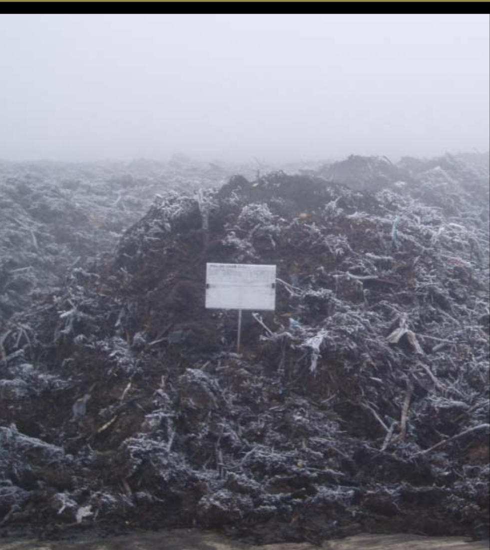
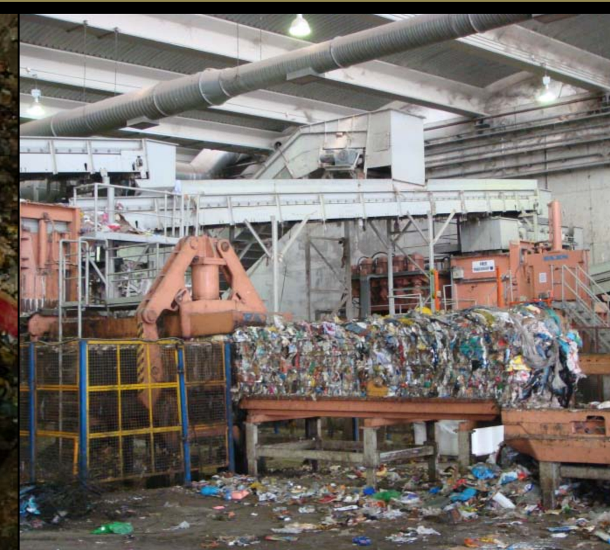
Different indices to express biodegradability in organic solid wastes. Application to full scale waste treatment plants



PhD Thesis

Tesis Doctoral

Sergio Ponsá Salas

Bellaterra, November 2010

UNIVERSITAT AUTÒNOMA DE BARCELONA

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Sergio Ponsá Salas

PhD Thesis

Different indices to express biodegradability in organic solid wastes. Application to full scale waste treatment plants

Diferentes índices para expresar la biodegradabilidad de residuos sólidos orgánicos. Aplicación a plantas de tratamiento de residuos a escala industrial

Diferents índexs per a determinar la biodegradabilitat de residus sòlids orgànics. Aplicació a plantes de tractament de residus a escala industrial

PhD Thesis by

Sergio Ponsá Salas

Bellaterra, November 2010

Antoni Sánchez Ferrer profesor titular del Departamento de Ingeniería Química de la Universitat Autònoma de Barcelona y **Teresa Gea Leiva** profesora lectora del mismo centro.

Certifican: que el ingeniero **Sergio Ponsá Salas** ha realizado bajo nuestra dirección el trabajo que, con el título "Different indices to express biodegradability in organic solid wastes. Application to full scale waste treatment plants", se presenta en esta memoria, la cual constituye su Tesis para optar al Grado de Doctor por la Universitat Autònoma de Barcelona.

Y para que se tenga conocimiento y conste a los efectos oportunos, presentamos en la Escola d'Enginyeria de la Universitat Autònoma de Barcelona la citada Tesis, firmando el presente certificado.

Bellaterra, Octubre de 2010.

Dr. Antoni Sánchez Ferrer　　　　　Dra. Teresa Gea Leiva

-Tenemos que admitir, Holmes, que una explicación sobrenatural en este caso, es teóricamente posible.
-Sí. Estoy de acuerdo. Pero, es un inmenso error hacer teorías sin tener suficientes datos. Inevitablemente, uno deforma los hechos para que encajen con las teorías, en vez de alterar las teorías para que concuerden con los hechos.

Sherlock Holmes

All our dreams can come true, if we have the courage to pursue them

Walt Disney

Three things in human life are important: the first is to be kind; the second is to be kind; and the third is to be kind.

Henry James

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Del mismo modo, esta Tesis ha recibido el apoyo de dos proyectos de investigación: CTM2006-00315/TECNO (Ministerio de Educación y Ciencia) y CTM2009-14073-C02-01 (Ministerio de Ciencia e Innovación).

Esta Tesis me toca firmarla a mí, pero sin duda es fruto del trabajo, esfuerzo y dedicación de mucha gente, sin la cual habría sido imposible la realización y redacción de esta memoria. Podría dedicar otra Tesis entera simplemente en palabras de agradecimiento y gratitud a todas las personas que me han acompañado en este camino, que ha durado más de 10 años, desde que en 1999 aterricé en la Universitat Autònoma de Barcelona. Han sido los mejores años de mi vida y esta Tesis sólo es uno de los miles frutos que ha dado el trabajo de estos años.

Escribir esta memoria era la meta final, pero por el camino he conocido a gente maravillosa, he vivido momentos irrepetibles con ellos: hemos aprendido juntos miles de cosas, hemos pasado días sobre pilas de lodos a temperaturas bajo cero, hemos pasado muchísimos días muestreando en los Ecoparcs, dentro de túneles, bajo la cintas de las que nos caían restos de diferentes residuos, vestidos con nuestros monos blancos (al principio) y que terminaban el día de color negro y nuestras máscaras de astronauta! Nos han caído purines encima, hemos estado sobre montañas de estiércol, hemos estado en decenas de EDARs y todo tipo de plantas de tratamiento de residuos. Y a pesar de todo, no ha habido ni un solo día en el que no hayamos disfrutado de todo eso! Jamás nadie hubiera imaginado que este trabajo tuviera un lado divertido, pero gracias a todos vosotros así ha sido siempre. Y el trabajo en el laboratorio no ha sido menos divertido, escuchando y bailando con nuestra música, bromeando y contando miles de historias que hacían que las horas pasaran sin darnos cuenta. Si en los momentos de trabajo siempre hemos encontrado la forma de divertirnos, que decir de nuestras cenas, fines de semana y los

innumerables momentos que hemos vivido juntos fuera de las paredes de la UAB, simplemente, han sido fantásticos!

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Y por último, me gustaría dedicar esta Tesis a *Velilla*, porque al igual que siempre, todo lo que hago en mi vida lo sigo haciendo pensando en lo que más quiero…

ABSTRACT

Biodegradable waste receives especial attention in the European Legislation (*Revised Framework Directive 2008/98/CE*) and this has been also reflected in Spanish Legislation in the *Plan Nacional Integrado de Residuos 2008-2015 (PNIR)*, due to the high importance that this municipal solid waste fraction has on the waste treatment environmental impact when it is not treated correctly and the possibility of recycling the biodegradable waste, to finally obtain compost or/and biogas that means green energy. For this purpose is necessary to develop suitable facilities for all waste treatments and assure the correct and efficient operation of such treatment and management facilities or plants.

The correct determination of process efficiency in these facilities requires a reliable measure of the biodegradable organic matter content of the wastes and their stability. This measure would allow: i) to establish a waste classification based on the biodegradability and stability; ii) the correct evaluation of plant and facilities performance; iii) the design of new and optimum facilities and waste treatments; and iv) to determinate the environmental impact of the final products of these facilities.

The information given by the analysis carried out just considering physical and chemical parameters is not able to reflect the correct biological nature of the wastes. It is really considerable the bibliographic references regarding the description, use and evaluation of biological indices, both aerobic and anaerobic, to characterize organic wastes. Additionally, these indices have already been proposed in some European countries' Legislations.

In this Thesis, new methodologies have been developed to determine aerobic and anaerobic biological indices, trying to optimize the already published methodologies by detecting their weaknesses, proposing improvements and increasing their utility. The indices obtained using these methodologies are: aerobic respirometric indices, expressed as the oxygen consumption rate and cumulative oxygen consumption during a given time and anaerobic indices, expressed as cumulative biogas and methane production during a given time or total biogas or methane production.

These methodologies have been assessed, evaluated and verified in different facilities, different treatments and in several works with different aims:

1) Optimization of the composting process of dewatered wastewater sludge, determining the minimum ratio of pruning waste used as bulking agent to obtain a hygienized and stabilized product in full scale facilities.
2) Complete assessment of a mechanical-biological treatment (MBT) plant treating 240.000 tones each year of municipal solid wastes. Process monitoring an determination of process efficiency regarding organic matter biodegradation.
3) Specific study of the mechanical pretreatment in a MBT plant and how it affects to the biodegradable organic matter removal.
4) Determination of the biogas production potential using anaerobic biological indices, measured in a short experimental time.
5) To obtain correlations between aerobic and anaerobic indices. Additionally, to correlate aerobic indices among them and analyzing the different information that they provide.
6) Using the information provided by aerobic respiration indices to completely characterized organic wastes.
7) Establishment of a standardized protocol to determine the biodegradability of organic wastes, from different origin and nature using aerobic biological indices to Agència de Residus de Catalunya.

The results obtained in all works and studies confirm the suitability of biological indices to be measure the biodegradable organic matter content and stability of solid wastes. Additionally, these indices can be considered as key parameters to design and control waste treatment facilities and processes.

RESUMEN

Los residuos biodegradables reciben una atención especial en el marco legislativo europeo actual (*Revised Framework Directive 2008/98/CE)* y en su transposición en España a través del *Plan Nacional Integrado de Residuos 2008-2015 (PNIR)*, debido al significativo impacto ambiental derivado cuando no son tratados correctamente y a su potencial uso como recursos renovables mediante la obtención de compost y biogás. Para ello, es imprescindible el desarrollo de instalaciones y plantas de tratamiento eficaces y eficientes.

La correcta evaluación de la efectividad y eficiencia de estas instalaciones requiere una medida fidedigna del contenido de materia orgánica biodegradable de los residuos y por consiguiente de su estabilidad. Esta medida permitiría: i) establecer una clasificación de residuos y productos en base a su biodegradabilidad y a su estabilidad; ii) la correcta evaluación de las plantas en funcionamiento; iii) el diseño de nuevas y optimizadas instalaciones; y iv) la determinación del potencial de impacto ambiental de los productos finales.

La información obtenida mediante el análisis de parámetros puramente físicos o químicos de los residuos no es capaz de reflejar la naturaleza biológica de los residuos. Es muy amplia la bibliografía que describe, propone y evalúa el uso de índices biológicos, aerobios y anaerobios, para caracterizar los residuos orgánicos. Asimismo, éstos índices han sido propuestos en diferentes normativas de países europeos.

En esta Tesis se han desarrollado nuevas metodologías para la determinación de índices biológicos aerobios y anaerobios, optimizando las metodologías ya referenciadas, eliminando sus limitaciones y ampliando su utilidad: índices respirómetricos aerobios, expresados como velocidad de consumo de oxígeno y su consumo acumulado durante un tiempo determinado e índices anaerobios expresados como producción acumulada de biogás y metano durante un tiempo determinado o total.

Estas metodologías se han evaluado y verificado mediante las siguientes aplicaciones:

1) Optimización del proceso de compostaje de lodos procedentes de EDARs urbanas, determinando la relación de estructurante-lodo mínima necesaria para obtener un producto final higienizado y estabilizado a escala industrial.

2) Completa evaluación de una planta de tratamiento mecánico-biológico (MBT) con capacidad para tratar 240.000 toneladas/año de residuos municipales, monitorización del proceso y determinación de las eficacias de eliminación de materia orgánica en cada etapa.
3) Estudio específico del pretratamiento mecánico de una MBT y su influencia en la eliminación de materia orgánica biodegradable.
4) Determinación de potenciales totales de producción de biogás mediante el análisis de índices biológicos anaerobios de corta duración.
5) Determinación de correlaciones entre índices aerobios y anaerobios. Determinación de correlaciones entre diferentes índices aerobios y discusión sobre la diferente información que proporcionan.
6) Caracterización completa de residuos basándose en la diferente información proporcionada por los índices respirométricos aerobios.
7) Redacción de un protocolo estandarizado para la determinación de la biodegradabilidad de residuos orgánicos de diferente origen y tipología para la Agència de Residus de Catalunya basándose en la determinación de índices biológicos aerobios.

Los resultados obtenidos en todos estos trabajos confirman la idoneidad del uso de índices biológicos como medida real del contenido de materia orgánica biodegradable de los residuos y por lo tanto de su estabilidad. Además pueden considerarse como un parámetro clave para el diseño y control en plantas de tratamiento de residuos.

RESUM

Els residus biodegradables reben una atenció especial en el marc legislatiu europeu actual (*Revised Framework Directive 2008/98/CE)* i en la seva transposició a Espanya a traves del *Plan Nacional Integrado de Residuos 2008-2015 (PNIR)*, degut al significatiu impacte ambiental derivat quan aquestos residus no són tractats correctament i al seu potencial ús com recursos renovables mitjançant l'obtenció de compost i biogàs. Pel correcte tractament d'aquestos residus és imprescindible el desenvolupament d'instal·lacions i plantes de tractament eficaces i eficients.

La correcta avaluació de l'efectivitat i eficiència d'aquestes instal·lacions requereix una mesura fidedigna del contingut de matèria orgànica biodegradable dels residus i per tant de la seva estabilitat. Aquesta mesura permetria: i) establir una classificació dels residus i productes en base a la seva biodegradabilitat i estabilitat; ii) la correcta avaluació de les plantes de tractament en funcionament; iii)el disseny de noves i optimitzades instal·lacions, i iv) la determinació del potencial impacte ambiental dels productes finals.

La informació obtinguda mitjançant l'anàlisi de paràmetres purament físics o químics dels residus no es capaç de reflectir la naturalesa biològica dels residus. És molt extensa la bibliografia que descriu, proposa i avalua l'ús d'índexs biològics, aerobis i anaerobis, per caracteritzar els residus orgànics. De la mateixa manera, aquestos índexs, han estat proposats en diferents normatives de paises europeus com paràmetres d'estabilitat.

En aquesta Tesis s'han desenvolupat noves metodologies per a la determinació d'índexs biològics aerobis i anaerobis, optimitzant les metodologies ja referenciades, eliminant les seves limitacions i ampliant la seva utilitat: índexs respiromètrics aerobis, expressats com velocitat de consum d'oxigen i consum acumulat durant un temps determinat i índexs anaerobis, expressats com producció acumulada de biogàs i metà durant un temps determinat o total.

Aquestes metodologies s'han avaluat i verificat mitjançant les següents aplicacions:

1) Optimització del procés de compostatge de fangs procedents d'EDARs urbanes, determinant la relació d'estructurant-fang mínima necessària per obtenir un producte final higienitzat i estabilitzat a escala industrial.

2) Completa avaluació d'una planta de tractament mecànic-biològic (MBT) amb capacitat per tractar 240.000 tones/any de residus municipals, monitoratge del procés i determinació de les eficàcies d'eliminació de matèria orgànica en cada etapa.
3) Estudi específic del pretractament mecànic d'una MBT i la seva influencia en l'eliminació de matèria orgànica biodegradable.
4) Determinació de potencials totals de producció de biogàs mitjançant l'anàlisi d'índexs biològics anaerobis de curta durada.
5) Determinació de les correlacions entre indexs aerobis i anaerobis. Determinació de les correlacions entre els diferents indexs aerobis i discusió sobre la diferent informació que poden proporcionar.
6) Caracterització completa de residus basant-se en la diferent informació proporcionada pels indexs respiromètrics aerobis.
7) Redacció d'un protocol estandarditzat per a la determinació de la biodegradabilitat de residus orgànics de diferent origen i tipologia per l'Agencia de Residus de Catalunya, basant-se en la determinació d'índexs biològics aerobis.

Els resultats obtinguts en tots aquestos treballs i estudis confirmen la idoneïtat de l'ús dels índexs biològics com mesura real del contingut de matèria orgànica biodegradable dels residus i per tant de la seva estabilitat. A més es poden considerar com un paràmetre clau pel disseny i control de plantes de tractament de residus.

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ABBREVIATIONS AND SYMBOLS

AcOH	Acetic acid	
ADS	Anaerobic digested sludge	
AFP	Air filled porosity	%
AT	Aerobic cumulative index	$g\ O_2\ kg\ DM^{-1}$
AT_{24h}	AT in the 24h of maximum activity	$g\ O_2\ kg\ DM^{-1}$
AT_4	Cumulative O_2 uptake during 4 days	$g\ O_2\ kg\ DM^{-1}$
ATP	Adenosine triphosphate	
AT_u	total cumulative oxygen consumption	$g\ O_2\ kg\ DM^{-1}$
B	Bottle working volume	L
BAT and BREFs	Best available techniques	
BD	Bulk density	$kg\ L^{-1}$
BMP	Biological methane potential in n days	$NL\ CH_4\ kg\ OM^{-1}$
BOD	Biological oxygen demand	$g\ O_2\ kg^{-}\ OM^{1}\ h^{-1}$
C	Carbon	
C/N	Carbon to nitrogen ratio	
C/P	Carbon to phosphorous ratio	
$CaCO_3$	Calcium carbonate	
C_C	Cumulative CO_2–C mineralized	%
CH_4	Methane	
C_I	Inert fraction	%
CO_2	Carbon dioxide	
COD	Chemical oxygen demand	$mg\ L^{-1}$
C_R	Rapidly mineralizable fraction	%
C_S	Slowly mineralizable fraction	%
C_W	Remaining carbon in the sample	%
DM	Dry matter	%
DRI_{1h}	average DRI_t in the one hour of maximum activity	$g\ O_2\ kg\ DM^{-1}\ h^{-1}$
DRI_{24h}	average DRI_{1h} in the 24 hours of maximum activity	$g\ O_2\ kg\ DM^{-1}\ h^{-1}$
DRI_{max}	maximum DRI_t obtained	$g\ O_2\ kg\ DM^{-1}\ h^{-1}$

DRI_t	Dynamic Respiration Index for a given time	$g\ O_2\ kg\ DM^{-1}\ h^{-1}$
EPA	Environmental Protection Agency (US)	
EU	European Union	
F	Volumetric airflow	$ml\ min^{-1}$
GB_{21}	Cumulative biogas production in 21days	$NL\ biogas\ kg\ DM^{-1}$
GB_n	Biogas potential in n days	$NL\ biogas\ kg\ DM^{-1}$
GB_u	Total cumulative biogas production	$NL\ biogas\ kg\ DM^{-1}$
GGE	Greenhouse gases emissions	
H_2O	Water	
H_2S	Hydrogen sulfide	
He	Helium	
HRT	Hydraulic retention time	days
IPPC	Integrated Pollution Prevention and Control	
K	Potassium	
K_{CH}	Chen-Hosshimoto kinetic constant	
k_R	Rapid rate constants	day^{-1}
k_S	slow rate constants	day^{-1}
M	Cumulative BMP	$NL\ CH_4\ kg\ OM^{-1}$
MBT	Mechanical biological treatment (plants)	
MC	Moisture content	%
MSW	Municipal solid waste	
N	Nitrogen	
N_2	Nitrogen gas	
NH_3	Ammonia	
NH_4^+	Ammonium	
NO_2	Nitrogen dioxide	
O_2	Oxygen	
OD_{20}	cumulative O_2 uptake during 20 h	$g\ O_2\ kg\ OM^{-1}\ h^{-1}$
OFMSW	Organic fraction of municipal solid waste	
OM	Organic matter	%, db
OUR	Oxygen uptake rate	$g\ O_2\ kg\ OM^{-1}\ h^{-1}$ or $g\ O_2\ kg\ DM^{-1}\ h^{-1}$
P	Phosphorous	
P	Maximum methane potential	$NL\ CH_4\ kg\ OM^{-1}$
PDRI	Potential dynamic respiration index	$g\ O_2\ kg\ OM^{-1}\ h^{-1}$
PNIR	Plan Nacional Integrado de Residuos	

P_r	Atmospheric pressure	atm or bar
R	Ideal gas constant	0.082061 atm L mol^{-1} K^{-1}
RDRI	Real dynamic respiration index	g O_2 kg OM^{-1} h^{-1}
R_f	Refractory coefficient	
RI_{37}	O_2 uptake rate at 37ºC	g O_2 kg OM^{-1} h^{-1}
RI_T	O_2 uptake rate at process temperature	g O_2 kg OM^{-1} h^{-1}
R_{max}	Maximum methane production rate	NL CH_4 kg OM^{-1} $days^{-1}$
S_{inoc}	Wet weight of the inoculums in mixtures	kg
SOUR	Specific oxygen uptake rate	g O_2 kg OM^{-1} h^{-1}
SRI	Static respirometric index	g O_2 kg OM^{-1} h^{-1} or g O_2 kg DM^{-1} h^{-1}
t	Time	hours or days
T	Temperature	K or ºC
t_F	time when GB_u is reached	days
t_{MAX}	Time during R_{MAX} is maintained	days
TNK	Total nitrogen Kjeldahl	
TOC	Total organic carbon	%, db
V	Volume	L or ml
$V_{37°C,n}$	V of biogas (or methane) produced during n days	L
VFA	Volatile fatty acids	
$V_{net\ 37°C,}$	Net V of biogas (or methane) produced during n days	L
VS	Volatile solids	%, db
W	Total wet weight of the mixture	kg
$W_{inoc,i}$	Total wet weight of inoculums in blanks	kg
X	Wet weight of material test aliquot	g
Z	DM of sample loaded	kg
λ	Lag phase	days
μ_m	Max. specific growth rate of microorganisms	day^{-1}

CHAPTER 1. INTRODUCTION

CHAPTER 1. INTRODUCTION

1.1 Overview of the problem

Growth in the European Union (EU) and North America, together with the new potential economies in development such as China, India and South America, are strongly accompanied by increasing amounts of waste, causing unnecessary losses of materials and energy, environmental damage and negative effects on health and quality of life. This is becoming a worldwide problem and all societies should be concerned about the consequences of non controlled industrial and urban design and social growth.

Waste generation and management is one of the most serious problems in modern societies, and consequently nowadays strong policies on waste issues are coming up in developed countries. Waste uncontrolled disposal and inappropriate management lead to severe impacts in the environment, causing water, soil and air pollution, contributing to climate change and affecting negatively to the ecosystems and human health. However when waste is appropriately managed it becomes a resource that contributes to raw materials saving, natural resources and climate conservation and sustainable development.

In the last 20 years waste has been at the centre of EU environment policy and substantial progress has been made. Heavily polluting landfills and incinerators are being cleaned up. New techniques have been developed for the treatment of hazardous waste (COM (2005) 666, Commission of the European Communities, 2005). With time, waste is increasingly seen as valuable resource for industry and approaches such as re-use, recycling and energy recovery are starting to be applied to regulate wastes. The waste management and recycling sector has a high growth rate and has an estimated turnover of over € 100 billion for EU. It is labour-intensive and provides between 1.2 and 1.5 million jobs (COM (2005) 666, Commission of the European Communities, 2005).

However, despite these successes, waste remains a problem. Waste volumes continue to grow. Legislation is, in some cases, poorly implemented and there are significant differences between national approaches. In addition EU waste law often remains unclear and has been the subject of considerable litigation on its interpretation. The potential for waste prevention and recycling is not yet fully tapped. The emerging knowledge about the environmental impact of resource use is not yet fully reflected in waste policy.

Taking all this into consideration European Commission has been working as it was prescribed in the Sixth Environment Action Programme (EAP) (Decision n° 1600/2002/EC of the European Parliament and of the Council of 22 july 2002) in a Waste Framework Directive that finally came out in the form of the Revised Waste Framework Directive (2008/98/CE).

The Revised Framework Directive (2008/98/CE) requires that all waste must be treated in a way that protects the environment and human health by preventing or reducing the adverse impacts of the generation and management of waste and by reducing the overall impacts of resource use and improving the efficiency of such use. Waste policy has to apply a five-step waste management hierarchy as a priority order. Highest priority is given to waste prevention, followed by preparation for reuse, recycling, other recovery and disposal. Member States shall bring into force the laws, regulations and administrative provisions necessary to comply with this Directive by 12 December 2010.

Member States have to work hardly to accomplish the new Directive datelines. Each Member State shall ensure that their competent authorities establish the corresponding waste management plans (one or more) and waste prevention programs covering the entire geographical territory of the Member State concerned. Furthermore, in the new Directive specific goals on biodegradable waste management are proposed. In addition, each Member State must have suitable facilities for all waste treatments and assure the correct and efficient operation of such treatment and management facilities or plants.

1.2 Current situation of waste management and legislation

At present in the EU municipal waste is disposed of through landfill (49%), incineration (18%), recycling and composting (33%)(COM (2005) 666, Commission of the European Communities, 2005). Current EU waste policy is based on a concept known as the waste hierarchy. This means that, ideally, waste should be prevented and what cannot be prevented should be re-used, recycled and recovered as much as feasible, with landfill being used as little as possible.

The legal framework underpinning this strategic approach includes horizontal legislation on waste management: Revised Waste Framework Directive (2008/98/CE) and Hazardous Waste Directive (91/689/EEC). These are complemented by more detailed legislation concerning waste treatment and disposal operations, such as the Landfill (99/31/EC) and Incineration Directives (2000/76/EC) and legislation to regulate the management of specific waste streams (waste oils, batteries, etc). In Figure 1 main directives and regulations are listed as well as the waste that is under consideration.

Despite the considerable progress that has been made and although recycling and incineration are increasing, overall waste volumes are growing and the absolute amount of waste going to landfill is not decreasing because of the growth in waste generation. For example, the amount of plastic waste going to landfill increased by 21.7% between 1990 and 2002 while the percentage of plastic waste being landfilled dropped from 77% to 62%.

Although waste prevention has been the main objective of both national and EU waste management policies for many years, neither the Community nor the national targets set in the past have been satisfactorily met.

Current EU waste management policies (2008/98/CE) are intended for developing recycling and recovery together with preventing waste generation. Consequently the resource efficiency of the European economy would increase and the negative impact of natural resources use would be reduced. In addition the current European legislation is also focused in correcting the weak key points considered in past legislations. These key points are: the full implementation of the existing and current legislation, taking legal actions when necessary; the simplification and modernization of existing legislation; the introduction of life-cycle thinking into waste policy; promotion of more ambitious waste prevention policies; better knowledge and information; development of common reference standards for recycling; and further elaboration of the EU's recycling policy. All these will contribute to the long-term goal for the EU, which is to become a recycling society that seeks to avoid waste and uses waste as a resource. It would mean that less waste goes to landfill and more energy is recovered from waste as well as more compost is obtained after waste treatment.

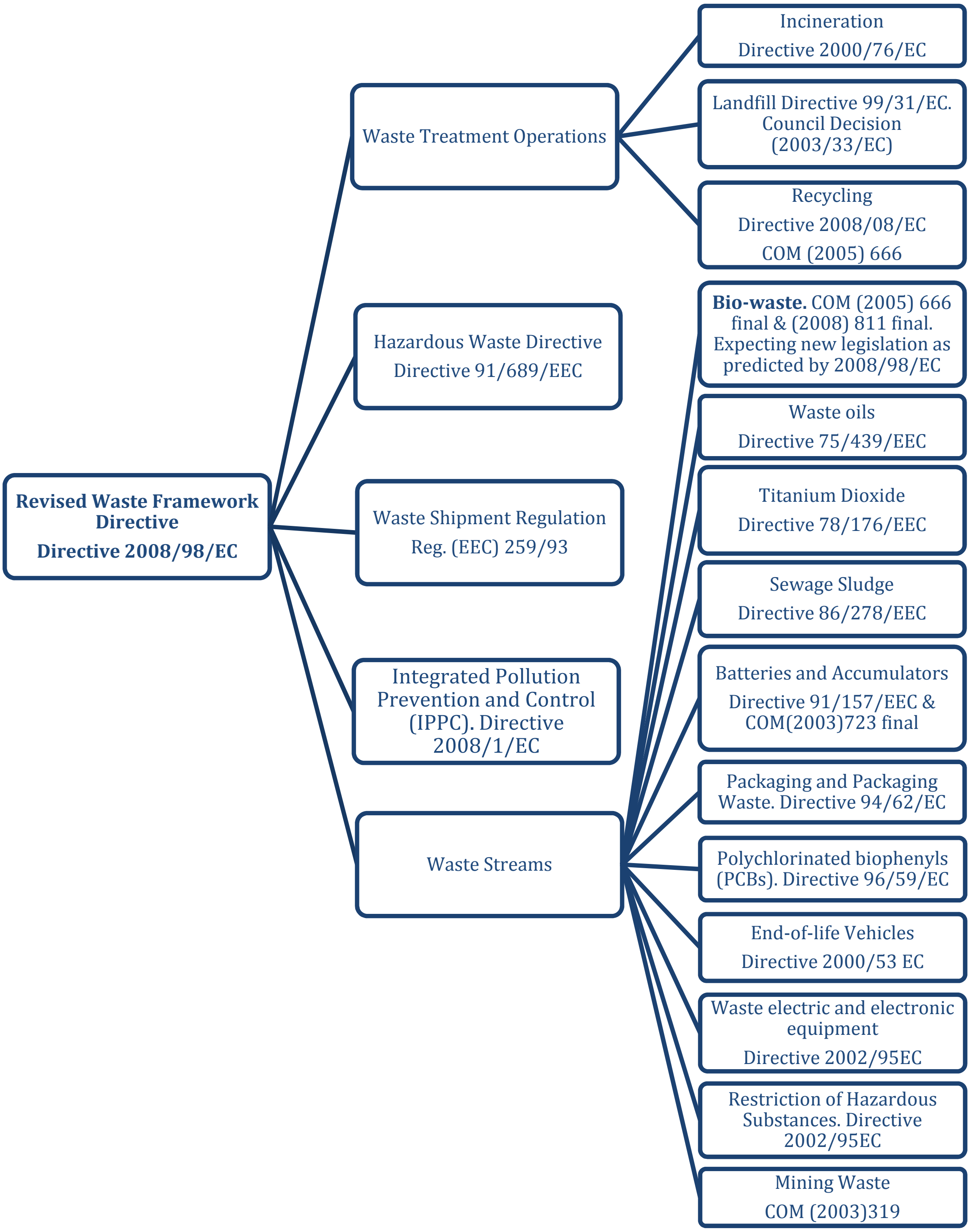

Figure 1.1. Directives and Legislation to be applied in EU and the wastes under concern.

Most developed economies and many developing countries are pursuing the objective of improving the waste management requirements. For example in Japan there is an extensive legislation related to waste and other sustainable production and consumption policies under the “3Rs reducing, re-using and recycling” umbrella. These include laws setting targets for general waste prevention, waste recycling and avoidance of final disposal. Japan aims to recycle 24% of municipal waste and to limit final disposal of waste to 50%. In addition, Japan has developed a number of recycling laws, some mirroring the objectives of EU recycling Directives.

The USA have developed policies at Federal and State levels. The Federal Government has set a long-term indicative target of a national recycling rate of 35% of municipal waste and is supporting this through a number of mainly voluntary programs. This includes efforts to foster smart design and reduce environmental impact of products. Several individual States have developed legislation restricting landfill and promoting the recycling of various waste flows.

China has enacted a number of laws that relate to waste management. In particular, these are pursuing the objective of promoting “the circular economy”. Currently China is developing medium-term and long-term plans for the development of this concept. There is also growing demand in China for recyclable materials.

In Spain, accordingly with the Revised Framework Directive (2008/98/CE) and previous European Legislation, the competent Spanish authorities have established the corresponding waste management plan and waste prevention program in the form of “Plan Nacional Integrado de Residuos 2008-2015” (PNIR) which was approved by the “Consejo the Ministros” the 26th of December of 2008 and published in the “Boletin Oficial del Estado” the 26th of February of 2009 (BOE Núm. 49 Sec. I. Pág. 19893). This Plan has as main goals the management and treatment of: municipal solid waste (MSW), wastes to which specific legislation is applied (hazardous, end-of-life vehicles, tires, batteries and accumulators, waste electric and electronic equipment, mining wastes, demolition wastes and sewage sludge), contaminated soils, wastes coming from agriculture and industry classified as non-hazardous. This Plan specifically highlights the importance on the management and treatment of biodegradable wastes, including an explicit strategy for this purpose ("Estrategia de Reducción de Vertido de Residuos Biodegradables").

Spanish and European authorities are really concerned on climate change, so the present legislation is also intended to fight for reducing the Greenhouse Gases emissions (GGE) derived from waste management and treatment. Although wastes contribution to Climate Change is slight compared to other industrial and social sectors (in 2006 it was just 2.8% of total GGE), there is still an important potential for reducing the emissions derived from wastes. Wastes GGE consists mostly of methane (CH_4) coming from landfills and to a lesser extend of nitrogen dioxide (NO_2) from waste waters and carbon dioxide (CO_2) from incineration. Pursuing this objective Spanish current legislation fixes that in 2016 municipal biodegradable waste landfilled must be less than 35% of the biodegradable waste generated in 1995. In addition, Directive 1999/31/EC already provided for redirecting two thirds of biodegradable municipal waste from landfills and required all Member States to establish and regularly review national strategies for management of the waste diverted from landfill.

PNIR also considers the five-step waste management hierarchy as a priority order (waste prevention, preparation for reuse, recycling, other recovery and disposal). The targets set in PNIR and based in (2008/98/CE) are the next:

- In 2015 it must be established source selected collection for at least paper and cardboard, metals, plastics and glass fractions.
- In 2020, waste preparation for reuse and recycling must be increased at least to 50% of the total amount collected for paper and cardboard, metals, plastics and glass fractions.
- Several measures for promoting source selected organic fraction or bio-waste collection must be adopted. It will promote and improve composting and anaerobic digestion treatments. Requirements on bio-waste management and treatment as well as quality requirements for digestate and compost must be established.

Biodegradable waste receives especial attention in the European Legislation (2008/98/CE, Article 22) and it has been also reflected in Spanish Legislation in the "Estrategia de Reducción de Vertido de Residuos Biodegradables" included in the PNIR section 18 (BOE

Núm.49 Sec. I. Pág. 19965). This is due to the high importance that this municipal solid waste fraction has on the waste treatment environmental impact when is not treated correctly and the possibility of recycling the biodegradable waste, to finally obtain compost or/and biogas that means green energy.

1.3 Waste classification and listing

The European Directive 2008/98/CE defines "waste" as any substance or object which the holder discards or intends or is required to discard.

Different classifications of wastes can be done. On the one hand wastes can be basically distinguished between urban or municipal wastes and industrial wastes depending on the origin where are generated. Municipal waste is defined as waste from households, as well as other waste, which, because of its nature or composition, is similar to waste from households (99/31/EC). Industrial waste comprises many different waste streams arising from a wide range of industrial processes. These streams are made of materials discarded from industrial operations or derived from manufacturing processes and may be liquid, sludge, solid, or hazardous waste. Industrial waste has detailed legislation that regulates its management and treatment.

Municipal waste management and treatment are regulated by 2008/98/CE. Specific source separated at origin waste flows, such as bio-waste, glass, plastics and metals have appropriate legislation, as it has been mentioned before.

Bio-waste is defined as biodegradable garden and park waste, food, and kitchen waste from households, restaurants, caterers and retail premises, and comparable waste from food processing plants. It does not include forestry or agricultural residues, manure, sewage sludge, or other biodegradable waste such as nature textiles, paper or processed wood. It also excludes those by-products of food production that never become waste.

In this document biodegradable waste will be treated in its integrity without taking into consideration the distinction of different fractions in what it can be classified. Figure 1.2 shows the different fractions that compose biodegradable waste.

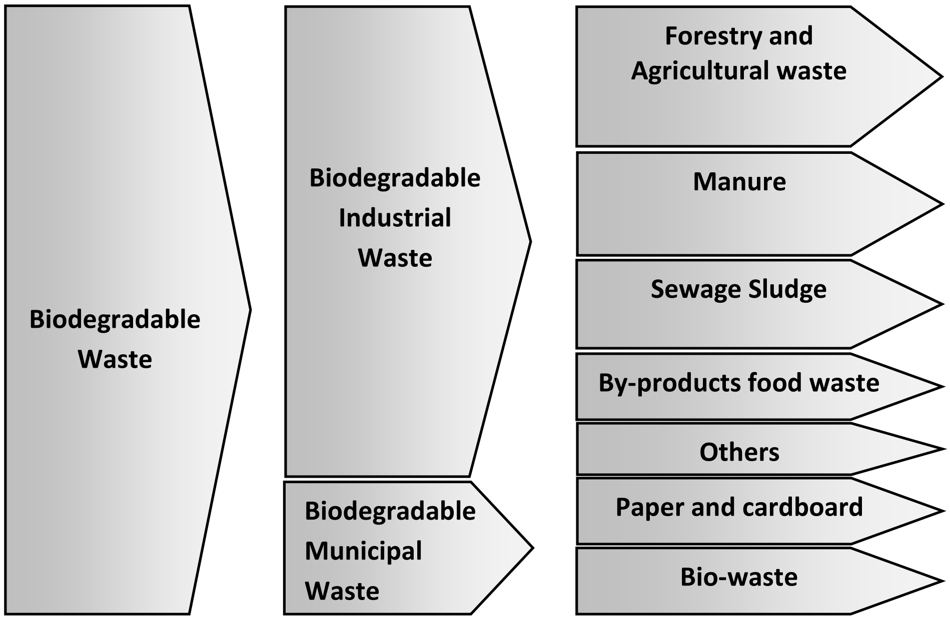

Figure 1.2. Composition of biodegradable waste

Concerning industrial waste, EU adopted in 1996 a set of common rules for permitting and controlling industrial installations in the Integrated Pollution Prevention and Control (IPPC) Directive (1996/61/EC). This IPPC Directive was codified in 2008 in the IPPC Directive (2008/1/EC). The purpose of this Directive is to achieve an integrated prevention and control of pollution arising from the activities listed in Annex I of this Directive (energy industries, production and processing metal industries, mineral industries, chemical industries, waste management industries and plants and other activities). It lays down measures designed to prevent or, where that is not practicable, to reduce emissions in the air, water and land from the abovementioned activities, including measures concerning waste, in order to achieve a high level of protection of the environment taken as a whole, without prejudice to Directive 85/337/EEC and other relevant Community provisions. Operators of industrial installations covered by Annex I of the IPPC Directive are required to obtain an authorization (environmental permit) from the authorities in the EU countries. About 52.000 installations are covered by the IPPC Directive in the EU.

The IPPC Directive is based on several principles, being the most important an *integrated approach* and *best available techniques (BAT)*. The *integrated approach* means that the permits must take into account the whole environmental performance of the plant, covering for example, emissions to air, water and land, generation of waste, use of raw materials, energy efficiency, noise, prevention of accidents, and restoration of the site upon closure. The purpose of the Directive is to ensure a high level of protection of the environment taken as a whole. *Best Available Techniques (BAT)* are the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole. To assist the licensing authorities and companies to determine BAT, the Commission organizes an exchange of information between experts from the EU Member States, industry and environmental organizations. This work is coordinated by the European IPPC Bureau of the Institute for Prospective Technology Studies at EU Joint Research Centre in Seville (Spain). This results in the adoption and publication by the Commission of the BAT Reference Documents (the so-called BREFs).

On the other hand wastes can be classified depending on the composition but contemplating the origin. European Legislation, by means of Decision 2000/532/EC, proposed a detailed list of waste where all sort of wastes are codified.

Waste can also be classified, as established in Directive 2008/98/CE, in hazardous and non-hazardous waste. Hazardous waste is waste which displays one or more of the hazardous properties listed in Annex III of the Directive 2008/98/CE, for example, explosive, oxidizing, highly flammable, irritant, toxic, harmful and carcinogenic substances amongst others. The Environmental Protection Agency of United States (EPA) defines hazardous waste as waste that is dangerous or potentially harmful to our health or the environment. Instead non-hazardous waste is waste which does not feature on the list of hazardous waste in current European Directive, and consequently is not considered as dangerous or potentially harmful to our health or the environment (EPA). Hazardous waste is under specific European Legislation (Directive 91/689/EEC) as it is considered in 2008/98/CE.

Finally, a waste classification, depending on the state of matter in which the waste is mostly presented, can be made. The distinction can be done between solid, liquid and gas wastes. European Council Directive 96/62/EC and Directive 2008/50/EC regulate gas emissions and pollutants. Council Directive 91/271/EEC concerns to urban or municipal waste waters (and some industrial waste waters under specific regulation) and Directive 2008/1/EC regulates industrial waste waters. Solid waste is regulated by Directive 2008/98/CE and other legislation related but also included in this Framework Legislation.

1.4 Solid waste management and treatments

A detailed description of the present scenario has been presented in this document, with the goal of giving an appropriate overview of the problem concerning waste management and treatment in Spain, in EU and even in some head countries of the world. Many attentiveness and thoughtfulness are shared in Legislation concerning the different wastes, and its consideration as a whole will give a general connection among all nature of wastes.

However, at this point, it is necessary to establish the boundary of the present work, since is not possible to cover the whole sphere concerning all waste treatment processes. Specifically, this document will be focused in **solid waste management, treatment and technology** and all the results, discussions and conclusions will be of special interest for **solid waste field**.

As it has been mentioned above, solid waste management and particularly the management of the organic fraction is one of the priorities for the competent administrations in developed countries around the world. In European Union, between 76.5-102 Mt/year of organic fraction of municipal solid waste (OFMSW) are generated, which would correspond to 30-40% of total municipal solid waste generated (European Commission, 2008). For example, at Catalan level, 1.59 Kg per capita per day of solid waste was generated in 2008, from which 45-55% corresponded to the organic fraction (Agència de Residus de Catalunya, 2009).

Industrial waste management and treatment is based, as established in European and Spanish Legislation, on the polluter-pays principle. That means that the waste producers are responsible of the management and treatment of the waste that they produce. In consequence, they can use BREFs documents to develop a waste treatment or they can send their wastes to external waste management plants. Obviously, wastewaters, gas emissions and solid wastes that cannot be transported must be treated in the plants or industries where are generated.

The management of municipal or urban wastes must be clearly distinguished in two steps: collection and later treatment or elimination. The treatment facilities design, in terms of capacity, plant operation and facilities useful life, directly depend on the way that collection is carried out, source selected (one or more fractions) or mixed, and on the collection system efficiency.

There are different collection models, considering the source separated fractions or separated collection system, resulting always a mixed fraction whose composition is variable and dependent on how and what has been previously separated in households (glass, paper and cardboard, packaging, bio-waste).

In Spain, in 2006 only the 14% of total municipal solid waste was collected in specific containers (separated collection) and the 86% was collected integrating the mixed fraction. In Table 1.1 a more detailed list of separated collection amounts of each fraction, is showed.

Table 1.1. Detailed generation and composition of municipal solid waste in Spain.

Collection system			**Tones**	**Percentage**
Separated collection	Household separation:		2.519.340	11%
		Paper and cardboard	934.062	4%
		Glass	562.000	2%
		Packaging	606.200	3%
		Bio-waste	417.078	2%
	Specific waste (green points)		697.432	3%
Mixed waste collection			20.431.260	86%

Source: Ministerio de Medio Ambiente y Medio Rural y Marino (2006)

Other collection systems are recently being applied to obtain a better separation of the organic fraction and recyclable materials in its origin. This is the so called door to door collection systems. However, although is one of the best systems in terms of quality of source separated wastes, it is not always feasible to carry out, since it is expensive and depends on the town and country planning. It consists on source separation but also on source collection, forcing people to separate as well as possible, otherwise, they would be fined.

Technology to treat wastes is being developed successfully to treat each kind of waste in the way with less environmental impact.

Packaging, glass, and paper and cardboard wastes collected selectively are sorted in classification plants and sent to recyclers. In some waste treatment plants where mixed waste is processed, specific flows of these materials are sometimes obtained and sent to classification plants and subsequently sent to recyclers.

Mixed municipal solid waste has been usually landfilled without any other previous treatment, but at present due to the problems associated with uncontrolled landfilling and related with CH_4 emissions due to anaerobic degradation of biodegradable organic matter and water contamination with landfill leachate, this fraction is exhaustively treated before landfilling.

Treatments applied to MSW are definitely necessary and are in accordance to new Legislation (European and Spanish levels), that establishes strong targets on the reduction of biodegradable organic matter going to landfill.

In addition, biodegradable organic matter must be considered as a renewable source of energy, since it can be anaerobically treated obtaining biogas as product or aerobically treated to finally obtain compost as product. Furthermore, a combination of these treatments can be used for a more intensive treatment. This possibility is considered in present legislation concerning the use and promotion of renewable sources of energy (Directive 2009/28/EC). This Legislation together with the Kyoto Protocol to the United Nations Framework Convention on Climate Change, establish a target of at least 20% share energy from renewable sources in the Community's gross final consumption of energy in 2020.

When possible and feasible MSW and OFMSW are generally treated in integrated waste treatment plants which consist on different treatments which main goal is to reduce the organic matter sent to landfill and maximize the amount of materials recovered for recycling. These plants are often called mechanical biological treatment (MBT) plants since both mechanical and biological treatments are combined.

1.5 Mechanical treatments for solid waste

Different mechanical treatments have been designed to condition the waste flows prior to biological treatments and to obtain recoverable materials to be sent to recyclers. Other mechanical treatments are used to prepare the refuses to landfilling or to storage or transport the recyclable materials.

When treating the MSW or OFMSW fractions in MBT plants, the first step commonly consists on a mechanical separation of recyclable materials and biodegradable organic matter. In this step a flow composed mainly of biodegradable organic matter, but also with other small inert materials that cannot be separated, is obtained. Other flows containing the different fractions in which solid recyclable waste can be sorted, such as plastics, metals, glass, paper and cardboard and huge objects are also derived. Finally a flow called “refuse” that is composed essentially by inert materials that the mechanical pre-treatment cannot classify in recyclable waste flows goes to landfill.

Some steps included in the mechanical pre-treatment in MBT plants are hand sorting, trommel screening, ballistic separation, magnetic separation of iron, separation of aluminum and glass among others. Figure 1.3 shows the flow scheme of an existing MBT plant as an example.

Before being landfilled, refuse is occasionally pressed and packaged with a special air permeable film in cubic bales, reducing the space in the landfill and avoiding anaerobic areas and therefore methane emissions from remaining biodegradable organic matter. If this packaging is not carried out, refuse is directly sent to landfill. In addition, recyclable material flows are sent to recycle plants for its recovery.

The flow containing biodegradable organic matter continues the treatment intended to stabilize the organic matter and finally obtain compost or, in general, stabilized materials.

OFMSW, if collection system is as good that assures a minimum amount of impurities (door to door systems), can be sent directly to biological treatments. Occasionally, OFMSW is pre-treated in the way to removed non-biodegradable materials, and just the refuse and biodegradable organic matter flows are obtained.

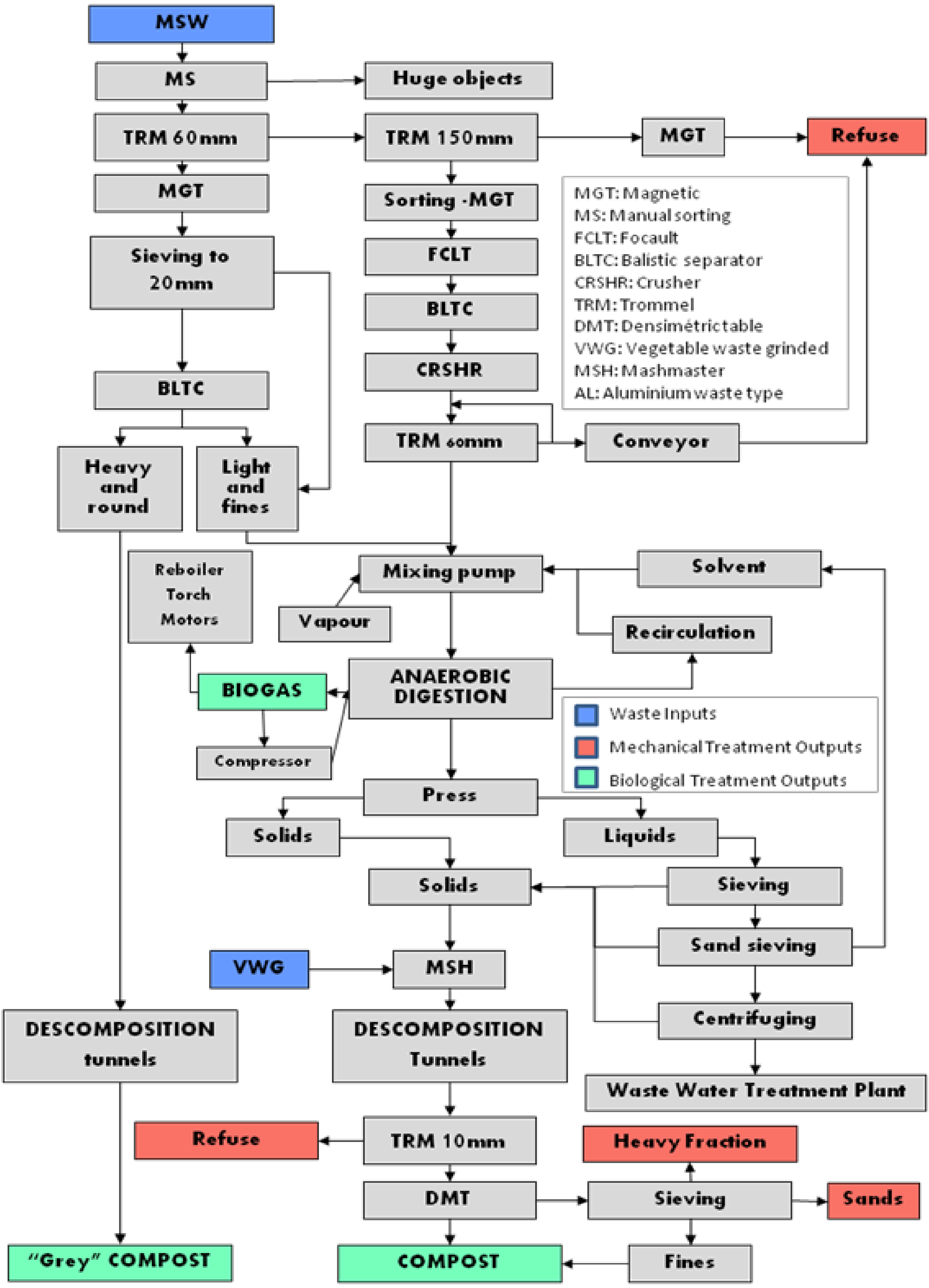

Figure 1.3. Detailed flow-scheme of operations in a MBT plant treating MSW

1.6 *Biological processes for solid waste*

Biological treatment processes, such as composting and anaerobic digestion have been widely studied around the world (Haug, 1993; Ahring, 2003) and at present they are the main biological treatments applied to stabilize the biodegradable organic matter of solid wastes. In the following sections both biological treatments will be described in detail.

1.6.1 Composting

Aerobic biological treatment is called *composting*, and is defined as follows: "is a biotechnological process by which different microbial communities initially degrade organic matter into simpler nutrients and, in a second stage complex organic macromolecules such as humic acids are produced, forming an organic fertilizer known as compost" (Hsu and Lo, 1999). Likewise, composting is also defined as an aerobic process that requires oxygen for microbial degradation and optimal conditions of moisture and porosity to produce thermophilic temperatures; where the maintenance of thermophilic temperatures is the primary mechanism for pathogen inactivation and seed destruction (Haug, 1993). Tchobanoglous et al. (1994) presented an equation (Figure 1.4) that summarizes the composting process:

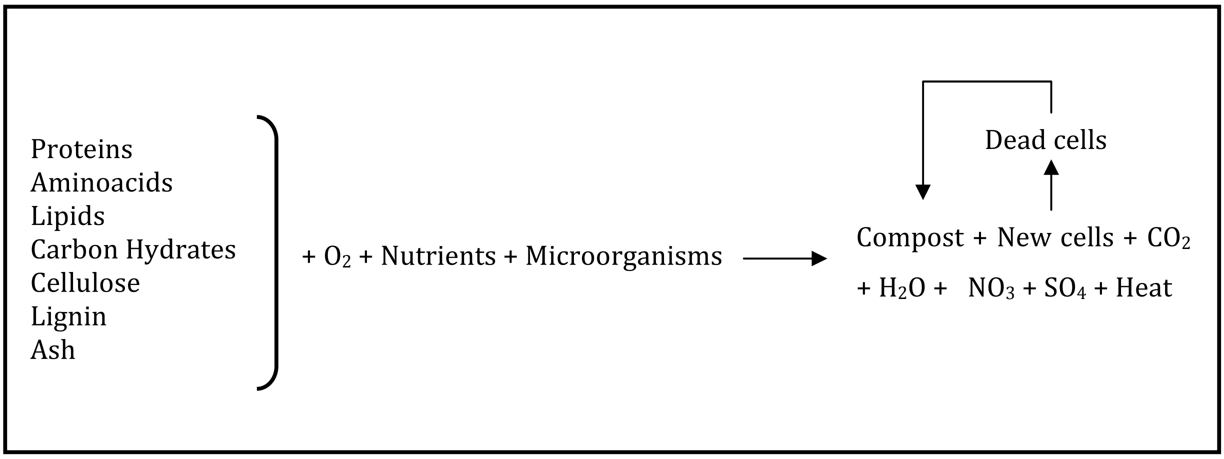

Figure 1.4. General equation for the composting process (Tchobanoglous et al., 1994)

Composting can be applied to treat organic wastes with different aims, being the main ones the following (Soliva, 2001; Adani et al., 2004):

- To produce high quality compost that permits the maintenance of soil fertility, the production of high quality crops and the conservation of the environment.
- To produce low-grade compost with limited application or for the application to degraded lands.
- To reduce the biodegradability, odour potential, moisture content, weight and volume of a material before landfill.
- To increase the calorific potential of the material via removal of the moisture content by the natural draft and the thermophilic temperature produced by the biological activity.

1.6.1.1 Description of the process

Haug (1993) divided the composting process in four different stages: 1) pre-processing; 2) high-rate decomposition; 3) curing phase; and 4) post-processing, as it is shown in Figure 1.5.

In the composting process it is important to maintain the biological, chemical and physical requirements of microorganisms to finally reach the maximum degradation levels throughout the stages of the process. The composting process generally occurs in two biological stages (high rate stage and curing phase) and two mechanical stages, the so called pre and post treatment, as it can be noted from Figure 1.5.

I. Pre-processing stage

MSW and OFMSW are heterogeneous wastes with a wide range of unwanted (non-biodegradable) material content, depending on the collection system. Some instruments are needed to separate those non-compostable fractions from organic fraction. In this sense a pre-processing stage is generally intended to mechanically pre-treat raw materials (as it has been mentioned in Section 1.5 and so often is the first stage in MBT plants) to sieve and reduce particle size (trommel screening and sieving), separate non-compostable or biodegradable components from compostable components (for example, hand sorting, magnetic separation of iron, separation of aluminum and glass). But pre-processing stage includes other important operations that are involved in providing the optimum composting conditions to the bulk mixture. These operations include moistening the mass to optimum values and blending feed components among others. Four approaches to blending feed components are widely used at full scale composting facilities (as show in Figure 1.5): i) addition of amendment; ii) recycling of compost product (seed microbes); iii) addition of bulking agent (new or recycled from the system); and iv) a combination of the above.

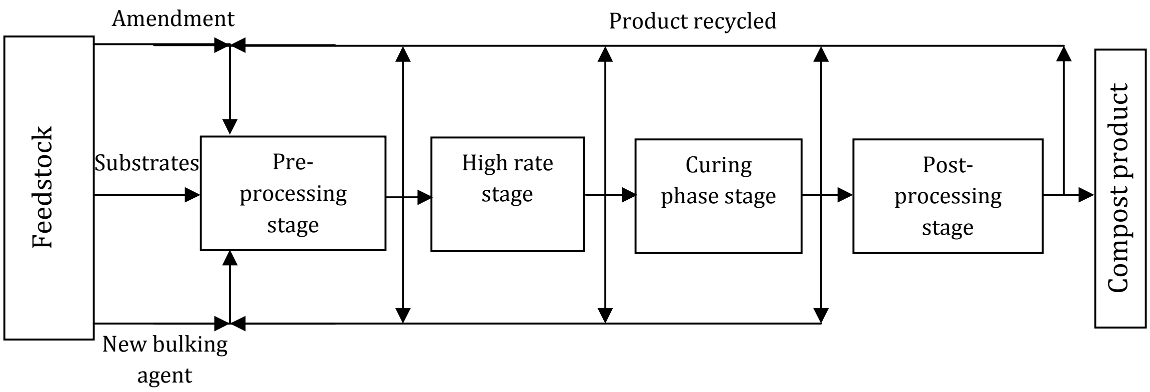

Figure 1.5: Generalized process diagram for composting showing inputs of feed substrates, amendments and bulking agents (Haug, 1993).

Figure 1.3 shows the typical scheme of a MBT plant treating MSW (similar scheme would present the process for treating OFMSW) including detailed operations implied in the pre-processing stage that in these plants is equivalent to the mechanical treatment.

After non-compostable materials removal, the remaining organic fraction (substrate) needs to be structured by adding bulking agent, which is generally organic and composed by wood chips, pallets refuses and pruning waste (Larsen and McCartney, 2000; Wong and Fang, 2000). Occasionally inorganic materials are used as bulking agent such as small perforated plastic cylinders. Adding bulking agent the matrix would reach the optimum physical and chemical conditions for composting process, in terms of structure, porosity or free air space, moisture content, nutrients and C/N ratio. If it is necessary amendment is also mixed with substrate and bulking agent. Amendments can be classified into structural or energy. A structural amendment is an organic material added to reduce bulk weight and increase air voids allowing for proper aeration, as sawdust or straw. An energy or fuel amendment is an organic material added to increase the quantity of biodegradable organics in the mixture and, thereby, increase the energy content of the mixture, as manure and yard waste (Haug, 1993). This is often achieved by the use of other wastes as co-substrates (Ruggieri et al., 2008).

This is a critical phase since the good process performance depends of the initial matrix properties and if they are not appropriate, the process cannot even begin.

II. High-rate stage decomposition

This stage is also called decomposition phase because during this stage occurs the decomposition of complex biodegradable organic matter into simpler organic and inorganic molecules by microorganisms (Hsu and Lo, 1999) and it is characterized by high oxygen uptake rates.

After forming the composting matrix (pre-processing stage) the materials are at room temperature. When decomposition starts, as result of microorganisms' metabolic activity, heat is produced since these are exothermic biological processes (Haug, 1993). The first phase of high-rate stage is known as the mesophilic stage where temperatures raise to 45°C and mesophilic populations are dominant throughout the composting mass. These microorganisms use available oxygen to oxidize carbon from the composting matrix to obtain energy and organic materials to build new biomass and in this process they produce carbon dioxide (CO_2) and water. While heat is produced, the matrix temperature raises and when it is over 45°C mesophilic microorganisms die or become dormant (awaiting more suitable conditions). Accordingly, at this point thermophilic microorganisms become active, consuming the materials that are readily available and multiplying rapidly replacing mesophilics in most sections of the material. Thermophilics generate greater quantities of heat than mesophilics and temperature can reach values up to 70°C. This second phase is known as thermophilic phase and it is considered to be the most important for the material pathogen inactivation and seed destruction (The U.S. Environmental Protection Agency, 1995). To meet the Environmental Protection Agency regulations, aerated static piles and in-vessel systems must be maintained at a minimum operating temperature of 55°C for at least 3 days and windrow piles must be maintained at a minimum operating temperature of 55^{o}C for 15 days or longer (considering at least 5 turnings during this period). Excessive composting matrix temperatures (over 70^{o}C) must be controlled because of its ignition risk, the limitation of microbiological activity and the ammonia (NH_3) emissions that are enhanced by high temperature and turnings (Soliva, 2001; Pagans et al., 2006).

When sources of readily available carbon are depleted, thermophilic activity decreases and temperature drops. Mesophiles begin to dominate the process once again until all readily available energy sources have been consumed.

This stage may take composting facilities between a few weeks and months depending on the materials to be composted and the system used.

III. Curing stage

At the end of the high-rate stage, due to the slow microbial activity, temperatures start to decrease till 40 °C and the curing stage begins. This stage provides the time required for the degradation of the more refractory compounds and texture of the material becomes dry and powdery (Haug, 1993). At the end of this stage the material is considered stabilized or mature, which is the reason to also know this stage as maturation stage (Haug, 1993). Finally the material reaches room temperatures and macroorganisms may appear. This stage is important because is when nitrogen obtained from dead biomas is incorporated into high molecular weight compounds that are resistant to the microbial decomposition, forming the nitrogen reserve (Tchobanoglous et al., 1994; Haug, 1993). This stage is less demanding in terms of oxygen and humidity than the high-rate stage and results in a net loss of total organic matter and inorganic constituents. The composting system used in the curing stage is usually an open windrow larger than the used in the previous stage with lower turning frequency and fewer aeration and homogenization requirements. The main products of the composting process are fully mineralized such as CO_2, H_2O, mineral ions, ash and stabilized organic matter (i.e. humic substances) (Haug, 1993).

IV. Post-processing stages

As high is the quality of initial feedstock as high will be the quality of the final compost (Haug, 1993). When treating heterogeneous substrates, with high percentage of inorganic materials or non-compostable matter, more work is needed to carry out the process and obtain final quality compost. Previous pre-processing stage is not fully effective and consequently some non-compostable or inert materials are not separated in this stage. Since principal aim of post-processing is to obtain high quality final compost, the removal of refuse materials and remaining fraction of bulking agent is carried out in this stage. Trommel screening and ballistic separators are usually used for this purpose (Haug, 1993). Physicochemical characteristics of the compost vary depending on the nature of the original material to be composted, the composting process conditions, composting technology and the decomposition magnitude. Some characteristics that differentiate compost from other organic materials are (Tchobanoglous, 1994): i) brown colour, sometimes dark brown; ii) low C/N ratio; iii) cation exchange and water absorption high capacities; and iv) low respiration activities.

1.6.1.2 Composting technologies

There are different technologies used in composting to treat solid waste. The most commonly full-scale composting methods currently employed are: i) Passive piles; ii) Turned windrows; iii) Aerated static piles; and iv) In-vessel systems.

- **Passive piles**

Passive piles, as the name suggests, are piles that remain static without alteration and may occasionally be turned during the process (EPA, 1997). Passive piles have a delta or trapezoidal cross section with length exceeding width and height. For most materials the ideal height is between 1.5 to 2 meters with a width of 4.3 to 4.8 meters. Although this method is simple and generally effective, it is not applicable under all conditions or for all types of waste. Composting under these conditions is very slow and it is satisfactory or sufficient for materials that are relatively uniform with respect to particle size. Passive piles can theoretically be used for composting vegetable waste or MSW. In the case of MSW or large quantities of vegetable waste, odor may be a problem (EPA, 1997).

Passive piles require low investment and technology. The piles should be constructed so they are large enough to conserve sufficient heat but not so large that they overheat (EPA, 1997). Passive piles have the advantage of low operating costs, however the time required for obtaining the finished product is much longer than it is for more intensive composting methodologies. For more intensive techniques, a finished product is obtained within a few weeks to a few months, whereas for passive piles over a year is needed for the composting process to be complete. In addition, the minimal turning of piles results in formation of anaerobic conditions and thus odor emissions.

- **Turned windrow**

Turned windrows are elongated composting piles that are turned frequently to maintain aerobic composting conditions and it is considered as a dynamic and extensive system. The frequent turning promotes uniform decomposition of the materials as cooler outer layers of the compost pile are moved to inner layers where the material is exposed to high temperatures and intensive microbial activity. This method achieves a finished product in 3 months to a year (UConn CES, 1989).

As with passive piles, the recommended height for turned windrows is between 1.5 and 1.8 meters width between 2.4 and 3.6 meters (Saña and Soliva, 1987; CRS, 1989). However, the windrow height varies depending on the materials being composted, the season, the region where it is composted, the tendency of the material to compress and the type of machinery used. The width of the windrow is usually twice its height.

- **Forced aerated static piles**

Aerated static pile composting implies forcing or pulling air through a trapezoidal compost pile, which minimizes the need for turning and it is considered as static and extensive system. To better manage odors, piles are often covered with a textile layer.

On average aerated piles are 2 to 2.6 meters in height. To facilitate aeration, wood chips are placed over the aeration pipes at the base of the windrow (Rynk et al., 1992). The composting process using this method takes 3 to 6 months.

An alternative technology which has been implemented in Spain in the last years is the aerated trench. Waste is confined in between two walls, thus pile sections become rectangular and plant capacity increases. Forced aeration is supplied to the trench and no turning is applied to the material.

- **Channels system**

Channels system is a dynamic and intensive system that consists on many parallel channels where initial matrix is led on one side of the channel and the final composted material is obtained on the other side. Channels have a rectangular cross section and a forced aeration system through the matrix. The material in these systems is frequently turned while it moves along the length of the channel. The turning frequency is established depending on the material, and the time required to make the final high-rate stage composting process coincide to the end of the channel length.

- **Tunnel system reactors**

Tunnel system is a high-technology method in which the composting process is conducted and controlled within a fully enclosed structure and it is considered as static and intensive system. Tunnels' dimensions are variable but commonly they are around 4 meters height, from 5 to 6 meters width and around to 20 meters length. Composting parameters such as aeration, moisture and temperature are mechanically controlled. Composting materials are usually retained in the system for 6 to 28 days and then cured in windrows for 1 o 2 months, but the range of time may vary depending on the composition of the material (EPA, 1997).

1.6.1.3 Principal process variables

Several parameters such as temperature, oxygen and moisture content are often selected as control variables of the composting process along with other physical, chemical, biochemical or microbiological properties such as enzymatic activity or respiration indices (Diaz et al., 2002, Saviozzi et al., 2004; Barrena et al., 2005; Mohee and Mudhoo, 2005; Tiquia, 2005).

- **Temperature**

When aeration is controlled, the temperature in the compost pile is determined by the level of activity of the heat-generating microorganisms (Richard, 1992a). The effective temperature in the process is between 45 and 59°C (Richard, 1992b). Temperatures below 20°C, inhibit the activity of microorganisms lowering their decomposition capacity (Strom, 1985; Finstein et al, 1986). The regulatory machinery of cell metabolism is affected by temperatures below the minimum requirement for a group of organisms. A typical temperature profile of a composting process is shown in Figure 1.6 along with the active microorganisms in each temperature range. Microorganisms tend to decompose materials most efficiently within their temperature tolerance range. Although composting occurs within a range of temperatures, the optimum temperature range of thermophilic microorganisms is preferred for two reasons: it promotes rapid composting and it destroys pathogens and weed seeds. The rates of microbial decomposition therefore increase when the temperature rises to an absolute upper limit. For this reason, it is important to maintain high temperature ranges without reaching process inhibition during the decomposition phase (Richard, 1992a; Rynk et al., 1992). As shown in Figure 1.6 at the beginning of the composting process, materials are at room temperature and then, as explained above, temperature gradually begins to rise due to the activity of microorganisms. But this only occurs if proper feeding conditions for aerobic microorganisms are present, such as an adequate porosity that allows oxygen diffusion and appropriate moisture contents for the aerobic activity, amongst others. As can be seen in this figure, psychrophilic and mesophilic microorganisms are present throughout the process and thermophilic microorganisms are active at higher temperatures. As explained before, the populations of microorganisms change from mesophiles to thermophiles when temperatures raise over 45°C. The activity of thermophiles generates greater quantities of heat than that of mesophiles leading to higher temperatures in the composting mass (Figure 1.6). Thermophilic microorganisms continue decomposing as long as energy and nutrients are plentiful. When sources of energy and nutrients become depleted, thermophilic microorganisms die. As the temperature drops mesophilic microorganisms become active once again and consume the remaining nutrients (Richard, 1992a; Rynk et al., 1992). If temperature profile results different to those expected for a correct performance (Figure 1.6), operators must take some corrective actions controlling the feedstock material and process conditions. An adequate feed conditioning and control of the process variables are required for a correct process development.

- **pH**

The optimal pH for a biological process is normally in the range of 6 to 7.5 for bacteria and 5.5 to 8 for fungi (Boyd, 1984). If the pH is below 6, microorganisms, particularly bacteria, die off and decomposition slows down (Wiley, 1956). If the pH rises above 9, ammonium becomes ammonia, which is toxic for microorganisms (Rynk et al., 1992). Like temperature, pH follows a typical profile throughout the composting process. As shown in Figure 1.6, most of the decomposition phase occurs at a pH between 5.5 and 8 (Rynk et al., 1992, Gray et al., 1971a). In the first stage these acids tend to accumulate and thus the pH decreases promoting the fungal bloom and the degradation of the cellulose and lignin. After that, a gradual increase in alkalinity occurs as a result of the phenolic and carboxyl group's decomposition. Likewise an abrupt rise in pH level might promote ammonia release, by influencing the $NH_3 - NH_4^+$ equilibrium in spite of its direct influence on biological activity (Liang et al., 2006).

If the system became anaerobic, the acid accumulation could decrease the pH level under 4 and thus limit the microbiological activity. If this happens the operator must aerate the system by turnings or pumping air to return the system to aerobic conditions.

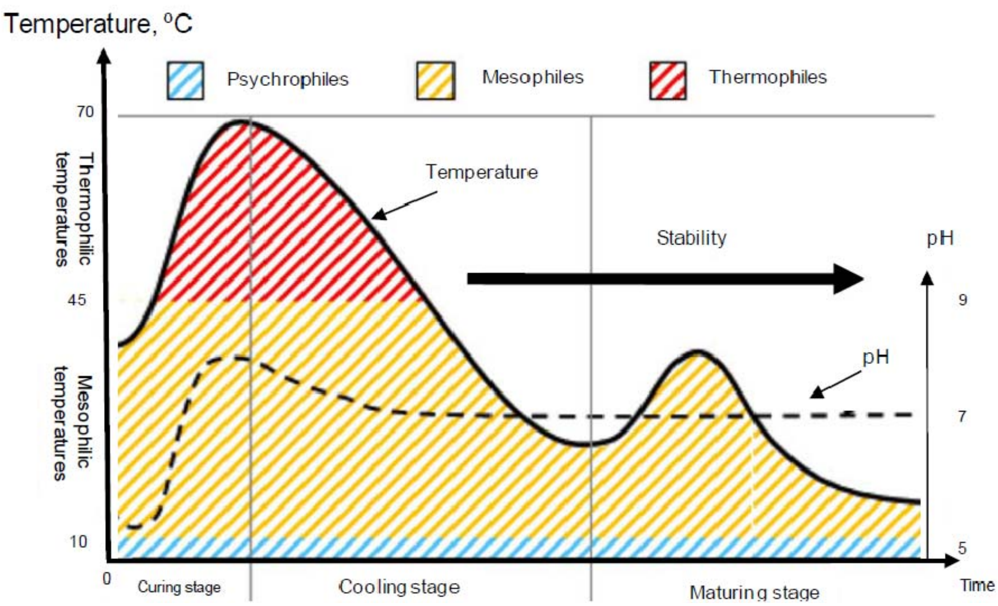

Figure 1.6 Typical temperature and pH profiles through the composting process

- **Nutrients and C/N content**

Microorganisms require specific nutrient balances in an available form, proportion and proper concentration to perform composting efficiently. The essential nutrients that microorganisms require in large quantities include carbon (C), nitrogen (N), phosphorus (P) and potassium (K). Chemoheterotrophic microorganisms require carbon as energy source, C and N to synthesize proteins, build cells and to reproduce. P and K are necessary for the reproduction of cells and for metabolism. In composting systems, C and N are usually the limiting factors for efficient decomposition (Richard, 1992a).

An initial C/N ratio of 15 to 30 is recommended as an optimum for composting materials (Haug, 1993). Lower values will promote N losses in the form of NH_3 while higher values can slow down the composting process due to lack of nitrogen to support microbiological activity. Some substrates may require additional nutrients to sustain rapid microbial growth rates. Likewise, many have a high N concentration as different types of manure and sewage sludge, while other cellulose materials such as woodchips, sawdust, leaves, etc. have a high C content. Operators can control the C/N ratio by co-composting different substrates to compensate the ratio, by adding one or the other of these if necessary or other sources of N or C. However, it is important to point out that the bioavailability of nitrogen and carbon should be considered in the calculation of the C/N ratio. While nitrogen present in the majority of wastes is mainly found in biodegradable forms, carbon can be present in recalcitrant form (Zhang et al., 2004; Komilis, 2006; Sánchez, 2007). The proportion of readily, moderately and slowly biodegradable organic matter will influence the process kinetics.

An adequate concentration of phosphorous, potassium and trace minerals i.e. calcium, iron, copper, etc, is also necessary for the microbial metabolism (Boyd, 1984). Although these nutrients are present in sufficient quantities, they may be present in a form, which makes them unavailable for some microorganisms (Gray et al., 1971b).

- **Oxygen and Aeration**

The main functions of aeration in composting processes are to supply the oxygen needed by aerobic microorganisms, to facilitate the regulation of excess moisture by evaporation, to remove heat to control process temperatures and to remove CO_2 and NH_3 (Haug, 1993; Soliva, 2001; Richard et al., 2004). An oxygen concentration of 10 to 15% is considered adequate in a composting matrix, although a minimum concentration of 5% can be sufficient for microbial activity.

With very wet substrates the requirement for moisture removal will tend to govern, whereas the requirement for heat removal will become dominant if substrates with high easily biodegradable organic matter content are treated. The air supplied can be by natural draft ventilation or inducted by turnings or mechanical blowers.

Monitoring the oxygen content within the composting matrix allows operators to control the process by aerations feedbacks. Composting first stage is characterized by high oxygen consumption, but in the maturation stage lower oxygen consumption is present as the microorganisms are less active. For that reason, when evaluating the performance of the process or maturity of a final material, respirometric techniques that measure consumed O_2 are increasingly used as indicators of the biological activity in the process. Respirometric techniques allow to measure oxygen uptake rate (OUR) (g O_2 kg^{-1} OM h^{-1}) or cumulative O_2 consumption (g O_2 kg^{-1} OM^{-1}) (Barrena et al., 2006a). According to the literature (Adani et al., 2004; California Composting Quality Council, 2001), materials with respiration index values between 0.5 and 1.5 g O_2 kg^{-1} OM^{-1} are considered stable, while respiration index values greater than 1.5 g O_2 kg^{-1} OM^{-1} correspond to unstable materials.

Already existing and new developed respirometric techniques to control and monitor composting processes are described in Section 1.7.

- **Moisture**

Microorganisms require moisture to absorb nutrients, metabolize and produce new cells because they can only use organic molecules if they are dissolved in water. Under conditions of low humidity, the composting process slows down. High moisture conditions can reduce and even stop the transfer of oxygen. Microorganisms also produce water as part of the decomposition process. Water is removed via aeration or evaporation (Gray et al., 1971a). The recommended range of moisture during the process is between 40-60%. The moisture content is usually maintained at this level by watering with leachate during the decomposition stage (high-rate phase) and rainfall water or other in the maturation stage (curing phase) to avoid contamination of the sanitized material if leachate was used (Haug, 1993). Below 20% humidity, very few bacteria are active (Haug, 1980).

- **Particle size and air filled porosity**

Particle size significantly affects the composting process. In general, small particles have a greater surface area to volume ratio. This means that much of the particle surface is exposed directly to decomposition by the microorganisms in the early composting stages (Gray et al. 197la). The optimum particle size is that providing enough surface area for rapid microbial activity, but also enough void space to allow air to circulate for microbial respiration and material decomposition (EPA, 1994). The particles should be large enough to prevent compaction, thus excluding the oxygen in the voids. For yard trimmings or municipal solid wastes, the desired combination of void space and surface area can be achieved by particle size reduction.

Air filled porosity (AFP) is defined as the ratio of air volume to total volume of the sample (Haug, 1993). This parameter depends on particle size, the structure of the particle and water content (Agnew and Leonard, 2003). There is a wide range of AFP recommended optimum values (Ruggieri et al., 2009) and all seem to be dependent on the type of material to be composted; as 25-30% for Jeris and Reagan (1973) and Haug (1993), and a range between 30-60% for Annan and White (1998) and Ruggieri et al. (2008), among other authors.

1.6.2 Anaerobic Digestion

Anaerobic digestion is a biological process that has been used for over 100 years to stabilize materials such as wastewater sludge, municipal solid waste and other industrial refuses (Burke, 2001; Ferrer et al., 2008). Anaerobic digestion is a microbiological process that occurs naturally in the environment, for example lagoons or in the stomach of ruminants. Under anaerobic conditions, organic materials are biodegraded through a complex microbiological process leading to the productions of a more stabilized organic material and biogas composed mainly of methane (CH_4) and carbon dioxide (CO_2) content that can be used for electricity generation (Lissens et al., 2001).

The technological applications of this process in bioreactors gives an appropriate solution for the treatment of organic wastes such as municipal solid wastes, by-products such as sewage sludge and other industrial refuses (Burke, 2001; Ferrer et al., 2008). The effluent of bioreactors can be used as an organic fertilizer as long as it meets the current legislation for land application. Habitually anaerobic digestion processes have to be complemented with a subsequent composting process to treat the effluent and completely stabilize organic matter, since not all organic matter biodegradable under aerobic conditions can be degraded in an anaerobic environment. When anaerobic digestion process is well implemented, performed and a high grade of stabilization is achieved the composting process can be substituted by a drying process (thermal or mechanical).

In recent years, anaerobic digestion has become an interesting technology because it provides a clean fuel from a renewable feedstock and thus leads to the partial replacement of fossil fuels for energy production (Adani et al., 2001; Chynoweth et al., 2001). In addition investors in biogas technologies have received investment subsides or fiscal instruments as incentives in the last years as consequence of the implementation of European Directives establishing national targets for energy from renewable sources (Directive 2009/28/EC; Directive 2006/12/EC).

1.6.2.1 Description of the process

The process takes place in an enclosed reactor on absence of oxygen, where degradation of organic materials occurs through four consecutive stages, namely hydrolysis, acidogenesis, acetogenesis and methanogenesis (Figure 1.7).

- **Hydrolysis**

In the first stage, facultative hydrolytic bacteria using extracellular enzymes hydrolyze and fragment undissolved particles and complex molecules (proteins, carbohydrates and lipids) to soluble and simpler compounds (amino acids, sugars, long chain fatty acids, alcohols, CO_2 and H_2) (Pavlostathis and Giraldo-Gómez, 1991; Ponsá et al., 2008).

- **Acidogenesis**

This phase involves the transformation of hydrolyzed compounds into volatile fatty acids (mainly acetate, propionate and butyrate), alcohols and other products including ammonia, hydrogen and carbon dioxide. The bacteria in this stage are facultative and proteolytic bacteria, which are abundant in nature. Acidogenic bacteria are fast growing compared to other groups used in anaerobic digestion (Ponsá et al., 2008).

- **Acetogenesis**

In acetogenesis, alcohols, fatty acids and aromatic compounds are degraded to produce acetic acid, carbon dioxide and hydrogen that will be used by methanogenic bacteria in the final anaerobic digestion stage (Archer, 1983; Ponsá et al., 2008).

- **Methanogenesis**

During methanogenesis, anaerobic methanogenic microorganisms produce methane from acetate, carbon dioxide and hydrogen (Madigan et al., 1998). Considering that methanogenic bacteria are slow growing compared to other hydrolytic-acidogenic bacteria, special attention to hydraulic retention time must be given in order to prevent methanogens wash-out (Ponsá et al., 2008).

1.6.2.2 Anaerobic digestion technologies

Different classifications of anaerobic digestion technologies and systems can be done depending on the: i) number of stages: single-stage or multistage systems; ii) dry matter content: dry or wet systems; and iii) operational temperature: psychrophilic, mesophilic or thermophilic systems.

I. Number of stages

Most anaerobic systems consist of a single-stage digester, which means that all stages take place in the same reactor. In such situation, environmental conditions (i.e. pH, redox potential, temperature, etc.) may favor the development of certain group of bacteria, but it is important to maintain equilibrium to ensure a balanced degradation process. For this reason, the control of environmental conditions is a key factor, especially regarding methanogenic microorganisms, which are strict anaerobes, with the lowest growth rate and are the most sensitive to sudden changes in environmental conditions.

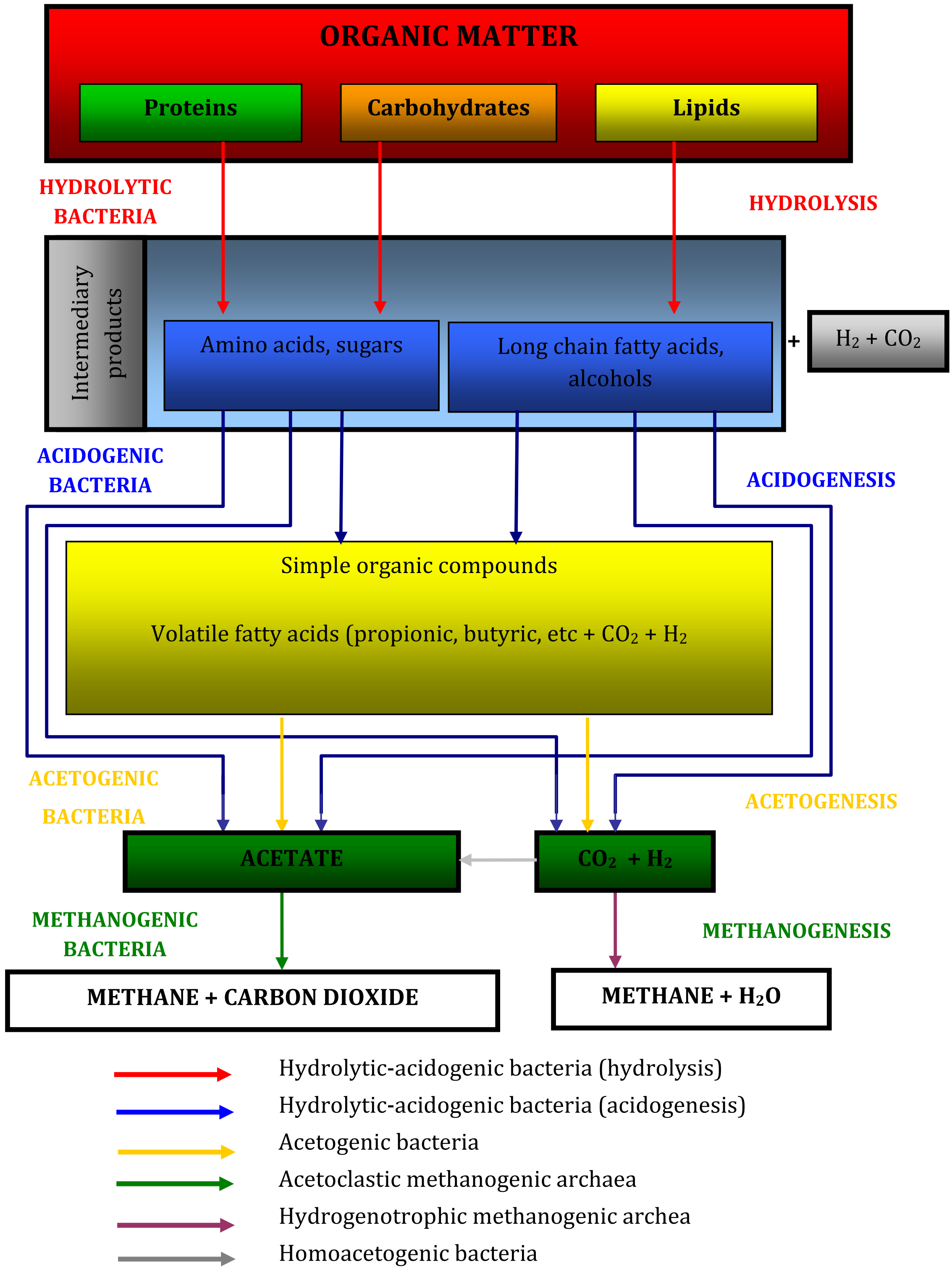

Figure 1.7. Stages and bacterial populations involved in anaerobic digestion (Pavlostathis and Giraldo-Gómez, 1991).

Some plants have implemented two-stage systems in which hydrolysis-acidogenesis and methanogenesis are separated. This allows for different environmental conditions in each reactor promoting the development of different microbial population in each reactor, which is reported to guarantee more stable process performance (Pavan et al., 1999). The high capital cost of installing multistage systems has resulted in a reduction in the number of these types of facilities. Currently, the installed capacity of multistage systems in European countries is 7% (De Baere and Mattheeuws, 2009). According to the last reference, at the end of 2010, multistage systems will represent only 2% of the European capacity, thus most of capacity for anaerobic digestion will be derived from single stage systems.

II. Dry matter content

Regarding dry matter content two different technologies can be considered: wet and dry processes.

In wet processes the dry matter content of the feeding and in the digester is maintained between 4-10% by diluting the feedstock with water (Hartmann and Ahring, 2005). Some wet processes adjust the feed dry matter content by co-digestion of materials with different dry solid content, for example conventional slurry systems usually function by co-digestion with animal manure, OFMSW, MSW or other feedstock to a final value around 10% (Braber, 1995).

The dry matter content for dry process systems is between 20-40% and no dilution is needed for feedings since normally raw materials fed such as OFMSW, MSW or other feedstock are comprised in this range (Poggi-Varaldo, 1997).

Between 2000 and 2005 a large number of full-scale wet treatment plants were installed in European countries, but since 2005, more dry anaerobic digestion plants were installed (De Baere and Mattheeuws, 2009). In recent years, dry anaerobic digestion has provided nearly 54% of the European capacity while wet anaerobic digestion represents 46% of total current capacity (De Baere and Mattheeuws, 2009).

III. Operational temperature

There are three conventional operational temperature levels for anaerobic digesters: psychrophilic (15-19°C), mesophilic (20-45°C) or thermophilic (45-70°C).

Anaerobic microorganisms can grow at psychrophilic temperatures (15-19°C). However, low biogas production is achieved for anaerobic digestion at these temperatures and thus industrial anaerobic digestion processes does not normally operate in the psychrophilic range (Lettinga, 1995).

In mesophilic systems, anaerobic digestion takes place between 20°-45°C and operates optimally between 37-41°C (Song et al., 2004).

Finally for optimal thermophilic processes operational temperature must be between 50-52°C, but in some systems it is possible to reach temperatures as high as 70°C (Song et al., 2004). Usually the range of temperatures considered for thermophilic systems is between 50 and 65°C (Nopharatana et al., 1998).

In general, the higher temperature, the faster the reaction rate and consequently lower retention time and volume required.

Until the early nineties, all plants operated under mesophilic conditions. Nowadays, mesophilic systems continue to be used more than thermophilic systems, since mesophilic bacteria are more tolerant to changes in environmental conditions than thermophilic bacteria. However, operating at higher temperatures facilitates greater hygienisation of the materials and higher gas production rates (Huyard et al., 2000). In 2004, 77% of the treatment capacity in Europe was provided by mesophilic plants (De Baere and Mattheeuws, 2009). However, a large number of thermophilic plants were built in 2005 and 2006 and it was estimated that between 2006 and 2010, 41% of the plants in Europe would operate under thermophilic conditions (De Baere and Mattheeuws, 2009).

As occurs for composting process, for anaerobic digestion it is also necessary to pre-process some feedstock such as OFMSW or MSW to increase its digestibility. The most common pre-treatment methods are sorting and particle size reduction. The same pre-treatment operations that are used for composting are generally used previous to anaerobic digestion.

In wet anaerobic digestion, depending on the quality and stabilization of the material, it can either be applied directly to farmland or may be separated into solid and liquid phases. Solids can be composted and the liquid phase can be treated in a wastewater treatment plant.

Wastes treated by dry process are sometimes composted with other farm or MSW materials or may be centrifuged and then composted (Braber, 1995).

1.6.2.3 Principal process variables

As in composting processes, there are some main operating parameters in anaerobic digestion systems. These parameters determine the microbial activity and thus influence/affect the anaerobic degradation efficiency. Process parameters can be split into the so–called environmental parameters (pH, redox potential, alkalinity, concentration and nature of organic and inorganic compounds, C/N ratio and C/P ratio) and operating parameters (temperature, retention time, organic loading rate and mixing).

As mentioned before, anaerobic biological activity can be developed for temperatures ranging from 5 to 70°C. However, there are generally two temperature ranges used at the full-scale industrial level providing optimum digestion conditions for methane production: the mesophilic and thermophilic ranges. The mesophilic range is between 20-40°C but the optimum temperature is considered to be 30-35°C. The thermophilic temperature range is between 50-65°C (Cecchi et al., 1993), but the processes are normally undertaken at 50-55°C. It is of special importance to keep constant temperature in the digesters and avoid rapid changes of temperature since it could lead to a thermal shock to microorganisms and a consequent stability loss.

The pH has a large influence on the biodegradation process because it affects the process velocity and the selectivity of the microorganisms that can be developed in the medium (Ratledge, 1991). The optimum operational ranges of pH have been widely studied. pH between 6.5 and 7.5 is considered an optimum and stable value for anaerobic digestion (APAT, 2005) but no general consensus on this issue exists. In literature, different ranges of optimum pH for hydrolytic and acidogenic bacteria are established. Flotats (2000) determined that a pH around 7-7.2 was the optimal, while others considered that optimal pH was slightly acid, between 5.5 a 6.5 (Zoetemeyer et al., 1982; Joubert and Britz, 1986; Kisaalita et al., 1987; Yu et al., 2003). However all authors agree that methanogens in particular are very sensitive to acidic conditions and unsuitable pH levels can inhibit their growth (Ratledge, 1991).

Alkalinity is a direct measure of the buffering capacity of the digester. The optimum range of alkalinity is between 1.5-3 g $CaCO_3$ L^{-1}, but to really ensure the digester stability is recommended to keep alkalinity up to 2.5 g $CaCO_3$ L^{-1} (Fannin, 1987). Alkalinity allows for indirect detection of digester acidification. A redox potential under -300 mV is recommended since it would indicate a reductive atmosphere in the system.

The optimal C/N ratio in anaerobic digestion is approximately 30. However in a range of 15-30 it is accepted. A high C/N ratio is an indicator of rapid consumption of nitrogen by methanogens and results in lower reaction rates and lower gas production while a low C/N ratio may cause inhibition, due to the accumulation of ammonia and pH values exceeding 8.5, which is toxic for methanogenic bacteria (Boone et al., 1987). To achieve an optimum C/N ratio, co-digestion of different materials, for example combining OFMSW with sewage or animal manure may be done.

Volatile fatty acids (VFA) concentration in the digester is one of the most important parameters for anaerobic digestion reactors because instability of the system is often marked by a rapid increase in the VFA concentration, which signals methanogenic phase inhibition (Ianotti and Fisher, 1984). According to Angelidaki (1992) carbohydrate and protein hydrolysis are limited by high VFA concentrations. VFAs are expressed as concentration of acetic acid (AcOH) in the feedstock and, depending on the type of material treated, this value can range from 200 to 2000 mg AcOH L^{-1}.

The retention time for completion of the anaerobic digestion reactions varies in relation to feedstock composition, anaerobic digestion technology and process temperature. The retention time for biomass treated using mesophilic digestion ranges from 10 to 40 days, while biomass treated in thermophilic reactors requires a minimum of 14 days (Bello-Mendoza and Shararrat, 1999).

Some experiments have shown that in order to operate smoothly an adequate degree of mixing in the reactor must be achieved (Campos, 2001). The purpose of mixing is to blend the fresh material with the digestate that contains microorganisms. The mixture reduces the phenomena of matter transfer limitation of substrate or nutrients within the liquid phase to the microbes. A 60% reduction in the degree of mixing may cause as much as a 50% decrease in treatment efficiency (Bello-Mendoza and Shararrat, 1999). Mixing systems vary in terms of reactor type and solid content in the digester (Campos, 2001). However an excessive agitation in the reactor could also lead to a process failure, since the flakes composed by the aggregation of microorganisms (mainly methanogens) could result broken and inefficient (Kim et al., 2002).

Biogas is the most important and valuable product obtained during the anaerobic digestion process. This product is mainly composed of methane and CO_2, but inert gases (N_2) and sulfur compounds (H_2S) are also present but at lower concentrations. Habitually, 100 to 200 m^3 of biogas is produced per ton of OFMSW digested (Braber, 1995). The composition of wastes affects the yield and biogas quality as well as the digestate quality. Typical biogas compositions are presented in Table 1.2.

Table 1.2. Composition of biogas produced from anaerobic digestion of different wastes.

Component	Organic Wastes	Sewage Sludge	Industrial Wastes	Biogas from Landfill
CH_4	50-80%	50-80%	50-70%	45-65%
CO_2	20-50%	20-50%	30-50%	34-55%
H_2O	saturated	saturated	saturated	Saturated
H_2	0-2%	0-5%	0-2%	0-1%
H_2S	100-700 ppm	0-1%	0-8%	0,5-100 ppm
NH_3	traces	traces	traces	Traces
CO	0-1%	0-1%	0-1%	Traces
N_2	0-1%	0-3%	0-1%	0-20%
O_2	0-1%	0-1%	0-1%	0-5%
Organic Compounds	traces	traces	traces	5 ppm

Source: Muñoz-Valero et al., 1987

1.7 Introduction to biological indices and their uses

The analysis of waste treatment efficiency requires a reliable measure of the biodegradable organic matter content of organic wastes and thus, their stability defined as the extent to which readily biodegradable organic matter has been decomposed (Lasaridi and Stentiford, 1998). This measure would permit the evaluation of current working plants, the improvement of the biological treatment process, the design of optimized facilities and the potential environmental impact assessment of the final products.

On the one hand, some biochemical parameters such as volatile solids (VS) (equivalent to organic matter), total and dissolved organic carbon (TOC, DOC) and chemical oxygen demand (COD) have been used to monitor the evolution of biological processes (Papadimitriou and Balis, 1996; Komilis and Ham, 2003; Fontanive et al., 2004; Ros et al., 2006). These parameters lack precision when are determined on heterogeneous materials such as MSW or OFMSW because of the presence of non-biodegradable volatile or oxidizable materials. On the other hand, several biological and biochemical indices such as ATP content, enzyme activity and total bacterial counts among others (Tiquia, 2005) are particularly useful since they can relate biological processes to metabolic activity.

However, aerobic respirometric techniques which determine CO_2 production or O_2 consumption and methanogenic activity assays which determine biogas or methane production of a given sample have been widely proposed and used (Ianotti et al., 1993; Scaglia et al., 2000; Ligthart and Nieman, 2002; Adani et al., 2004; Hansen et al., 2004; Tremier et al., 2005; Barrena et al., 2006a). These assays will give as result a direct measure of the biological activity that can be related to the biodegradability grade of the sample. Nevertheless, there is not a general consensus about the key assay parameters, such as the use of an inoculum, the amount of sample to be used and its preparation and structuration, the assay temperature (mesophilic or thermophilic) and the test duration. Even the expression of the results (oxygen uptake rate or cumulative consumption) and the units (dry or volatile solids basis) are different among the tests published (Barrena et al., 2006a).

For example considering the temperature, when choosing the assay optimum value, it is necessary to take into account that this variable is directly related to the biological activity rate. Even, sometimes, temperature is not controlled and varies throughout the assay. Many authors have reported different optimum temperatures for maximum biological activity determination through the composting process evolution (Lasaridi et al., 1996; Barrena et al., 2005).

Notwithstanding the amount and quality of the work referred to, there is no consensus for biodegradable organic matter content and stability measurements within the research community in the solid waste treatment field (Barrena et al., 2006a).

Some aerobic respirometric techniques and anaerobic activity assays have been proposed in national regulations by some European countries such as Germany (Federal Government of Germany, 2001), Italy (Favoino, 2006) and England and Wales (Godley et al., 2005), as well as they have been included in the European legislation drafts (European Commission, 2001).

1.7.1 Aerobic respirometric techniques

Methods based in O_2 consumption can be classified into dynamic and static methods depending on if there is a continuous air/oxygen supply or not (Adani et al., 2001). In addition they can also be classified into those that determine the oxygen uptake rate and those that measure cumulative oxygen consumption during a fixed time or if they measure O_2 consumption or CO_2 production (Barrena, 2006).

Dynamic methodologies have some advantages over static methods. The most significant are the increasing of oxygen diffusion rate to liquid phase (which is the oxygen available for microorganisms) and consequently reducing mass transfer limitations and the possibility of obtaining a continuous profile of the oxygen consumption or carbon dioxide production during the whole biodegradation process (Adani et al., 2003; Tremier et al., 2005; Barrena et al., 2006a). The profile and all the indices that are inferred from this profile permit a deeper knowledge and understanding of the characteristics of the sample studied in term of biodegradable organic matter content and stability.

Nevertheless, static respirometric indices (SRI) can be used as an indicators or first approximation of the potential biological activity of an organic material, being of great utility because of its rapid determination and its practical utilization at waste treatment facilities where longer and more complex methodologies such as dynamic techniques, are not possible to determine (Barrena, 2006).

Oxygen rate or oxygen uptake rates can be measured directly by sensors or by using pressure gauge or electrolytic respirometers, as well as measuring the variation of oxygen concentration by gas chromatography or oxygen electrodes. In addition, some techniques measure the oxygen in the gas phase while others measure the oxygen dissolved in aqueous solutions.

Determinations of carbon dioxide production can be obtained following simple methodologies, usually cheap and that have already been widely used in laboratories. For example a methodology frequently used consists on bubbling the outlet gas containing CO_2 produced in alkaline solutions in order to fix the CO_2. Solvita ® is a common industrial method based on the last principle. In addition there are some other complex methods for CO_2 determinations based on colorimetric or chromatographic techniques (California Compost quality Council, 2001; Brewer and Sullivan, 2003).

However, these methodologies present some important limitations that lead to think that they are not suitable indices for measuring biodegradability or stability. The main limitations are: i) the no distinction between the carbon dioxide produced aerobically or anaerobically; ii) the solubility of carbon dioxide in water and its dependence on the pH; and iii) the quantification of carbon dioxide produced by organic matter chemical oxidation (Gea et al., 2004).

These methodologies assume that the ratio oxygen consumed to carbon dioxide produced may be 1, but experimentally this ratio varies during the biodegradation process (Lasaridi and Stentiford, 1998).

There is a wide range of commercial equipment to measure aerobic respiration indices. For example the most used are: Costech, Oxytop and Micro-Oxymax among others. These equipments typically need a frequent maintenance and calibration and they are really expensive. There are many works in literature describing different methodologies to determine aerobic respiration indices. They have been also considered in the legislation of some European countries as well as they were proposed in European legislation drafts (European Commission, 2001). The main methodologies are summarized in Table 1.3.

Iannotti et al. (1993) measured changes in O_2 concentration in the head space of a closed flask containing a solid sample of known volume and mass at determined temperature and state and atmospheric pressure. The decline in O_2 content in the air is monitored with an O_2 electrode.

Table 1.3. Summary of already published aerobic methodologies for index determinations.

Index	Name	Reference	Type	Units	Sample				Assay conditions	
					State	Weight	Sieveing	Moisture	Time	Temperature
O_2 uptake	O_2 uptake	Iannotti et al., (1993)	Static	g O_2 kg OM^{-1}	Solid	60 g	< 9.5 mm	50-55% w/w	16 h incubation + 1 h assay	37°C
SOUR	specific oxygen uptake rate	Lasaridi and Stentiford, (1998)	Static	g O_2 kg OM^{-1} h^{-1}	Liquid	3-8 g	< 9.5 mm	In suspension	5-6 h	30°C
OD_{20}	cumulative O_2 uptake during 20 h		Static	g O_2 kg OM^{-1}	Liquid	3-8 g	< 9.5 mm	In suspension	20 h	30°C
Solid SOUR	SOUR in solid sample		Static	g O_2 kg OM^{-1} h^{-1}	Solid	3-8 g	< 9.5 mm		20 h	30°C
DRI	Dynamic respirometric index	Adani et al., (2001) European Commission, 2001	Dynamic	g O_2 kg OM^{-1} h^{-1}	Solid	From few grams up to industrial scale	< 50 mm if necessary	Adjustment to 75% water holding capacity	4 days but only data recorded during 24 h is used	Self-heated
SRI	Static respirometric index		Static	g O_2 kg OM^{-1} h^{-1}	Solid	From few grams up to industrial scale	< 50 mm if necessary	Adjustment to 750 g kg^{-1} water holding capacity	3 h	Self-heated
RDRI	Real DRI		Dynamic	g O_2 kg OM^{-1} h^{-1}	Solid	From few grams up to industrial scale	< 50 mm if necessary	No adjustment	4 days but only data recorded during 24 h is used	Self-heated
PDRI	Potential DRI		Dynamic	g O_2 kg OM^{-1} h^{-1}	Solid	From few grams up to industrial scale	< 50 mm if necessary	Optimal moisture	4 days but only data recorded during 24 h is used	Self-heated
AT_4 Sapromat	Cumulative O_2 uptake during 4 days	Binner and Zach (1998)	Static	g O_2 kg OM^{-1}	Solid	50 g	< 10 mm	Saturation	4 days	20°C
RI_T	O_2 uptake rate	Barrena et al., (2005)	Static	g O_2 kg OM^{-1} h^{-1}	Solid	250 ml	< 10 mm	40-55%	4 h incubation + 1.5 h assay	Process
RI_{37}	O_2 uptake rate		Static	g O_2 kg OM^{-1} h^{-1}	Solid	250 ml	< 10 mm	40-55%	18 h incubation + 1.5 h assay	37°C
AT_4	Cumulative O_2 uptake during 4 days	Favoino, 2006; European Commission, 2001	Dynamic	mg O_2 g OM^{-1}	Solid	500 g	< 10 mm	50%	4 days expandable	58°C
AT_4	Cumulative O_2 uptake during 4 days	Federal Government of Germany, 2001	Static	mg O_2 g DM^{-1}	Solid	50 g DM	< 10 mm	Saturation	4 days + lag phase	20°C
DR_4	Cumulative O_2 uptake during 4 days	Godley et al., 2005 (UK Environ. Ag.)	Dynamic	mg O_2 g DM^{-1} or mg O_2 g OM^{-1}	Solid	400 g DM	< 10 mm	50%	4 days	35°C

Lasaridi and Stentiford, (1998) technique is based in the biological oxygen demand (BOD) typically used in water analysis. This method permits to obtain two different indices: i) a measure of the specific oxygen uptake rate (SOUR) expressed as g O_2 kg OM^{-1} h^{-1} and ii) a measure of cumulative oxygen uptake during 20 hours (OD_{20}) expressed as g O_2 kg OM^{-1}. For these determinations, a dissolved O_2 probe is used to measure changes in O_2 concentration of a sample suspended in water under optimal conditions and at temperature of 30°C. The SOUR for a solid sample is calculated as described by Iannotti at al., (1993), but the assay is carried out at 30°C for its comparison with SOUR results.

Adani et al., (2001) determines the dynamic respirometric index (DRI) expressed as g O_2 kg OM^{-1} h^{-1} by measuring the different oxygen content in the inlet and outlet air-flow passing throughout the bioreactor containing a solid sample. DRI is calculated from the average of 12 measurements taken every 2 hours, during the 24 h of maximum activity during 4 days. Depending on the assay conditions, authors distinguish between real dynamic respiration index (RDRI) performed with no moisture adjustment of the sample and potential dynamic respiration index (PDRI) when sample moisture is adjusted to the optimum value. Also static respirometric index (SRI) is determined by stopping aeration and measuring the air oxygen content decline, taking readings every 5 minutes during 3 hours with an oxygen electrode in the head space volume of the bioreactor. According to Iannotti et al., (1993) also the measurement of the AFP is required. The process is carried out in an adiabatic bioreactor and therefore all data is recorded at process temperature.

Barrena (2006) established new conditions for static respirometric techniques. The sample is adjusted (if necessary) to moisture between 40-55% and the bioreactor is placed in a water bath at controlled temperature. Oxygen content decline is measured by an oxygen electrode in the headspace of the bioreactor and data is recorded every minute. The respirometric index (RI_{37}) is carried out at 37°C while RI_T is performed at the same temperature of the material from which the sample was taken. Previously to the oxygen content data recording, sample is incubated at test temperature during 18 and 4 hours for RI_{37} and RI_T respectively while is continuously aerated.

In the legislation of some European countries as well as in European legislation drafts (European Commission, 2001) cumulative oxygen uptake has been widely proposed to measure wastes' stability. The index that these methodologies describes represent the cumulative oxygen consumed during 4 days and expressed in mg O_2 g DM^{-1} or mg O_2 g OM^{-1}. However these methodologies differ in many key points. Diverse moisture adjustments, different working temperatures and sample treatments and even the use of inoculums in some methodologies are the most significant differences between methodologies proposed.

1.7.2 Anaerobic techniques

Anaerobic methodologies have not been as widely used and studied as aerobic technologies to determine biodegradability or stability in solid samples. However they are of special interest since despite usually being long tests, these techniques are cheap and with a simple performance. In addition they give a reliable measure of the organic matter which is potentially biodegradable under anaerobic conditions. Besides, the anaerobic indices can provide essential information for optimal design and performance of anaerobic digestion facilities, since not all biodegradable organic matter under aerobic conditions is anaerobically biodegradable, and consequently when analyzing or designing anaerobic digestion facilities, anaerobic indices are more recommendable that aerobic respirometric indices.

These methodologies allow the determination of biogas or methane produced by anaerobic microorganisms while organic matter is biodegraded. Different anaerobic indices can be obtained:

i) Biogas potential (GB as it is named in German legislation) represents the cumulative volume (liters) of biogas produced at a fixed time (usually 21 days, GB_{21}) per kg of dry matter feed. Also longer or total determinations of biogas potential are can be carried out. So the test will last until no significant biogas production is observed, usually up to 100 days (GB_{100}).

ii) Biological methane production (BMP) corresponds to the cumulative volume of methane (liters) produced per kg of dry matter or organic matter feed. The determination of this index implies the biogas composition analysis, generally by gas chromatography. BMP can also be expressed at different fixed times.

iii) Maximum methane production rate (Rmax) is expressed as NL CH_4 kg OM^{-1} $days^{-1}$ and obtained when adjusting experimental BMP data to Gompertz model (Equation 1.1.) (Zwietering, et al., 1990; Lay, et al., 1998).

$$M = P \cdot \exp\left\{-\exp\left[\frac{R_{max} \cdot e}{P}(\lambda - t) + 1\right]\right\} \quad \text{Equation 1.1}$$

In Gompertz model: M is the cumulative BMP (NL CH_4 kg OM^{-1}); P is the maximum methane potential (NL CH_4 kg OM^{-1}); t is the time (days); R_{max} (NL CH_4 kg OM^{-1} $days^{-1}$) and λ is the lag phase (days).

Anaerobic indices have been suggested in national regulations by some European countries such as Germany (Federal Government of Germany, 2001), Italy (Favoino, 2006) and England and Wales (Godley et al., 2005).

Table 1.4 shows the test conditions for some of the national standards defined for biological stability determination under anaerobic conditions.

Table 1.4. National standards for anaerobic index determinations.

Reference	Inoculation	Water Content	Temperature	Test duration	Results expression
Federal Government of Germany, 2001			Abfallablagerungsverordnung – AbfAblV		
GB_{21}	yes	50 g DM + 50 mL inoculum + 300 mL water	35°C	21 days + lag phase	L kg DM^{-1}
Godley et al., 2005			United Kingdom Environment Agency		
BMP_{100}	yes	20 g OM + 50 mL inoculum + 200 mL solution	35°C	100 days	L kg OM^{-1}

Both aerobic and anaerobic biological techniques have been satisfactory used up today in several applications, as it is confirmed by the large number of publications reported in the bibliography, and they have been firmly considered in national and European legislations.

However, these methodologies require some modifications and despite they have already been widely used, new applications can be developed. In this thesis work, the development of new methodologies and their successful applications to real cases will be presented.

CHAPTER 2. RESEARCH OBJECTIVES

CHAPTER 2. RESEARCH OBJECTIVES

The main objective of this work is to develop and apply biological indices (aerobic and anaerobic) as a reliable measure of biodegradable organic matter content in organic wastes.

In order to reach this main objective, many specific objectives were also proposed and are presented below:

- To update the review conducted by Barrena et al., (2006a) to establish the most common and reliable respirometric methodologies to determine biodegrable organic matter content and stability.

- To prove that already published respirometric methodologies can be used to monitor the biological activity during the waste treatment process by different technologies and to determine the stability of the final product.

- To identify and detect weaknesses of the already published methodologies in the literature and propose improvements.

- To develop systematical methodologies and design and construct the equipment necessary to determine a more reliable measure of biodegradability and stability of a given sample.

- To compare the indices proposed when are used in real waste treatment facilities and to discern about the different information that they provide.

- To determine the correlations among the developed methodologies.

- To study the overall efficiency of the waste treatment processes and the specific efficiency of every single process step regarding the biodegradable organic matter content by using the different methodologies proposed.

- To monitor complete waste treatment facilities and to assess the results obtained.

- To establish the most suitable form of expression for those indices and discuss about the wide range of information that indices can provide.

- To prove the use of those new respirometric indices for improving the performance and operation of waste treatment facilities and single processes but also for determining the stability of final products.

- To determine which could be the optimum treatment for organic wastes, using the biodegradable organic matter content by means of respirometric indices, as main decision tools.

- To define a standardized methodology and make a protocol for its implementation in industrial facilities.

CHAPTER 3. MATERIALS AND METHODS

Chapter 3. Materials and methods

3.1 Solid sampling procedure

Different sampling methodologies were applied depending on the characteristics of the material to be analyzed.

When sample must be taken from a composting pile, the bulk-integrated sample is obtained from eight different locations of each pile giving a final volume of approximately 24 liters. Then, the integrated sample is manually mixed in the laboratory and reduced using the quartering method to several sub-samples of 1.5–2 litters (approximately 1–1.5 kg) (Keith, 1996), which were used to carry out the analytical procedures.

When enough material is available, 2 tonnes of material are initially treated to finally obtain a sample of 25-30 kg. The quartering method is used to obtain 500 kg of mixed material. The final sample is obtained by mixing four or five subsamples of about 5-6 kg each, taken from different points of the 500 kg bulk of material.

Frequently, when not enough amount of material was available or sampling was too complicated (for example when sampling the continuous flow of organic matter coming from the mechanical pretreatment and going to the anaerobic digester in a MBT plant), different techniques were used to finally obtain a representative sample. For example in continuous flows, a subsample of around 5-6 kg was taken every 5 minutes, to finally obtain a sample of 30-40 kg.

3.2 Sample treatment

The original sample, in its entirety, must be wet-crushed to < 15 mm. Sample preparation must be completed and the test started within the following 48 hours following sampling. During this period temperatures over 4°C are permissible for no more than 12 hours. If it is not possible to ensure compliance with this procedure, the sample shall be frozen within 12 hours after sampling at -18°C to -20°C. Freezing of samples shall be documented in connection with evaluation. Thawing of samples must last no longer than 24 hours at room temperature but never exceeding 25°C.

3.3 Analytical methods

Routine parameters were determined according to the standard procedures included in the "Test Methods for the Examination of Composting and Compost" (US Department of Agriculture and US Composting Council, 2001). Results were calculated as a mean of three replicates.

- **Moisture content (MC) and dry matter (DM)**

MC and DM were analyzed calculating the water loss, as shown in Equations 4.1 and 4.2. The sample was oven dried at 105°C for 18-24 hours.

$$\mathrm{MC} = \frac{(\mathrm{P_i} - \mathrm{P_f})}{(\mathrm{P_i} - \mathrm{P_0})} \cdot 100 \quad \text{(Equation 3.1)}$$

$$\mathrm{DM} = 100 - \mathrm{MC}\ (\%) \quad \text{(Equation 3.2)}$$

where: MC, moisture content of the sample (%); P_i, initial wet weight of the sample; P_f, final dry weight of the sample; P_0, beaker weight.

- **Total organic matter (OM, equivalent to volatile solids content, VS)**

OM was analyzed by sample ignition at 550°C in the presence of excess air for 2.5 hours, calculated as equation 4.3 shows.

$$OM = \frac{(P_i - P_f)}{(P_i - P_0)} \cdot 100 \quad \text{(Equation 3.3)}$$

where: OM, organic matter of the sample (%); P_i, initial wet weight of the sample; P_f, final dry weight of the sample; P_0, beaker weight

- **pH**

pH was determined as follows: A slurry of waste and deionized water was blended at a ratio of 1:5, w/w or v/v basis. The sample was shaken for 20 minutes at room temperature to allow the salts to solubilize in the deionized water. The pH was measured with an electrometric pH meter (Crison, micropH200) directly in the compost/water slurry or in the extracted solution on a solid waste distilled water extract using a 1:5 weight ratio.

- **Total nitrogen Kjeldahl (TNK)**

TNK was determined following the next three principal steps:

i) Sample digestion. This process converts all the organic nitrogen into ammonia. This change is achieved by exposing the sample to concentrated sulfuric acid in the presence of a catalyst at a high temperature.
ii) Distillation. The $N - NH_4^+$ from an aliquot is transformed into $N - NH_3$ by distillation in the presence of excess of base into a test tube containing an excess of boric acid at a known concentration.
iii) Titration. The difference between the equivalents of acid initially present and those remaining after distillation equal the equivalent of acid neutralized by ammonia, i.e. the equivalent of ammonia from both the N-organic and the $N - NH_4^+$ existing in the initial sample. Unlike the $N - NH_4^+$content of the sample, the amount of organic nitrogen can be determined.

Total nitrogen Kjeldhal (TNK) was determined using 0.5 g of the sample. The sample was digested for 1.5 hrs at 400°C using 25 mL of concentrated sulphuric acid in 100 mL Kjeldhal tubes using a Bloc Digester 6 (with six tubes capacity) (J.P. Selecta S.A., Barcelona, Spain). To speed up the digestion, a catalyst (Kjeltab®) was added. Each digestion block contained two blank tubes that contained the standard amount of acid described above and a catalyst tablet (Kjeltab®). After allowing the sample to cool, the sample was diluted using deionised water. A Büchi Distillation Unit K-355 (Flawil, CH) was used for sample distillation with an excess of NaOH (35%). The condensate was placed in a conical flask with 100 mL of boric acid (4%) with mixed indicator. A colorimetric assay was used to measure the amount of nitrogen formed by adding, HCl and an acid indicator. TNK was calculated using Equation 3.4.

$$TNK = \frac{(V_i - V_0)\cdot N \cdot 14}{W_{wb}} \quad \text{(Equation 3.4)}$$

Where: TNK, total N-Kjeldhal (%); V_i, HCl volume consumed (mL) in sample titration; V_0, volume of HCl consumed (mL) in control titration; N, normality of the HCl used in determination; and Wwb, sample weight in wet basis (g).

- **Bulk density (BD)**

BD is defined as the weight per unit of volume of sample. BD was calculated on wet basis dividing the sample weight by the sample volume as shown in Equation 4.6.

$$BD_W = \frac{W_S}{V_S} \quad \text{(Equation 3.5)}$$

where: BD_w, wet bulk density (kg L^{-1}); W_s, sample weight (kg); V_s, sample volume (L).

- **Composting material maturity**

Maturity was measured using the Dewar® self-heating test (U.S Department of Agriculture and the U.S Composting Council, 2001). The principle is based on the heating potential of a composting material, where the less mature materials will reach higher temperatures. The method consists into precisely record the highest temperature achieved after placement of composting material into a Dewar vessel for several days. Interpretation of the results is based on division into five-levels of 10°C increments of the material temperature. For example, Class V (highest maturity) refers to 10°C, IV is 20°C and the lowest level of maturity (grade I) is 50°C heating over room temperature (Weppen, 2002).

- **Fat, protein and carbohydrates content**

Fat, protein and carbohydrates content were determined according to official methods in Spain (Spanish Ministery of Agriculture, Fishing and Food. Official Analysis Methods) by an external laboratory.

- **Biogas composition**

Biogas composition was determined by gas chromatography, based on Standard Methods procedure 2720C (APHA, 1999). The chromatograph (Perkin-Elmer AutoSystem XL Gas Chromatograph) was equipped with a thermal conductivity detector and a packed column (Hayesep 3m 1/8" 100/120) into which biogas samples were injected. The carrier gas was

Helium (He) in splitless mode (column flow: 19 ml · min^{-1}). The oven was maintained at a constant temperature of 40°C. Injector and detector temperatures were 150°C and 250°C, respectively. The system was calibrated with pure samples of methane (99.9% CH_4) and carbon dioxide (99.9% CO_2). Retention time was 1.5 and 3 minutes for CH_4 and CO_2, respectively. The total time of each run was 10 minutes.

- **Static respirometric index (SRI)**

SRI was determined by using a custom made respirometer developed by Barrena (2006). The static respirometer was built according to the original model described previously (Ianotti et al., 1993) and following the modifications and recommendations given by The US Department of Agriculture and The US Composting Council (2001). A detailed description of the respirometer can be found elsewhere (Barrena et al., 2005; Barrena 2006). Approximately 250 mL of sample were placed in 500 mL Erlenmeyer flasks on a nylon mesh screen that allowed the air movement under and through the solid samples. The setup included a water bath to maintain the temperature at 37 °C during the respirometric test. Prior to the assays, samples were incubated for 24 h at 37 °C. During the entire incubation period, samples were aerated with previously humidified air at the sample temperature. The drop of oxygen content in a flask containing a sample was monitored with a dissolved oxygen meter (Lutron 5510, Lutron Co. Ltd., Taiwan) connected to a data logger. The rate of respiration of the sample (Oxygen Uptake Rate, OUR, based on dry matter content or organic matter content) was then calculated from the slope of oxygen level decrease versus time according to the Equation 3.6 (Ianotti et al., 1993). Results of the static respirometric index are expressed as g O_2 kg OM^{-1} h^{-1} and are presented as a mean of three replicates.

$$SRI = \frac{V \cdot P_r \cdot 32 \cdot m \cdot 60}{R \cdot T \cdot X \cdot DM \cdot OM} \quad \text{(Equation 3.6)}$$

where,

SRI= respiration index (g O2 kg OM^{-1} h^{-1}),

V= volume of air in flask (mL),

P_r= atmospheric pressure at elevation of measurement (atm),

m= slope of change in percent O_2 saturation per minute divided by 100,

R= ideal gas constant (0.082061 atm L mol^{-1} K^{-1}),

T= temperature (K),

X= wet weight of material test aliquot (g),

DM= fraction of total solid of a parallel sample aliquot (g DM g X^{-1}), and,

OM= fraction of organic matter of a parallel sample aliquot in dry basis (g OM g DM^{-1}).

CHAPTER 4. BIOLOGICAL INDICES AND NEW METHODOLOGY DEVELOPED

CHAPTER 4. BIOLOGICAL INDICES. NEW METHOLODOLGY DEVELOPED

As it was described in Chapter 2, some specifics objectives concerning new methodologies for biological indices determinations are proposed. These new methodologies are intended to be improvements of the already published and adopted methodologies. The first step consists on analyze the weaknesses and the strengths of the already published methodologies.

Many weaknesses and differences were found in literature, being the most significant:

- The disparity of methodology proposed.
- The different assay conditions, in terms of temperature, sample amount, use of inoculums, etc. These different assay conditions make the results incomparable among them, since, for example, the biological activity is strongly dependent on the temperature.
- The discrepancy when expressing results, in DM or OM basis. OM is always quantified as percentage of volatile solids in the sample, including the non or low biodegradable organic materials, such as plastics and polymers, fabrics, etc. This would lead to a wrong analysis of the results, since not all organic matter is biodegradable and biodegradability would be also referred to an unknown amount of non-biodegradable organic matter. In addition, indices are expressed as cumulative production or consumption during a fixed time, or as a rate, measured as an average for an interval of time, or as a single measure (maximum value or after a giving time).
- The different pretreatments given to initial sample to be analyzed. Some methodologies do not even treat the sample, while others make intensive treatments, such as sorting, drying, crushing and sieving. Some methodologies also imply moisture adjustment, while in others the analysis is carried out in water suspension, or with any moisture adjustment.
- Static indices are considered imprecise by different reasons: i) when sample is incubated during a fixed time, the respirometric results are being conditioned since for example different incubation times would be required to obtain the maximum biological activity depending on the nature of the sample. Additionally, when determining oxygen uptake rate (OUR) in an static respirometer, is usual to measure

the rates during a fixed time, and give as a result the maximum OUR in this time. However, values of respirometric indices varies with time depending on the stage of biodegradation and consequently is unknown if this value corresponds to a maximum, minimum or an intermediate respirometric value; ii) static conditions directly limit the oxygen transfer from gas to liquid (or biofilm) phase. Continuous flows would favor the mass transfer through the phases, and as high the air flow is, higher the mass transfer will be (De Guardia et al., 2010).

The strengths of SRI are the simplicity and relative low cost of the equipment, the rapid determination, the practical use as first approach and the straightforward mathematical calculus.

New methodologies developed in this work must be an improvement of the already proposed techniques, giving the most appropriate conditions to obtain a reliable measure of the biological activity and correcting the diffuse or tedious points detected. In addition, adequate equipments must be designed and constructed and systematical methodologies must be described and assessed.

Two methodologies have been completely studied and assessed with different wastes and different assay variables to finally establish the most suitable techniques to carry out biological activity determinations. These measures will be a reliable measure of biodegradable organic matter content and sample stability.

The two methodologies proposed in this work consist of:

I. Continuous determination of biological activity under aerobic conditions and expressed as O_2 consumption rate and as cumulative O_2 consumed during a fixed time.
II. Continuous determination of biogas and methane production under anaerobic conditions during a fixed time and total biogas or methane production as well as maximum methane and biogas production rates by adjusting experimental data to a Gompertz model.

4.1 Aerobic indices: Dynamic Respiration Indices (DRI) and cumulative indices (AT).

Sampling has as main goal to obtain a representative amount of matter to be analyzed. Strict and hard strategies have been designed to reach this goal in the initial sampling as described in Section 3.1. However this effort would be in vain if a correct procedure is not established to process the sample ***previous to analysis***. Subsequently, different crushing strategies have been assessed to allow the sample being completely mixed.

Manual sorting of inert materials and grinding was initially carried out but the characteristics of the initial sample were notably modified and the particle size was remarkably heterogeneous, and consequently this option was discarded.

In order to homogenize particle size, a garden grinder was used obtaining a uniform particle size around 5 mm. However particle size was considered too small for maintaining a good porosity and matrix structure. In addition, garden grinder was not able to grind plastic, glass or metals, and previous manual sorting was also required thus modifying initial sample characteristics.

Finally an industrial grinder was used to grind original sample in its entirely (without any material sorting) obtaining an initial sample size between 10-15 mm. This technique does not modify sample characteristics since any sorting is carried out because the grinder used was able to grind all kinds of objects, such as plastic film, metals and glass bottles. This size was considered as optimal to increase available surface and maintain enough porosity and matrix structure (Ruggieri et al., 2009).

As established by the German Institute for Standardization, sample preparation must be completed and the test starts within the following 48 hours after sampling. During this period temperatures over 4°C are permissible for no more than 12 hours. If it is not possible to ensure compliance with this procedure, the sample shall be frozen within 12 hours after sampling at -18°C to -20°C. Freezing of samples shall be documented in connection with evaluation. Thawing of samples must last no longer than 24 h and at room temperature but never exceeding 25°C.

A currently work undertaken by the co-researcher Michele Pognani shows that aerobic indices could be influenced by the time during which the most active samples, such as OFMSW or similar, are frozen. It is being demonstrated that for freezing times longer than 90 days, aerobic indices slightly decrease, and after being one year frozen, aerobic indices could decrease between 30-40% of the initial value previous to freezing. If storing time for frozen samples is below 90 days, aerobic indices are not affected and values are statistically the same. Special attention must receive final results obtained by Pognani in this work, since they can be of special interest for being included in the aerobic indices methodology.

Next point to study was the establishment of the amount of sample necessary for a correct and representative indices determination. An excessive amount of sample could entail a compaction of the sample in the reactor and the loss of structure and porosity while a moderate amount of sample could result in a non representative index results.

An OFMSW sample was used for determining the optimal amount of sample to be analyzed. Three different amounts of sample were studied, considering lab scale working conditions. The amounts assessed were: i) 50-55 g; ii) 110-120 g; and iii) 420-430 g. The results obtained for DRI and AT4 determinations are shown in Table 4.1. After analyzing the results, some considerations can be done:

I. The highest standard deviation for all indices studied corresponds to the experiment with the least amount of sample (50-55 g), indicating that such a low quantity may be not representative enough for index determinations.
II. Lowest values for all indices studied were obtained for the experiment with the most amount of sample, suggesting that a compaction of material and mass transfer limitations could occur during the determinations of respirometric indices.
III. When using around 115 g of sample, low standard deviations were obtained among the three replicates and values were higher than those obtained for the experiment with around 420 g of sample. It could be stated that analyzing 115 g of matter, sample would be representative enough and undesirable setbacks, such as compaction and consequent mass transfer limitation, would not occur.

Table 4.1 Aerobic respiration indices for different amounts of a sample of OFMSW.

Amount of sample (g)	Dynamic respiration indices (mg O_2 g DM^{-1} h^{-1})			Cumulative index during 4 days (mg O_2 g DM^{-1})
	DRI_{MAX}	DRI_{1H}	DRI_{24H}	AT_4
50-55	3.2±0.4	3.2±0.4	3.0±0.4	259±39
110-120	2.8±0.2	2.8±0.1	2.68±0.08	220±19
410-420	2.5±0.1	2.4±0.2	2.2±0.1	177±12

DRI_{MAX}: maximum DRI obtained. DRI_{1H}: average DRI in the 1 hour of maximum activity. DRI_{24H}: average DRI_{1H} in the 24 hours of maximum activity.

The procedure established for aerobic indices determination and calculation was based on previous work by Adani et al. (2003, 2004, and 2006), Barrena et al. (2005) and on the procedure described by the German Institute for Standardization reported in the Ordinance on the Environmentally Compatible Storage of Waste from Human Settlements and on Biological Waste-Treatment Facilities (2001).

Figures 4.1-4.4 show a scheme and some pictures of the experimental set up built for dynamic respiration index determination and designed with the aim to analyze twelve samples simultaneously.

Before carrying out the analysis moisture content must be adjusted if it is necessary to a minimum value of 45% by adding tap water. This would be the normal procedure when analyzing final materials such as composts.

Around 100-120 g of waste sample correctly pretreated as described above, are initially placed in a 500 mL reactor. In the case of low porosity materials such as sludge, modification have been included in order to adequate the methodology to all kind of wastes. These modifications are described in Section 4.1.1.

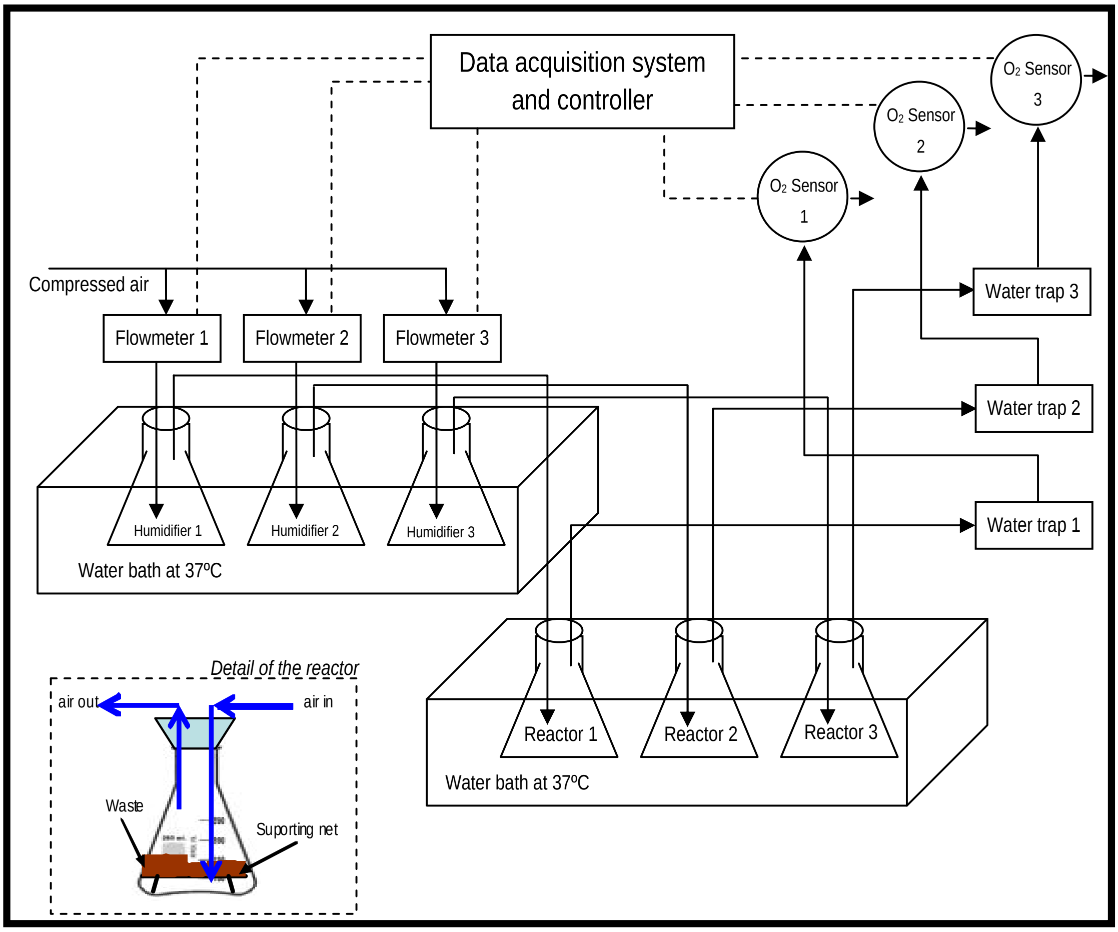

Figure 4.1. Scheme of experimental set-up for analyzing a sample in triplicate.

Reactors consisted of an Erlenmeyer flask, containing a plastic net to support the organic waste and provide an air distribution chamber, placed in a water bath at 37°C (Barrena et al., 2005).

Airflow in the reactors is manually adjusted by means of an air flow controller (Bronkhorst Hitec, The Netherlands) to provide constant airflow, and modified when necessary to ensure minimum oxygen content in exhaust gases of 10% v/v (Leton and Stentiford, 1990). Airflow is previously humidified at the sample temperature to avoid the sample drying during experiment length. According to the biodegradability of the samples, initial air flow selected was between 30-45 mL min^{-1} for active samples and 15-25 mL min^{-1} for more stable samples such as compost.

Figure 4.2. Picture of the 12 reactors and waster traps.

Figure 4.3. Picture of the 12 flow-meters and electro-valves of the experimental set-up for analyzing 12 samples

Figure 4.4. Picture of the O_2 and CO_2 sensors and data acquisition system.

Exhaust air from the reactors was sent to oxygen and carbon dioxide sensors prior dehumidification in a water trap. Both air flow meters and oxygen sensors were connected to a data acquisition system to continuously record these values.

Data concerning air-flow, and O_2 and CO_2 content in the exhaust gas for all reactors is registered at least once every 15 minutes.

Dynamic respiration index can be calculated from oxygen and air flow data for a given time as shown in Equation 4.1, derived from steady state mass balance.

$$DRI_t = \frac{(O_{2,i} - O_{2,o}) \times F \times 31.98 \times 60 \times 1000^a}{1000^b \times 22.4 \times DM} \qquad \text{(Equation 4.1)}$$

Where: DRI_t, Dynamic Respiration Index for a given time t, mg $O_2 \cdot g^{-1}$ $DM \cdot h^{-1}$; ($O_{2,i}$-$O_{2,o}$), difference in oxygen content between airflow in and out the reactor at that given time, volumetric fraction; F, volumetric airflow measured under normal conditions (1 atm and 273 K), ml min^{-1}; 31.98, oxygen molecular weight, g mol^{-1}; 60, conversion factor, minutes/hour; 1000^a, conversion factor, mg g^{-1}; 1000^b: conversion factor, mL L^{-1}; 22.4, volume occupied by one mol of ideal gas under normal conditions, L; DM, dry mass of sample loaded in the reactor, g.

A dynamic respiration index curve can be built from on-line collected data as shown in Figure 4.5. From these data, several respiration indices can be calculated as follows, divided into the two abovementioned categories: oxygen uptake rate indices and cumulative consumption indices.

Oxygen Uptake Rate Indices - DRI

- DRI_{max}: maximum DRI_t obtained.

- DRI_{1h}: average DRI_t in the one hour of maximum activity.

- DRI_{24h}: average DRI_{1h} in the 24 hours of maximum activity (Adani et al., 2003).

Cumulative Consumption Indices - AT

- AT_n: Cumulative oxygen consumption in n days calculated as shown in Equation 4.2:

$$AT_n = \int_{t_l}^{t_l+n} DRI_t \cdot dt \qquad \text{(Equation 4.2)}$$

Where t_l is time when lag phase finishes. Lag phase (Federal Government of Germany, 2001) ends when oxygen uptake rate, expressed as a 3-hour mean, reaches 25% of the maximum uptake rate calculated as the average of three hours (Figure 4.5). The weight of the oxygen consumed during the lag phase is subtracted from the weight of the oxygen consumed throughout the entire test (lag phase + n days), and for AT_4 calculations must not be more than 10% of the overall value. If this condition is not fulfilled, determination may not be carried out.

- AT_4: cumulative oxygen consumption in four days (after lag phase).

- AT_{24h}: cumulative oxygen consumption in the twenty-four hours of maximum activity, i.e., the twenty-four hours period when DRI_{24h} is calculated.

- AT_u: total cumulative oxygen consumption, until no significant oxygen consumption is observed.

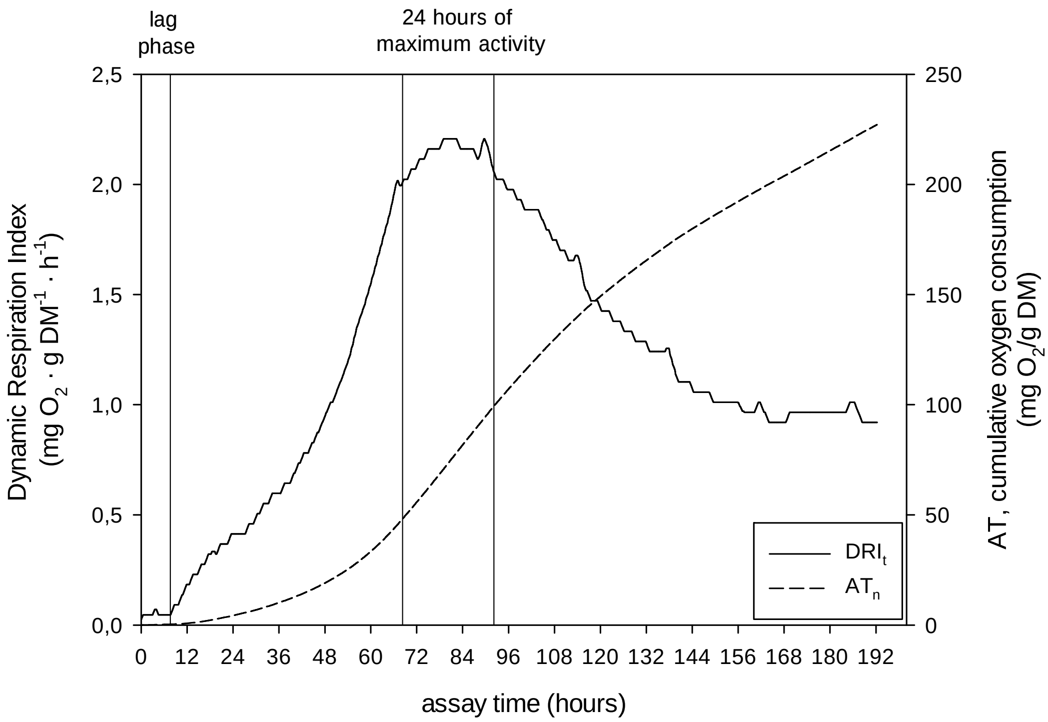

Figure 4.5. Typical curve for dynamic respiration indices evolution and calculation.

Results are expressed as mg O_2· g DM^{-1}. Both the mean and the standard deviation are to be listed. If possible, three replicates are recommended. However a minimum of two replicates must be always analyzed for each sample and a third replicate must be undertaken when deviation among duplicates is over 20%.

As discussed in Section 1.7.1, respirometric indices based on CO_2 production data, seems to be more erratic, and a different purpose for this data is intended. This data would be useful for determining the C/N ratio, but concerning only the C biodegradable that would correspond to the carbon emitted in form of CO_2. This is the goal of a current work which is being undertaken with co-researchers.

Test temperature is an important parameter to establish since biological activity is strongly dependent on it and methodologies already published differ in this parameter. In order to decide the optimal temperature for aerobic test determinations, an experiment was carried out. This experiment consisted of determining the aerobic indices for a sample of OFMSW after the mechanical pretreatment in a MBT plant, at three different temperatures, one in each temperature level: psychrophilic (15-19°C); mesophilic (20-45°C) and thermophilic (45-70°C). This sample was almost free of inert and undesirable materials. Results obtained are shown in Table 4.2.

Table 4.2 Aerobic respiration indices obtained for a sample of OFMSW after mechanical pretreatment, at different test temperatures.

Test temperature	**Dynamic respiration indices ($mg\ O_2\ g\ DM^{-1}\ h^{-1}$)**			**Cumulative index during 4 days ($mg\ O_2\ g\ DM^{-1}$)**
	DRI_{MAX}	DRI_{1H}	DRI_{24H}	AT_4
20°C	4.1±0.5	4.0±0.4	3.4±0.5	185±23
37°C	5.5±0.2	5.5±0.2	3.8±0.1	275±14
55°C	0.83±0.05	0.81±0.05	0.68±0.03	19.0±0.3

DRI_{MAX}: maximum DRI obtained. DRI_{1H}: average DRI in the 1 hour of maximum activity. DRI_{24H}: average DRI_{1H} in the 24 hours of maximum activity

Some conclusions can be obtained after analyzing these results:

I. When working at 55°C it is observed that biological activity is always extremely low and considering that the waste studied has a high content in biodegradable organic matter and higher respirometric indices were expected, it can be concluded that the thermophilic range of temperatures is not adequate for aerobic indices determination. Although it was not assessed, it is though that at this temperature would not be possible to discriminate between poorly or highly biodegradable wastes.

II. When working at 37°C, the highest results in all indices measured are obtained. In addition standard deviation is very low and results correspond to the values expected for this kind of wastes. A very important point to highlight is the short time required for determining DRI indices, being this time the half of the time required for the determination at 20°C. The times needed to calculate the indices were: DRI_{MAX}, 19 hours; DRI_{1h}, 19,5 hours; DRI_{24h}, 36 hours. Lag phase for AT_4 determinations were 6.5 hours at 37°C and 12 hours when working at 20°C.

III. When working at 20°C, similar results to the values obtained were guessed. However high dispersion in results is observed, they are lower than the results obtained at 37°C and long times are required for index determinations.

To sum up and considering the above results and discussion, it is possible to establish that 37°C is the optimal temperature for aerobic indices determinations since it allows to develop the maximum biological activity and consequent organic matter biodegradation in the shortest time compared to the other temperatures tested.

4.1.1 Test modifications when analyzing high moisture and low porosity wastes

The above described methodology is not always valid for all kind of wastes and some modifications must be done when analyzing wastes with high moisture content (higher than 70%) and low porosity, such as sewage sludge. For the determination of aerobic respirometric indices it is crucial to ensure a good structure and porosity of the sample to make the oxygen available for microorganisms and avoid anaerobic areas.

To solve this problem the addition of inert bulking agent is required. This bulking agent must be considered inert (not biodegradable) during the assay time.

Different options were initially considered to be used as bulking agent. This bulking agent must have the appropriate characteristics to provide a good matrix structure but also to absorb moisture from the sample. The materials provisionally considered as possible bulking agent were: i) wooden rods; ii) small pieces (20mm) of ceramic in a canal shape; iii) small strips (25 mm length, 10 mm width) of fiber dishcloths.

These three materials were assessed for the determination of aerobic indices. Two sewage sludges were chosen to carry out the experiment: digested sludge and raw sludge coming from different waste water treatment facilities.

First step was the determination of the optimal mixture ratio for each bulking agent. Different mixtures were made with all bulking agents and the sludges proposed. Some mixtures were initially discarded since they did not provide correct structure and porosity. Those that apparently provide enough matrix structure were compared for each bulking agent. At this point, it is important to make some observations. The mixtures were designed considering a minimum amount of sample of 100 g, since although these wastes seem to be very homogeneous, the high moisture content imply that almost all wet weight of the sample is water and what it is pursued by the methodology is the evaluation of solids' biodegradation. Therefore, a minimum of 30 g of DM of sample is required for aerobic indices determination. In addition, density of bulking agent is usually really low (except for ceramic pieces), and the matrix volume increases significantly after mixing. The volume of the reactors is 500 ml and porosity (air filled porosity) must be up to 40% (Ruggieri et al., 2009) so these two limitations may be considered when choosing the bulking agent-sludge ratio.

The best ratios for each bulking agent were those that gave the maximum values of DRI and AT_4 determinations, since it would mean that they provide the best conditions for aerobic biodegradation.

The ratios bulking agent/sludge in wet weight selected were: i) 1/4 for wooden rods; ii) 1:1 for ceramic pieces; and iii) 1:10 for dishcloth strips.

Afterward, the best material to work as bulking agent was to be determined. Thus, results obtained for the three bulking agents studied at the optimal ratios found were compared and discussed (Figure 4.6).

Comparing the results obtained when using ceramic pieces and dishcloth strips, which are for sure totally inert and non biodegradable, it can be observed results for ceramic pieces are always lower than for dishcloth strips. Therefore, it can be stated that ceramic pieces are not suitable enough to be used as bulking agent. The reason can be the high water holding capacity of ceramics, which dries the sludge excessively.

When using wooden roots and dishcloth strips similar (statistically the same) results were obtained for DRI_{MAX} and DRI_{24h}. However, when determining AT_4, results differ significantly, being always higher when using wood roots. This may lead to think that for long determinations of aerobic respirometric indices, wood roots cannot be considered inert materials, since wood is slightly biodegradable after a certain period of time. To clarify this fact, a respirometric experiment just using a real pruning waste was set up, obtaining that DRI_{MAX} of 0.91 mg O_2 g ST^{-1} h^{-1} is obtained after 26 hours of experimental running. Results for DRI_{24h} and AT_4 were also determined, obtaining values of 0.82 mg O_2 g ST^{-1} h^{-1} and 61.03 mg O_2 g ST^{-1} respectively. Consequently, wood roots may not be used as bulking agent for index determinations which imply a long period of time (up to 24-30 hours). Normally DRI_{24h} determinations for sludge samples are obtained within the first 24-30 hours after respirometry starting.

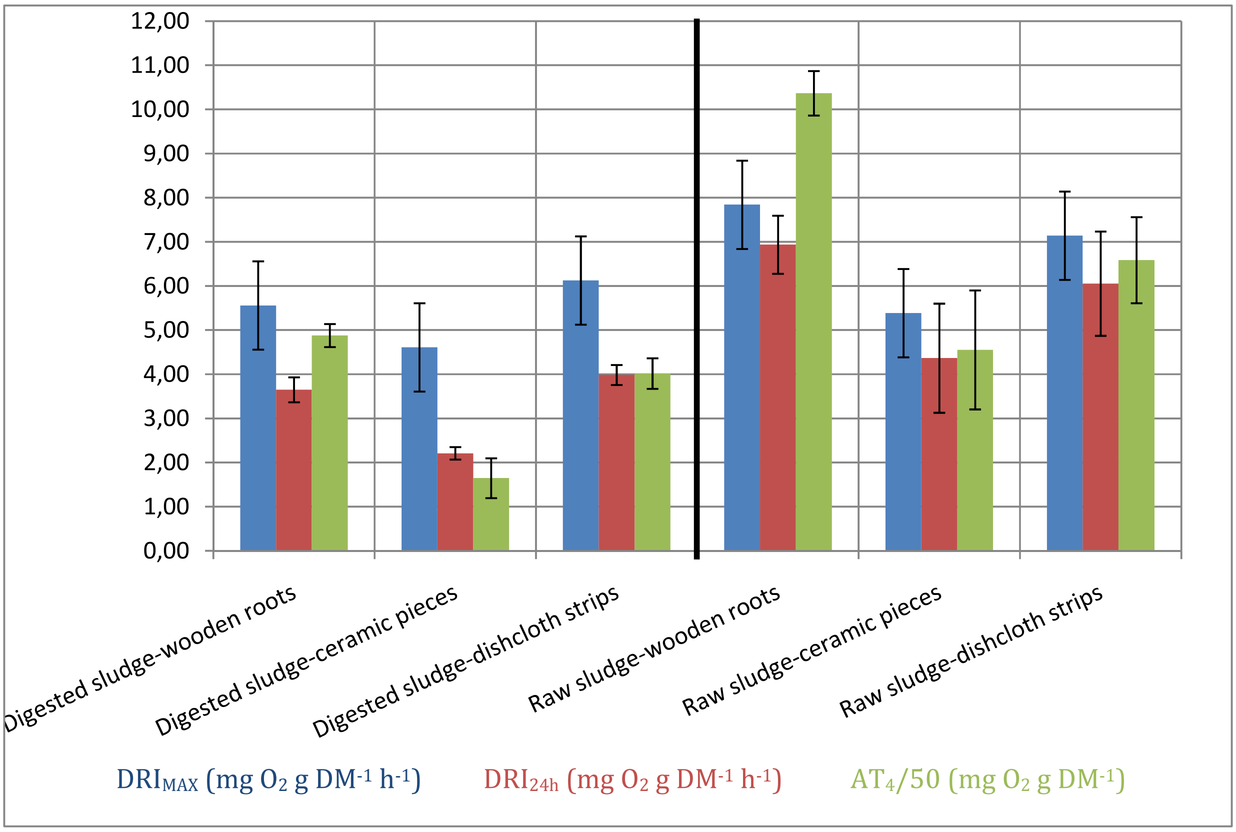

Figure 4.6. Results obtained when analyzing DRI and AT4 for raw and digested sludges using different materials as bulking agents.

Therefore, although wood roots are simpler to use as bulking agent and could be used for short index determinations, dishcloth strips are the material most recommended to be used as bulking agent when analyzing this high moisture and low porosity of wastes.

To conclude this section, when waste to analyze presents high moisture content and low porosity the next procedure must be followed.

Prior to introduce the sample in the reactor (Erlenmeyer flask), a mixture with dishcloth strips (25 mm length, 10 mm width) must be carried out in a wet weight ratio 1/10 dishcloth strips (bulking agent)/sludge. Next, mixture must be introduced in the reactor quantifying the amount of sample (waste) that remains in the glass beaker. This matter must be subtracted from the sample mass initially weighted when considering the total DM of the sample loaded in the reactor.

The methodology for determining the DRI and test modifications established in section 4.1.1. make up an standard procedure that was requested for the Agència Catalana de Residus (ARC), which is the organization responsible for managing the waste generated throughout Catalonia. This procedure was described in Catalan and it is currently used and applied for the ARC for stability determinations and biological activity measurements. The Standardized Protocol to determine DRI is presented in Chapter 9, Annex, in the same format and language in which it was originally written.

4.1.2 Assessment of biodegradable organic matter fractions through biodegradation kinetics modeling

In order to completely characterize the biodegradable organic matter content of a given waste by means of quantitative measures of the easily and slowly biodegradable organic matter and biodegradation kinetic rate constants, the data of cumulative CO_2 produced or mineralized was fitted to the four models described by Tosun et al. (2008). The four models are described below:

- First-zero-order kinetic model

The first-zero-order kinetic model is expressed as:

$$C_C = C_R(1-\exp(-k_R t)) + C_S k_s t \qquad \text{(Equation 4.3)}$$

where, C_C is cumulative CO_2–C mineralized (%) at time t (days), C_R, C_S are percentage of rapidly and slowly mineralizable fraction, respectively, and k_R and k_S are rapid and slow rate constants (day^{-1}), respectively.

- First-first-order kinetic model

The first-first-order kinetic model is expressed as:

$$C_C = C_R(1-\exp(-k_R t)) + C_S(1-\exp(-k_s t)) \qquad \text{(Equation 4.4)}$$

- Chen and Hosshimoto's kinetic model

The model is expressed by the following equation as suggested by Tosun et al. (2008):

$$C_C = 100 - 100 \times (R_f + (1-R)K_{CH} / (\mu_m t - 1 + K)) \qquad \text{(Equation 4.5)}$$

where R_f is the refractory coefficient, K_{CH} is Chen and Hosshimoto dimensionless kinetic constant, and μ_m is maximum specific growth rate of microorganisms, day^{-1}.

- Levi-Minzi kinetic model

Levi-Minzi model expresses net mineralization with an exponential kinetic

$$C_C = kt^m \qquad \text{(Equation 4.6)}$$

where k is a constant that characterizes the units used for the variables and m is a constant that characterizes the shape of the curve.

However, these models present some limitations, being the most important the consideration of the non-biodegradable organic matter or organic carbon as slowly biodegradable fraction which obviously leads to non completely reliable results.

Two additional models which permit for the characterization of easily and slowly biodegradable organic matter fractions were also considered. Model suggested by Komilis

(2006) was found more complete than those described by Tosun et al. (2008) but it requires additional chemical analysis (final TOC and initial DOC) so it was discarded in the first assessment. Model suggested by Tremier et al. (2005) was also fitted to experimental data. This model had been optimized for a sludge:bulking agent mixture and provided good results for sludge experimental data. However, the model did not properly adjust to the respirometric profile of the rest of wastes.

Trying to sort out the limitations that the first-zero-order and first-first-order models described by Tosun present, a new simple model was developed to obtain after fitting the data the three different fractions in which organic matter or carbon can be classified: Cr, Cs and inert fraction (Ci) and the biodegradation kinetics rates (k_r and k_s).

If keeping the concept of the Tosun model, the mathematical expression is unable to predict the inert fraction. However, instead considering the evolution of the carbon emitted in form of CO_2, the carbon that has not been degraded yet can be also followed, assuming that the initial TOC corresponds to the 100% of the carbon in the sample and subtracting the carbon emitted from this initial value. The remaining carbon in the sample can be expressed as percentage of the initial TOC (Annex, Article VII).

The mathematical modeling of these data would correspond to the next expression:

$$C_W = C_R \times \exp(-k_R t) + C_S \times \exp(-k_S t) + C_I \qquad \text{(Equation 4.6)}$$

where, C_W is the remaining carbon in the sample (%) at time t (days), C_R and C_S are the percentages of rapidly and slowly mineralizable fractions respectively, C_I is the inert fraction , and k_R and k_S are rapid and slow rate constants (day^{-1}), respectively. This expression consists of two exponential decay terms and an independent and constant term.

4.2 Anaerobic indices: Biogas production during a fixed time (GBn), Biological Methane Potential during a fixed time (BMPn)

All procedures described in section 4.1 concerning sampling and sample treatment and storage must be also strictly applied for anaerobic indices determination.

The aim of these indices determinations is to determine the biodegradability of organic wastes under anaerobic conditions by measuring the production of biogas and methane during given times.

To analyze the biogas and methane production of the different samples, a new analytical method was set up by adapting the procedure described by the German Institute for Standardization (Federal Government of Germany, 2001) and initially using the reactor concept proposed by Ferrer et al. , (2004). The German standard procedure provides the parameter GB_{21} expressed as normal liters of biogas (temperature: 273K and pressure 1.01325 bar) produced per kg of total solids (NL kg DM^{-1}) during 21 days. In the developed test, biogas production was monitored at different times and the test was finished when no significant biogas production was observed (never before 100 days). Thus, biogas production GB_n could be obtained for n days of analysis. Results were expressed both as normal liters of biogas produced per kg of dry matter and volatile solids (NL kg VS^{-1}). In addition biogas composition was analyzed to obtain the biochemical methane production (BMP_n) by gas chromatography (Perkin-Elmer AutoSystem XL Gas Chromatograph) with a thermal conductivity detector and using a column Hayesep 3m 1/8" 100/120. The details of biogas analysis can be found in Section 3.3.8.

To obtain the anaerobic biodegradability of the samples, the use of anaerobic inoculum is required. The inoculum was always collected from an anaerobic digester treating OFMSW (4500 m^3 of capacity, working temperature of 37°C and hydraulic retention time of 21 days) in MBT plant. The reactor was continuously fed with a mixture of OFMSW/recirculated sludge in a ratio 1/2 (dry basis). Specifically the inoculum consists of the liquid fraction after centrifugation of digester output material. This fraction may have a minimum of 8-10 % of DM. The anaerobic inoculum, that can never be frozen, must be kept at 37°C during two weeks to remove any remaining easily biodegradable fraction.

At present (and as future trends indicate) almost all digesters work under mesophilic temperatures, being 37°C the most usual. Consequently, the most useful biogas or methane production determinations would be under the same conditions that are industrially used. For that reason, test temperature was established at 37°C. In addition, inoculum was obtained from a digester working at 37°C, so mesophilic populations are already present and no acclimatization is needed.

When making the mixtures inoculum-sample (waste) the organic loading rate must be carefully taken into account. The main problem that can appear along the experiment duration is the medium acidification and inhibition of microorganisms by volatile fatty acids accumulation. This would occur when content of easily hydrolysable organic matter in the sample was excessive. Therefore, different inoculum/sample ratios could be defined to carry out the experiments, since all samples have different composition characteristics. In this sense, the inoculum/substrate ratio in dry basis could range from 0.4/1 to 4/1. However, in order to define a standard procedure valid for all kind of wastes, a single ratio must be established. Two main points were considered when establishing the most suitable ratio: i) the sample amount analyzed must be enough for being considered as representative (a minimum of 70-80 g of sample); and ii) the no acidification of the media must be assured.

Different experiments were carried out to sort out the quandary. Finally a ratio of 2/1 inoculum/substrate in dry basis was assessed as the most suitable for biogas and methane production determination for all kind of wastes. This ratio coincides with the ratio used in the MBT plant for feeding the digester mixing the waste with the digester output material.

Sealed aluminum bottles of 1 liter of working volume will be used for carrying out the anaerobic tests (Figure 4.7). The mixture is directly made in the bottles by adding the correspondent amounts of inoculum and sample to finally obtain 600 ml of mixture and around 400 ml of headspace (depending on the bulk density of the mixture) in the bottles. The mixtures were incubated in a temperature controlled room at 37°C. Before each experiment, the bottles were purged with nitrogen gas to ensure anaerobic conditions. The bottles had a ball valve which can be connected to a pressure digital manometer (SMC model ZSE30, Japan) allowing for the determination of the biogas pressure. The bulk density of the mixture was previously determined (in triplicate) to calculate the headspace volume of the bottles which was assumed constant along the experiment. During the test, the bottles were shaken once a day.

Biogas and methane productions were calculated according to the ideal gas law from the pressure measured in the bottle and considering the headspace volume previously measured.

To avoid excessive pressure in the bottle the biogas produced was purged periodically (typically 25-30 times during the experiment). This way pressure was not allowed to reach a value over 2 bar. This contributes to minimize the possible solubilization of carbon dioxide since methane is hardly soluble in aqueous media. Nevertheless, final biogas production at long times should not be affected by this effect.

All biogas production tests were carried out in triplicate. The results are expressed as an average with standard deviation. If one of the bottles presented a deviation higher than 20%, it was discarded for the biogas potential calculation.

Figure 4.7. Set up for anaerobic index determination: sealed aluminum bottles.

A biogas production test containing only inoculum was analyzed in triplicate to be used as a blank. The blank is also useful to have a quantitative measure of inoculum activity. Biogas and methane production from inoculum samples must be subtracted from the biogas and methane production of the waste samples. That would mean that results of GB_n and BMP_n represent only the biogas or methane produced by degrading anaerobically the organic matter contained in the sample and without considering the remaining organic matter that can content the inoculum.

In Figure 4.8, the results obtained for 3 different OFMSW are showed, as average of the 3 replicates and standard deviation. Also the GB_n for inoculum (blank) is plotted in the graph for comparison.

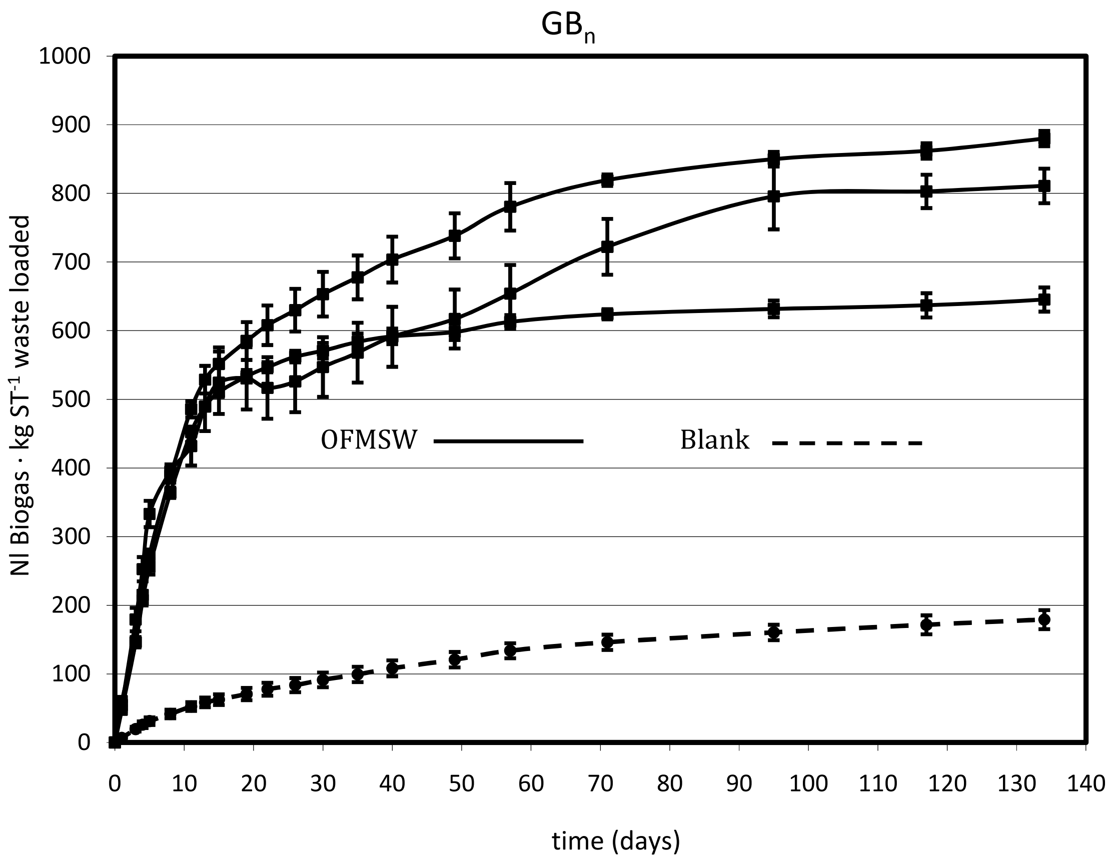

Figure 4.8. Example of GB_n evolution (average and standard deviation) for 3 different samples of OFMSW from different origin and the blank.

The procedure to determine GB_n and/or BMP_n is described below.

i) The volume of biogas or methane produced at 37°C and 1 atm in each experiment is calculated as follows (Equation 4.3)

$$V_{37°C,n} = \frac{\left[B-\left(W/_{BD_w}\right)\right]\times\sum_{i=0}^{n} P_i}{1.032502} \quad \text{(Equation 4.7)}$$

Where $V_{37°C,n}$ is the volume of biogas (or methane) produced in a bottle after n days (L); B is the bottle working volume (L); W is the total wet weight of the mixture introduced in the bottle (kg); BD_w is the wet bulk density of the mixture (kg · L^{-1}) ; P_i is the pressure measured after pressure release (bar); n is the days after experiment started; 1.032502 is the atmospheric pressure (bar).

ii) The net volume of biogas (or methane) produced, after subtracting the biogas (or methane) produced by the blank is calculated as follows (Equation 4.8)

$$V_{net\ 37°C,n} = \left[V_{37°C,n}\right] - \left[\left(\sum_{i=0}^{3} {V_{37°C\ inoc.,i}}/_{W_{inoc,i}}\right)\Big/ 3\right] \times S_{inoc} \quad \text{(Equation 4.8)}$$

Where $V_{net\ 37°C,n}$ is the net volume of biogas (or methane) produced in a sample bottle after n days (liters); $V_{37°C\ inoc.,i}$ is the volume of biogas (or methane) produced in each blank triplicate after n days (liters); $W_{inoc,i}$ is the total wet weight of inoculum initially introduced in each blank triplicate (g); S_{inoc} is the wet weight of the inoculums used when making the initial mixture waste-inoculum (g).

iii) The biogas production during n days (GB_n) and biological methane potential during n days (BMP_n) is finally determined using Equation 4.9

$$GB_n\ (BMP_n) = \left[\left({V_{net\ 37°C,n}}/_{Z}\right) \times \frac{273.15}{310.15}\right] \quad \text{(Equation 4.9)}$$

Where GB_n is the net volume of biogas produced from a waste sample after n days (NL biogas·kg DM^{-1}); BMP_n is the net volume of methane produced from a waste sample after n days (NL methane·kg DM^{-1}); Z is the amount of DM of sample initially loaded in the reactor (kg DM); 310.15 is the temperature measured in Kelvin at which the experiment is carried out (310.15 K) and equivalent to 37°C; 273.15 is the temperature in Kelvin which corresponds to normal conditions (273.15 K) and equivalent to 0°C.

CHAPTER 5. RESULTS

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This chapter contains the articles that have been published in indexed international journals

Article I: Composting of dewatered wastewater sludge with various ratios of pruning waste used as a bulking agent and monitored by respirometer.

Article II: Comparison of aerobic and anaerobic stability indices through a MSW biological treatment process.

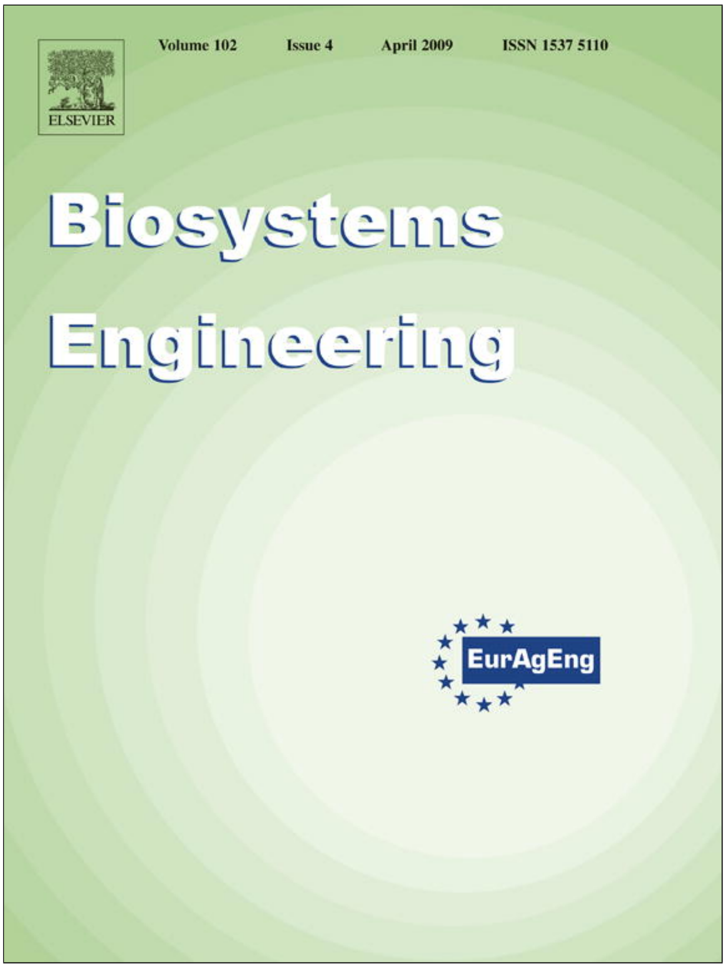
Article III: The effect of storage and mechanical pretreatment on the biological stability of municipal solid wastes.

Article IV: Different indices to express biodegradability in organic solid wastes.

Article I

Composting of dewatered wastewater sludge with various ratios of pruning waste used as a bulking agent and monitored by respirometer.

Sergio Ponsá , Estela Pagans, Antoni Sánchez
Biosystems Engineering. 2009. Vol (102), p. 433-443.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Research Paper: SE—Structures and Environment

Composting of dewatered wastewater sludge with various ratios of pruning waste used as a bulking agent and monitored by respirometer

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The effects of different volumetric ratios of wastewater sludge to bulking agent on the performance of full-scale composting were studied. Volumetric ratios of wastewater sludge to pruning waste, used as a bulking agent, were 1:2 (Pile 1), 1:2.5 (Pile 2) and 1:3 (Pile 3). Experiments were carried out in an uncovered plant using windrow composting with weekly turning. To monitor the evolution of the three composting piles, routine parameters such as temperature and interstitial oxygen level, chemical parameters such as organic matter, moisture and C/N ratio, and biologically related indices such as respiration indices at process temperature ($RI_{process}$) and at 37 °C (RI_{37}) were monitored. Different responses were observed in the three piles; Pile 1 did not accomplish the necessary requirements in terms of sanitation and $RI_{process}$ for a typical composting process; Piles 2 and 3 presented a similar behaviour, reaching thermophilic temperatures for a long period and, due to their high biological activity, high $RI_{process}$. The quality of the product obtained in the three piles in terms of stability (RI_{37} and the Rottegrade self-heating test) and maturity (germination index) were measured, with compost from Pile 3 the most stable. To achieve satisfactory stability and sanitation for application to land, optimisation of the sludge to bulking agent ratio used to process wastewater sludge into compost appears to be crucial.

1. Introduction

In 1998, Spain produced about 0.6–0.8 × 10^6 Mg of dry wastewater sludge and it is expected that during 2006 the production will reach 1.5 × 10^6 dry Mg per year (Ministerio de Medio Ambiente, 2001). Catalonia, located in the northeast of Spain, is one of the regions with the highest production of sludge. At present, land application is the main disposal mode used for wastewater sludge, and there are unique legal restrictions for application to soil related to heavy metal content and the presence of potentially toxic compounds. Also, the spreading of sludge onto land must be carried out using methods that ensure the effective elimination of pathogens and the maximisation of agronomic benefits.

Wastewater sludge composting with the use of bulking agents can enhance the stability of organic matter, inactive pathogens and parasites (Larsen *et al.*, 1991; Furhacker & Haberl, 1995; Wei *et al.*, 2001; Wang *et al.*, 2003), and enable the production of a quality product that may be used as a soil conditioner or as an organic fertiliser (Tremier *et al.*, 2005). A

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Nomenclature

C/N	carbon to nitrogen ratio
CBAR	critical bulking agent requirement
RI	respiration index
RI_{37}	respiration index at a fixed temperature of 37 °C (mg [O_2] g^{-1} [VS] h^{-1})
$RI_{process}$	respiration index at the *in situ* temperature of the pile (mg [O_2] g^{-1} [VS] h^{-1})
VS	volatile solids
w/w	weight to weight ratio

long list of waste materials have been proposed as bulking agents, although the most widely used materials are wood chips and pruning waste (Atkinson *et al.*, 1996; Jokela *et al.*, 1997; Wong *et al.*, 1997; Larsen & McCartney, 2000). Common volumetric ratios of bulking agent to sludge are approximately 2:1 to adjust C/N ratio to 25 (Wong *et al.*, 1997). The study conducted by Eftoda & McCartney (2004) presented a systematic approach concerning the critical bulking agent requirement (CBAR) in sludge composting, by simulating the compressive load occurring in full-scale composting conditions. Although bulking agents are not believed to degrade significantly under composting conditions, because of their high lignin content, some recent works have reported a certain biodegradability of wood chips (Mason *et al.*, 2004). The optimisation of the sludge-bulking agent mixtures for urban or industrial sludge composting has been extensively studied (Milne *et al.*, 1998; Miner *et al.*, 2001; Gea *et al.*, 2003). The agronomical quality of compost produced is limited mainly by their chemical composition as well as by the stability and maturity of the organic matter (Govi *et al.*, 1993; Sesay *et al.*, 1997; Bernal *et al.*, 1998a; Grigatti *et al.*, 2004). Stability is related to the presence of easily biodegradable compounds in the composting process and can be measured by the respiration index (RI) (Iannotti *et al.*, 1993; Chica *et al.*, 2003). RI is commonly determined at mesophilic temperatures (30–37 °C) and it is an indicator of the biological activity of the composting process (Adani *et al.*, 2003). However, since predominant active microbial populations evolve according to composting temperature profile, if RI is estimated at process temperature it can be used as an indicator of the evolution of the biological activity during composting (Barrena *et al.*, 2005, 2006a). In fact, recent results have shown weak correlations between RIs determined under mesophilic conditions and process temperature in full-scale composting of organic fraction of municipal solid wastes (Barrena *et al.*, 2006b) and sludge composting Eftoda & McCartney (2004). Other authors have proposed the use of dynamic respiration tests to overcome oxygen transfer limitations, although the cost of this type of test is considerably higher (Barrena *et al.*, 2009). However, there are few references to the use of RIs in composting of wastewater sludge. In comparison to stability, maturity is normally defined in relation to compost application and plant growth (Cooperband *et al.*, 2003) and it is usually determined by means of germination experiments (Weppen, 2002; Tang *et al.*, 2006).

Windrow composting is the most common method to produce compost from organic wastes (Avnimelech *et al.*, 2004). In windrow composting systems, the major source of aeration is natural convection, when air moves through interstitial voids (porosity) in the pile supplying oxygen to the microorganisms (Eftoda & McCartney, 2004). However, the need for porosity and, in consequence, the use of bulking agents increases the operational costs for composting plants. The cost of purchasing bulking agents and the cost of transportation may be particularly relevant in regions where there are no available gardens or forest areas, between 20 and 30 € Mg^{-1} of total cost, according to Spanish prices and providers (Ruggieri *et al.*, in press). At the same time, bulking agent requirements can result in space limitation as they increase the volume of material to process.

For this reason, when conditioning a high moisture content substrate (such as wastewater sludge) in a full-scale composting process, the minimum amount of bulking agent required to maintain an adequate oxygen level in the pore space of the compost matrix is key to ensuring optimum performance because it saves costs and it reduces the requirement for land. Several recent studies have highlighted the necessity of performing full-scale studies to obtain reliable conclusions about the composting process (Eftoda & McCartney, 2004; Ruggieri *et al.*, 2008). However, such studies conducted at full-scale are rare in the literature.

The objectives of this research were to: (i) determine the optimal bulking agent to sludge volumetric ratio on a full-scale composting process of wastewater sludge using mechanical turning; (ii) study the overall efficiency of the composting process, in terms of stabilisation of organic matter, (iii) monitor the biological activity of the composting process, by using different respiration techniques, and (iv) determine the final compost maturity, based on germination indices.

2. Materials and methods

2.1. Composting materials

Dewatered wastewater sludge was obtained from several urban wastewater treatment plants located in the region of Lleida (Catalonia, Spain); they are usually processed at the composting plant at Alguaire (Lleida). The average composition of wastewater sludge is presented in Table 1. The concentration of other nutrients was (dry weight basis): N–NH_4^+: 0.99%; Ca: 4.8 (% CaO); Fe: 0.98%; P: 2.5 (% P_2O_5); Mg: 1.0 (% MgO); K: 1.1 (% K_2O), showing no limitation of the nutrients in the composting process. The heavy metal content was (ppm, dry weight basis): Cd: 1.9, Cu: 130, Cr: 60, Hg: 0.8, Ni: 42, Pb: 54, Zn: 470; well below the international limits for sludge application to soil in Europe (European Commission, 2000). Pruning wastes were used as a bulking agent since this was the typical bulking agent used at the composting plant in Alguaire. Table 1 shows the main characteristics of the wastes composted.

Table 1 – Properties of the initial mixtures for the three composting experiments and characteristics of bulking agent and wastewater sludge

Material	Moisture content (%)	Organic matter (db, %)	Organic C (db, %)	Organic N (db, %)	C/N	pH	Electrical conductivity ($mS\ cm^{-1}$)	RI_{37} (mg [O_2] g^{-1} [VS] h^{-1})
Sludge	84.7 ± 0.1	75.0 ± 0.1	41.2	5.96	7.0	N/M	N/M	7.3 ± 0.2
Bulking agent	17.3 ± 0.1	58.1 ± 0.3	32.0	0.71	44.9	N/M	N/M	1.3 ± 0.2
Pile 1[a] (1:2)	62.7 ± 0.9	51.3 ± 0.4	28.5	2.68	10.6	8.04	2.65	2.08 ± 0.04
Pile 2[a] (1:2.5)	63.9 ± 0.4	55.4 ± 0.4	30.7	2.09	14.7	8.64	2.49	1.7 ± 0.1
Pile 3[a] (1:3)	43 ± 5	52.0 ± 0.6	28.9	1.65	17.5	8.16	3.10	2.1 ± 0.2

db: dry basis; N/M: not measured.
a Properties determined once the pile was built (after 1 week).

2.2. *Composting experiments*

Composting experiments were carried out at the uncovered composting plant of Alguaire (Lleida, Spain). The environmental conditions (average daily temperature and precipitation) during the course of the experiments are shown in Fig. 1.

Three composting piles were built simultaneously by mixing approximately 55–60 Mg of sludge with pruning wastes in three different volumetric ratios (sludge:bulking agent): 1:2 (Pile 1); 1:2.5 (Pile 2) and 1:3 (Pile 3). The initial ratios were selected according to the normal operation of the composting plant, from a low ratio (1:2), in terms of available porosity, and a high ratio (1:3), which was selected as the maximum value because of the availability of bulking agent at the plant. The approximate amounts, volumes and bulk densities of sludge and bulking agent mixtures used for each pile are presented in Table 2 and the main characteristics of the composted mixtures are shown in Table 1. It should be borne in mind that it took approximately one week to build the three piles, so it is probable that some degradation occurred during this period. Initial bulk densities for the mixtures tested can be considered high, as the sludge ash content was also high in comparison with other wastewater sludge (Haug, 1993). The base time for composting experiments was the day when all three piles were fully formed.

The approximate dimensions of the piles were as follows: base: 4 m; height: 1.5 m; length: 30–40 m, and they were trapezoidal in shape. The piles were built on a slopped concrete floor and they were not sheltered from the rain according to the normal operation of the plant. Sludge and pruning wastes were initially mixed as follows. Sludge was firstly deposited onto a 40–50 mm bed of pruning wastes with a particle size smaller than 30 mm. The remainder of pruning wastes, necessary to reach each of the three selected ratios, was then added on top of the mixture and then mixed using a turner (Backhus Model 15.50, Edewecht, Germany). Once the process was finished, and the wastes were well mixed, three passes of the turner were necessary to build-up each pile to the specified dimensions. The composting experiment was carried out from the 7th November, 2005 to the 31st January, 2006 (i.e. 85 days). All the piles were turned weekly and forced aeration was not provided.

Temperature and oxygen content of the piles were measured *in situ* at 1.00 and 1.50 m depth in four points of each

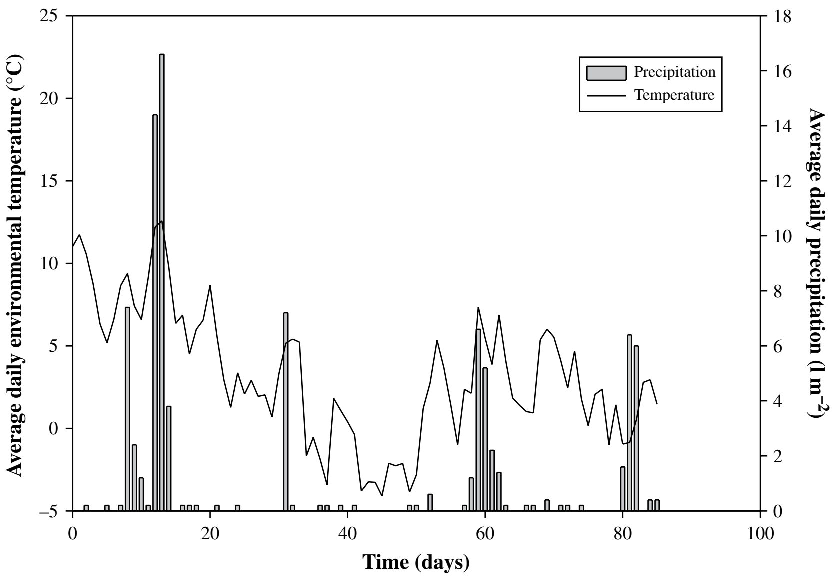

Fig. 1 – Average daily environmental temperature and average daily precipitation during the course of the experiments in the composting plant of Alguaire.

Table 2 – Properties of the three piles studied. Sludge and bulking agent weights and total volume of the piles were experimentally determined

Pile	Bulking agent (w/w, mg)	Sludge (w/w, mg)	Initial percentage of sludge (%, weight basis)	Total volume (m^3)	Bulk density ($Mg\,m^{-3}$)
Pile 1	30.2	64.1	68.0	90	1.05 ± 0.2
Pile 2	43.7	74.2	63.0	120	0.98 ± 0.1
Pile 3	42.3	59.8	58.6	105	0.97 ± 0.1

w/w: wet weight.

pile. The temperature and oxygen values presented are average values and the standard deviation is shown. Temperature was measured with a portable Pt-100 sensor (Delta Ohm HD9214, Caselle di Selvazzano, Italy) and oxygen concentration was measured with a portable O_2 detector (Oxy-ToxiRAE, RAE, San Jose, USA) connected to a portable aspiration pump.

2.3. *Analytical methods*

Moisture, total organic matter (expressed as volatile solids, VS), organic nitrogen content, carbon/nitrogen ratio (C/N), nutrient content, heavy metal content, pH, electrical conductivity, bulk density, germination indices and the results from the Rottegrade self-heating test were all determined using an integrated sample and using standard procedures (US Department of Agriculture and US Composting Council, 2001). This bulk-integrated sample was obtained from eight different locations of each pile giving a final volume of approximately 24 l. Then, the integrated sample was manually mixed in the laboratory and reduced using the quartering method to several sub-samples of 1.5–2 l (approximately 1–1.5 kg) (Keith, 1996), which were used to carry out the analytical procedures. The sub-samples were stored at 4 °C for less than 24 h prior to analysis.

Moisture content was determined by drying a moist sample in a forced-air oven set at 105 °C until constant sample weight and expressed on a wet weight basis. Total organic matter was determined by ignition of a dry sample in a muffle furnace at 550 °C for 2 h and expressed on a dry weight basis. Organic nitrogen content was determined by digestion using sulphuric acid at 420 °C for 1.5 h followed by distillation according to Kjeldahl method. Electrical conductivity and pH were determined using a mixture of compost and deionised water blended to a ratio of 1:5 (w/w) (US Department of Agriculture and US Composting Council, 2001). Bulk density was determined using the water displacement method. Results from the Rottegrade self-heating test were determined by measuring with a Pt-100 sensor the maximum temperature produced by a sample of compost incubated for 10 days in a 1.5 l Dewar vessel. Carbon content was based on the total organic matter of the samples and considering that, for biological materials, the carbon content is 55% of the volatile solid fraction (Tiquia et al., 1996). All the analyses mentioned above were triplicated with each replicate coming from a different sub-sample. The standard deviations of the replicated measurements are presented with all experimental data. Where no standard deviation is shown, the errors can be considered negligible.

2.4. *Respiration tests*

Static RIs were determined using a respirometer, which was built to the design of the original model (Iannotti *et al.*, 1993) but including the modifications and recommendations given by the US Department of Agriculture and US Composting Council (2001). A detailed description of the respirometer and its design was published by Barrena *et al.* (2005).

The experimental setup also included a water bath to maintain the selected temperature during the respirometric test (total duration was 1 h). Respirometer tests were assayed at the *in situ* temperature of the pile during sampling in order to obtain the real biological activity of the process (i.e. under the same conditions, without incubation to avoid hydrolysis of organic matter). Results of the static respiration related to the stability of the material (carried out during the last sampling) were also measured at a fixed temperature value of 37 °C after an incubation period of 24 h, as this is the usual temperature and incubation period used for the prediction of compost stability (Iannotti *et al.*, 1993). In addition, in Pile 2 the RI at 37 °C was measured for comparison purposes, since previous results with municipal solid wastes have demonstrated that it does not change significantly during composting (Barrena *et al.*, 2005). Our previous results (Barrena *et al.*, 2006b), obtained during full-scale composting of municipal solid wastes, have demonstrated that the use of the actual process temperature to determine the RI is necessary to accurately determine the biological activity, whereas mesophilic conditions are only able to predict compost stability.

RI is expressed as the amount of oxygen consumed per unit of total organic matter of the sample per hour (mg [O_2] g^{-1} [VS] h^{-1}). Values of RI are presented as the mean of three replicates. Standard deviation is also presented; usually in the range of 5–10%.

2.5. *Phytotoxicity*

Aqueous extracts of the three piles final samples were prepared by adding two parts of deionised water per part of sample weight (on a dry matter basis). The phytotoxicity of these extracts (filtered by 0.45 μm) was evaluated by the seed germination technique (Tiquia *et al.*, 1996; Tiquia & Tam, 1998). Cucumber (*Cucumis sativus*) was used for the test. Using 10 seeds of cucumber incubated in the extracts at 25 °C for 5–7 days, the seed germination percentage (germination index) and root length of the cucumber seeds were determined. Seed germination percentage and root elongation in distilled water were also measured as a control. The percentages of relative seed germination, relative root elongation and combined germination index were calculated as follows:

$$\text{Relative seed germination (\%)} = \frac{\text{No. of seeds germinated in final compost extracts}}{\text{No. of seeds germinated in control}} \times 100 \quad (1)$$

$$\text{Relative root growth (\%)} = \frac{\text{Mean root length in final compost extracts}}{\text{Mean root length in control}} \times 100 \quad (2)$$

$$\text{Combined germination index} = \frac{(\text{\% Relative seed germination})(\text{\% Relative root growth})}{100} \quad (3)$$

All germination indices were calculated using three replications.

3. Results and discussion

3.1. *Evolution of temperature and interstitial oxygen*

Weather conditions affect the performance of the composting process since parameters such as interstitial oxygen and moisture content are dependent on the average daily environmental temperature and the average daily precipitation. The profiles of average daily environmental temperature and average daily precipitation are plotted in Fig. 1. Low temperatures and high precipitation were recorded during the composting experiments. Few studies have been published about the influence of cold weather and precipitation conditions on the composting performance but McCartney & Eftoda (2005) found a positive correlation between snowfall and oxygen supply and pile moisture content.

The temperature profiles of the three composting piles are shown in Fig. 2. No significant differences were observed between oxygen and temperature measurements obtained at different depths of the material. The standard deviations for temperature values were in the range of 2–8 °C, whereas in the case of oxygen they were in the range of 1–4% (Fig. 3). However, the initial values of temperature had a high degree of variability because the construction of the piles took 1 week.

The thermophilic range of temperatures was easily reached by Piles 2 and 3 despite the low ambient temperatures (<0 °C for several weeks) and the poor weather conditions (rain, fog and high humidity). In Pile 3 average temperatures over 55 °C were measured for more than 70 days, which was a positive indication for sanitation of the material. Also, Pile 2 had average temperatures over 55 °C for at least 15 days. Turning of the piles was carried out once a week, in excess of that required by the regulations for sanitation (US Environmental Protection Agency, 1995). Therefore, the material composted in Piles 2 and 3 met the international requirements on compost sanitation, which are based on time–temperature conditions (US Environmental Protection Agency, 1995; European Commission, 2000). However, as shown in Fig. 2, according to international regulations the material in Pile 1 was not sanitised. Nevertheless, a microbial study would be necessary to ensure the absence of pathogen microorganisms in the three piles.

Fig. 3 shows the evolution of interstitial oxygen of the material for each pile. Initially a drop in the oxygen values for the three piles could be observed until a minimum value of 10, 5.5 and 8% for Piles 1, 2 and 3, respectively. These drops in the values of oxygen content could mostly be attributed to the high initial biological activity of the material in Piles 2 and 3, as it was observed by the rapid temperature rise, which is the

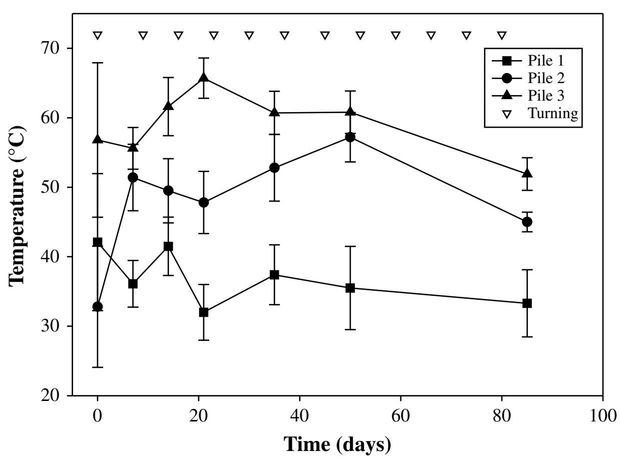

Fig. 2 – Temperature profiles (average values) during the course of the experiment for Piles 1, 2 and 3. Error bars show the standard deviation.

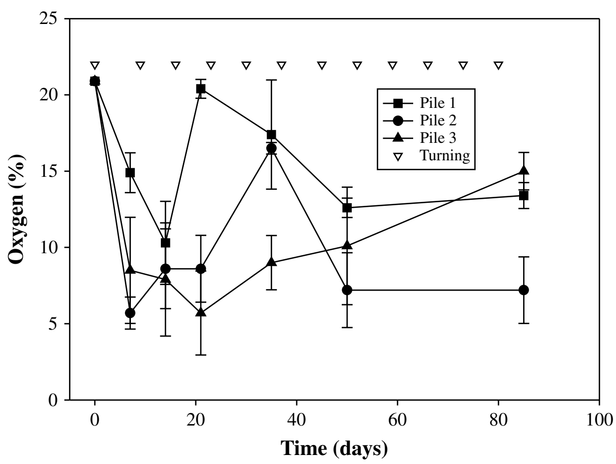

Fig. 3 – Oxygen content profiles (average values) during the course of the experiment for Piles 1, 2 and 3. Error bars correspond to standard deviation.

typical composting profile for highly biodegradable wastes (Gea et al., 2004). In Pile 1, the reason for oxygen depletion may be related to high moisture content and a resulting low-porosity, as it can be observed in Fig. 4, since biological activity was always low for this Pile 1, as will be explained later. Pile 3 followed a typical interstitial oxygen profile; initially a drop followed by an increase as temperature decreases. This indicated a reduction in the biological activity due to the progressive diminution and exhaustion of biodegradable organic matter. Furthermore, it is necessary to point out that the interstitial oxygen level in Pile 1 was always slightly higher, which could be because of the lower biological activity as will be discussed later. During days 20–40, an increase in oxygen content was observed for all three piles. This could be due to a reduction in the moisture content (Fig. 4), which implies an increase in the porosity that allowing better air circulation, as has been reported for other organic wastes (Ruggieri et al., 2008). During the next period (from day 40) a slight decrease of oxygen for Piles 1 and 2 was observed, even when moisture content was stable. A possible explanation of this might be a progressive compaction of the material and a loss of free air space, which is often related to a lack of bulking agent (Miner et al., 2001; Gea et al., 2003; Eftoda & McCartney, 2004).

On the other hand, some values of interstitial oxygen detected during the experimental period can be considered as low. Although these values can be considered to limit the composting process, there has been some evidence of good composting performance when a mechanical system with frequent turning is used (Barrena et al., 2006b; Ruggieri et al., 2008). It appears that having an adequate set of conditions for the start-up of a composting process with wastewater sludge (moisture, porosity, etc.) is not the only requirement necessary to ensure a successful process performance. It is possible that, in order to achieve the desired temperature profiles, there is a minimum level of respiration activity or, in our words, a high oxygen uptake rate, necessary for the first stages of composting at full-scale, as will be discussed later.

3.2. Physico-chemical parameters

Initial and final properties of the three composting mixtures are shown in Tables 1 and 3, respectively. Evolution of moisture content during composting is shown in Fig. 4. Because of the weather conditions, environmental humidity and a total precipitation of 90 mm (Fig. 1), an increase in moisture content during the first week was observed in all three piles. It is probable that the initial mixture of sludge and bulking agent was not water-saturated and consequently some rainwater

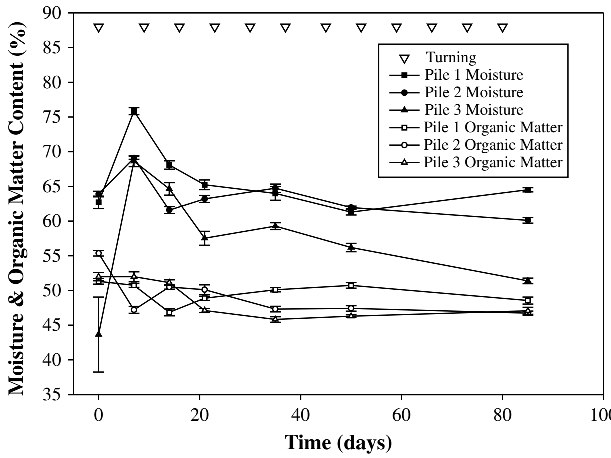

Fig. 4 – Evolution of moisture on wet weight basis (solid symbols) and organic matter on dry matter basis (open symbols) content during the course of the experiment for Piles 1, 2 and 3. Error bars show the standard deviation.

was retained thereby increasing moisture content. In addition, the temperature of the piles was not high enough to evaporate the excess of water. However, contrary to the results obtained by other authors (McCartney & Eftoda, 2005), no significant correlation ($p < 0.05$) was found between precipitation and moisture content. The abnormally low initial moisture content of Pile 3 can be due to a sampling error, as this value is not feasible according to the initial moisture values of sludge and bulking agent. Unfortunately, no sample was available to repeat this analysis. The effect of the increasing moisture, combined with the aerobic biological activity, was reflected in a drop of the interstitial oxygen level for the three piles. However, after the first week, a decreasing trend was observed with the three experiments reaching final values of 51% for Pile 3 and 60% for Piles 1 and 2. Nevertheless, moisture levels were over 40% during the composting experiments for the three piles, which is considered as the minimum value for optimal composting piles. Thus, composting was not limited by moisture content (Haug, 1993). Dry matter reductions are shown in Table 4, with values in the range of 5.4–16.3% being obtained. However, a significant correlation could not be determined between dry matter reduction and the extent of the composting process.

Organic matter evolution is shown in Fig. 4, and total reductions of organic matter content are presented in Table 4. No conclusions could be drawn from the results for organic matter since the bulking agent (which is mostly organic) was

Table 3 – Properties of final products obtained from the three composting experiments

Pile	Moisture content (%)	Organic matter (db, %)	Organic C (db, %)	Organic N (db, %)	C/N	pH	Electrical conductivity ($mS\ cm^{-1}$)	RI_{37} ($mg\ [O_2]\ g^{-1}\ [VS]\ h^{-1}$)	Stability grade
Pile 1	64.5 ± 0.3	48.6 ± 0.5	26.97	2.22	12.1	8.14	2.14	1.01 ± 0.04	V
Pile 2	60.1 ± 0.4	46.7 ± 0.3	25.96	1.48	17.5	8.27	1.65	1.16 ± 0.09	V
Pile 3	51.4 ± 0.4	47.1 ± 0.5	26.15	0.79	32.8	8.10	1.62	0.7 ± 0.1	V

db: dry basis.

Table 4 – Dry matter and organic matter reduction for the three composting experiments. Data presented are calculated from an overall mass balance, considering the principle of ash content conservation (Haug, 1993)

Material	Dry matter reduction (%)	Organic matter reduction (%)
Pile 1	5.5	10.5
Pile 2	16.3	29.5
Pile 3	8.1	15.5

not significantly degraded. Nevertheless, organic matter reductions, for Piles 2 and 3 were higher than for Pile 1 because of the more active process that occurred in Piles 2 and 3. Other authors have studied the reduction in organic matter in the different sludge composting systems. For instance, a 10% reduction was obtained with a pile-scale aerated static bin (Zhu, 2006), whereas other authors obtained high values of reduction (55%) for a full-scale aerated pile (Baeta-Hall *et al.*, 2005). Recently, other authors have reported reductions in the range of 30–50% depending on the type of bulking agent using the Rutgers system, forced ventilation and mechanical turning (Alburquerque *et al.*, 2006).

The trends for pH and electrical conductivity are presented in Tables 1 and 3 and Fig. 5. All the values obtained had a low standard deviation and agreed with typical values for the composting processes with a slight decrease of electrical conductivity (Pagans *et al.*, 2006). The trend for pH was typical of that related to fatty acid production, and ammonia generation and release. Initially, pH was relatively high compared to other organic wastes (e.g. municipal solid wastes) (Gea *et al.*, 2004), which is usual for wastewater sludge because of its high free ammonia content (Weppen, 2002). Then, during the most active part of the composting process (0–20 days) ammonia is stripped as gas and the possible formation of fatty acids provokes a slight decrease in pH (Pagans *et al.*, 2006; Sundberg *et al.*, 2004). After the active phase, the decrease in temperature results in a lower vaporisation of ammonia and the biodegradation of fatty acids, which leads to an increase in pH to an alkaline value. As it can be observed, only slight differences were detected among the three piles, therefore it can be

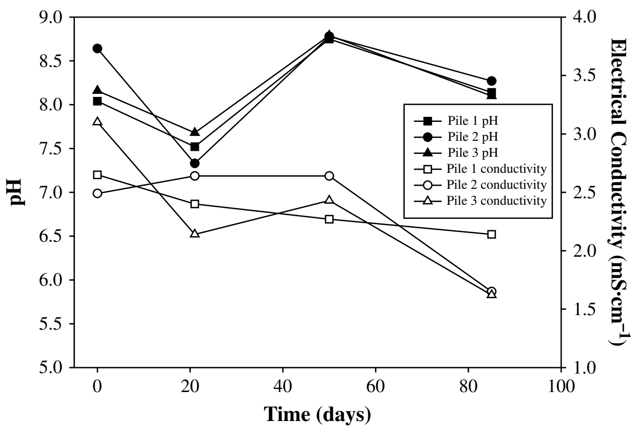

Fig. 5 – Evolution of pH (solid symbols) and electrical conductivity (open symbols) during the course of the experiment for Piles 1, 2 and 3.

concluded that bulking agent ratio did not have a significant influence on these parameters.

In relation to C/N ratios presented in Tables 1 and 3, the initial values were slightly lower than those recommended for composting (Jokela *et al.*, 1997; Wong *et al.*, 1997; Larsen & McCartney, 2000). The highest initial C/N ratio was 17.5 for Pile 3, which is very close to the optimal reported values for C/N ratio (Jokela *et al.*, 1997). The C/N ratio increased during the composting process resulting in a relatively high C/N ratio, which may have been caused by high rates of ammonia emission. In fact, low C/N ratios have been proposed as a measure of compost stability (Bernal *et al.*, 1998a, b). However, it must be pointed that C/N ratios in initial mixtures for composting are usually formulated on a total C/N basis, whilst not all the C is biodegradable (Sánchez, 2007). However, the C/N ratio results demonstrated that none of the piles was nitrogen limited.

3.3. *Biological activity indices*

Different RIs were measured during the experimental period. Respirometry usually refers to the aerobic biological activity of the material and was determined at two different temperatures: RI at process temperature ($RI_{process}$), which is an indicative parameter of the real process activity at operating conditions, or RI at 37 °C (RI_{37}), which is related to the material stability in the maturation phase (Barrena *et al.*, 2005). It is also generally considered that values of RI_{37} below 1 mg $[O_2]$ g^{-1} [VS] h^{-1} correspond to a stable compost (California Compost Quality Council, 2001). On the other hand, the Rottegrade self-heating test gives information in form of a stability grade. In Europe, this test is commonly used to characterise the stability of compost, with a range from I (fresh material) to V (mature compost) (US Department of Agriculture and US Composting Council, 2001). The test is based in determining the increase of temperature of a compost sample in an adiabatic Dewar vessel. However, the Rottegrade test is used routinely with municipal solid wastes (Barrena *et al.*, 2005) and no information is available on the performance of this test with wastewater sludge.

Trends for $RI_{process}$ for the three piles were determined and monitored during the experimental period. However, RI_{37} was only determined for Pile 2, since this pile was built according to the usual composting pile recipe (i.e. sludge:bulking agent ratio) and was used as a control sample. Furthermore, RI_{37} and Rottegrade self-heating test were determined for the final material of the three piles to measure the final stability of the compost obtained.

Trends for $RI_{process}$ are shown in Fig. 6. Initially, the $RI_{process}$ for the three piles was similar and close to 2 mg $[O_2]$ g^{-1} [VS] h^{-1}. After the first week of composting, the maximum value of $RI_{process}$ was reached in Piles 2 and 3. For large masses, the time necessary to reach the maximum value of respiration activity is because it is necessary to have a homogenous distribution of microbial population and biodegradable organic matter. This phenomenon is not usually observed in laboratory scale composting experiments (Gea *et al.*, 2004; Barrena *et al.*, 2005). A maximum $RI_{process}$ values close to 12 mg $[O_2]$ g^{-1} [VS] $h^{-1}$and close to 5 mg $[O_2]$ g^{-1} [VS] h^{-1} were reached in Piles 3 and 2, respectively. These can be considered

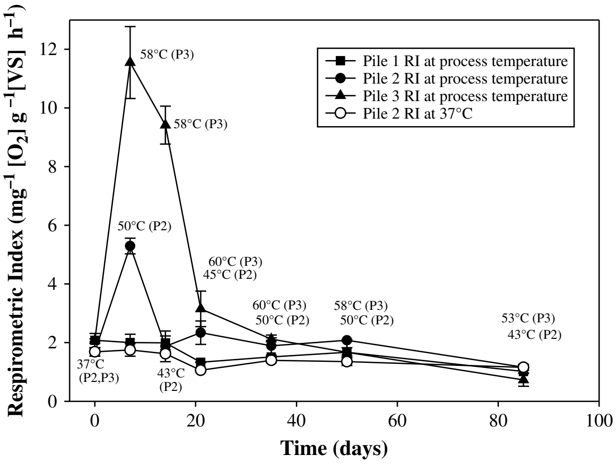

Fig. 6 – RI at process temperature for Piles 1, 2 and 3 jointly with the temperature of each sample. RI at 37 °C for Pile 2 (open circle) during the course of the experiment. Error bars show the standard deviation.

as being very high values of RI, and they correspond with values found for other biodegradable organic wastes such as organic fraction of municipal solid wastes and paper sludge (California Compost Quality Council, 2001; Barrena *et al.*, 2006a). However, $RI_{process}$ for Pile 1 did not increase as was expected, given the high values of RI found for wastewater sludge (Table 1) and low values of $RI_{process}$ were obtained. Therefore, it is evident that a high level of porosity is necessary for the composting of high moisture organic wastes such as wastewater sludge at full-scale. However, other studies on composting of wastewater sludge at laboratory scale have shown that with a relatively low volumetric bulking agent:sludge ratio (1:1 or 2:1) it is possible to obtain a successful composting process (Gea *et al.*, 2003, 2004). It is remarkable to note that the optimal bulking agent volumetric ratios found in the present study are very close to those of laboratory composting experiments systematically conducted with the objective of determining CBAR by simulating the compressive load that occurs at full-scale. In this case, the key was to include vertical loadings in the small-scale simulations to obtain results representative of full-scale conditions (McCartney & Chen, 2001; Eftoda & McCartney, 2004). This again reinforces the necessity of carrying out composting experiments at full-scale when the process is to be implemented on an industrial scale. Because of their influence on the composting process, it is also necessary to carry out full-scale experiments under representative weather conditions.

After reaching the maximum value, the $RI_{process}$ for Piles 2 and 3 showed an important decrease during the two following weeks, according to the progressive stabilisation of organic matter; confirming that a significant amount of oxygen was consumed during the first stage. However, during this period no variation in $RI_{process}$ was observed for Pile 1, which confirms the low biological activity found in this pile, even 3 weeks after the composting pile was built and despite the weekly turnings. This is again evidence of the key role that bulking agent ratio plays in the performance of wastewater sludge composting. It is possible to attribute the initial low activity found in Pile 1 to an excessive moisture content. Nevertheless, after the third week, moisture content in Pile 1 was similar to that in Piles 2 and 3, which showed the maximum $RI_{process}$ values. As a consequence, during the remainder of the composting process, it was evident that a low ratio of bulking agent was responsible for the low biological activity observed.

In the final 2 months of the composting a slight decrease of $RI_{process}$ was observed for Piles 2 and 3, which could be probably attributed to the degradation of slowly biodegradable compounds. Thus, it can be concluded that a higher level of biological activity takes place during the first phase, when easily biodegradable organic matter is available for the microorganisms. After this, when the pool of organic matter is exhausted, biological activity remains practically constant at low level or with a slightly decreasing tendency because the less-easily biodegradable organic matter requires lower oxygen consumption (Barrena *et al.*, 2006c). After 3 months, Pile 1 continued showing a constant $RI_{process}$, which possibly implies that basal respiration was maintained during the entire composting period.

Comparing $RI_{process}$ data with pile temperature profiles during the first stage, it can be observed that initially they are well correlated. The pile with the highest biological activity (Pile 3), in terms of $RI_{process}$, reached the highest temperature in a short period. Pile 2, which showed significant biological activity, also reached the thermophilic range of temperature during the first week of process. Pile 1, on the other hand, did not show an increase in biological activity and never reached the thermophilic range.

However, during the maturation phase (from day 30 onwards), biological activity was low and practically constant even when the pile temperature was high and occasionally within the thermophilic range (Piles 2 and 3). This was probably due to the thermal properties of the compost material (low heat transfer rates as a consequence of low thermal conductivity and heat retention) and should not be related to biological activity, as it has also been observed in the maturation phase of other organic wastes (Gea *et al.*, 2005; Barrena *et al.*, 2006c). Therefore, temperature should not be used in the maturation stage to predict compost stability or the stage of organic matter degradation.

Comparing $RI_{process}$ data with interstitial oxygen data, it can be observed that the initial decrease in the level of interstitial oxygen could be due to the increase of moisture content (which implies a loss of porosity) but also to the increase in biological activity (especially in Piles 2 and 3). The level of moisture (and consequently porosity) has been found to be critical for the composting of wastewater sludge in general (Haug, 1993; Gea *et al.*, 2003) and also specific studies (Richard *et al.*, 2002; Eftoda & McCartney, 2004).

The final cumulative oxygen consumption at the end of the process (90 days) was also determined in terms of mass of O_2 consumed per mass of initial VS in sludge for the three composting piles by considering that the bulking agent used was not significantly degraded. In fact, this value can be calculated by means of a numerical integration of the $RI_{process}$ values versus time at any given process time (Fig. 6) using the Simpson method (Yakowitz & Szidarovszky, 1989). When the total process time is considered, this value can be an indicator for good performance of the composting process and a measure of the stability of a final compost product. A very high organic matter degradation would then imply a total oxygen uptake of 23.355 g $[O_2]$ g^{-1} [initial sludge VS] (value obtained in Pile 3). A significant degradation would occur for values of 13.360 g $[O_2]$ g^{-1} [initial sludge VS] (value obtained in Pile 2). Whereas for values below 8.100 g $[O_2]$ g^{-1} [initial sludge VS] (value obtained in Pile 1), the composting process could not be considered finished and the organic matter would not be stabilised. This is, to our knowledge, the first attempt to use the cumulative oxygen consumption to predict compost stability, but the application of this index should be related to the effectiveness of organic matter degradation in a composting process and the extent at which composting occurs. A very interesting feature of the cumulative oxygen consumption is that it can differentiate using initial and final samples, which is not possible using single RI determinations, and this is important because at the initial stage composts show low respiration activity because their biological activity is still starting-up (the typical lag phase of biological processes). The evolution of cumulative oxygen uptake is shown in Fig. 7 for the three piles. It is clear from Fig. 7 that the highest level of oxygen consumption occurred in Pile 3, followed by Piles 2 and 1, which is in agreement with temperature profiles and the discrete RI measurements (Fig. 6). From Fig. 7, it is interesting to note that after a stabilisation of organic matter, basal respiration was observed for all the materials composted. This has been shown with other composting studies dealing with different organic wastes (Barrena *et al.*, 2005; Gea *et al.*, 2005).

RI_{37} evolution for Pile 2 is also plotted in Fig. 6. This parameter was only determined for Pile 2 in order to compare it with $RI_{process}$. It showed practically constant values close to 1 mg $[O_2]$ g^{-1} [VS] h^{-1} for the entire period of the experiment. As expected, when RIs were determined at 37 °C and at process temperature, differences between both indices were more significant during the first thermophilic phase than in the final maturation phase, when temperature was closer to 37 °C. In fact, RI_{37} values were just slightly different from $RI_{process}$ from day 30 onwards (corresponding to the maturation phase), as shown in Fig. 6. From 0 to 30 days (the active phase of composting) the thermophilic microorganisms only exhibited a limited growth at 37 °C (which implies a low RI) due to the kinetics imposed by low temperatures, whereas the mesophilic population only exhibits a limited respiration activity (Barrena *et al.*, 2005). At process temperature, the RI was determined under real operating conditions (i.e. thermophilic range) and the microbial populations present in the material were fully active, resulting in high values of RI. It can be concluded that the $RI_{process}$ can be used for monitoring the biological activity of the composting process; however, it should be determined at process temperature, whereas determinations at 37 °C (mesophilic temperature) should be exclusively used as a stability parameter in the maturation phase. Similar results have been also obtained in laboratory or pilot scale composting experiments with several organic wastes (Gea *et al.*, 2004; Barrena *et al.*, 2005). At full-scale, although some weak correlations between RI, measured at mesophilic conditions, and temperature have been observed in the composting of organic fraction of municipal solid wastes (Barrena *et al.*, 2006b) and sludge composting (Eftoda & McCartney, 2004), $RI_{process}$ is a more accurate parameter to show the biological activity of composting mixtures. Another possible approach is the use of dynamic respiration tests, in which the oxygen transfer limitations can be completely overcome, although the cost of these tests can be considerable (Barrena *et al.*, 2009). However, the use of $RI_{process}$ as a measure of biological activity is of special relevance for full-scale facilities (especially in the maturation stage) where temperature is maintained in the thermophilic range because of the limited heat transfer of the compost material (low thermal conductivity) although biological activity is limited (Barrena *et al.*, 2006b). Therefore, in these situations, the RI provides an accurate measure of the biological activity of the compost material.

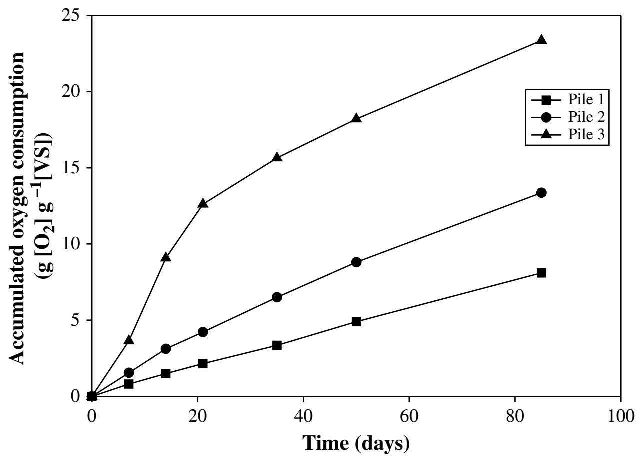

Fig. 7 – Cumulative oxygen consumption for Piles 1, 2 and 3 during the course of the experiment.

3.4. *Final compost stability*

In the final samples, RI_{37} was measured for all three piles. The results are shown in Table 3. Despite all the materials having the same final low RI_{37} value, this was not indicative of similar compost properties, because it is necessary to consider temperature and $RI_{process}$ trends. Consequently, it is possible to affirm that final material in Pile 1 was not significantly composted. Although the three piles had a similar final RI_{37} close to 1 mg $[O_2]$ g^{-1} [VS] h^{-1}, only Pile 3, with a RI_{37} of 0.73 mg $[O_2]$ g^{-1} [VS] h^{-1}, had a value of below the limit established to qualify the compost as stable material (California Compost Quality Council, 2001). These results indicate that fully stable and mature compost from wastewater sludge can be obtained in 60 days in a large-scale facility, if the bulking agent ratio is properly adjusted. In the case of Pile 2 a short curing process could have a positive effect on the stability of the compost.

Rottegrade stability grade for the three composts is also shown in Table 3. All the composts presented a Rottegrade value of V, which corresponds to the maximum stability grade. However, it is necessary to point out these values can lead to wrong conclusions, as no evidence of process development is available using this test. Rottegrade test and RI_{37} values should therefore be considered with care as

Table 5 – Germination indices for the final compost of three piles

Material	Relative seed germination (%)		Relative root growth (%)		Combined germination index (%)	
	5 days	7 days	5 days	7 days	5 days	7 days
Pile 1	100	100	128.3	137.3	128.3	137.3
Pile 2	100	100	123.2	149.3	123.2	149.3
Pile 3	100	100	118.2	130.1	118.2	130.1

parameters to predict and determine stability of composts from wastewater sludge, especially if no data from the composting process are available. Parameters based on cumulative oxygen consumption appear to be more reliable in terms of measuring the effectiveness of the composting process and organic matter biodegradation.

3.5. *Phytotoxicity analysis*

In relation to the phytotoxicity of compost, seed germination tests indicate the presence of significant quantities of phytotoxins (Tiquia *et al.*, 1996; Tiquia & Tam, 1998). The results of phytotoxicity analysis are presented in Table 5. The relative seed germination results were in all the cases 100%, which meant that no phytotoxic compounds were present in compost. Additionally, all the relative root growth results were greater than 100%. It has been suggested that a combined germination index (a product of relative seed germination and relative root elongation) over 80% indicates the absence of phytotoxins in composts (Tiquia *et al.*, 1996). Moreover, a relative root growth over 100% indicated that compost had a positive effect on plant growth. In the case of Pile 1 compost, which also presented a high germination index, a possible explanation is that the original sludge did not contain any important plant growth toxins, and therefore the germination indexes are high even with unfinished compost. Further studies on wastewater sludge composting might consider the determination of germination indices in initial or some intermediate stages of the composting process.

4. Conclusion

The performance of three full-scale composting processes using different bulking agent ratios has been systematically studied. Results revealed that the selection of an appropriate bulking agent ratio is critical for the correct development of the composting process in low-porosity organic wastes such as municipal wastewater sludge. Optimum values of volumetric ratio bulking agent:sludge are within the range 2.5–3. RIs are the most suitable parameters to monitor the composting process, as they reflect the biological activity of the composting process. Other physico-chemical measures should be carefully considered and they often need information of the process evolution to be correctly interpreted. According to cumulative respiration values, high organic matter degradation corresponds to 13–23 g [O_2] g^{-1} [initial sludge VS], when high volumetric ratios of bulking agent are used. In fact, cumulative oxygen consumption is able to predict the effectiveness of organic matter degradation in a composting process and the extent at which composting occurs. Finally, by using the adequate volumetric ratio, the compost obtained from wastewater sludge presents a high level of maturity.

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Article II

Comparison of aerobic and anaerobic stability indices through a MSW biological treatment process.

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Comparison of aerobic and anaerobic stability indices through a MSW biological treatment process

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Abstract

A complex mechanical–biological waste treatment plant designed for the processing of mixed municipal solid wastes (MSW) and source-selected organic fraction of municipal solid wastes (OFMSW) has been studied by using stability indices related to aerobic (respiration index, RI) and anaerobic conditions (biochemical methane potential, BMP). Several selected stages of the plant have been characterized: waste inputs, mechanically treated wastes, anaerobically digested materials and composted wastes, according to the treatment sequence used in the plant. Results obtained showed that the main stages responsible for waste stabilization were the two first stages: mechanical separation and anaerobic digestion with a diminution of both RI and BMP around 40% and 60%, respectively, whereas the third stage, composting of digested materials, produced lesser biological degradation (20–30%). The results related to waste stabilization were similar in both lines (MSW and OFMSW), although the indices obtained for MSW were significantly lower than those obtained for OFMSW, which demonstrated a high biodegradability of OFMSW. The methodology proposed can be used for the characterization of organic wastes and the determination of the efficiency of operation units used in mechanical–biological waste treatment plants.

1. Introduction

The bulk municipal solid waste stream (MSW, which can contain a range of 35–50% of organic materials) and the source-selected organic fraction of municipal solid waste (OFMSW, with an organic content over 80%) have received special attention from the European authorities. As a result, at present there is an increasing number of facilities such as composting, anaerobic digestion and mechanical–biological treatment plants whose main goal is to reduce the biodegradable organic matter content of these organic wastes and stabilize them by means of biological processes.

The analysis of waste treatment efficiency in these plants requires a reliable measure of the biodegradable organic matter content of organic wastes and thus, their stability defined as the extent to which readily biodegradable organic matter has decomposed (Lasaridi and Stentiford, 1998). This measure would permit the evaluation of current working plants, the improvement of the biological treatment process, the design of optimized facilities and the potential environmental impact of the final products.

Some biochemical parameters such as volatile solids (VS), total and dissolved organic carbon (TOC, DOC) and chemical oxygen demand (COD) have been used to monitor the evolution of biological processes (Fontanive et al., 2004; Komilis and Ham, 2003; Papadimitriou and

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Balis, 1996; Ros et al., 2006). These parameters lack precision when determined on heterogeneous materials such as MSW or OFMSW because of the presence of non-biodegradable volatile or oxidizable materials.

Biological activity measurements have been widely suggested in the literature as a measure of biodegradable organic matter content or stability. In this sense, aerobic respirometric techniques and methanogenic activity assays have been proposed (Adani et al., 2004; Barrena et al., 2006; Hansen et al., 2004; Ianotti et al., 1993; Ligthart and Nieman, 2002; Scaglia et al., 2000; Tremier et al., 2005). The suggested methodologies differ in key assay parameters, such as temperature, which is directly related to the biological activity rate. Indeed, changes in the optimum temperature value have been reported for maximum biological activity determination through the composting process evolution (Barrena et al., 2005; Lasaridi et al., 1996). Some comparisons between a few of the proposed aerobic methods have been made (Adani et al., 2003, 2006; Gea et al., 2004), concluding that respirometric indices are suitable for biological process monitoring. On the other hand, only one recent reference (Cossu and Raga, 2008) has presented a good correlation between an accumulative aerobic respiration method and the biogas potential for landfill excavated waste. Furthermore, a number of standards have been already proposed (ASTM, 1996; Cooper, 2005; US Department of Agriculture and US Composting Council, 2001). Notwithstanding the amount and quality of the work referred to, there is no consensus for stability measurements within the research community in the solid waste treatment field (Barrena et al., 2006).

Some of the above-mentioned methods have been considered in the European legislation drafts (European Commission, 2001) and adopted in national regulations by some European countries such as Germany (Federal Government of Germany, 2001), Italy (Favoino, 2006) and England and Wales (Godley et al., 2005). Table 1 shows the test conditions for some of the national standards defined for biological stability determination under aerobic and anaerobic conditions and the proposed stability limits. As can be observed, the methodologies proposed differ in many key aspects such as the use of an inoculum, the amount of sample to be used and its preparation, the assay temperature (mesophilic or thermophilic) and the test duration. Even the expression of the results (oxygen uptake rate or cumulative consumption) and the units (dry or volatile solids basis) are different among the tests published.

The objectives of this research are therefore: (i) to study the suitability of the aerobic respiration index and the methane potential for the determination of the biodegradable organic matter content and biological stability in samples from a selected MBT plant (Ecoparc de Montcada, Barcelona, Spain), which were obtained at different stages of their biodegradation process; (ii) to compare the two indices proposed (aerobic and anaerobic); (iii) to determine the correlations among the methods studied; and (iv) to determine the efficiency of the treatment of biodegradable organic matter in the evaluated MBT plant, based on the selected indices.

2. Materials and methods

2.1. Materials

Samples were obtained from a mechanical–biological treatment (MBT) plant (Ecoparc de Montcada, Montcada i Reixach, Barcelona) that treats mixed MSW ($63 \pm 11\%$ dry matter content, $63 \pm 12\%$ volatile solids content) and OFMSW ($39 \pm 5\%$ dry matter content, $67 \pm 11\%$ volatile solids content). Samples were collected during April–May 2006. Analytical methods were carried out on a representative sample (approximately 20 kg) obtained by mixing four

Table 1
Stability indices proposed in some European regulations

Reference[a]	Inoculation	Water content	Temperature	Test duration	Results expression[b]	Stability limit
European Commission (2001), Italia (Lombardia), Favoino (2006)			Biological treatment of biowaste, second draft			
DRI	No	10–13 kg, 75% water holding capacity	Self-heated	<4 days	mg O_2 kg VS^{-1} h^{-1}	1000
AT_4	Yes	500 g, 50% moisture	58 °C	4 days expandable	mg O_2 g VS^{-1}	10
Federal Government of Germany (2001)			Abfallablagerungsverordnung – AbfAblV			
AT_4	No	40 g, saturation + empty filtration	20 °C	4 days + lag phase	mg O_2 g DM^{-1}	5
GB_{21}	Yes	50 g DM + 50 mL inoculum + 300 mL water	35 °C	21 days + lag phase	L kg DM^{-1}	20
Godley et al. (2005)			United Kingdom Environment Agency			
DR_4	Yes	400 g, 50% MC	35 °C	4 days	mg O_2 g DM^{-1} or mg O_2 g VS^{-1}	No limit proposed
BM_{100}	Yes	20 g VS + 50 mL inoculum + 200 mL solution	35 °C	100 days	L kg VS^{-1}	No limit proposed

[a] DRI, AT_4 and DR_4 are respiration indices (oxygen consumption), whereas GB_{21} and BM_{100} are anaerobic indices (biogas production).
[b] DM: dry matter; VS: volatile solids.

subsamples of about 5 kg each, taken from different points of the bulk of material.

2.2. Mechanical–biological treatment plant

The MBT plant studied is located in Montcada (Barcelona, Spain) and it is denominated Ecoparc de Montcada. Mixed MSW and OFMSW, consisting of kitchen and garden wastes coming from the metropolitan area of Barcelona, are treated in this plant. MSW and OFMSW are treated separately in two independent lines. The capacity of the plant is 240,000 tonnes/yr (70,000 tonnes/yr of OFMSW and 170,000 tonnes/yr of MSW). A schematic diagram of the MBT plant and the sampling points is shown in Fig. 1. The treatment of wastes includes three main phases:

Step 1: Mechanical pretreatment: both OFMSW and MSW are treated to remove inorganic materials such as plastics, metal, glass and stones, which are recycled. The mechanical pretreatment includes: trommel screens (to remove large impurities), magnetic separator (to remove ferric materials), Foucault separator (to remove aluminum), ballistic separator (to remove large density materials) and shredder. After this pretreatment sequence, the organic materials are essentially free of inorganic contaminants.

Step 2: Anaerobic digestion: organic matter is anaerobically digested in three digesters of 4500 m^3 of capacity. The plant uses the Valorga process (Bonhomme and Pavia, 1986), in which the material is processed in solid state and under mesophilic conditions (38 °C). Mixing is provided by biogas injection along the reactor. Retention time is set at 21 days.

Step 3: Composting: material coming from anaerobic digesters is mixed with bulking agent (pruning wastes at a ratio 2:1) and composted in a tunnel composting system (17 tunnels) during 3 weeks to stabilize and sanitize the material. During this period, operational parameters (temperature, oxygen and moisture content) are monitored and controlled. Final compost (from OFMSW) or stabilized waste (from MSW) is stockpiled before commercialization.

Samples were collected from the most significant points of the MBT plant (Fig. 1), and for both lines (MSW and OFMSW). The samples selected for the study of the plant were: input material, pretreated material, digested material, composted material and final material (compost or stabilized waste), which resulted in ten samples (five for each line). Samples were immediately frozen and conserved at −20 °C after collection. Before analysis, samples were thawed at room temperature for 24 h.

2.3. Analytical methods

Water content, dry matter and organic matter or volatile solids (OM or VS) were determined according to the standard procedures (US Department of Agriculture and US Composting Council, 2001).

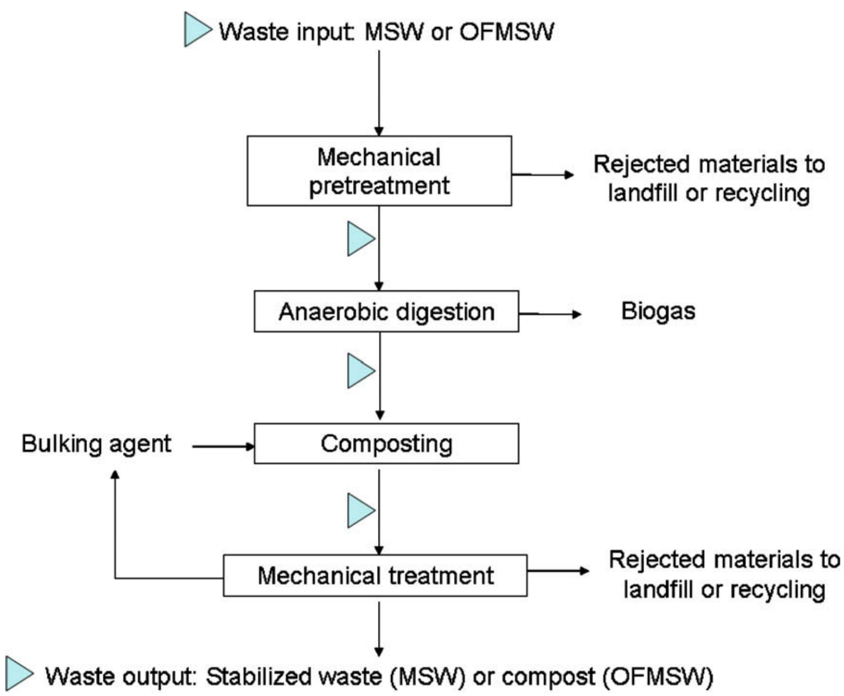

Fig. 1. Scheme of the mechanical–biological treatment plant. Triangles indicate sampling points.

2.4. Respirometric tests

A static respirometer was built according to the original model described previously (Ianotti et al., 1993) and following the modifications and recommendations given by US Department of Agriculture and US Composting Council (2001). A detailed description of the respirometer can be found elsewhere (Barrena et al., 2005). Approximately 250 mL of sample were placed in 500 mL Erlenmeyer flasks on a nylon mesh screen that allowed air movement under and through the solid samples. The setup included a water bath to maintain the temperature at 37 °C during the respirometric test. Prior to the assays, samples were incubated for 24 h at 37 °C. During the entire incubation period, samples were aerated with previously humidified air at the sample temperature. The drop of oxygen content in a flask containing a sample was monitored with a dissolved oxygen meter (Lutron 5510, Lutron Co. Ltd., Taiwan) connected to a data logger. The rate of respiration of the sample (Oxygen Uptake Rate, OUR, based on dry matter content) was then calculated from the slope of oxygen level decrease according to the standard procedures (Ianotti et al., 1993). Results of the static respirometric index are expressed as $g\,O_2\,kg\,DM^{-1}\,h^{-1}$ and are presented as an average of three replicates.

2.5. Biochemical methane potential

A 200 g sample of a wet representative waste was used in this test. The sample was mixed at a 1:1 weight ratio with an inoculum coming from the output of the anaerobic digester of the MBT plant except for fresh input OFMSW and MSW samples where a 10:1 weight ratio of inoculum:sample was used to avoid acidification and inhibition caused by volatile fatty acids accumulation. No water was added to this mixture except for the final dry samples (compost and stabilized MSW) to reach a minimum moisture content of 40%.

The mixture was incubated in a water bath at 37 °C in a sealed aluminum bottle with a working volume of 1 L. Before each experiment, the bottles were purged with nitrogen gas to ensure anaerobic conditions. The bottle was provided with a ball valve connected to a pressure digital manometer, which allowed determination of the biogas pressure. The bulk density of the mixture was determined in triplicates in order to calculate the headspace volume of the bottles. During the test, the bottles were shaken once a day. The results on biogas production were obtained from the pressure in the bottle and the headspace volume. Excessive pressure in the bottle was released by purging the biogas produced (25–30 times during the experiment). Biogas composition was also routinely measured.

The tests were carried out in triplicate and the results obtained at 21 days (BMP_{21}) and at the end of the test when no significant biogas production was detected (BMP_F) are expressed as biogas volume (L) produced and measured at normal conditions ($T = 273$ K, $P = 1$ bar) per kg of dry matter. A triplicate measure of the biogas production of the inoculum was carried out as a blank and deducted from the biogas production of the waste samples. The deviation found for inoculum biogas production was low (10%). Biogas production in 21 days (BMP_{21}) for the inoculum used was within 60–70 L of biogas per dry kg of inoculum. In fact other standardized methods recommend a minimum level activity of the inoculum in order to obtain good results (Federal Government of Germany, 2001).

Biogas composition was analyzed by gas chromatography (Perkin–Elmer AutoSystem XL Gas Chromatograph) with a thermal conductivity detector and using a column Hayesep 3 m 1/8 in. 100/120. Volatile fatty acids (VFA) were determined by gas chromatography (Perkin–Elmer AutoSystem XL Gas Chromatograph) with a flame ionization detector (FID) and a column HP Innowax 30 m × 0.25 mm × 0.25 μm. The details of biogas and VFA analysis can be found elsewhere (Fernández et al., 2005). Typical values of methane percentage in biogas were around 55–65%, whereas VFA were not detected.

3. Results and discussion

3.1. Respirometric study

The results of the evolution of respiration index for OFMSW and MSW treatment lines in the MBT plant are shown in Fig. 2. The values presented of RI and BMP are expressed on a dry matter basis, because the content of the samples varied significantly as biodegradation process occurred (Barrena et al., 2005). Organic matter basis has been exclusively used in the expression of final materials stability for comparison with some national stability limits.

Similar evolution trends can be observed for both lines, indicating a progressive stabilization of the material. In general, respiration indices found for OFMSW are higher than those of MSW, which is expected since OFMSW contains a higher content of labile organic compounds. It is important to note that these differences are more significant in initial samples (input and materials mechanically pretreated), whereas the differences are minimal after biological treatment (digested and composted materials), when labile organic matter has been biodegraded.

Specific results from the main steps in the studied MBT are presented in Table 2. These results indicate that there is a significant loss of biodegradable organic matter in the mechanical pretreatment (43% for OFMSW and 28% for MSW, respectively). This fact is somewhat surprising since mechanical pretreatment occurs in a short time (no more than 2 days). It is probable that the sequence of operations used in mechanical pretreatment (several trommel screens and separators) favors the presence of oxygen and acts as an aerobic biodegradation process. As the mechanical pretreatment is an essential part of a MBT plant, it can be concluded that the loss of biodegradable organic matter in this

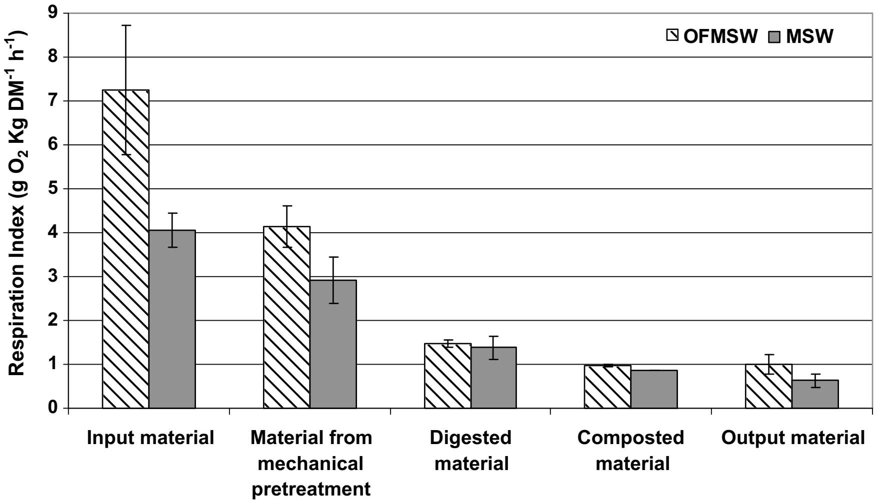

Fig. 2. Evolution of respiration index in the mechanical–biological treatment plant. Average of triplicates is presented jointly with standard deviation.

Table 2
Successive reductions of respiration index and biochemical methane potential (at 21 days) in selected points of the mechanical–biological treatment plant

Point of the plant	OFMSW (% index reduction)		MSW (% index reduction)	
	RI	BMP_{21}	RI	BMP_{21}
Material from mechanical pretreatment	43	45	28	0
Anaerobically digested material	69	56	53	71
Composted material	33	45	38	0

part of the process should be considered in future MBT designs, especially when estimating the efficiency of the next steps, for instance, potential biogas production for anaerobic digestion or aeration requirements for composting. In any case, mechanical pretreatment should be the focus of future studies.

After mechanical pretreatment, the reduction of RI observed in anaerobic digestion is also very high (Table 2). In fact, anaerobic digestion is the main step regarding biodegradable organic matter reduction for both OFMSW and MSW. The reductions of RI observed show that a considerable part of aerobically biodegradable organic matter can be anaerobically digested. The values observed are in accordance with volatile solids reductions found for anaerobic digesters at laboratory (Fernández et al., 2005) and industrial scale (Fruteau et al., 1997; Lissens et al., 2001; Luning et al., 2003). Finally, composting contributed to organic matter stabilization of 33% and 38% for OFMSW and MSW, respectively (Table 2).

In any case, the methodology proposed in this work can be of interest for application in any configuration of waste treatment plant to identify the most important operations related to organic matter stabilization and efficiency. Since there is no evidence on other published works with different technologies or treatment sequences, further studies are necessary to determine the optimal configuration for MBT plants.

3.2. Methane potential study

The results obtained for the biochemical methane potential at 21 days (BMP_{21}) are shown in Fig. 3 for OFMSW and MSW. BMP_{21} for OFMSW shows a parallel evolution to RI (Figs. 2 and 3). Again, there is a considerable loss of methane potential in mechanical pretreatment, and the role of anaerobic digestion is prevalent in organic matter stabilization, whereas the third step in the process, composting, acts as a final stabilization process (Table 2). However, the results of BMP_{21} obtained for MSW appear to be more erratic. As expected, there is a large reduction of methane potential in anaerobic digestion (71%, Table 2), which again indicates the importance of this process in a combined anaerobic–aerobic MBT plant. However, a reduction of BMP_{21} in mechanical pretreatment or composting is not observed. A possible explanation is that the time spent in these operations does not permit the degradation of organic matter in a less biodegradable material such as mixed MSW.

3.3. Correlation among stability indices

3.3.1. Duration of BMP test

In this work, several samples from the treatment of OFMSW were analyzed in terms of BMP obtained at 21 days and final BMP obtained when biogas production was not detected (more than 100 days). Results are shown in Fig. 4. Although the dispersion is high, the correlation between BMP_{21} and BMP_F was highly significant, with a correlation ratio of 0.9998 and a slope of 0.729. According to these results, methane produced during 21 days corresponds to the 73% of ultimate potential methane. Although no values have been found for solid wastes, this value is

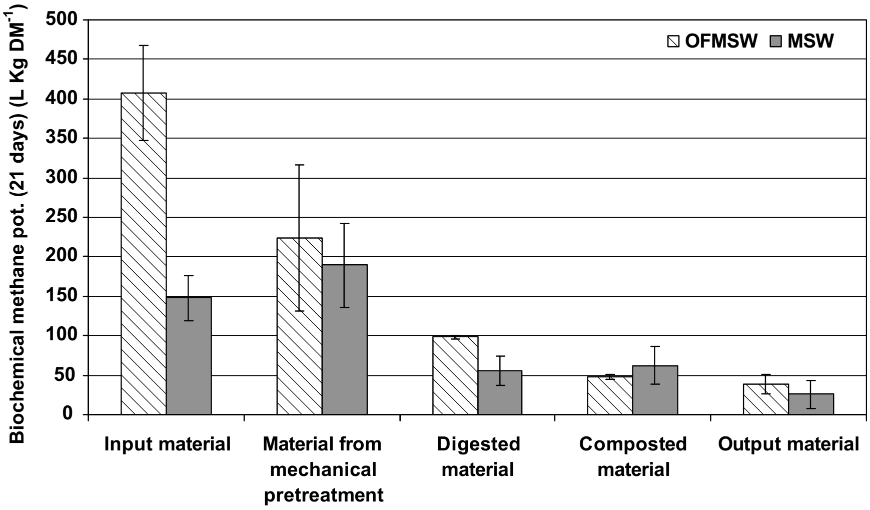

Fig. 3. Evolution of biochemical methane potential (21 days) in the mechanical–biological treatment plant. Average of triplicates is presented jointly with standard deviation. Biochemical methane potential from inoculum has been deducted.

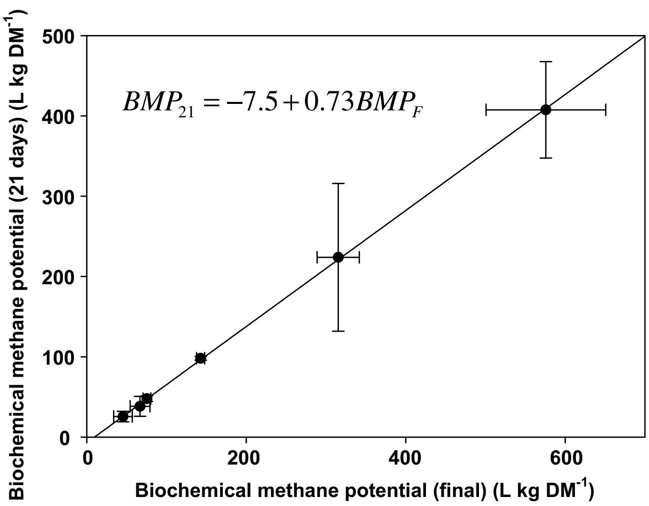

Fig. 4. Correlation between biochemical methane potential obtained at 21 days and final biochemical methane potential. Average of triplicates is presented jointly with standard deviation. Biochemical methane potential from inoculum has been deducted.

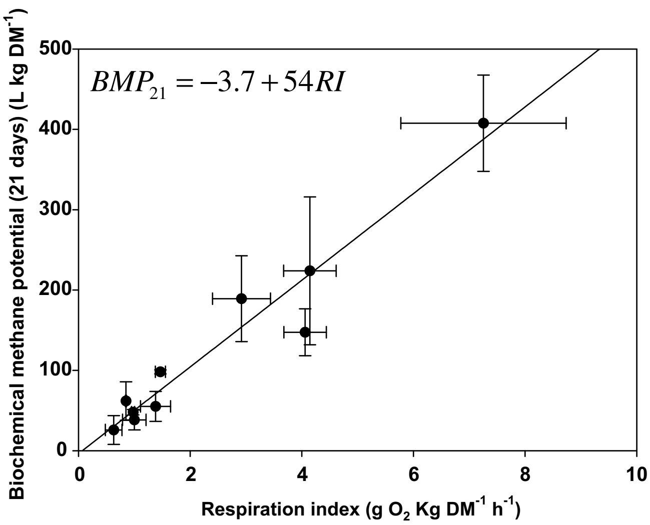

Fig. 5. Correlation between biochemical methane potential obtained at 21 days and respiration index. Average of triplicates is presented jointly with standard deviation. Biochemical methane potential from inoculum has been deducted.

similar to those used for the characterization of wastewater biodegradability by means of biochemical oxygen demand (Metcalf and Eddy, 2003). According to this test, the ratio DBO_5/DBO_F is within the range of 60–70%. Another value of interest obtained in this experiment is the determination of total methane potential for OFMSW, which resulted in 572 L biogas per dry kg of OFMSW, with a percentage of methane of 60%. This value is in accordance with other values found for food wastes (Eleazer et al., 1997) and source-separated municipal solid waste (Hansen et al., 2003).

3.3.2. Aerobic and anaerobic indices

Correlation between RI (aerobic) and BMP_{21} (anaerobic) is presented in Fig. 5 for all of the samples analyzed (including MSW and OFMSW samples). A linear correlation between RI and BMP_{21} with a slope of 54.0 can be obtained, with a high level of statistical significance (correlation coefficient: 0.94, $p < 0.0001$). This is an indication that both indices are suitable to predict waste stability, although from a practical point of view, respiration index is more recommendable in terms of time required, no need of seed, etc. Thus, aerobic indices could be used for the monitoring of the degree of degradation in anaerobic processes in waste treatment plants. Although some correlations between aerobic indices have been reported (Adani et al., 2003), this is, to our knowledge, one of the first studies where aerobic and anaerobic stability indices are correlated for organic solid wastes in different stages of biodegradation.

Table 3
Respiration index and biochemical methane potential (at 21 days) for final materials

Test	Compost from OFMSW	Stabilized material from MSW
Respiration index (g O_2 kg DM^{-1} h^{-1})	1.00 ± 0.21	0.63 ± 0.05
Respiration index (g O_2 kg VS^{-1} h^{-1})	2.11 ± 0.44	1.19 ± 0.09
Biochemical methane potential (biogas volume (L) produced at normal conditions ($T = 273$ K, $P = 1$ bar) per kg of dry matter)	38 ± 3	26 ± 5
Biochemical methane potential (biogas volume (L) produced at normal conditions ($T = 273$ K, $P = 1$ bar) per kg of volatile solids)	80 ± 6	49 ± 9

3.4. Final materials stability

Values of RI and BMP_{21} for the final materials (compost from OFMSW and stabilized material from MSW) are presented in Table 3. RI and BMP_{21} in Table 3 are expressed on a dry matter basis and organic matter basis, since some national regulations on stability use organic matter (often expressed as volatile solids) as the basis for stability measurements (Table 1). As can be seen in Table 3, values obtained for stabilized material sampled from the mixed MSW treatment line are very close to those proposed in different national regulations, being respiration index 1.19 g O_2 kg VS^{-1} h^{-1} for a limit of 1 g O_2 kg VS^{-1} h^{-1} proposed in Italian regulation, and 26 L kg DM^{-1} for the biogas production when the limit proposed in German legislation is 20 L kg DM^{-1}.

The values of stability obtained for compost from source-selected OFMSW are, on the contrary, far from those presented in some national regulations and in the second draft of biological treatment of biowaste (European Commission, 2001). Thus, respiration index is 2.11 g O_2 kg VS^{-1} h^{-1} (the proposed limit is 1 g O_2 kg VS^{-1} h^{-1}) and the biogas production is 38 L kg DM^{-1} (the proposed limit is 20 L kg DM^{-1}). It appears that composting time in the MBT plant should be extended for more effective compost stabilization. Nevertheless, it should be kept in mind that the limits proposed in most of the regulations are intended for stabilization of mixed MSW prior to landfilling or incineration, which is not the case for the MBT plant studied.

4. Conclusions

The study carried out has demonstrated that the methodology proposed can be used for the monitoring of stabilization of organic matter in mechanical–biological waste treatment plants. Both aerobic and anaerobic indices can be used for the estimation of the biodegradable organic matter content of solid waste samples, and the correlation between both indices is good. However, aerobic indices are recommended because of the shorter duration of the assay.

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Article III

The effect of storage and mechanical pretreatment on the biological stability of municipal solid wastes.

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The effect of storage and mechanical pretreatment on the biological stability of municipal solid wastes

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ABSTRACT

Modern mechanical–biological waste treatment plants for the stabilization of both the source-separated organic fraction of municipal solid wastes (OFMSW) and the mixed stream of municipal solid wastes (MSW) include a mechanical pretreatment step to separate recyclable materials such as plastics, glass or metals, before biological treatment of the resulting organic material. In this work, the role of storage and mechanical pretreatment steps in the stabilization of organic matter has been studied by means of respiration techniques. Results have shown that a progressive stabilization of organic matter occurs during the pretreatment of the source-separated OFMSW, which is approximately 30% measured by the dynamic respiration index. In the case of mixed MSW, the stabilization occurring during the reception and storage of MSW is compensated by the effect of concentration of organic matter that the pretreatment step provokes on this material. Both results are crucial for the operation of the succeeding biological process. Finally, respiration indices have been shown to be suitable for the monitoring of the pretreatment steps in mechanical–biological waste treatment plants, with a strong positive correlation between the dynamic respiration index and the cumulative respiration index across all samples tested.

1. Introduction

MSW and OFMSW are treated in industrial facilities of different configurations such as mechanical–biological treatment (MBT), anaerobic digestion and composting plants. An objective of these plants is to reduce the biodegradable organic matter in order to minimize the environmental burdens related to the landfill of wastes (odor problems, methane emissions or leachate generation). It has been reported that biological stability of organic matter is positively correlated with low environmental impacts associated to waste management (Muller et al., 1998).

MBT plants are of different configurations. They can include aerobic (composting), anaerobic processes or the combination of both (Ponsá et al., 2008a; Wagland et al., 2009). Nevertheless, they all include a first mechanical pretreatment step with a double objective: to recover recyclable materials (glass, plastics and metals) and to prepare the organic matter for biological treatment. Although scientific literature is full of references on the performance, monitoring and optimization of the biological steps involved in the treatment of MSW, to the authors' knowledge, no studies have been published on the possible effect of the mechanical pretreatment on the stabilization of organic matter. This is an interesting point since any stabilization occurring in this first step could have a critical influence on the biological process behavior afterwards. For instance less biogas production would be expected in anaerobic digestion or less aeration requirements would be necessary in a composting-like treatment. These both aspects are crucial in the configuration of a MBT plant.

The analysis of a waste treatment plant requires a reliable measure of the biological activity of the organic matter or, similarly, its stability defined as the extent to which readily biodegradable organic matter has decomposed (Lasaridi and Stentiford, 1998). In this field, the application of respiration indices has proven to be very useful in the monitoring of waste treatment plants and for the prediction of the stability of final products such as stabilized material for landfill or compost (Adani et al., 2006; Barrena et al., 2009). For instance, Ruggieri et al. (2008) reported the stabilization reached during the composting of OFMSW using several aeration modes and Ponsá et al. (2009) have recently presented the use of respirometry for the optimization of the amount of bulking agent used for porosity adjustment in wastewater sludge composting at full-scale. In relation to the techniques used for the determination of respiration index, several studies have reported the suitability of dynamic methods to overcome possible problems of mass transfer limitations in solid-state respirometry (Adani et al., 2003; Barrena et al., 2006; Tremier et al., 2005), which is crucial when very active materials are studied (for instance, raw OFMSW and MSW).

In a previous work (Ponsá et al., 2008a), we carried out the complete respirometric monitoring of a complex MBT plant that included in this order, mechanical pretreatment, anaerobic

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digestion and composting and we observed that the main step for organic matter stabilization was anaerobic digestion. However, a significant decrease of stability was observed in the pretreatment operations. The main objective of this study is to investigate the possible effect of mechanical pretreatment on both the OFMSW and MSW stabilization.

2. Materials and methods

2.1. Mechanical–biological treatment plant

The MBT plant studied is located in Barcelona province. Mixed MSW and OFMSW consisting of kitchen and garden wastes from the Metropolitan Area of Barcelona are treated in this plant. MSW and OFMSW are treated separately in two independent lines. The capacity of the plant is 240,000 t/year (70,000 t/year of OFMSW and 170,000 t/year of MSW). The treatment of organic wastes includes three main processes:

Process 1: mechanical pretreatment: both OFMSW and MSW are treated to remove inorganic materials such as plastics, metal, glass and stones, which are recycled. The mechanical pretreatment includes in this order: two trommel screens (to remove large impurities, first cut off 60 mm, second cut off 150 mm, Masias Recycling SL Girona, Spain), a magnetic separator (to remove ferric materials), a Foucault separator (to remove aluminum), a ballistic separator (to remove large density materials) and a shredder. After this pretreatment sequence the organic materials are essentially free of inorganic contaminants.

Process 2: anaerobic digestion: organic matter is anaerobically digested in three digesters of 4500 m^3 of capacity. The plant uses the Valorga process, in which the material is processed in solid-state and under mesophilic conditions (38 °C) during 21 days.

Process 3: composting: material coming from anaerobic digesters is mixed with bulking agent (pruning wastes in a ratio 2:1) and composted in a tunnel composting system (17 tunnels) during three weeks to stabilize and sanitize the material. Final compost (from OFMSW) or stabilized waste (from MSW) is stockpiled before commercialization.

2.2. Sampling

Three campaigns were carried out in this study, C1 on October 2008, C2 on December 2008 and C3 on January 2009. In each of these campaigns waste samples were collected from the three significant points of the pretreatment process for both MSW and OFMSW lines: Step 1 – waste collected as received in the plant from the transport truck; Step 2 – waste from the collection pit, where the maximum retention time is two days, and Step 3 – waste after the entire mechanical pretreatment, which takes approximately four hours to completion. The total number of samples analyzed was: 2 lines (MSW and OFMSW) $\times$ 3 sampling points (Steps 1, 2 and 3) $\times$ 3 campaigns (C1, C2 and C3) = 18 samples.

Analytical methods were carried out on a representative sample (approximately 100 kg) obtained by mixing sub-samples of about 25 kg each, taken from at least four different points of the bulk of material. All samples were entirely ground to 10 mm particle size to increase the available surface and maintain enough porosity and matrix structure. The separation of large objects was not carried out because the grinder used was able to grind all kinds of objects, such as plastic film, metals and glass bottles.

Next, the ground samples were vigorously mixed in the laboratory and approximately 10 kg of each sample were immediately frozen and conserved at −20 °C. Before analysis, samples were thawed at room temperature for 24 h.

2.3. Analytical methods

Water content or dry matter (DM) and organic matter content were determined according to the standard procedures (The US Department of Agriculture and The US Composting Council, 2001, TMECC 0309 and TMECC 0507, respectively). All the results are presented as an average of three replicates with standard deviation.

2.4. Respirometric tests

A dynamic respirometer has been built as described by Adani et al. (2006). A sample of 100 g of organic material was obtained by randomly taking different small sub-samples from the 10 kg of thawed material after vigorous remixing. This sample was placed in a 250 mL Erlenmeyer flask and incubated in a water bath at 37 °C. The starting organic material moisture was adjusted to a range of 50–60%, if necessary. Air was continuously supplied to the samples using a mass flowmeter (Bronkhorst Hitec, The Netherlands) to ensure aerobic conditions during the experiment (oxygen concentration higher than 10%). Oxygen content in the exhaust gas from the flask was measured using a specific probe (Xgard Crowcon, UK) and recorded in a personal computer equipped with commercial software (Indusoft Web Studio, version 2008, USA). No lag-phase was detected in any of the respirometric analysis carried out. From the curve of oxygen concentration vs. time, two respiration indices can be calculated:

(a) *Dynamic respiration index (DRI):* calculated as explained in Adani et al. (2004). It represents the average oxygen uptake rate during the 24 h of maximum activity observed during the respiration assay. It is expressed in mg of oxygen consumed per g of dry matter and per hour.
(b) *Cumulative respiration index (CRI):* explained in Cossu and Raga (2008) and calculated as in German Federal Ministry for the Environment (2001). It represents the cumulative oxygen consumption during the four days of maximum respiration activity without considering the lag initial phase and under the same conditions of DRI. It is expressed in mg of oxygen consumed per g of dry matter.

2.5. Statistical methods

An ANOVA test was performed to compare different sampling points. If the ANOVA test resulted in statistically significant differences, a Tukey test was performed in pairwise comparisons. About 95% confidence level was selected for all statistical comparisons. Statistical tests were conducted with SPSS 15.0.1 (SPSS Inc., USA).

3. Results and discussion

3.1. Respirometric study

The general properties of the samples studied are reported in Tables 1 and 2. Although OFMSW presented higher values of moisture and total organic matter content than those of MSW, no trend was observed when analyzing the different points of the pretreatment process. Other authors have previously demonstrated that the use of compositional methods such as dry matter or organic matter content for the evaluation of biodegradability of municipal solid wastes is not recommended (Sánchez, 2009; Wagland et al., 2009).

Fig. 1 shows the evolution of DRI in the samples collected from the selected points of the mechanical pretreatment and for both

Table 1
General properties determined during pretreatment process for OFMSW. Step 1: waste collected as received in the plant from the transport truck; Step 2: waste from the collection pit and Step 3: waste after the entire mechanical pretreatment. Results from triplicates are presented as mean ± standard deviation.

Step	Campaign	Moisture content (ww) (%)	Organic matter content (DM) (%)
1	1	58 ± 2	74 ± 2
	2	58 ± 3	59 ± 2
	3	67 ± 2	79 ± 6
	Mean	61 ± 5	71 ± 10
2	1	61 ± 4	74 ± 3
	2	62 ± 5	80 ± 2
	3	60 ± 3	75 ± 4
	Mean	61 ± 1	76 ± 3
3	1	56 ± 2	68 ± 2
	2	67 ± 4	65 ± 2
	3	57 ± 4	68 ± 4
	Mean	60 ± 6	67 ± 2

ww: wet weight.
DM: dry matter.

Table 2
General properties obtained during pretreatment process for MSW. Step 1: waste collected as received in the plant from the transport truck; Step 2: waste from the collection pit and Step 3: waste after the entire mechanical pretreatment. Results from triplicates are presented as mean ± standard deviation.

Step	Campaign	Moisture content (ww) (%)	Organic matter content (DM) (%)
1	1	46 ± 1	56 ± 4
	2	49 ± 7	70 ± 2
	3	43 ± 2	71 ± 6
	Mean	46 ± 3	65 ± 8
2	1	39 ± 4	65 ± 4
	2	49 ± 3	76 ± 4
	3	44 ± 9	46 ± 8
	Mean	44 ± 5	62 ± 15
3	1	51 ± 3	58 ± 6
	2	45 ± 3	48 ± 5
	3	49 ± 2	73 ± 6
	Mean	48 ± 3	60 ± 13

ww: wet weight.
DM: dry matter.

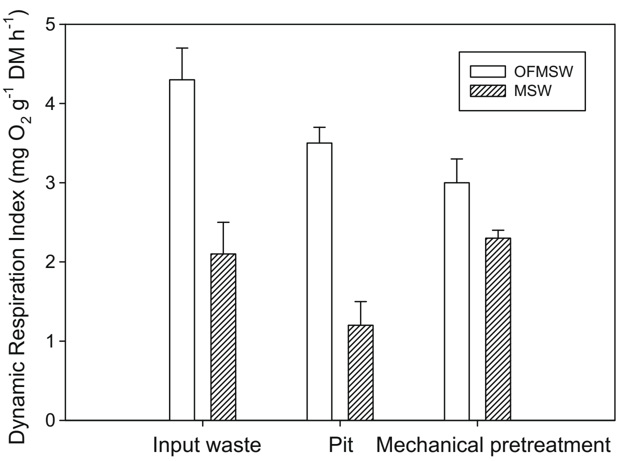

Fig. 1. Evolution of dynamic respiration index (DRI) during the pretreatment process of MSW (mixed municipal solid wastes) and OFMSW (source-separated organic fraction of municipal solid wastes).

Table 3
Respiration indices obtained during pretreatment process for OFMSW. Step 1: waste collected as received in the plant from the transport truck; Step 2: waste from the collection pit and Step 3: waste after the entire mechanical pretreatment. Different letters in the row of "mean" imply statistically different results. Results from triplicates are presented as mean ± standard deviation.

Step	Campaign	Dynamic respiration index (mg O_2 g^{-1} DM h^{-1})	Cumulative respiration index (mg O_2 g^{-1} DM)
1	1	4.0 ± 0.7	268 ± 80
	2	4.1 ± 0.2	219 ± 27
	3	4.7 ± 0.9	359 ± 79
	Mean[a]	4.3 ± 0.4	282 ± 70
2	1	3.4 ± 0.3	184 ± 15
	2	3.6 ± 0.3	254 ± 37
	3	3.7 ± 0.1	284 ± 16
	Mean[b]	3.5 ± 0.2	241 ± 51
3	1	3.1 ± 0.5	202 ± 20
	2	2.7 ± 0.1	183 ± 5
	3	3.2 ± 0.4	187 ± 19
	Mean[c]	3.0 ± 0.3	190 ± 10

DM: dry matter.

Table 4
Respiration indices obtained during pretreatment process for MSW. Step 1: waste collected as received in the plant from the transport truck; Step 2: waste from the collection pit and Step 3: waste after the entire mechanical pretreatment. Different letters in the row of "mean" imply statistically different results. Results of triplicates are presented as mean ± standard deviation.

Step	Campaign	Dynamic respiration index (mg O_2 g^{-1} DM h^{-1})	Cumulative respiration index (mg O_2 g^{-1} DM)
1	1	1.8 ± 0.1	127 ± 6
	2	1.9 ± 0.4	129 ± 33
	3	2.5 ± 0.3	201 ± 28
	Mean[a]	2.1 ± 0.4	152 ± 40
2	1	1.2 ± 0.4	82 ± 30
	2	0.8 ± 0.1	64 ± 4
	3	1.5 ± 0.4	123 ± 34
	Mean[b]	1.2 ± 0.3	90 ± 30
3	1	2.4 ± 0.4	150 ± 22
	2	2.2 ± 0.1	163 ± 2
	3	2.2 ± 0.4	179 ± 36
	Mean[a]	2.3 ± 0.1	164 ± 14

DM: dry matter.

lines of OFMSW and MSW. All sampling points following the pretreatment process were statistically different in terms of respiration activity at 95% confidence level except in one case (Table 4). However, different trends were observed when considering OFMSW and MSW.

In the case of OFMSW, the trend is a gradual decrease of DRI, from 4.3 to 3.01 mg O_2 g^{-1} DM h^{-1}, which corresponds to a 30% decrease (Table 3). It is evident that both operations involved in pretreatment (pit storage and mechanical removal of inorganic impurities) provoke the biodegradation of the most rapidly biodegradable fraction contained in this material. In the case of the OFMSW pit the maximum residence time is two days, which is adequate for plant operation and to adapt the plant to the logistics of the source-separated collection systems that are being implemented (Tanskanen and Kaila, 2001). However, this study reveals that this time is long enough to affect the waste respiration activity. The last step in pretreatment, although shorter than pit storage, involves separation processes and transport between them. This clearly acts as aerobic treatment for OFMSW. In fact, several composting systems are based on the use of drum aerated composters, which resemble trommels and some of the mechanical pretreatment operation units used in modern MBT (Kalamdhad and Kazmi, 2009).

In the case of MSW, the observed trend is similar in the pit, with an important decrease of the respiration activity (from 2.1 to 1.2 mg O_2 g^{-1} DM h^{-1}, Table 4). Although the reason for this behavior is not clear, it can be hypothesized that the higher level of porosity of mixed MSW because of the presence of inert large materials when compared to OFMSW contributes to enhance the biodegradation of organic matter during pit storage, as porosity has an important effect on oxygen uptake rate (Ruggieri et al., 2009). However, the respiration activity is completely recovered after mechanical pretreatment (Fig. 1).

This "recovery" of respiration activity needs to be carefully interpreted. Theoretically, respiration activity in MBT cannot increase and, in consequence, the only way to explain this increase is the concentration effect associated to mixed MSW mechanical selection, that is, inorganic materials (glass, metals) and inert non-biodegradable organic materials (plastics) are removed and biodegradable organic materials (that are responsible for respiration) are then concentrated. According to the values obtained from mechanical pretreatment, this concentration effect is around 1.9 (from 1.2 to 2.3 mg O_2 g^{-1} DM h^{-1}, Table 4). However, another possible hypothesis could be that the pretreatment step can act as a hydrolytic step for biodegradable organic matter and consequently increase the respiration activity as it has been observed in anaerobic sludge pretreatment (Ponsá et al., 2008b).

According to plant manager information the MSW line has 50% rejected materials to landfill while OFMSW line has only 20%. The reason for this difference is that MSW presents an average weight composition of food and green waste (38%), paper (21%), plastics (16%), glass (8%), metals (5%) and others (12%) when directly obtained from collection trucks, while the OFMSW presents an average level of impurities of 15% (Catalan Environment Agency, 2009). Finally, it must be noted that in the case of OFMSW, although this concentration effect is also possible, the lower content of inorganic or inert organic materials does not permit its quantification and, in fact, the respiration activity slightly decreases (Fig. 1). Unfortunately, no results on mechanical pretreatment operations related to uptake of oxygen have been found in literature for comparison with DRI values of this study.

3.2. Correlation between cumulative and non-cumulative respiration indices

As there is no consensus in the scientific community on the way to express and report respiration indices (Barrena et al., 2006), both dynamic (DRI) and cumulative respiration indices (CRI) have been used in this study. In fact, previous results have shown good correlations between both indices (Barrena et al., 2009) and significant correlation between aerobic and anaerobic indices such as GB_{21} (Cossu and Raga, 2008; Ponsá et al., 2008a; Wagland et al., 2009). In this study, the correlation between both indices presented in Tables 3 and 4, with all samples considered, is presented in Fig. 2. It is evident that the correlation is good with the correlation coefficient (R^2) of 0.93. These values indicate that DRI and CRI can be positively correlated with highly active raw MSW samples, although more evidence to generalize this would be necessary for other organic wastes or MSW in different stages of the stabilization process in MBT plants. Moreover, it is also clear that the level of activity for mixed MSW and source-separated OFMSW are significantly different. These results have been also reported in other studies (Ponsá et al., 2008a) and they again highlight the need to consider different plant designs for both wastes, especially when biological operations are to be selected.

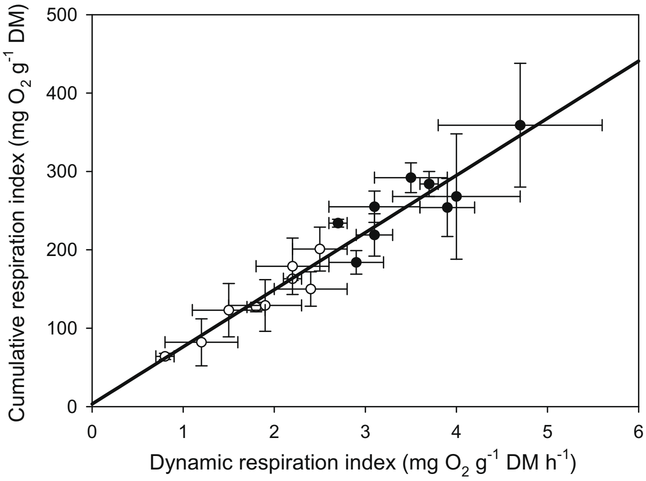

Fig. 2. Correlation between dynamic respiration index (DRI) and cumulative respiration index (CRI) for all the analyzed samples. Black-filled symbols correspond to OFMSW samples and white-filled symbols correspond to MSW samples.

3.3. Implications for plant operation

The demonstration that the pretreatment process provokes a significant stabilization of organic matter has important implications in the design of MBT plants. For instance, in the case of OFMSW the pretreatment process implies a loss of around 30% of respiration activity (Table 3), which can have different implications depending on the further biological process to be applied. In the case of anaerobic digestion (the case of the studied plant) this loss is expected to provoke a decrease in the biogas yield when compared to the untreated input material, which is the value typically considered when designing anaerobic reactors. If an aerobic composting-like process is selected for OFMSW stabilization, a lower aeration requirement is expected, since respiration activity is directly related to oxygen uptake rate (Tremier et al., 2005).

In the case of MSW, the first decrease of respiration activity after reception is compensated by the concentration effect of organic matter after the pretreatment step. It is evident that the removal of large amounts of inorganic matter during this pretreatment step causes a concentration effect in organic matter; therefore the respiration level after pretreatment is due to a similar amount of organic matter that is now in a higher percentage than that of the input material. However, if no stabilization had occurred during the entire pretreatment process, the respiration activity after this process would have been higher than that of the input waste, due to a considerable amount of inorganic materials that would have been removed. This is not really the case since both activities are very similar (Table 4). Therefore, it can be concluded that the losses of easily biodegradable organic matter are higher than those reported for the case of OFMSW (about 40% when comparing respiration activity for Steps 1 and 2).

4. Conclusions

The results obtained in this study can be summarized in the following conclusions:

(1) Complex mechanical pretreatment results in a progressive stabilization of organic matter in mechanical–biological treatment plants. In the case of source-separated OFMSW this stabilization is approximately 30%, whereas in the case of mixed MSW a first stabilization is observed during the reception and storage of MSW, which is compensated by

the effect of concentration of organic matter by pretreatment processes.

(2) This unexpected degree of stabilization has to be considered in the design of mechanical treatment plants because it implies a lower biogas yield if anaerobic digestion is selected as biological treatment or a shorter operation time/lower aeration requirements if composting is proposed.
(3) Dynamic respiration indices are a suitable technique to measure the effect of mechanical pretreatment on the stabilization of municipal solid wastes that are intended to be biologically treated.
(4) The great variability observed in the samples of MSW suggests a need to extend this work to other plants and other municipalities.
(5) Other biological phenomena involved in the pretreatment stages should be the focus of further studies. The role of the collection system should be also analyzed.

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Article IV

Different indices to express biodegradability in organic solid wastes.

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Different Indices to Express Biodegradability in Organic Solid Wastes

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Respiration indices are suggested in literature as the most suitable stability determination and are proposed as a biodegradability measure in this work. An improved dynamic respiration index methodology is described in this work. This methodology was applied to 58 samples of different types of waste including municipal solid wastes and wastewater sludge, both raw materials and samples collected in a mechanical-biological treatment plant at different stages of biodegradation. The information obtained allowed to establish a qualitative classification of wastes in three categories: highly biodegradable, moderately biodegradable, and wastes of low biodegradability. Results were analyzed in terms of long and short-term indices and index expression: dynamic respiration indices expressed as average oxygen uptake rate (mg O_2 g^{-1} dry matter [DM] h^{-1}) at 1 and 24 h of maximum activity (DRI_{1h}, DRI_{24h}); and cumulative oxygen consumption in 24 h of maximum activity and 4 d (AT_{24h}, AT_4). The statistical comparison of indices and wastes is also presented. Raw sludge presented the highest biodegradability followed by the organic fraction of municipal solid waste and anaerobically digested sludge. All indices correlated well but different correlations were found for the different wastes analyzed. The information in the dynamic respiration profile allows for the calculation of different indices that provide complementary information. The combined analysis of DRI_{24h} and AT_4 is presented here as the best tool for biodegradable organic matter content characterization and process requirements estimation.

The number of treatment facilities based on biological processes has been increasing the last years. These installations are receiving municipal and industrial organic wastes with the common main goal of reducing their biodegradable organic matter content. Composting, anaerobic digestion, and mechanical-biological treatment plants contribute to organic matter recycling and energy recovery and avoid unstable organic matter landfilling.

The general goal of those facilities would then be to stabilize the organic wastes. Stability is defined as the extent to which readily biodegradable organic matter has decomposed (Lasaridi and Stentiford, 1998). A consensus has not been reached yet about which shall be the most suitable measurement of the biodegradable organic matter content in a solid organic waste. The measure of biodegradable organic matter content is of most importance for the proper analysis and design of the above mentioned treatment facilities and it is required to evaluate their efficiency. Some references can be found where different methodologies are suggested as a measure of biodegradable organic matter, based on chemical and biological assays. However, some of those methodologies such as the volatile solids content are suitable only as a total organic matter measurement. They cannot express the potential biodegradability since they include volatile materials which are not degraded in the operation time (e.g., the bulking agent in a composting plant) or are not biodegradable at all (e.g., plastics present in municipal solid wastes) (Wagland et al., 2009). The methodologies based on biological assays appear as more suitable and some standards have been suggested by different authors or European countries legislation documents (Barrena et al., 2006).

Among the biological methodologies suggested, aerobic respiration indices have been highlighted as the most suitable tool for biodegradabity and/or stability assessment (Barrena et al., 2009; Wagland et al., 2009). Indeed, they have been used in recent works to analyze the performance of different treatment processes. For instance, Ponsá et al. (2008) used the static respiration index (SRI) proposed by Barrena et al. (2005) and based on a previous work by Iannotti et al. (1993) to assess the efficiency of a mechanical-biological treatment (MBT) plant treating municipal solid waste

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Abbreviations: ADS, anaerobically digested sludge; AT_{24h}, cumulative oxygen consumption in the 24 hours of maximum activity (corresponding to DRI_{24h}); AT_4, cumulative oxygen consumption in 4 days after lag phase; DM, dry matter; DRI_{1h}, dynamic respiration index as an average of the 1 hour of maximum activity; DRI_{24h}, dynamic respiration index as an average of the 24 hours of maximum activity; DRI_{max}, maximum dynamic respiration index; MBT, mechanical-biological treatment; MSW, municipal solid waste; MBT-MSW, samples from a MBT treating MSW; MBT-OF, samples from a MBT treating OF; OF, source-selected organic fraction of municipal solid waste (mainly food and yard wastes); RS, raw sludge; SRI, static respiration index.

(MSW) and source-selected organic fraction of municipal solid waste (OF). Ruggieri et al. (2008) used the same index to compare the performance of different aeration systems to enhance OF composting. Ponsá et al. (2009) also applied this methodology to analyze the composting system of wastewater treatment sludge when using different bulking agent ratios.

Besides the obvious usefulness of this SRI as demonstrated by the above mentioned works, other authors have suggested dynamic approaches for respiration activity measurement (Adani et al., 2003; Tremier et al., 2005). Furthermore, SRI correlates well with dynamic respiration index (DRI) (Barrena et al., 2009) and with anaerobic indices such methane generation potential (Ponsá et al., 2008). The main difference among static and dynamic methodologies is that SRI presents a single value of biological activity potential while the dynamic approach generates an activity profile which might permit a deeper analysis of organic materials biodegradability: this should include both total biodegradable organic matter content and information on at which rate the biodegradation can occur. Biodegradation rate is an aspect that is still unknown for organic solid wastes, since many steps (mass and energy transfer, microbiological communities, etc.) can be a limiting stage.

In this work, an improved dynamic methodology is presented with the objective to offer a reliable measurement of the biodegradable organic matter content in organic solid materials, useful for researchers and industrial operators. The aim of this work is to establish whether respiration indices can be used as a measure of the biodegradable organic matter content and stability of organic materials as well as to define the most suitable form of expression for those indices.

Materials and Methods

Organic Wastes

Fifty-eight samples of different organic wastes collected at different stages of biodegradation were used in this work. Raw materials were: OF (mainly food and garden wastes); MSW; and sludge from wastewater treatment plant, both raw sludge (RS) and anaerobically digested sludge (ADS). Additional samples were collected at different processing points in a MBT plant treating MSW (MBT-MSW) and OF (MBT-OF). This plant has been previously described elsewhere (Ponsá et al., 2008) and the main processing steps are mechanical pretreatment, anaerobic digestion, and composting, in this order. Table 1 shows the average dry and organic matter content for each type of raw material. Values for MBT samples are not included because they present a high deviation since this label includes diverse materials such as MSW after mechanical pretreatment, digestate from anaerobic digestion or final compost.

Samples were collected and analyzed along 1 yr period (2008). All OF and MSW samples were grinded to 15 mm particle size to increase available surface and maintain enough porosity and matrix structure (Ruggieri et al., 2009). All samples were frozen at −18°C within the first 12 h after sampling. Before analysis samples were thawed at room temperature for 24 h.

Dynamic Respiration Index

The procedure established for dynamic respiration indices determination and calculation was based on previous work by Adani et al. (2003, 2004, and 2006) and Barrena et al. (2005) and designed with the aim to analyze three replicates simultaneously. Figure 1 shows a scheme of the experimental set up built for dynamic respiration index determination with capacity for three samples. A 100 g waste sample was placed in a 500 mL reactor. In the case of low porosity materials such as sludge, porosity was corrected manually by mixing 25 g of wooden rods (cut in two) for 100 g of sludge and the resulting 125 g of mixture were used for DRI determination. Wooden rods are considered inert material since their biodegradation is negligible in the time of assay. Reactors (Fig. 1) consisted of an Erlenmeyer flask, containing a plastic net to support the organic waste and provide an air distribution chamber, placed in a water bath at 37°C (Barrena et al., 2005). Airflow in the reactors was manually adjusted by means of an air flow controller (Bronkhorst Hitec, the Netherlands) to provide constant airflow, and modified when necessary to ensure a minimum oxygen content in exhaust gases of 10% v/v (Leton and Stentiford, 1990). According to the biodegradability of the samples, initial air flow selected was 30 mL min^{-1} for active samples and 20 mL min^{-1} for more stable samples such as compost. Exhaust air from the reactors was sent to an oxygen sensor prior dehumidification in a water trap. Both air flow meters and oxygen sensors were connected to a data acquisition system to continuously record these values for DRI calculation.

Dynamic respiration index (DRI) can be calculated from oxygen and air flow data for a given time (Eq. [1]).

$$\mathrm{DRI}_t = \frac{(O_{2,i} - O_{2,o}) \times F \times 31.98 \times 60 \times 1000^a}{1000^b \times 22.4 \times \mathrm{DM}} \qquad [1]$$

where: DRI$_t$, dynamic respiration index for a given time t, mg O_2 g^{-1} DM h^{-1}; ($O_{2,i}$-$O_{2,o}$), difference in oxygen content between airflow in and out the reactor at that given time, volumetric fraction; *F*, volumetric airflow measured under normal conditions (1 atm and 273 K), mL min^{-1}; 31.98, oxygen molecular weight, g mol^{-1}; 60, conversion factor, minutes h^{-1}; 1000^a, conversion factor, mg g^{-1}; 1000^b: conversion factor, mL L^{-1}; 22.4, volume occupied by one mol of ideal gas under normal conditions, L; DM, dry mass of sample loaded in the reactor, g.

A dynamic respiration index curve can be built from on-line collected data as shown in Fig. 2. From these data, several respiration indices can be calculated as follows, divided into two categories: oxygen uptake rate indices and cumulative consumption indices.

Oxygen Uptake Rate Indices—Dynamic Respiration Index

- DRI$_{max}$: maximum DRI$_t$ obtained.
- DRI$_{1h}$: average DRI$_t$ in the 1 h of maximum activity.
- DRI$_{24h}$: average DRI$_{1h}$ in the 24 h of maximum activity (Adani et al., 2003).

Cumulative Consumption Indices—Cumulative Oxygen Consumption

- AT$_n$: Cumulative oxygen consumption in n days calculated as shown in Eq. [2]:

$$AT_n = \int_{t_l}^{t_l+n} DRI_t \cdot dt \quad [2]$$

where t_l is time when lag phase finishes. Lag phase (Federal Government of Germany, 2001) ends when oxygen uptake rate reaches 25% of the maximum uptake rate calculated as the average of 3 h (Fig. 2).

- AT_4: cumulative oxygen consumption in 4 d (after lag phase).
- AT_{24h}: cumulative oxygen consumption in the 24 h of maximum activity, that is, the 24 h period when DRI_{24h} is calculated.

Two replicates were analyzed for each sample. A third replicate was undertaken when deviation among duplicates was more than 20%.

Analytical Methods

Water content, DM and organic matter content were determined according to the standard procedures (USDA and the U.S. Composting Council, 2001). Three replicates were analyzed for each sample.

Statistics

ANOVA test was performed to compare different indices and substrates. Mean values for the different DRI were compared for a given substrate. In addition, OF, RS, and ADS mean values were compared for a given index. If ANOVA test resulted in statistically significant differences, Tukey test was performed in pairwise comparisons. A confidence level of 95% was selected for all statistical comparisons. Statistical tests were conducted with SPSS 17.0.0 (SPSS Inc., Chicago, IL).

Table 1. Dry matter and volatile solids content for the different types of sample considered, expressed as average with standard deviation in brackets.

Sample code	Type of sample	No. of samples	Dry matter	Volatile solids
			%	%, dmb†
OF	organic fraction of municipal solid waste	6	36.2 (5.4)	73.7 (8.8)
RS	raw sludge	10	21.4 (6.0)	73.3 (7.7)
ADS	anaerobically digested sludge	10	21.4 (3.7)	55.4 (8.8)
MBT-MSW	samples from a MBT plant treating municipal solid waste	12	–	–
MBT-OF	samples from a MBT plant treating OF	20	–	–

† dmb: dry matter basis.

Results and Discussion

Respiration Indices Values and Correlations

Figure 3 presents DRI_{max}, DRI_{1h}, and DRI_{24h} and Fig. 4 presents AT_{24h} and AT_4 for the 58 samples analyzed. It was not possible to calculate AT_4 in all cases due to insufficient test time. In general higher indices values are observed for OF and RS samples. In the case of MBT samples, the high variability among indices values reflects the different stage of stability of samples collected along a mechanical-biological treatment process.

From the presented values, a qualitative classification of indices can be established, based on the intrinsic characteris-

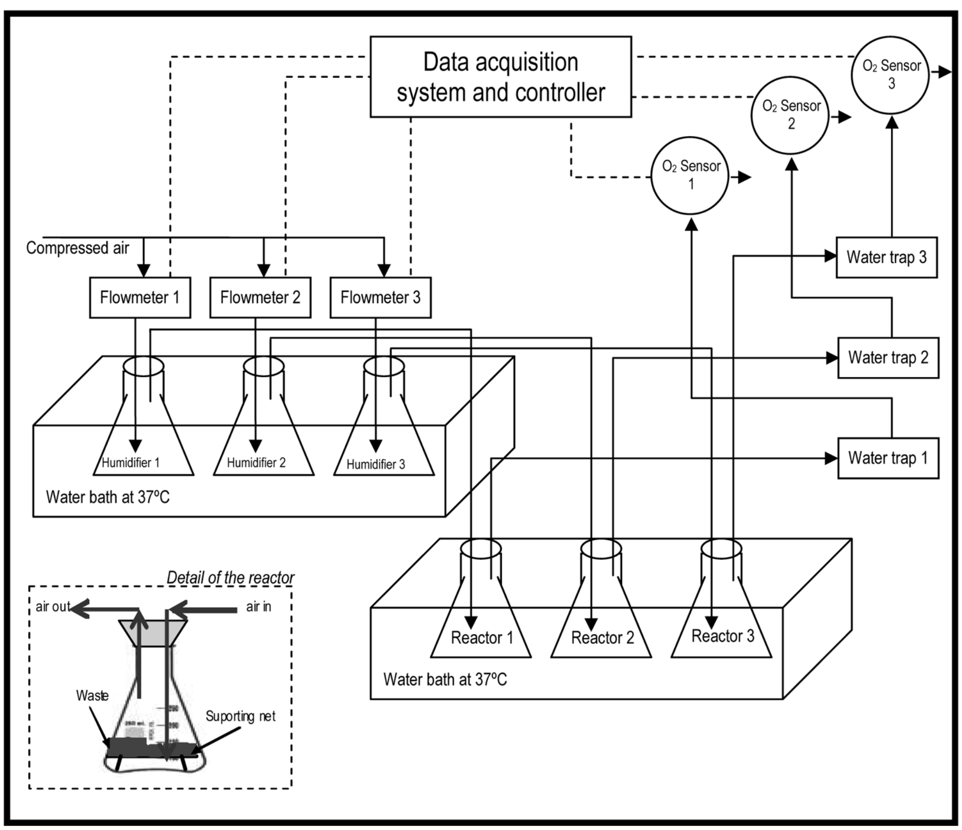

Fig. 1. Experimental set up for dynamic respiration indices determination.

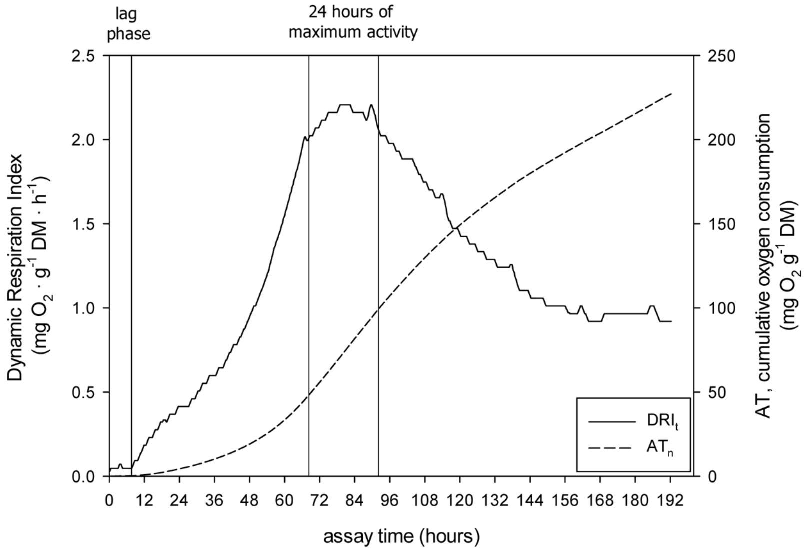

Fig. 2. Typical curve for dynamic respiration index (DRI) evolution and calculation.

tics of the materials, the existence of a pretreatment or storage stage, the sample history, and the analyzed indices values:

i. *highly biodegradable wastes*, respiration activity higher than 5 mg O_2 g^{-1} DM h^{-1} (which includes source-selected organic fraction of municipal solid waste, nondigested municipal wastewater sludge and animal by-products);

ii. *moderately biodegradable wastes*, respiration activity within 2 to 5 mg O_2 g^{-1} DM h^{-1} (including mixed municipal solid waste, digested municipal wastewater sludge, and several types of manure);

iii. *wastes of low biodegradability* (respiration activity lower than 2 mg O_2 g^{-1} DM h^{-1}).

The indices in Fig. 3 and 4 were analyzed to establish whether they correlate. Indices were analyzed together and divided into groups according to the type of material. Results obtained for linear correlation, slope, p and R^2, are presented Table 2. For instance, for OF and MBT-OF samples, AT_4 and DRI_{24h} correlated according to $AT_4 = 71.8137 \times DRI_{24h}$, with a R^2 of 0.9063 and $p < 0.0001$. All indices correlated significantly when all data from the 58 samples were considered. When respiration indices were analyzed according to the type of sample, the correlations found were different but still significant, except for the case of ADS where a high dispersion was observed and no significant linear correlation was found among the five different indices considered. The observed variability in ADS could be explained by the different biodegradation level achieved in anaerobic digesters working under different conditions (retention time, type of technology, etc.). In general the slope for the linear correlation among DRI_{1h} and DRI_{max} was close to 1 for the different materials analyzed. DRI_{24h} was the 65% of DRI_{max} when all data was considered. However this ratio varied between 49.3 and 89.3% depending on the type of sample. This variation was also observed for DRI_{24h} or DRI_{1h} with AT_4 (65.8 for all data and 71.8 to 101.2 for different types of waste). Short-term indices obtained for one type of waste have been correlated to long-term ones and proposed as useful prediction tools (Mohajer et al., 2009). The observations here presented and discussed highlight the need for specific correlations for each material. They also indicate that although strongly correlated the indices considered might provide different information. Thus, a deeper analysis of their meaning and expression form was undertaken and it is presented in the following sections.

Oxygen Uptake Rate Indices—Dynamic Respiration Index

Figure 5 presents the statistical comparison of DRI_{max}, DRI_{1h}, and DRI_{24h} for three different organic wastes typologies, OF, RS, and ADS. The indices DRI_{max} and DRI_{1h} were not statistically different for the three materials considered. The index DRI_{24h} was statistically different to and lower than the other two indices for ADS while it was found not different for OF and RS. In the case of highly biodegradable wastes as OF and RS, high respiration activity can be maintained for longer periods of time. In these cases, DRI_{max}, DRI_{1h}, and DRI_{24h} are equivalent. Contrary, moderately biodegradable materials as ADS can reach a considerable activity at a given moment but the lack of enough metabolic energy content will not allow for the maintenance of that respiration level. In this case, a long-term index as DRI_{24h} is expected to be lower than DRI_{max} and DRI_{1h}, as demonstrated in this work (Fig. 5). In consequence, DRI_{24h} is considered more sensitive to discriminate among different biodegradability levels. This conclusion points to the hypothesis that a longer time index such as AT_4 could be more sensitive too and a better tool for stability and/or biodegradable organic matter content determination.

Cumulative Consumption Indices

Figure 6 presents the variation with time of cumulative oxygen consumption (AT_n) expressed as a ratio of long time oxygen consumption test (AT_{12}, cumulative consumption in 12 d). These results were obtained correlating AT_n to AT_{12} for 22 organic samples including OF, RS, ADS, MBT-OF, and MBT-MSW.

Data in Fig. 6 was fitted to the modified Gompertz model (Eq. [3]), which describes microbial growth and is often used in anaerobic digestion systems (Buendía et al., 2009; Zwietering et al., 1990).

$$AT_n / AT_{12} = P \cdot \exp\left\{ -\exp\left[\frac{R \cdot \exp}{P} (\lambda - t) + 1 \right] \right\} \quad [3]$$

where AT_n/AT_{12} is the ratio of cumulative oxygen consumed at time t (days) to the final cumulative oxygen consumption; P is the ratio of the ultimate oxygen consumption potential (dimensionless); R is maximum oxygen uptake rate, d^{-1}; and λ is the lag phase (days).

The results of the Gompertz fitting were P = 1.01, $R = 0.13$ d^{-1} and $\lambda = -0.92$ d ($p < 0.0001$, $R^2 = 0.9921$). The absence of a lag phase (mathematically, a negative lag phase) indicates the rapid growth of aerobic microorganisms in highly biodegradable substrates. Accordingly, an aerobic method is expected to allow for a more rapid biological activity estimation than an anaerobic procedure (Ponsá et al., 2008). Gompertz model should be used when a lag phase is observed, for instance, when processing long time frozen samples.

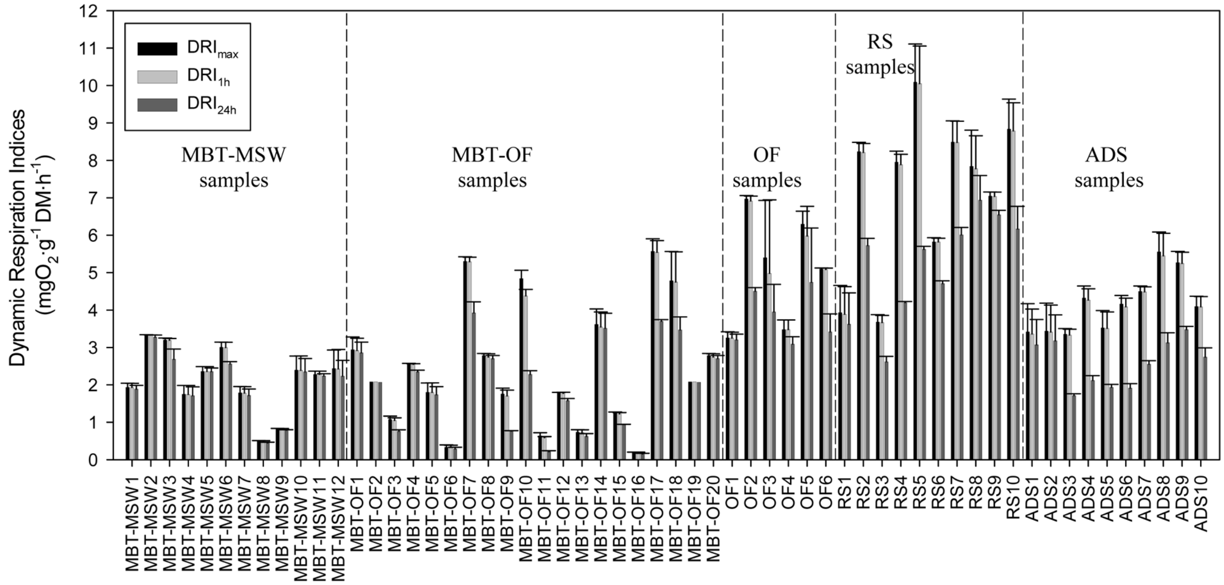

Fig. 3. Dynamic respirometric indices (DRIs) for 58 organic waste samples, expressed as: DRI_{max}, maximum DRI measured; DRI_{1h}, DRI average of the 1 h of maximum activity; DRI_{24h}, DRI average of the 24 h of maximum activity. Vertical lines separate different waste typology.

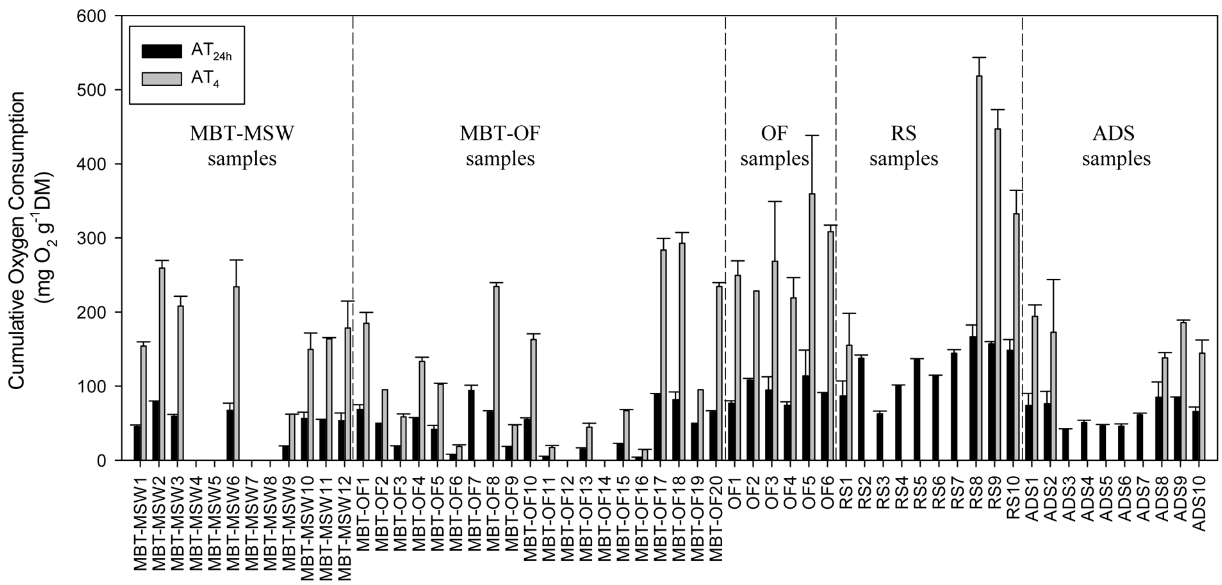

Fig. 4. Cumulative oxygen consumption indices for 58 organic waste samples, expressed as: AT_{24h}, cumulative consumption in the 24 h of maximum activity; AT_4, cumulative consumption in 4 d. Vertical lines separate different waste typology.

In the cases where a lag phase is not observed a simple exponential rise model (Eq. [4]) is considered more suitable to model AT evolution. Figure 6 shows data fit to this model.

$$AT_n / AT_{12} = P \times \left[1 - \exp\left(-R \times t\right)\right] \qquad [4]$$

Experimental data in this study fitted well to the exponential model ($p < 0.0001$ and $R^2 = 0.9956$). Model parameters obtained were $P = 1.07$ and $R = 0.22$ d^{-1}. The expression obtained is valid for all the analyzed samples which include different organic materials collected at different stages of biodegradation. Consequently this model can be considered a general expression suitable for aerobic biodegradation process modeling.

As observed in Fig. 6, AT_4 corresponds to 65% of the final cumulative oxygen consumption. In the wastewater field the parameter biological oxygen demand at 5 d (BOD_5) is widely used (Metcalf and Eddy, 2003). The BOD_5 represents a 65% of total biological oxygen demand for municipal wastewater. Hence, 4 d is a convenient duration for the respiratory test in solid phase since it quantifies a considerable amount of total oxygen consumption avoiding longer analysis times.

Dynamic Respiration Index vs. Cumulative Oxygen Consumption—Which Index Should Be Used?

Figure 7 shows the statistical comparison of the biodegradability of three different types of organic wastes according to the index selected to express it. According to Fig. 7, OF and ADS would be considered as equivalent in terms of biodegradability when considering DRI_{max}, DRI_{1h}, DRI_{24h}, or AT_{24h}. However, when a longer time cumulative index as AT_4 was used, the classification

Table 2. Linear correlations ($Y = s \times X$) found among different dynamic indices according to type of waste (n: number of samples; s: slope; Y: dependent variable; X: independent variable; dynamic respiration index (DRI), mg O_2 g^{-1} dry matter (DM) h^{-1}; cumulative oxygen consumption (AT), mg O_2 g^{-1} DM).

OF and MBT-OF samples†
n = 24, *p* < 0.0001 for all correlations

Y → / X ↓	DRI_{1h}	DRI_{24h}	AT_{24h}	AT_4
DRI_{max}	s:0.9698 R^2:0.9965	s:0.6687 R^2:0.8857	s:16.1484 R^2:0.8991	s:47.4244 R^2:0.8017
DRI_{1h}		s:0.6927 R^2:0.8970	s:16.7315 R^2:0.9114	s:49.2708 R^2:0.8116
DRI_{24h}			s:24.1736 R^2:0.9972	s:71.8137 R^2:0.9063
AT_{24h}				s:2.9787 R^2:0.9154

RS samples
n = 10, *p* < 0.05 for all correlations, except ‡ *p* < 0.0001 and § *p* > 0.10

Y → / X ↓	DRI_{1h}	DRI_{24h}	AT_{24h}	AT_4
DRI_{max}	s:0.9968‡ R^2:0.9999	s:0.4904 R^2:0.5528	s:11.8046 R^2:0.5547	s:4.2057 R^2:0.9132
DRI_{1h}		s:0.4928 R^2:0.5547	s:11.8618 R^2:0.5556	s:53.4010§ R^2:0.5074
DRI_{24h}			s:24.0276‡ R^2:1.0000	s:101.2485 R^2:0.9142
AT_{24h}				s:4.2057 R^2:0.9132

MBT-MSW samples
n = 12, *p* < 0.0001 for all correlations, except ¶ *p* < 0.001

Y → / X ↓	DRI_{1h}	DRI_{24h}	AT_{24h}	AT_4
DRI_{max}	s:0.998 R^2:1.0000	s:0.8915 R^2:0.9663	s:20.5811¶ R^2:0.9192	s:71.7897¶ R^2:0.9246
DRI_{1h}		s:0.8934 R^2:0.9668	s:20.6284¶ R^2:0.9199	s:71.9317¶ R^2:0.9247
DRI_{24h}			s:23.8990 R^2:0.9714	s:80.0834¶ R^2:0.9017
AT_{24h}				s:3.3564¶ R^2:0.9313

ADS samples
n = 10, *p* > 0.10 for all correlations, except # *p* < 0.0001

Y → / X ↓	DRI_{1h}	DRI_{24h}	AT_{24h}	AT_4
DRI_{max}	s:0.9830# R^2:0.9985	s:0.3622 R^2:0.2008	s:11.3557 R^2:0.2901	s:-10.4543 R^2:0.1870
DRI_{1h}		s:0.3710 R^2:0.2038	s:11.5285 R^2:0.2894	s:-10.4712 R^2:0.1757
DRI_{24h}			s:25.6461§ R^2:0.9670	s:51.1704 R^2:0.2920
AT_{24h}				s:0.2315 R^2:0.0054

All data
n = 58, *p* < 0.0001 for all correlations

Y → / X ↓	DRI_{1h}	DRI_{24h}	AT_{24h}	AT_4
DRI_{max}	s:0.9900 R^2:0.9986	s:0.6325 R^2:0.8496	s:15.3432 R^2:0.8492	s:44.7059 R^2:0.7068
DRI_{1h}		s:0.6400 R^2:0.8539	s:15.5174 R^2:0.8496	s:45.6593 R^2:0.7135
DRI_{24h}			s:24.0525 R^2:0.9970	s:65.8188 R^2:0.8698
AT_{24h}				s:2.7205 R^2:0.8664

† OF: source-selected organic fraction of municipal solid waste; MBT: mechanical-biological treatment; RS: raw sludge; MSW: municipal solid waste; ADS: anaerobically digested sludge.

appeared different, being OF and RS not statistically different and ADS statistically less biodegradable. This last finding would be in agreement with the classification suggested in section 3.1 of this paper as well as with the behavior of these materials under composting conditions (Gea et al., 2004). As previously explained, highly biodegradable materials maintain a high activity level for a longer time than moderately biodegradable wastes. This is illustrated by the ratio AT_{24h}/AT_4, which is 34.2, 34.5 and 37.8% for OF, RS, and ADS respectively, as calculated from average data on Fig. 7.

Consequently, long time cumulative indices would better represent the overall biodegradable organic matter content of

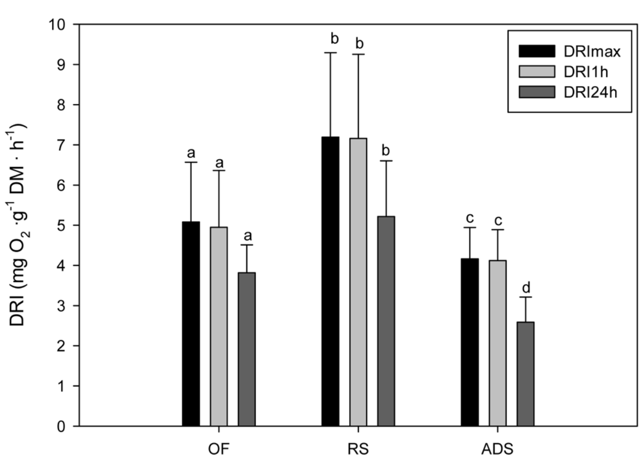

Fig. 5. Statistical comparison of different indices obtained for three different organic wastes. Different letters indicate statistically different means.

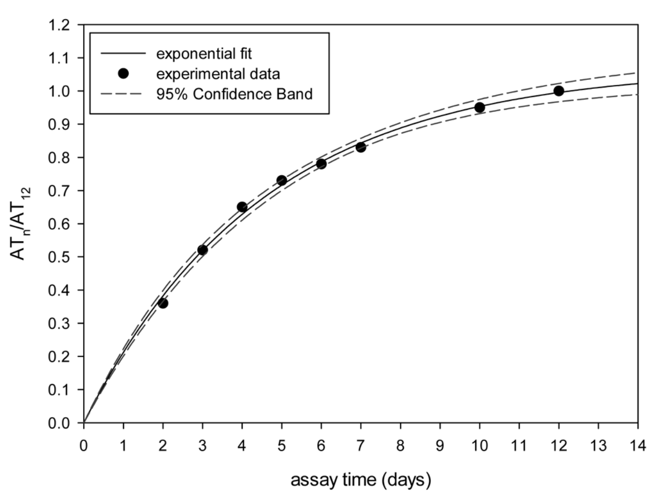

Fig. 6. Evolution with time of cumulative oxygen consumption as a fraction of ultimate cumulative oxygen consumption: experimental data and exponential fit.

a given sample than short term indices, either cumulative or rates. Consequently, AT_4 provides a reliable measure of biodegradable organic matter. However, it is crucial to know the maximum biodegradation rates for a complete biodegradability assessment and in the initial stage of a treatment process to optimize operation. Dynamic respiration methodology allows for a complete biodegradability analysis combining DRI_{max}, DRI_{24h} and AT_4 information, that is, biodegradation rate and biodegradable organic matter content. If one index shall be selected, DRI_{24h} is sensitive enough to discriminate among highly and moderately biodegradable wastes and can be determined in a short period of 24 h. Afterward, correlations presented in section 3.1 can be used for AT_4 estimation from DRI_{24h} values specifically for the different types of wastes presented here.

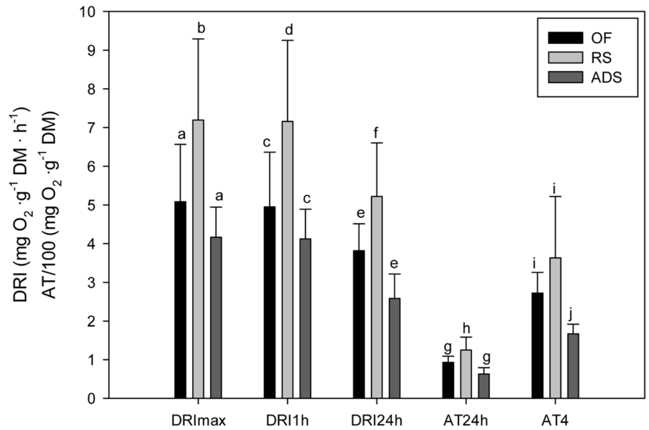

Fig. 7. Statistical comparison of three different organic wastes dynamic indices. Different letters indicate statistically different means.

Conclusions

All indices obtained from dynamic respiration methodology correlate well but can reveal differences among organic substrates in a diverse manner. The information provided by DRI profile is a useful tool for a precise biodegradability analysis. The index DRI_{24h} shall be selected as a fast and sensitive measure of biodegradability level while AT_4 quantifies the biodegradable organic matter content of a given sample. The combined information provided by both indices should be used whenever possible. Specific correlations for a given material should be used as prediction tools avoiding general relationships.

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CHAPTER 6. GENERAL DISCUSSION

CHAPTER 6. GENERAL DISCUSSION

A general discussion of the results will be done in this section but trying to give a solution to the main problems presented in Chapter 1 and also stating that the goals proposed in Chapter 2 have been successfully achieved.

During the body of this chapter results presented in Chapter 5, corresponding to already published articles, will be used, as well as results presented in Chapter 9, which correspond to the articles that have been already submitted for publication in international journals.

The next discussion will be structured in the next typology fields:

- Update bibliography of already published respirometric methodologies (revising Barrena et al., (2006a), assess their use to monitor biological processes and determine the stability of final products, and propose improvements for these methodologies.
- The development of standardized methodologies and equipments needed for obtaining a reliable measure of biodegradable organic matter content.
- Comparison and evaluation of the new indices proposed and determination of correlations among them.
- Assessment of the use of these indices in industrial facilities.

6.1. Assessing the appropriateness of the use of the already proposed biological indices

The research group in which this thesis has been developed has long experience in the determination of the aerobic respiration indices of several organic wastes. In fact some co-researches have already completed their thesis in the field of aerobic respirometries and have published many articles in international journals: Gea et al., 2004; Barrena et al., 2005; Barrena et al., 2006a; Barrena et al., 2006b; Barrena et al., 2006c; Ruggieri et al., 2008. Barrena et al., 2009.

In the background of the research group a methodology for determining SRI was developed by Dr. Barrena and other co-researchers, based in the methodology previously described by

Iannotti et al., (1993). Therefore this methodology was widely used in a varied range of applications, such as an assessment for co-digestion (Barrena et al., 2007), for monitoring composting processes (Gea et al., 2004; Gea et al., 2005; Barrena et al., 2006a); for comparing composting technologies (Ruggieri et al., 2008); and for testing some composting improvements (Barrena et al., 2006b) among other uses.

Some other methodologies have been reported in this thesis (Section 1.7) to be used in the waste treatment field with different aims. However and as was previously mentioned, the comparison of the results is unfeasible since methodologies differ in so many key points which definitely make impossible to formulate global conclusions of all data found in literature.

In order to give continuity to the work already done by the researching group, new goals to improve the methodology were proposed and as reflects this thesis, they were finally reached.

In the first stage, the assessment of the already developed methodology for determining SRI was carried out at industrial full scale as it is stated in Article I and Article II.

From results obtained in Article I, the evidence that SRI may not give enough information for a complete process monitoring is observed. SRI cannot discern between final products with a different grade of stability or different biodegradable organic matter content, since the same results of SRI are obtained for all samples. Respirometric indices are intended to give information about the biodegradable organic matter content, biological activity of the sample and a degree of stability. Nevertheless SRI as a single measure cannot give all this information.

When analyzing biodegradable organic matter content, SRI can only be used as a first approach, since the procedure described does not permit the comparison of the results obtained from samples of different origin and different physical and chemical characteristics. This is because the treatment and the analysis procedure for the wastes must be in accordance to their initial characteristics. For example, depending on the sample, different incubation times would be necessary to reach the maximum OUR. The most suitable result to be compared among the diverse wastes would be the maximum OUR maintained for a given time. However, depending on the material analyzed, different times would be necessary to reach these values. These times range from a few hours to a 4-5 days, depending on the nature of the waste and the time that has been stored frozen.

In addition, and as was corroborated in Article I, to make the results comparable among them in terms of stability and biodegradable organic matter content, it is necessary to give optimal conditions for measuring the respirometric indices, since just the absolute maximum respirometric value will provide this information. Biodegradable organic matter content correspond to the content of organic matter which could be susceptible of being biodegraded, and to obtain comparable and interpretable results, the tag of “at optimal conditions” should be added. In this sense, it is obvious that samples from Pile 3 described in Article I, were not analyzed at optimal conditions because moisture was excessive and there were not enough structure nor porosity. A similar discussion could be done for stability results. Stability will give a measure of the potential biodegradable matter content in a sample. A stable material will have potential biodegradable matter content below the legislation limit as means of respirometric indices. Therefore, optimal conditions should be provided for its measurement by means of respiromtries. Also Rottegrade test, intended to give information about sample stability, does not provide reliable information, due to the not optimal conditions for organic matter biodegradation. To provide optimal conditions to low porosity materials, in Section 4.1.1. a detailed procedure has been described for sample treatment previously to its analysis. Rottegrade test would be applied successfully only for specific final products, such us compos previously mechanically treated (post treatment), but not as a stability measure of samples directly collected from composting piles or other processes.

In Article II, the lack of information provided by SRI is also confirmed. Since when comparing a cumulative methodology (BMP) with a non continuous index determination (SRI), different trends are obtained (in the case of MSW). The erratic results obtained in Article II concerning SRI, are definitely confirmed in Article III. In Article III, mechanical pretreatment was specifically studied and results given by DRI and AT_4 (continuous measures) verified that during mechanical pretreatment of MSW there is a concentration of biodegradable organic matter because non biodegradable materials are mechanically removed from the main waste flow. This would be in accordance with the results obtained in Article II when using BMP, but would disagree with results measured by SRI. This would also imply that SRI results should be carefully interpreted and they should be analyzed considering the limitations that this methodology entails.

Apart from not providing continuous optimal conditions and the limitations concerning the incubation time, SRI could be susceptible of other improvements. Instead having a discrete measure of OUR in a single period of time, it would be most useful to have a continuous determination of OUR, during such a long period of time that allows for reaching maximum OUR values. In this sense a measure of the cumulative oxygen consumption, will provide also important information, since although a waste could be slowly or hardly biodegradable, thus low SRI or DRI, during long biological processes such as composting, biodegradable organic matter could be also removed. Therefore both DRI and AT_n were chosen as better respirometric indices, since they can provide more reliable information related to biodegradable organic matter content and final product stability (Article IV).

However SRI seems to be useful and reliable for biological activity determinations, since it can provide the measure of the punctual biological activity of a sample at working conditions. This would allow to discern between the different processes and settle on the best conditions or choose the best performance variables.

6.2 The development of standardized methodologies and equipments needed for obtaining a reliable measure of biodegradable organic matter content.

Once the assessment of SRI methodology was carried out and weaknesses and strengths were detected, many improvements were designed, fulfilled and afterward assessed.

A new methodology was developed for measuring simultaneously DRI and AT_n. The new respirometer was built according to the design previously made trying to overcome all limitations that SRI presented. As described in Section 4.1, the equipment allows for analyzing 12 samples simultaneously.

As well as aerobic respirometric methodology was improved, anaerobic methodology was also significantly improved and a detailed and standardized procedure is described in Section 4.2.

New methodologies will permit a complete analysis of the wastes or materials, giving reliable information about biodegradability, stability and even biological activity as has been assessed in Articles III and IV (Chapter 5), and Articles V, VI and VII (in Chapter 9).

6.3 Comparison and evaluation of the new indices proposed and determination of correlations among them.

Different indices and diverse units for their expression have been defined in Chapter 4 and used in the Articles that make this thesis up. Long discussion could be done about the most appropriate index or about the most suitable form of expression. However, there is not a single and simple answer and the solution seems to be a combined used of indices, depending on the final goal of the analysis and a specific expression of results depending on the nature of the waste sample studied.

It seems clear that each index would provide different information. A particular discussion will be initially done distinguishing between aerobic and anaerobic indices. Subsequently, a global discussion will be carried out.

6.3.1 Aerobic indices

Starting with aerobic indices and considering the abovementioned, SRI can be a useful tool as first approach on the analysis of biodegradability and stability or even as a more reliable measure when determining biological activity, as has been confirmed in Article I and II.

However, DRI measured as DRI_{MAX}, DRI_{1h} and DRI_{24h} can provide a more complete analysis of the results. DRI_{MAX} would indicate the maximum oxygen consumption rate for a given sample what would mean that when composting, the aeration system must be able to supply enough oxygen to the mixture in order to avoid the process limitation by oxygen availability. DRI_{MAX} would give information about how easily biodegradable under aerobic conditions is the organic matter of the sample. DRI_{1h} would give similar information, since maximum OUR is normally maintained for more than one hour as it is shown in Article IV. However, these both indices must be carefully considered because sometimes easily oxidizable or hydrolysable materials are present in the wastes and high values of DRI_{MAX} and DRI_{1h} are obtained. In this sense, longer DRI determinations would overcome this inconvenient. Thus DRI_{24h} would be the most appropriate measure to give reliable information of the biodegradation rate and even of the biodegradability of the sample, and points to the hypothesis that longer experimental techniques could give more concise information on biodegradability and stability of the sample.

Specifically, in terms of biodegradability, meaning how biodegradable is the organic matter of the sample, dynamic respirometric indices, measured as DRI, could not be sensitive enough to make a correct classification. It could be justified by the fact that sometimes organic matter of a given sample can be of diverse nature. Organic matter could be classified in different fractions: easily biodegradable, hardly biodegradable or inert. The next discussion is based on the results obtained in Article IV and Article VII. In this sense, when analyzing samples of different origin and different nature diverse results are expected, since the characteristics of these samples are well known as well as the treatments to which they have been subjected. Therefore, the methodology proposed to be considered reliable and consistent, must provide enough information to establish an exact classification of the materials or wastes depending on the biodegradability, the stability, the biodegradation rate and finally determine the correspondent fractions of the organic matter of the sample.

Cumulative indices (AT_n) would provide more information on biodegradability and stability. In addition the profile of the cumulative oxygen consumed or the (theoretically) equivalent cumulative carbon dioxide produced could be used to determine the percentage of easily (or rapidly, Cr) and hardly (or slowly, Cs) biodegradable organic matter of the sample as well as the non biodegradable fraction of organic matter (Article VII). Given that AT_4 and longer AT results represent an absolute value of the oxygen consumed or the carbon dioxide produced, they could be used to definitely determine biodegradability and stability. This is confirmed in Article IV, when AT_4 was the parameter that allowed for differentiating between anaerobically digested sludge (ADS), which have already been subjected to a biological treatment so less biodegradability was expected, and raw sludge and OFMSW, which are fresh samples with high biodegradability expected.

Another parameter than could be of special interest for discussion is AT_{24h} when it is compared to AT_4. For moderately or low biodegradable materials, the ratio AT_{24h}/ AT_4 would be higher than for highly biodegradable materials, due to the fact that for highly biodegradable materials biological activity, what means OUR, is maintained at high values during longer times than for moderately and low biodegradable materials.

To sum up this part of the discussion, it can be stated that each index can provide different information but there is not a single index able to totally characterize a waste sample. The total characterization will be able when considering at least DRI_{MAX}, DRI_{24h} and AT_4.

DRI_{MAX} would be useful to optimize operation in the initial stage of the composting processes, when aeration can be the limiting parameter but is not sensitive enough to determine biological activity, biodegradability or stability. As longer is the analysis, more concise can be the information provided by the index determined. Therefore, DRI_{24h} can overcome the limitations of DRI_{MAX} and DRI_{1h} when determining biodegradability and stability. However for determining the real biodegradability or stability, AT_4 or longer analysis must be carried out.

As example two different degradation behaviors are shown in Figure 6.1. In this Figure, DRI and AT profiles are plotted for a sample of OFMSW and a sample of ADS. As can be observed, DRI_{24h} results would be similar and close to 2.1 mg O_2 g $DM^{-1}h^{-1}$ for both samples what would mean that the average of OUR during the 24 hours of maximum oxygen consumption results are the same. Although ADS reaches higher values of DRI_{MAX}, this high biological activity is only maintained during a few hours, while for OFMSW the biological activity is maintained at high values during a longer period of time. If only DRI_{24h} was considered, ADS and OFMSW would have the same level of biodegradability and it is also confirmed by results from Article VII, where Cr values are similar for OFMSW and ADS.

Therefore, for a reliable measure of biodegradability AT results must be also considered. The values of AT_4 obtained are 170 and 330 mg O_2 g DM^{-1} for ADS and OFMSW respectively. As can be noted, AT_4 values differ significantly making possible the distinction between a high biodegradable waste (OFMSW) and a moderate biodegradable waste (ADS).

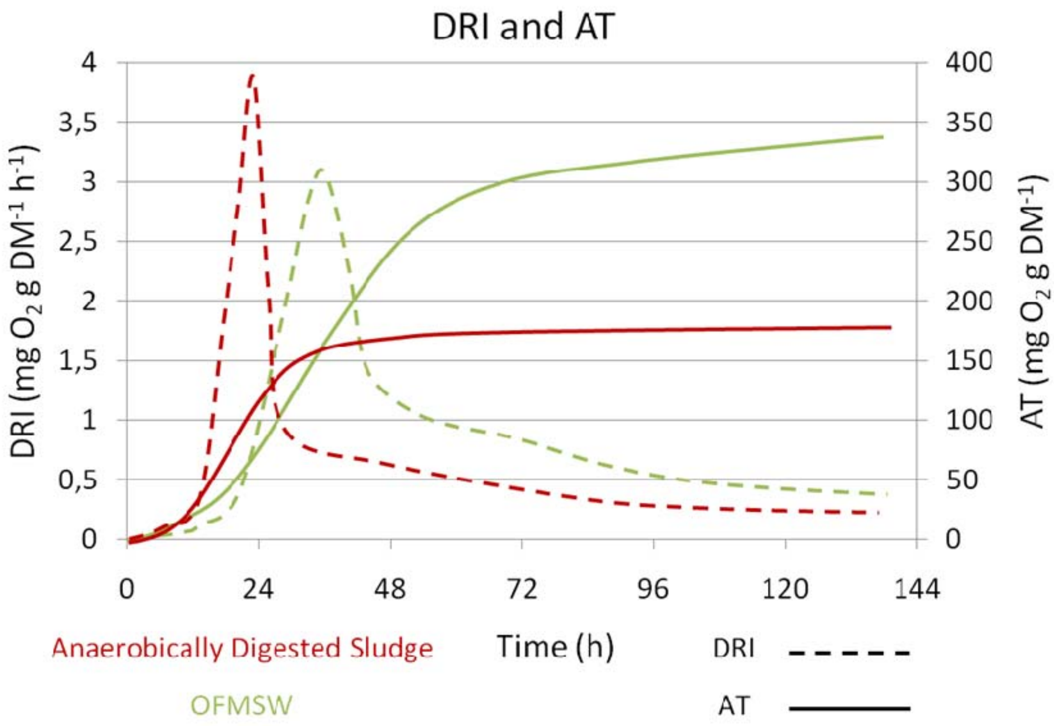

Figure 6.1. DRI and AT profiles for ADS and OFMSW samples.

A deeper analysis could be done regarding the nature of the wastes. The high OUR measured for ADS, would mean that a fraction of the organic matter of the sample is highly biodegradable, concretely this fraction corresponds to a 10% of the initial TOC with a kr of 0.65 $days^{-1}$. In fact when analyzing a sample of ADS, in Article VII, this is the only waste with a percentage of Cr higher than Cs. Probably this would be due to the presence of hydrolyzed organic matter that has not been degraded by methanogenic bacteria during anaerobic digestion and that is easily biodegradable under aerobic conditions. Table 6.1 summarizes the kinetic results obtained for these two wastes as presented in Article VII when using the new kinetic model.

On the contrary, the Cr of OFMSW is slowly biodegraded because: i) particle size is higher, so lower available surface; and ii) organic matter is composed by complex macromolecules which are hard to biodegrade. Although Cr values are similar, kr is much higher (55%) for ADS than for OFMSW, and consequently Cr is biodegraded at a higher rate, as it is reflected in Figure 6.1. Nevertheless, the percentage of slowly biodegradable carbon, Cs, (or equivalent organic matter) is extremely higher (85%) for OFMSW than for ADS. Concretely, as is proved in Article VII, the OFMSW is composed as an average by 40% of highly potentially biodegradable matter while ADS is only composed by 7%. Considering all these data it is expected similar values of DRI_{24h} but higher values of AT_4 for OFMSW than for ADS, as it has been abovementioned and confirmed in Figure 6.1.

Table 6.1. Kinetic parameters for new model developed in this work.

New kinetic model developed					
Model parameter	Cr (%)	Cs (%)	Ci (%)	kr (day^{-1})	ks (day^{-1})
OFMSW	13 ± 3	40 ± 2	46.0 ± 0.7	0.30 ± 0.03	0.08 ± 0.01
Digested Sludge	10 ± 1	7 ± 1	81 ± 2	0.65 ± 0.01	0.12 ± 0.04

OFMSW: Organic Fraction of Municipal Solid Waste. Cr: rapidly biodegradable carbon fraction on initial TOC. Cs: slowly biodegradable carbon fraction on initial TOC. Ci: inert carbon fraction on initial TOC. kr: rapid rate constant. ks: slow rate constant.

Additionally, regarding industrial usefulness of these results, some considerations could be done. When composting ADS, high aeration requirements will be required during the first stage, but the process will be completed in short times compared to other wastes such as OFMSW or raw sludges. In addition aerobic treatment of OFMSW will involve a more intensive process and aeration supply must be maintained for long times.

Respirometric methodologies are intended to give a reliable measure of biodegradability, stability and biological activity. However these methodologies would not be profitable if they did not have a practical use in industrial facilities for waste analysis or process monitoring. In this regard, short determinations would have an added value, since time required for having AT_4 results is always up to 4 days, and in treatment plants, such a long times are normally not possible for storing wastes prior to treatment and off line measures obtained after 5 days of sampling are not useful.

On the one hand, as it has been previously mentioned, AT_4 gives more reliable information on biodegradability and stability but on the other hand, DRI_{24h} requires shorter times for its determination. In this manner, some correlations between indices have been obtained, in order to allow for complete analysis in shorter times. In Articles III and IV, strong correlations between DRI and AT_4 have been defined. These correlations demonstrate that AT_4 values can be predicted by using DRI_{24} values with a correlation coefficient up to 0.9 in almost all cases. However, some restrictions must be pointed out. The most important is that correlations must be particularly calculated depending on the type of waste to be analyzed because, as discussed above and observed in Figure 6.1, the organic matter of the samples is of different nature and present different degradation kinetics. Moreover, for some type of wastes, such as ADS, correlations are not valid, since the different origins and anaerobic digestion technologies and treatments to which they are applied, lead to obtain diverse products that could even be considered as different wastes because their characteristics are mostly different and a particular correlation would be necessary for each sample.

The most reliable measure to determine the biodegradable organic matter content is AT_u (total cumulative oxygen consumption until no significant oxygen consumption is detected). AT_u definitely reflects the total amount of oxygen consumed to completely remove the biodegradable organic matter but it can also reflect the total carbon that has been mineralized and emitted in form of CO_2. Furthermore, after fitting experimental data to the new model developed (Article VII), it allows for Cr, Cs and Ci determinations, as well as the biodegradation constant rates, kr and ks, which finally leads to a complete waste characterization. However, this index is disesteemed for process monitoring, due to the long times needed for AT_u determinations (normally more than 30 days). But the utility of these determinations is remarkable in some cases, as it has been demonstrated in Article VII.

Additionally, the most suitable units in which indices must be expressed should be established. Different forms of expression have been reported in literature and almost all of them express the results on OM basis. This fact could lead to wrong interpretations of the results, since it is being assumed that all OM measured by ignition is biodegradable. Considering the heterogeneity of municipal solid wastes and their composition (Agencia de Residus de Catalunya, 2010) it seems clear that when igniting the sample, plastics, textiles and other synthetic organic materials are quantified as OM susceptible for biodegradation. In these regard, DM basis would be more reliable, since all matter of the material (except water) would be taken into account. On contrary when using OM basis, an unknown amount of inert organic matter would be evaluated together to biodegradable organic matter. As an example, using the OM basis would mean that when expressing the results, plastic bottles would be considered while aluminum cans would be not considered, being both materials non biodegradable at all. To avoid this controversy, DM was stated as the correct basis to which the indices must be referred to. In fact, the most suitable basis in which the indices must be referred would be the biodegradable organic carbon, measured as the total carbon emitted in form of CO_2 until no significant CO_2 production is detected. However these measures require long determinations and as it has been aforementioned, they are not recommended for monitoring purposes.

However, total CO_2 production and CO_2 production profiles can be used to obtain essential information, allowing for a reliable characterization of the organic matter contained in the wastes as it can be confirmed in Article VII.

Firstly, the knowledge of the total CO_2 production will permit to calculate the real amount of carbon susceptible to be biodegraded. This measure will definitely avoid the problems that the use of TOC presents, since not all organic carbon of the wastes can be biodegraded and the recalcitrant carbon can be sometimes greater than the biodegradable organic carbon (BOC). For example, the initial C/N ratio is one of the most important factors affecting the composting processes and the compost quality, but it is generally calculated using the TOC what irremediably leads to many process failures because, as stated above, not all organic carbon can be considered biodegradable.

Secondly, the CO_2 production profiles can be adjusted to a mathematical model to provide the kinetic parameters regarding aerobic biodegradation reactions which, for example, will be extremely helpful for determining the time required for a properly stabilization of the material. These parameters are the rapidly biodegradable (C_R) and slowly biodegradable (C_S) organic fractions under aerobic conditions as well as the inert fraction (C_I) and the kinetic rate constants associated to each fraction. They will provide valuable information for composting processes management and design.

6.3.2 Anaerobic indices

Anaerobic indices are of especial interest if wastes are to be treated in anaerobic biological processes. Aerobic indices cannot always give a reliable measure of how anaerobically degradable would be a waste. In this sense, when designing anaerobic treatments, estimating biogas productions and carrying out economical analysis, a more accurate measure is needed and anaerobic indices could provide this more precise information on anaerobic biological degradation and biogas and methane potential productions.

Anaerobic indices have not been as widely studied and used as aerobic indices. There are different reasons to justify this fact: i) methodologies were more complicated because inoculum was required and strong anaerobic conditions were necessary; ii) anaerobic biological kinetics are much slower than aerobic kinetics and long experiments were necessary; and iii) they are not a reliable measure of total biodegradable organic matter, since not all aerobically degradable organic matter can be degraded under anaerobic conditions.

The research group did not have experiences on anaerobic index determinations of solid wastes, thus a new methodology was developed to achieve this goal, taking as initial reference the methodology described by the Federal Government of Germany and the procedure described by Ferrer et al., (2004) as it has been described in Section 4.2.

The experimental anaerobic indices determined are both absolute values of cumulative biogas or methane produced in a DM basis. Subsequently, maximum biogas or methane production rate can be calculated by fitting the experimental data to the Gompertz model.

GB_n will provide information about the potential production of biogas (L) per unit of DM of the sample loaded (kg). Equivalently, BMP will provide the measure of the potential production of methane (L) per unit of DM of the sample loaded (kg). As they will measure the volumetric production of a compressible fluid, such as biogas or methane, results must be referred to specific temperature and pressure conditions. Normal conditions (273.15 K and 1atm) are the most widely used and therefore they are the conditions chosen for referring the results. Regarding the basis to which the results should be referred to, the same discussion done for aerobic indices is applicable in this Section. Final units for expressing anaerobic index results will be NL of biogas or methane per kg of DM loaded.

At present, there is a large number of anaerobic digestion facilities treating a wide range of wastes. However, also many facilities have failed because the previous analysis of the wastes was not properly carried out and consequently the anaerobic digesters design was not correct for the satisfactory treatment of the waste or even anaerobic digestion could have been not the appropriate treatment for some wastes.

In the case of municipal wastes, and considering MSW and OFMSW flows, specific characterizations of the wastes should be done for each country or region, since the waste characteristics would depend on the population lifestyle and habits. In addition the different legislation and collection systems will lead to diverse waste distinctivenesses. For these reason, and as an example, an anaerobic digester design for treating MSW generated in Germany could be not appropriate for treating MSW in Spain.

It seems clear that the analysis of GB and BMP could be crucial for deciding the most suitable biological treatment for a given waste. GB determinations will give a measure of the total biogas production and biodegradable potential while BMP determinations will provide information of the quality of the biogas produced (methane content) and will make possible the accurate economical analysis of the process.

Nevertheless, the analysis of these parameters is too long for being useful. And some correlations have been found to reduce the time required for their determinations as it has been described in Article III and in Pognani et al., 2010.

In Articles II and V specific correlations between GB_n and total or final GB were calculated and some discussion of the results can be done. As it was discussed in Section 6.3.1, different correlations must be done depending on the type of waste, since organic matter will be of different nature, depending on the waste. In this regard, in Article V correlations for MSW and OFMSW were described, trying to determine total or final GB when only knowing GB_n at shorter times of analysis.

For OFMSW good correlations (correlation coefficient, R^2, always close to 0.9) were obtained even for the shorter GB determined. Consequently it could be stated that only knowing the GB_3 (during 3 days), the total biogas production potential could be predicted. This will be of special usefulness, since time required for anaerobic index determinations would be the same than for aerobic indices and reliable information on anaerobic biodegradation of the material could be obtained.

On contrary, for MSW poor correlations were obtained for almost all times assessed. It could be due to the high heterogeneity of this wastes that make extremely difficult to compare the biodegration kinetics. However, for longer times of analysis, correlations become significant, since although organic matter is of different nature and consequently initial kinetics could be different, the organic matter content in this type of wastes is similar and for longer times the biogas or methane production profiles will tend to become similar. In consequence, good correlations are not obtained until analysis times up to 21 days, what means that at least GB_{21} will be necessary to predict the final or total biogas potential production of a MSW sample.

In addition, in a recent publication of the co-researcher Michele Pognani (Pognani et al., 2010), it has been stated that correlations differ significantly if they are calculated distinguishing also between raw and already biologically treated or partially stabilized materials.

To sum up this part of the discussion it could be stated, that for a reliable prediction of the total GB, a specific correlation considering the type of waste and the degree of stabilization should be used.

However, apart from knowing the final biogas or methane productions, is even more decisive to know the maximum biogas production rate (R_{MAX}), the time during which this rate is maintained (t_{MAX}), and the time when the final potential biogas production is reached (t_F) as it has been demonstrated in Article VI. It is important the amount of biodegradable organic matter which is susceptible of being anaerobically biodegraded (GB and BMP) but from and industrial useful point of view, it seems impossible to have digesters working with such a long hydraulic retention time (HRT), sometimes up to 100 days. In this sense, the R_{MAX} indicates how easily or rapidly biodegradable under anaerobic conditions are the wastes, as occurred when discussing the information provided by the kinetic parameters kr and ks under aerobic conditions. t_{MAX} can also give key information to decide the optimal HRT of the reactor because usually the production rate tends to decrease significantly after t_{MAX} so the process may become economically unviable because of the low biogas production. Additionally, if t_F is also considered, a complete characterization of the waste can be accomplished.

These parameters can be used to distinguish whether a waste is recommendable for being treated anaerobically or not. The difference between the GB after t_{MAX} and the GB at t_F will quantify the fractions of easily and moderately biodegradable organic matter under anaerobic conditions. As low was the difference between GB at t_{MAX} and GB at t_F, more content in organic matter easily biodegradable in the sample.

6.3.3 Correlations between aerobic and anaerobic indices

A good correlation was obtained between SRI and BMP in Article II with a correlation coefficient of 0.94. Therefore it could be stated that both indices are suitable for plant monitoring and predict waste stabilization. However these results have to be carefully interpreted because this correlation will probably not be appropriate for all organic wastes. There are many typologies of organic wastes, some of them coming from industries, which would present different biodegradability under aerobic or anaerobic conditions.

In a recent Article published by the co-researcher Michele Pognani, the correlation between DRI_{24h} and GB_{21} for OFMSW at different stages of biodegradation, has been demonstrated as even more reliable, with a correlation coefficient of 0.99 (Pognani et al., 2010). This will confirm the results obtained in Article II and the fact that longer and continuous methodologies (dynamic) give more precise results than static methodologies.

6.4 Assessment in the use of biological indices

As mentioned in Sections 1.1 and 1.2, strong policies are coming up in European countries on waste management and treatment fields. Waste going to landfills must be reduced and recyclable materials must be recovered and used as a resource. Environmental impacts derived from waste management and treatment must be also reduced and green energy coming from renewable sources, such as organic wastes, must be increased. Waste treatment facilities must become more effective and advanced studies must be carried out to further improve their performance.

The motivations that encourage the works of this Thesis were based on the abovementioned goals that should be pursued by all societies in the world or at least those that are developed enough to practice an environmental thinking culture and policies. In these regard, biological indices described and experiences and results presented in this thesis are of special relevancy.

The indices proposed can be used in a wide range of applications. They can be used to monitor biological processes, but also mechanical processes involved in organic waste treatments. They can be used to determine the efficiency of waste treatment processes and establish improvements. They may be considered as one of the key parameters for waste treatment designs since they provide a reliable measure of the biodegradable organic matter content. They can also be applied for developing process optimizations and increase green energy and resources coming from wastes. Furthermore, biological indices can be used to determine stability of the wastes and may be proposed in legislations as a reliable measure of stability limits. Finally they can be used to classify wastes, to decide the most appropriate treatment for each typology of waste and evaluate the quality of the final products. In the next subsections the assessment of the use of the biological indices will be discussed.

6.4.1 Biological indices to monitor waste treatments and establish improvements.

As described in Section 1.7, classical chemical or physical parameters seem to be not precise enough to provide reliable measures of processes or facilities performance and biological indices have been demonstrated to be effective parameters for this purpose as it is described in Articles I, II and III.

In Article I SRI were used to monitor the biological activity of three windrow composting piles of dewatered wastewater sludge with various ratios of bulking agent. The results obtained during the composting process were used to prove that composting process with less bulking agent was not even started despite having a final product with a grade of stability of V (Rottegrade self-heating test), which correspond to the most stabilized products, and a similar value of SRI that the other piles. The pile with the highest ratio bulking agent/sludge achieved the maximum degree of stabilization and sanitation, only described by the different biological activity profile measured by SRI at process temperature. In this study biological indices were used to assess the effectiveness of organic matter degradation and establish the optimal mixture ratio for an effective composting process

In Article II, the evolution of organic matter stabilization in a complex MBT plant was monitored for OFMSW and MSW using SRI and BMP. Using these biological indices the efficiency of each step regarding biodegradable organic matter reduction was evaluated. Concretely, anaerobic digestion was found as the main step with SRI reductions of 70% and 53% for OFMSW and MSW respectively. Some contradictory results were observed when studying the MSW treatment line and further studies were proposed (Article III). In any case, it was demonstrated that biological indices could be used to trustworthy monitor a complex waste treatment facility involving different biological and mechanical processes.

In Article III, the pretreatment process in a complex MBT plant, involving reception, pit storage and mechanical treatment, was studied for OFMSW and MSW lines. It was demonstrated that during the pretreatment of OFMSW the biodegradable organic matter content gradually decreases a 30% in terms of DRI_{24h}. Consequently it has to be considered when designing anaerobic digesters. Otherwise biogas production would result lower than the design values. When studying the MSW line a different DRI_{24h} profile was obtained. After a reduction up to 40% during pit storage an increasing of 52% was measured during mechanical treatment. This could be explained if considering that the effect of organic matter concentration in the mechanical treatment is more important than the organic matter biodegradation during the pretreatment stage. Again, these results must be considered in the next biological process designs (composting or anaerobic digestion).

6.4.2 Biological indices to be used as key parameters for waste treatment designs

Previous to the design and related to organic matter treatment plants, it is essential to decide which would be the main objective of the waste treatment: to stabilize organic matter or to produce green energy. Depending on the objective, the design will be notably different.

As an example, if a treatment plant is intended to maximize the production of green energy by anaerobic digestion, what would mean to feed as much easily biodegradable organic matter as possible to the digester, the design would be focused firstly on avoiding the organic matter biodegradation during the mechanical pretreatment of the waste, as it has demonstrated in Article III, and secondly on minimizing the content of biodegradable organic matter in the refuse flows. This would imply a complete different design of the mechanical pretreatment, which must be carried out in a shorter period of time as well as must occur for waste storage in the pit. Pretreatment operations should be designed to obtain the maximum efficiency and effectiveness but with less aeration and mixing. In this sense shorter transportation belts between operations and shorter residence times or lower turning speeds in trommels could be some adaptations to be considered when designing.

Since biological indices developed in this work provide a reliable measure of the biodegradable organic matter content they must be considered as key parameter to decide which could be the main objective of the treatment and also which could be the more suitable treatment and subsequently to through the most appropriate design. Considering all information provided by biological indices, it would additionally be possible to know how easily biodegradable is the organic matter of the sample, if it is anaerobically degradable, which is the biogas or methane potential and therefore an economical analysis could be conducted to discuss on the economical viability of the process.

It is of crucial importance to design a treatment to really obtain the desired final products, to maximize the separation of materials susceptible of recycling and maximize the quality of the organic matter flow going to biological treatment.

Biological indices can be also used as decision parameters to implement or not some modifications to improve the biological processes which are already working successfully, as it is reflected in Article VI. In this work, a deep study on the implementation of codigestion in an industrial digester that is treating OFMSW was carried out. The assessment consisted in to decide if the addition of a cosubstrate, which would imply a 25% of increasing in the organic loading, would lead to a process improvement, in terms of biogas production and organic matter biodegradation. Anaerobic biological indices together with the Gompertz modelization of the results allowed for a complete analysis of the codigestion processes. The results obtained established that vegetal oil was the best cosubstrate to be used in an already working industrial digester treating OFMSW, since all parameters analyzed were improved. Additionally the results obtained for the other cosubstrates analyzed made possible to detect some improvements but also some weaknesses of the biological process that may be considered in economical terms or depending on the next treatment steps. Thus, biological indices could be used as key parameters for codigestion processes designs as well as to study the efficiency of these treatments.

6.4.3 Stability determinations

At present, biological indices are the best tool to determine the stability of a given waste or product. Stability measurements are in fact the measure of the biodegradable organic matter content. To be considered as stable, a sample must contain a really low amount of organic matter. Generally, stability measurements are carried out for compost samples, since they are the final product of the organic matter treatment. Stable compost would mean that when it is applied to soil, no undesirable odors and leachates are produced, and no toxicity for vegetables is present. Additionally, compost sanitization and hygienization must be assured during the composting treatment previous to the application to soil.

Biological indices have been demonstrated to be the most suitable measure to determine the biodegradable organic matter content of a given sample. However it is necessary to define the particular biological index and the stability limit. In literature and as it has shown in Article II, there is a wide range of methodologies and stability limits. Some of them are included in some national regulations or in European legislation drafts. However, and as it has mentioned before, they differ significantly in many key parameters and some weaknesses have been detected in some methodologies.

In this sense a large number of compost samples have been analyzed and completely characterized in the different works presented in this thesis and in other related works. DRI_{24h} was determined as the best DRI to consistently characterize a waste or sample. It can be considered that a sample is stable when DRI_{24h} is lower than 0.8-0.7 g O_2 kg TS^{-1} h^{-1}. For samples with higher values an extra biological treatment is still needed. For example considering composting processes, it would imply that longer maturation times are required

CHAPTER 7. CONCLUSIONS

CHAPTER 7. CONCLUSIONS

In this thesis the use of respirometric indices has been assessed as a reliable measure of the biodegradable organic matter content in a given sample. These measures provide essential information about the nature of the waste and allows for the correct treatment design and biological process performance.

The weaknesses of the already proposed methodologies for the determination of biological indices, both aerobic and anaerobic, have been studied and several improvements have been proposed. As result, a new methodology has been developed and it can be considered, at present, as the best tool to characterize the wastes or other samples in terms of: biological activity, biodegradable organic matter content, stability and biodegradation kinetic analysis.

The main conclusions will be listed next:

AEROBIC BIOLOGICAL INDICES

- Static respirometric indices (SRI) can be used as a first approach to characterize the wastes, since it is an easy, cheap and quick technique. However it cannot be considered as the unique and reliable measure to monitor a biological process o even to determine final product stability.

- Dynamic respirometric indices (DRI) and cumulative indices (AT) are the most appropriate measures to completely characterize the nature of a waste. They allow for a reliable measure of biological activity, comparable among the samples and avoiding all limitations that SRI present.

- Biological activity, measured as DRI and AT, provides a detailed waste characterization, in terms of biodegradable organic matter content and stability.

- DRI and AT measures are the most useful tool to design new mechanical and biological processes according to the nature of the waste that is going to be treated. Additionally, they can be used to implement improvements in the facilities or processes that are already operating.

- DRI and AT determinations can be used as key parameter to monitor the biological processes but also mechanical treatments.

- DRI_{24h} is the most suitable measure to determine the biodegradability of a given sample since the time required for its determination is short and it allows for a reliable discernability. Nevertheless, AT_4 shall be selected to really quantify the biodegradable organic matter content of this sample.

- All indices obtained from dynamic respiration methodology correlate well but present differences among organic substrates in a diverse manner. That leads to determine specific correlations for each single material typology avoiding the use of general relationships.
- The simple mathematical model developed, based on organic carbon depletion monitoring, allows for a complete organic matter characterization and biodegradation kinetic analysis, providing the different fractions in which organic matter can be classified (rapidly and slowly biodegradable and inert matter) and the kinetic parameter for each fraction.

ANAEROBIC BIOLOGICAL INDICES

- The anaerobic biological indices are the most appropriate and reliable measure to determine the biogas and/or methane potential of a given waste.

- The biogas potential (GB) is the most suitable tool to establish how biodegradable under anaerobic conditions the organic matter of a given sample is. This is of special interest, since aerobic biological indices cannot completely predict anaerobic biodegradability (although some correlations have been proposed) because not all organic matter biodegradable under aerobic conditions is anaerobically biodegradable.

- Time required for total GB determinations is sometimes longer than 100 days and it will make unfeasible the use of GB measures to characterize wastes that are going to be treated in anaerobic digesters or to monitor anaerobic biological processes. However, satisfactory correlations have been obtained for OFMSW samples to determine the total GB just by knowing the GB_3. On contrary, for more heterogeneous wastes such as MSW, longer analyses are necessary (GB_{21}) to obtain acceptable correlations to predict the total GB.

- Information provided by GB measures is of special interest to correct design and operation of anaerobic digestion plants in terms of retention time and biogas and methane production.

- Anaerobic biological indices have been demonstrated as the most appropriate tools to assess the implementation of improvements and optimizations in anaerobic biological processes, such us codigestion of various organic wastes.

- In the same way as aerobic biological indices, the GB should be used to measure the biodegradable organic carbon (under anaerobic conditions) and be used instead TOC for C/N determinations.

- The methane and biogas productions can be fitted to the Gompertz model, allowing for a biodegradation kinetic analysis under anaerobic conditions.

- Kinetic parameters, together with total GB are valuable information that should be definitely used to design anaerobic biological treatments and optimize the facilities that are already operating.

In general, both aerobic and anaerobic biological indices provide a more reliable and valuable information than physical and chemical parameters. In addition, they can be reasonably correlated for each waste typology and nature.

The mathematical modelization allows for the correct measure of biodegradable organic carbon. This parameter should be used instead of total organic carbon (TOC) measures for C/N determinations.

Information provided by biological indices must be used in the future instead that one provided by physical or chemical analysis, since as it has been proved, biological indices allow for an advanced characterization of the wastes.

Well established, defined and proved methodologies have been described in the core of this thesis. In fact, the Agencia Catalana de Residus (ARC), entrust our group to present an standardized protocol to carry out the determination of DRI_{24h} and it is currently used by the ARC for the assessment of waste treatment facilities and as stability requirements. The original protocol is presented in Chapter 9.

The results presented in this Thesis, confirm the appropriateness of the biological indices, both aerobic and anaerobic, to be used as reliable measures stability and biodegradable organic content and they must be the key parameters for waste treatment designs and legislative regulations and limits.

Final results based on modelization of both aerobic and anaerobic biological activity determinations (C_R, C_S, C_I, k_R y k_S), establish a new frame of knowledge about organic waste characterization that will be fundamental for suitable, efficient and optimal desing of treatment systems for organic waste management.

CURRENT AND FURTHER RESEACRH WORK

Further research work derived from this Thesis and which is currently undertaken by some co-researchers is summarized next:

- Belen Puyuelo is currently studying the aerobic and anaerobic biodegradable carbon, the correlations between these measures and assessing their use as the most suitable measure for BOC/N ratios. Additionally she is developing a control and monitoring system for composting processes based on OUR analysis. We are also working on developing correlations between waste stability, measured as DRI_{24h}, and the properties derived from waste image analysis.
- Joan Colon is studying the different composting technologies through LCA (Life Cycle Assessment) tools, considering biological indices as measure of stability and biodegradability.
- Michele Pognani is analyzing the efficiency of different facilities where organic wastes are treated using different technologies. He is also studying the quality of the different compost obtained from different treatment systems, basing on information provided by aerobic biological indices.

CHAPTER 8. BIBLIOGRAPHY

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CHAPTER 9. ANNEX

Chapter 9. Annex

This part includes the unpublished work which has been submitted for publication and it is currently under revision. In addition, this part also includes the original protocol written for the ARC to determine DRI_{24h}.

Article V: Biogas and methane potential from samples of municipal solid wastes of different origin and treatment process

Article VI: Anaerobic co-digestion of the organic fraction of municipal solid waste with several organic co-substrates

Article VII: Development of a simple model for the determination of the biodegredable organic fractions in several organic wastes

Protocol to determine DRI. Protocol per a la determinació de l'estabilitat biològica mitjançant l'Índex Respiromètric Dinàmic (IRD) en mostres de residus urbans organics.

Article V

Biogas and methane potential from samples of municipal solid wastes of different origin and treatment process

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Biogas and methane potential from samples of municipal solid wastes of different origin and treatment process

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Abstract

Biogas (GB) and methane (BMP) potential were analyzed for samples of mixed municipal solid waste (MSW) and source-selected organic fraction of municipal solid waste (OFMSW) obtained at different stages of a mechanical-biological treatment plant which includes anaerobic digestion and composting. Biogas and methane potential were higher for OFMSW (270 – 575 Nl biogas/kg DM) than for MSW (130 – 260 Nl biogas/kg DM). The efficiency of the treatments applied in the plant was reflected in a progressive reduction of GB and BMP in the material. GB and BMP values obtained at different times were correlated. Biogas potential calculated for 3, 4, 5, 6, 7, 14, 21, 50 and 100 days correlated well for OFMSW samples. For MSW samples only GB values obtained for longer times than 14 days correlated well with final biogas production (100 days). The biogas potential analysed at 21 days accounted for the 77% of total biogas potential in OFMSW samples and for the 71% in MSW samples. These results are useful for the correct design and operation of anaerobic digestion plants in terms of retention time and biogas and methane production.

Keywords: Anaerobic digestion, Composting, Biogas potential, Greenhouse gas, Methane potential, Municipal solid waste.

1. Introduction

Generation of municipal solid wastes (MSW) is a worldwide problem for modern societies. Although waste management and treatment has received some attention in the last years, the solution of problems derived from collection, treatment and final disposal of wastes are still in a preliminary stage. Special attention has received the problem of biogas and methane generation from organic municipal solid wastes when they are landfilled without treatment, as methane is a powerful greenhouse gas [1-2]. The efforts in Europe to avoid methane emission from landfills have been regulated in the EC landfill directive (1999/31/EC), which progressively limits the admission of biodegradable organic matter from MSW that can be landfilled in the next years.

According to new regulations, technologies based on biological treatments to reduce the biodegradable organic matter content of MSW have gained popularity. Among them, anaerobic digestion, composting or the combination of both in form of mechanical biological treatment plants (MBT) are the most extended. The final products of these plants can be used as organic amendments (typically from source-selection collection systems) or simply disposed in landfills or incinerated as refuse derived fuels if agronomical quality is low (from mixed waste collection systems). Besides, as biogas and methane potential can be considered reliable measures of solid waste biological stability, limits for final disposal of wastes based on biogas production have been established or proposed in some European countries such as Germany [3], Italy [4], England and Wales [5] and it was previously considered in some European legislation drafts [6].

Different studies related to the production of biogas and methane from several organic wastes have been published. In the field of MSW, the main objective of the published works is to determine the potential of biogas or methane that can be obtained under optimal conditions for anaerobic digestion. For instance, values of 170 and 320 Nl of methane and biogas per kg of dry matter have been obtained using fresh mixed MSW, being this potential very low after few years of landfilling [7]. As source-separated collection systems for organic MSW have been implemented in different European states, the determination of biogas and methane potential of these wastes is of special interest. Higher values of biogas and methane production are often obtained when processing source-selected organic MSW in comparison to mixed MSW. Thus, values of methane production as high as 450-550 Nl of methane per kg of volatile solid have been reported for this fraction (the content of volatile solids for source-selected organic fraction of MSW is approximately 80-90% of dry matter) [8-9]. In other studies published, the aim of the work is to determine the optimal conditions of the biogas production tests [10-13]. These tests can now be considered well established since they have been adapted in some European regulations [3-5].

However, there is scarce information about the production of biogas from samples of municipal solid wastes collected with source-selection systems or, in general, samples that are being treated by modern mechanical-biological treatment plants. The objectives of this research are to explore in detail the biogas and methane potential of samples of municipal solid wastes obtained from different collection systems and processed by means of several biological treatment technologies. This is, to our knowledge, the first work where the complete range of biogas and methane potential are studied and the potential data from different times are correlated. The values obtained can be crucial for the selection of treatment technologies that are currently in process of development, design or operation.

2. Materials and Methods

2.1. Waste samples

Samples were obtained from different sources to have all the possible range of biogas and methane potentials. Table 1 shows the codification and treatment that correspond to each sample. Fresh (not treated) samples, corresponding to collection systems based on source-selected organic fraction of municipal solid wastes (OFMSW) and mixed municipal solid wastes (MSW) were directly obtained from collection trucks. 3 samples of each fraction were collected from 6 different municipalities. Treated samples were obtained from a mechanical-biological waste treatment plant located in Barcelona (Spain) with a total capacity of 240,000 tons of waste per year. Briefly, the plant operation is divided into three successive units: i) mechanical pretreatment (to extract non-organic materials such as plastics, glass and metals for recycling), ii) anaerobic digestion and iii) composting. The plant processes both OFMSW and MSW in two independent lines. Treated samples were obtained from different operations of the plant and from both lines to cover all the range of biogas potential: mechanically pretreated samples (OF-MPT and MSW-MPT), anaerobically digested samples (OF-AD and MSW-AD) and composted samples (OF-COM and MSW-COM). Additionally, two years old samples of baled landfilled municipal wastes were also analysed (MSW-LF) to cover the presumably lowest value of biogas and methane potential.

Samples were collected during April-June 2006. Analytical methods and biogas and methane production tests were carried out on a representative sample (approximately 40 kg). The sample was obtained by mixing four subsamples of about 10 kg each, taken from different points of the bulk of material (approximately 2000 kg). Samples were immediately frozen and conserved at -20 °C after collection. Before analysis, samples were thawed at room temperature during 24 hours.

Table 1: Codification and general characteristics of the samples analysed.

Sample codification	Source	Treatment
OF1	OFMSW	None
OF2	OFMSW	None
OF3	OFMSW	None
MSW1	MSW	None
MSW2	MSW	None
MSW3	MSW	None
OF-MPT	OFMSW	Mechanical pretreatment
MSW-MPT1	MSW	Mechanical pretreatment
MSW-MPT2	MSW	Mechanical pretreatment
OF-AD1	OFMSW	Anaerobic digestion
OF-AD2	OFMSW	Anaerobic digestion
MSW-AD	MSW	Anaerobic digestion
OF-COM1	OFMSW	Composting (4 weeks)
OF-COM2	OFMSW	Composting (4 weeks)
MSW-COM1	MSW	Composting (4 weeks)
MSW-COM2	MSW	Composting (2 weeks)
MSW-COM3	MSW	Composting (3 weeks)
MSW-COM4	MSW	Composting (4 weeks)
MSW-LF1	MSW	Sanitary landfill (2 years)
MSW-LF2	MSW	Sanitary landfill (2 years)

2.2. Biological methane production

To analyze the biogas and methane production of the different samples, a new analytical method was set up. This new method is based on the procedure described by the German Institute for Standardization reported in the Ordinance on the Environmentally Compatible Storage of Waste from Human Settlements and on Biological Waste-Treatment Facilities [3]. The developed test provides the parameter GB_{21} expressed as Nl of biogas produced per kg of total solids (Nl/kg DM) during 21 days, as it is also described in the Federal Government of Germany procedure [3], but in addition biogas production was monitored at different times, and the test was finished when no significant biogas production was observed (never before 100 days of duration). The main modifications in relation to the German test were: temperature was 37°C, the sample weight was increased to have a more representative sample, and the ratio inoculum:substrate was increased in some fresh samples to avoid acidification and inhibition by volatile fatty acids accumulation (the typical ratio inoculum:substrate ratio was 0.4:1 in dry matter basis, although in some cases it was increased up to 4:1).

Specifically, the mixtures were incubated in a water bath at 37°C in sealed aluminum bottles with a working volume of 1 L. The approximate weight of sample used was 0.250 kg. Before each experiment, the bottles were purged with nitrogen gas to ensure anaerobic conditions. The bottles have a ball valve connected to a pressure digital manometer (SMC model ZSE30, Japan), which allowed the determination of the biogas pressure. The bulk density of the mixture was previously determined (in triplicate) to calculate the headspace volume of the bottles. During the test, the bottles were shaken once a day. The results on biogas production were calculated from the pressure in the bottle and the headspace volume. Excessive pressure (more than 2 bar) in the bottle was released by purging periodically the biogas produced (typically 25-30 times during the experiment). Methane content of biogas was also routinely measured as explained below. In relation to the inoculum used, a very active inoculum from a Valorga dry anaerobic digester treating OFMSW and MSW (4500 m^3 of capacity, working temperature of 37°C and hydraulic retention time of 21 days) is directly mixed with the samples to be analysed and introduced in the bottles immediately after its collection. No lag phase was detected in the samples analyzed since the inoculum was already acclimatized to this kind of wastes.

All the tests of biogas production were carried out in triplicate. The results are expressed as an average with standard deviation. The typical deviation found in triplicate samples was in the range of 10-20%. If one of the bottles presented a deviation higher than 20%, it was discarded for the biogas potential calculation, as described in [3]. A biogas production test containing only inoculum is also analyzed in triplicate to be used as a blank. The blank is also useful to have a quantitative measure of inoculum activity. Biogas and methane production from inoculum samples is subtracted from the biogas and methane production of the waste samples. To illustrate the analysis, Figure 1 shows the cumulative biogas production obtained for three replicates corresponding to one MSW sample and one OFMSW sample.

Biogas composition was analyzed to obtain the biochemical methane production (BMP) by gas chromatography (Perkin-Elmer AutoSystem XL Gas Chromatograph) with a thermal conductivity detector and using a column Hayesep 3m 1/8" 100/120. The details of biogas analysis can be found elsewhere [14]. Typical values of methane percentage in biogas were around 55-65%.

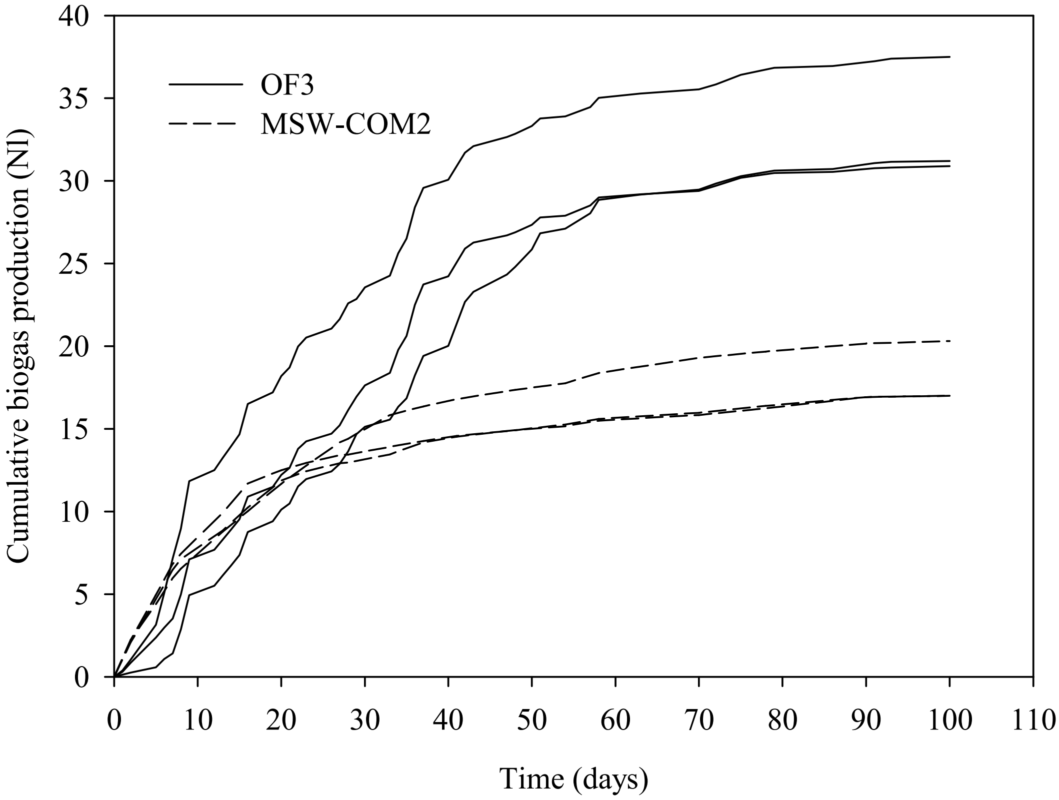

Figure 1: Examples of biogas cumulative production (triplicate) for one OFMSW sample (OF3) and one MSW sample (MSW-COM2).

2.3. Analytical Methods

Bulk density, water content, dry matter and organic matter (equivalent to volatile solids) were determined according to the standard procedures [15].

3. Results and Discussion

3.1. Biogas and methane potential for different municipal solid waste samples

Table 2 shows the values obtained for biogas (GB) and biological methane potential (BMP) at 21 and 100 days. Also the dry matter and volatile matter content of the samples is reported in Table 2. Values for GB_{21} and BMP_{21} were lower than for GB_{100} and BMP_{100} respectively, showing that the total biogas or methane potential can not be achieved in 21 days and longer periods are required for a complete estimation.

GB_{100} for OFMSW fresh samples ranged between 270 and 575 Nl biogas/kg DM and BMP_{100} values ranged from 150 to 385 Nl CH_4/kg DM. These values are similar to values previously reported by other authors for total biogas and methane potential [7-9]. Davidsson et al. [16] measured methane potential for source-sorted organic fraction of municipal solid waste and the experimental values obtained were very similar to theoretical methane potential calculated based on waste component composition. Thus, if biogas production is monitored for enough time the value obtained can be considered the total biogas potential of the sample.

GB_{100} and BMP_{100} values obtained for MSW were lower than for OFMSW due to the lower volatile and biodegradable matter content in the samples and also the highest presence of volatile non-biodegradable materials such as plastics (Figure 1).

As observed in Table 2, in general GB and BMP values decreased gradually at each stage in the waste treatment plant reflecting the efficiency of the different processes considered (mechanical pre-treatment, anaerobic digestion and composting) to stabilize the biodegradable organic matter present in the fresh materials.

Table 2: Biogas (GB) and methane potential (BMP) at 21 and 100 days, organic and dry matter content for the samples analysed.

Sample codification	GB_{21} (Nl biogas/kg DM)	GB_{100} (Nl biogas/kg DM)	BMP_{21} (Nl CH_4/kg DM)	BMP_{100} (Nl CH_4/kg DM)	Dry Matter Fraction	Volatile Solids Fraction
OF1	92 ± 33	270 ± 48	50 ± 18	148 ± 34	0.33 ± 0.04	0.87 ± 0.03
OF2	410 ± 60	575 ± 75	281 ± 38	385 ± 54	0.29 ± 0.06	0.78 ± 0.03
OF3	340 ± 40	372 ± 37	223 ± 8	245 ± 27	0.20 ± 0.04	0.88 ± 0.03
OF-MPT	224 ± 92	305 ± 26	125 ± 60	170 ± 19	0.40 ± 0.06	0.63 ± 0.03
OF-AD1	22 ± 7	51 ± 11	15 ± 4	32 ± 11	0.37 ± 0.02	0.50 ± 0.02
OF-AD2	98 ± 3	152 ± 5	59 ± 2	92 ± 3	0.26 ± 0.02	0.47 ± 0.02
OF-COM1	33 ± 12	68 ± 12	20 ± 8	41 ± 9	0.48 ± 0.01	0.47 ± 0.01
OF-COM2	48 ± 3	80 ± 5	28 ± 2	48 ± 3	0.49 ± 0.01	0.47 ± 0.02
MSW1	43 ± 10	129 ± 50	23 ± 5	79 ± 48	0.39 ± 0.02	0.86 ± 0.04
MSW2	156 ± 29	259 ± 128	91 ± 10	142 ± 82	0.39 ± 0.02	0.69 ± 0.05
MSW3	89 ± 7	128 ± 18	40 ± 3	66 ± 12	0.47 ± 0.02	0.57 ± 0.01
MSW-MPT1	221 ± 53	292 ± 57	130 ± 8	174 ± 34	0.30 ± 0.07	0.75 ± 0.02
MSW-MPT2	133 ± 20	207 ± 44	82 ± 12	127 ± 28	0.57 ± 0.03	0.50 ± 0.02
MSW-AD	120 ± 59	209 ± 90	73 ± 31	126 ± 53	0.18 ± 0.02	0.54 ± 0.03
MSW-COM1	47 ± 18	75 ± 20	27 ± 8	45 ± 14	0.49 ± 0.01	0.33 ± 0.02
MSW-COM2	64 ± 24	168 ± 21	41 ± 16	105 ± 12	0.56 ± 0.01	0.52 ± 0.02
MSW-COM3	97 ± 9	129 ± 15	64 ± 6	86 ± 10	0.71 ± 0.02	0.46 ± 0.03
MSW-COM4	81 ± 9	107 ± 14	54 ± 6	72 ± 9	0.83 ± 0.03	0.48 ± 0.02
MSW-LF1	73 ± 30	145 ± 40	48 ± 23	92 ± 25	0.56 ± 0.03	0.54 ± 0.06
MSW-LF2	120 ± 22	206 ± 36	74 ± 14	129 ± 23	0.51 ± 0.03	0.51 ± 0.02

The same trend can be observed for the total volatile matter content, although this parameter is not adequate for monitoring composting processes because of the addition of an organic bulking agent, which increases the organic matter content at the beginning of this process (Table 2).

Finally, biogas potential for compost from OFMSW was in the range of 68 – 80 Nl biogas/kg DM whereas stabilized material from MSW presented similar values, 75 – 107 Nl biogas/kg DM. In general, the reduction of biogas and methane potential after an intensive biological treatment (aerobic and anaerobic) is within the range of 80-90% for OFMSW and 40-50% for MSW. These reduction values can be considered as the most suitable parameters to describe the efficiency of a mechanical-biological treatment plant. At present, no data has been found in literature about the biological efficiency of such plants.

3.2. Biogas and methane potentials at different periods of time

It has been explained in the previous section how determining the total biogas or methane potential of a sample requires long periods of time up to 100 days. The disadvantages of such a long analysis are obvious for plant monitoring and a shorter determination would be helpful for plant managers. In this sense, values of biogas potential of all the samples obtained at different times of analysis were examined and compared in order to investigate if a shorter period of time could be representative of the total biogas and methane potential.

Table 3 shows the correlations found for biogas potential obtained at 3, 4, 5, 6, 7, 14, 21, 50 and 100 days of analysis, for OFMSW samples at different stages of biodegradation. As can be observed, all GB values correlated well (P values below 0.002 in all cases). According to Table 3, GB_{14} accounts for the 64% of total biogas potential, GB_{21} represents the 77% and GB_{50} is the 97%. It is also worthwhile to notice that using an active and acclimatized inoculum the total biogas and methane production from OFMSW can be estimated with only 3 days of test. This fact increases the utility of biogas and methane test for predicting the stability of OFMSW samples.

Table 4 shows the same correlations than Table 3 for mixed MSW samples. It can be observed how GB values obtained at few days of analysis do not correlate well with GB values obtained at longer periods. An explanation to this fact can be the inherent heterogeneity and variability on the composition of these samples. Biogas production rate can be considered as proportional to the concentration of substrate (in this case, biodegradable organic matter). For MSW samples, the presence of non-biodegradable matter like glass, plastics and other inert materials influences the initial rate of biogas production and in consequence, the relation between biogas production at short time and GB_{100} is erratic. However GB values tend to be equal at longer experimental time. In this sense, correlations for GB_{14}, GB_{21} and GB_{50} with GB_{100} are acceptable (Table 4). For MSW samples, GB_{14}, GB_{21} and GB_{50} account for the 38%, 71% and 94% of total biogas potential,

Table 3. Correlations for biogas production obtained at different assay times for samples of organic fraction of municipal solid waste.

Y↓ X→	GB_3	GB_4	GB_5	GB_6	GB_7	GB_{14}	GB_{21}	GB_{50}	GB_{100}
	GB_3	0.79x+2.06 P<0.0001 R^2=0.990	0.65x+3.67 P<0.0001 R^2=0.974	0.54x+2.96 P<0.0001 R^2=0.973	0.52x+0.77 P<0.0001 R^2=0.979	0.45x-7.53 P<0.0001 R^2=0.948	0.36x-8.07 P=0.0003 R^2=0.905	0.31x-17.7 P<0.0001 R^2=0.970	0.30x-21.6 P<0.0001 R^2=0.953
		GB_4	0.82x+1.68 P<0.0001 R^2=0.996	0.69x+0.79 P<0.0001 R^2=0.994	0.66x-1.74 P<0.0001 R^2=0.992	0.57x-11.6 P<0.0001 R^2=0.943	0.45x-10.9 P=0.0008 R^2=0.867	0.39x-23.2 P=0.0005 R^2=0.938	0.37x-27.9 P=0.0002 R^2=0.918
			GB_5	0.84x-1.06 P<0.0001 R^2=0.998	0.80x-3.92 P<0.0001 R^2=0.990	0.68x-15.3 P=0.0001 R^2=0.928	0.53x-13.5 P=0.0016 R^2=0.833	0.46x-28.6 P=0.0012 R^2=0.845	0.44x-33.9 P=0.0005 R^2=0.887
				GB_6	0.95x-3.57 P<0.0001 R^2=0.996	0.82x-17.9 P<0.0001 R^2=0.948	0.64x-15.7 P=0.0011 R^2=0.851	0.55x-32.7 P=0.0002 R^2=0.911	0.53x-39.1 P=0.0005 R^2=0.888
					GB_7	0.87x-16.1 P<0.0001 R^2=0.967	0.68x-15.1 P=0.0004 R^2=0.891	0.56x-31.5 P=0.0001 R^2=0.928	0.56x-38.2 P=0.0003 R^2=0.905
						GB_{14}	0.80x-1.06 P<0.0001 R^2=0.952	0.67x-16.5 P<0.0001 R^2=0.939	0.64x-24.4 P=0.0002 R^2=0.919
							GB_{21}	0.81x-13.8 P=0.0001 R^2=0.928	0.77x-23.1 P=0.0003 R^2=0.904
								GB_{50}	0.97x-13.9 P<0.0001 R^2=0.997
									GB_{100}

Table 4. Correlations for biogas production obtained at different assay times for samples of municipal solid waste.

Y↓ X→	GB_3	GB_4	GB_5	GB_6	GB_7	GB_{14}	GB_{21}	GB_{50}	GB_{100}
	GB_3	0.96x-2.70 P<0.0001 R^2=0.935	0.81x-2.73 P<0.0001 R^2=0.776	0.62x-0.49 P=0.0023 R^2=0.585	0.42x+1.33 P=0.0241 R^2=0.381	0.07x+10.8 P=0.4102 R^2=0.062	0.06x+9.83 P=0.2150 R^2=0.136	0.03x+0.03 P=0.4733 R^2=0.047	0.05x+8.11 P=0.2235 R^2=0.131
		GB_4	0.91x-1.35 P<0.0001 R^2=0.945	0.74x-0.13 P<0.0001 R^2=0.815	0.50x+2.12 P=0.0049 R^2=0.528	0.08x+13.9 P=0.3770 R^2=0.071	0.06x+13.4 P=0.2242 R^2=0.131	0.02x+15.9 P=0.5506 R^2=0.033	0.04x+13.4 P=0.3595 R^2=0.076
			GB_5	0.86x+0.21 P<0.0001 R^2=0.954	0.58x+2.89 P=0.0015 R^2=0.615	0.08x+17.1 P=0.3757 R^2=0.071	0.06x+17.0 P=0.2635 R^2=0.112	0.02x+20.2 P=0.6509 R^2=0.019	0.03x+18.8 P=0.5510 R^2=0.033
				GB_6	0.68x+3.03 P=0.0009 R^2=0.649	0.10x+19.6 P=0.3607 R^2=0.076	0.06x+20.3 P=0.3057 R^2=0.095	0.02x+23.9 P=0.7065 R^2=0.013	0.02x+23.7 P=0.7120 R^2=0.012
					GB_7	0.31x+12.2 P=0.0037 R^2=0.549	0.17x+16.8 P=0.0045 R^2=0.535	0.11x+18.7 P=0.0477 R^2=0.310	0.09x+18.5 P=0.0754 R^2=0.259
						GB_{14}	0.53x+16.4 P<0.0001 R^2=0.904	0.42x+8.46 P<0.0001 R^2=0.869	0.38x+6.21 P=0.0001 R^2=0.752
							GB_{21}	0.76x-10.9 P<0.0001 R^2=0.898	0.71x-17.6 P<0.0001 R^2=0.812
								GB_{50}	0.94x-11.3 P<0.0001 R^2=0.934
									GB_{100}

respectively. It is particularly remarkable that the value at 14 days is only the 38% of the total biogas produced, whereas for OFMSW the biogas produced at 14 days accounted for the 64% of GB_{100}.

In general, it should be highlighted that the fraction of total biogas potential produced within the same period of time is different for the two different types of wastes considered (OFMSW and MSW), being the disagreement higher for short times of analysis. This fact is interesting since it poses the problem that other organic materials could behave differently, although no data have been found in literature. Consequently, the amount of biogas produced with time should be investigated for each waste before deciding the most suitable analysis duration. Besides, from data of biogas production at different times, the retention time could be selected in full-scale anaerobic digestion process.

However, GB_{21} represents a similar fraction of GB_{100} for both materials (71-77%). In this sense, 21 days could be recommended as the duration of GB test. This period of time is already suggested in some standards [3]. Then, for municipal solid wastes, it would not be necessary to use 100 days as suggested by other references [5].

The findings reported in this paper are also useful for the determination of the optimum retention time in full-scale anaerobic digestion operation. The knowledge of the fraction of the total biogas potential produced for different periods of time permits to carry out the economical analysis required to determine the optimal retention time.

4. Conclusions

Several conclusions can be obtained from this work:

1. Biogas potential is 130 – 260 Nl biogas/kg DM for mixed MSW and 270 – 575 Nl biogas/kg DM for source-separated OFMSW.

2. Biogas and methane potential calculated for 3, 4, 5, 6, 7, 14, 21, 50 and 100 days correlated well for OFMSW samples. For MSW samples only biogas and methane production values obtained for longer times than 14 days correlated well with final production.

3. 21 days is recommended as the analysis time for biogas and methane determinations with OFMSW and MSW samples.

4. The results obtained are useful for the correct design and operation of anaerobic digestion plants in terms of retention time and biogas and methane production.

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Article VI

Anaerobic co-digestion of the organic fraction of municipal solid waste with several organic co-substrates

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ANAEROBIC CO-DIGESTION OF THE ORGANIC FRACTION OF MUNICIPAL SOLID WASTE WITH SEVERAL ORGANIC CO-SUBSTRATES

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Abstract

A strategy to improve the operation of working anaerobic digesters treating the organic fraction of municipal solid wastes (OFMSW) to increase biogas production is studied in this work. It consists on increasing the organic loading rate of the digesters by adding extra organic matter from some problematic organic wastes. Vegetable oil, animal fats, cellulose and protein were used as co-substrates and the co-digestion anaerobic process was analyzed in terms of the ultimate methane production, the methane production rate and the hydraulic residence time. The analysis of methane or biogas production led to different conclusions when expressing this parameter in a volatile solids basis or in a reactor volume basis. The need for a combined analysis is highlighted. In addition a new model to predict the biodegradability rate and evaluating the organic matter fraction susceptible of biodegradation was developed and proved as suitable for assessing anaerobic digestion processes. All four co-substrates used led to some operative improvements. Vegetable oil is the most suitable co-substrate to be anaerobically digested with OFMSW since all the parameters evaluated were extremely improved compared to the OFMSW digestion.

Keywords: anaerobic co-digestion; biogas; organic fraction of municipal solid waste; organic wastes; methane production; co-substrates.

1. Introduction

Biogas technologies (European Commission, 2009; 2006; Swedish Institute of Agricultural and Environmental Engineering, 2006; Jansen, 2004) are an attractive and well established alternative that allows the production of energy while processing different organic wastes or biomass and obtaining a solid product that can be used as an organic fertilizer or conditioner (Pain et al., 1988; Lema and Omil, 2001; McCarty, 2001; Lettinga, 2001; Murto et al., 2001; Neves et al., 2006; Neves et al., 2009; European Commission, 2001). In addition, the Landfill Directive 1999/31/EC (article 5) together with the Working document on Biological treatment of biowaste 2nd draft (European Commission, 2001) introduced years ago very restrictive targets for the reduction of biodegradable waste to landfill. In consequence, at present there is a large number of anaerobic digestion facilities treating different kinds of organic wastes such as municipal solid waste (MSW), source separated organic fraction of municipal solid waste (OFMSW, mainly food and yard wastes), manure, sewage sludge and different industrial organic wastes (IOW).

However, there are some poorly biodegradable IOW that cannot be digested alone due to their characteristics as, for instance, low solubility or incorrect carbon-to-nitrogen (C/N) ratio. Nevertheless, when mixed with other complementary wastes, the mixture becomes suitable for anaerobic co-digestion (Alatriste-Mondragón et al., 2006). There is abundant literature about co-digestion processes, such as co-digestion of OFMSW and agricultural residues (Converti et al., 1997; Kübler et al., 2000), organic wastes and sewage sludge (Neves et al., 2009; Fernández et al., 2005; Zhang et al., 2008) or more specific wastes (Buendía et al., 2009; Bouallagui et al., 2009).

A new strategy to be implemented in already operating plants could be the combined treatment of different kinds of IOW with OFMSW. Thus, on the one hand, a new waste would be valorized using working digesters and avoiding new investments. On the other hand, energy would be obtained. The most common problematic organic wastes produced from industry or municipalities are those that are rich in lipids, cellulose and proteins.

Lipids are characterized either as fats, oils or greases, coming mainly from food wastes and some industrial wastewaters, such as those from slaughterhouses, dairy industries or fat refineries (Li et al., 2002). Lipids are attractive for biogas production since they are reduced organic materials with a theoretical high methane potential. However, they also present several problems such as methanogenic bacteria inhibition and adsorption onto biomass that cause sludge flotation and washout (Neves et al., 2009).

Cellulose wastes (CW) come mainly from paper and cardboard industries (mostly composed by cellulose, hemicellulose and lignin) or from textile industries. CW are also part of the bulk MSW that is not source separated, which could be added to the organic waste flow again in order to be anaerobically treated. CW have a C/N ratio ranging from 173:1 to greater than 1000:1, while the suggested optimum C/N ratio for anaerobic digestion is in the range of 20:1 to 30:1 (Zhang et al., 2008). Therefore, the mixing of CW with OFMSW can provide suitable nutrients for the combined co-digestion (Zhang et al., 2008).

Those wastes with high protein content and consequent high nitrogen content come mainly from meat industries, slaughterhouses and farms (slurry and manure). Since these wastes have a high organic content, high biological oxygen demand and low C/N ratio, anaerobic co-digestion with OFMSW or sludge is recommended for their treatment (Buendía et al., 2009). In addition, large ammonia concentrations in animal wastes are found to inhibit anaerobic treatments (Nielsen et al., 2008). This problem is further accentuated for protein-rich wastes, for which the ammonia concentration rises significantly during their fermentation (Chen et al., 2008).

To the authors' knowledge, there is scarce information about high organic load co-digestion of lipids, cellulose and protein as co-substrates for OFMSW and its comparison and possible implementation in working digesters. In fact most of industrial co-digestion plants treat OFMSW together (in a relative small percentage) with sewage sludge (Rintala and Jarvinen, 1996; Mata-Alvarez, 2000). In addition, there is a really scarce industrial application of co-digestion (Mata-Alvarez, 2000), possibly due to the non-applicable studies published and only 7% of the overall anaerobic digestion of OFMSW capacity is at present co-digested. The aim of this work is to study the feasibility of the co-digestion of the OFMSW with different kinds of organic wastes such as vegetal oil (VO), animal fat (AF), cellulose and peptone (protein) and to assess the possibilities of implementing this co-digestion process in already working plants.

2. Materials and Methods

2.1. Waste sources and inoculum characteristics

Main properties of OFMSW, inoculum and co-substrates used are presented in Table 1. The OFMSW samples were obtained from a Mechanical-Biological Treatment (MBT) plant (Barcelona, Spain) that treats mixed MSW and OFMSW, in two separated lines, with a total capacity of 240,000 tons of waste per year. The OFMSW samples used were taken in the plant after mechanical pretreatment and prior to anaerobic digestion process. This material is essentially free of impurities, it is shredded to 20-30 mm and fed to the digester in the plant. A representative sample (approximately 40 kg) was obtained by mixing four subsamples of about 10 kg each, taken from different points of the bulk material. This sample was used for biogas and methane production tests and other analysis.

The four used co-substrates were: (i) commercial vegetable (coconut) oil (VO) ; (ii) animal fat (AF) (Trg Debo Fancy, KAO Corporation S.A., Spain); iii) cellulose (cellulose powder, 20 micron, Sigma-Aldrich); and protein (bacteriological peptone, Oxoid, 14% of total nitrogen). A 20% (dry basis) of the corresponding co-substrate was added to OFMSW to obtain the target mixtures, which were intended to achieve 20% of increase in the loading rate. Vegetable and animal fats were additionally characterized in order to know their main composition in terms of long chain fatty acids (LCFAs). VO is mainly composed by lauric acid (45.5%), myristic acid (18.5%), palmitic acid (10.4%) and oleic acid (8.7%). AF is mainly composed by oleic acid (38.0%), palmitic acid (30.0%) and stearic acid (17.0%).

The inoculum for anaerobic digestion was collected from the plant anaerobic digester treating OFMSW (4500 m^3 of capacity, working temperature of 37ºC and hydraulic retention time, HRT, of 21 days). The reactor was continuously fed with a mixture of OFMSW:recirculated sludge in a ratio 1:2 (dry basis). The anaerobic inoculum was kept at 37ºC during two weeks to remove any remaining easily biodegradable fraction.

2.2. Biological methane production

To analyze the biogas and methane production of the different samples, an analytical method was set up by adapting the procedure described by the German Institute for Standardization (Federal Government of Germany, 2001). This standard procedure provides the parameter GB_{21} expressed as normal liters of biogas (temperature: 273K and pressure 1.01325 bar) produced per kg of total solids (Nl kg

DM^{-1}) during 21 days. In the developed test, biogas production was monitored at different times and the test was finished when no significant biogas production was observed (after 135 days). Thus, biogas production GBn could be obtained for n days of analysis. Results were expressed both as normal liters of biogas produced per kg of dry matter and volatile solids (Nl kg VS^{-1}). Besides test length and results expression, temperature was changed to 37ºC. Additionally the ratio inoculum:substrate of the German standard test was not followed. Instead, the actual ratio of the industrial anaerobic digester, 1:2 OFMSW to inoculum (dry basis), was maintained. Since in all the experiments involving the use of co-substrates an extra 20% of dry matter was added by means of co-substrate dry matter addition, it was preferred not to change the original OFMSW to inoculum ratio. In fact, as stated before, one of our objectives was to analyze the behavior of the anaerobic digestion process without changing any of the operational parameters at industrial scale. Accordingly, the resulting ratio in the co-digestion experiments was a mixture 1:2:0.2 OFMSW:inoculum:co-substrate (dry basis).

The mixtures were incubated in a temperature controlled room at 37ºC in sealed aluminum bottles with a working volume of 1 liter. Before each experiment, the bottles were purged with nitrogen gas to ensure anaerobic conditions. The bottles had a ball valve which could be connected to a pressure digital manometer (SMC model ZSE30, Japan) allowing for the determination of the biogas pressure. The bulk density of the mixture was previously determined (in triplicate) to calculate the headspace volume of the bottles that was assumed constant during the experiment. During the test, the bottles were shaken once a day. Biogas production was calculated according to the ideal gas law from the pressure measured in the bottle and considering the headspace volume previously measured. To avoid excessive pressure in the bottle the biogas produced was purged periodically (typically 25-30 times during the experiment). This way pressure was not allowed to reach a value over 2 bar. This contributes to minimize the possible solubilization of carbon dioxide since methane is hardly soluble in aqueous media. Nevertheless, final biogas production at long times should not be affected by this effect.

All biogas production tests were carried out in triplicate (three different bottles for each sample). The results are expressed as an average with standard deviation. The typical deviation found in triplicate samples was in the range of 5-15%. If one of the bottles presented a deviation higher than 20%, it was discarded for the biogas potential calculation, as described in Federal Government of Germany (2001). A biogas production test containing only inoculum and other containing a mixture of inoculum and OFMSW (substrate:inoculum ratio 1:2 in dry basis) were also set up in triplicate to be used as a blank and control test respectively. Specifically the loading rates used were 57.2 g TS l^{-1} (37.4 g VS l^{-1}) for the blank containing only inoculum, 72.6 g TS l^{-1} (49.5 g VS l^{-1}) for the control, which is the operating loading rate of the industrial digester and close to 87 g TS l^{-1} (63.5 g VS l^{-1}) for all co-digestion experiments, what means an increase of 20% compared to control analysis. The blank is also useful to have a quantitative measure of inoculum activity. Biogas and methane production from inoculum samples was subtracted from the biogas and methane produced by the waste samples.

Biogas composition was analyzed to obtain the biochemical methane production (BMP) by gas chromatography (Perkin-Elmer AutoSystem XL Gas Chromatograph) with a thermal conductivity detector and using a column Hayesep 3m 1/8" 100/120. The details of biogas analysis can be found elsewhere (Fernández et al., 2005). Typical values of methane percentage in biogas were around 55-70%, although in specific experiments some values higher than 85% were reached.

The maximum methane production rate (R_{max}) and lag phase (λ) were determined by fitting the modified Gompertz model (Eq. 1) described by Zwietering et al. (1990) and Lay et al. (1998) to the experimental cumulative methane production curves.

$$M = P \cdot \exp\left\{ -\exp\left[\frac{R_{max} \cdot e}{P} (\lambda - t) + 1 \right] \right\} \quad (1)$$

Where M is the cumulative BMP (Nl CH_4 kg VS^{-1}); P is the maximum methane potential (Nl CH_4 kg VS^{-1}); t is the time (days); R_{max} (Nl CH_4 kg VS^{-1} $days^{-1}$) and λ (days).

Matlab v2007a software package (MathWorks Inc., Massachusetts, USA) was used for fitting the value of the model parameters in Equation 1 (P, R_{max} and λ).

2.3. Anaerobic biodegradation kinetics modeling

In order to completely characterize the biodegradable organic matter content of a given waste by means of quantitative measures of the easily and slowly biodegradable organic matter and biodegradation kinetic rate constants, the data of cumulative biogas produced could be fitted to the four models described by Tosun et al. (2008). It has to be noted that Tosun models were developed to fit data obtained under aerobic conditions and expressed as the percentage of carbon mineralized, calculated as the amount of cumulative C-CO_2 produced, by means of aerobic biodegradation, at a given time on initial total organic carbon (TOC), that is, a biodegradable organic carbon (BOC)/TOC ratio for a given time.

Although Tosun models are described to be used in aerobic biodegradation processes, they could also be used for describing and assessing the anaerobic biodegradation processes. However, Tosun models present some limitations, being the most important the consideration of the non-biodegradable organic matter or organic carbon as slowly biodegradable fraction which obviously leads to non completely reliable results.

Trying to sort out the limitations of the first-zero-order and first-first-order models described by Tosun, a new simple model was developed to obtain the three different fractions in which organic matter or carbon can be classified after fitting the data: rapidly biodegradable (Cr), slowly biodegradable (Cs) and inert fraction (Ci). In addition, instead of monitoring the carbon emitted in form of CO_2 when organic matter is aerobically degraded, the carbon contained in the biogas in form of CO_2 and CH_4 was considered.

If keeping the concept of the Tosun model, the mathematical expression is unable to predict the inert fraction. However, instead of considering the evolution of the carbon emitted, the carbon that still has not been degraded can be also followed, assuming that the initial TOC corresponds to the 100% of the carbon in the sample and subtracting the carbon emitted from this initial value. The remaining carbon in the sample can be expressed as percentage of the initial TOC.

The mathematical modeling of these data would correspond to the following expression:

$$C_W = C_R \times \exp(-k_R t) + C_R \times \exp(-k_R t) + C_I \qquad (2)$$

where, C_W is the remaining carbon in the sample (%) at time t (days), C_R and C_S are the percentages of rapidly and slowly mineralizable fractions respectively, C_I is the inert fraction, and k_R and k_S are rapid and slow rate constants (day^{-1}), respectively. This expression consists of two exponential decay terms (first order kinetics) and an independent and constant term.

2.3. Analytical Methods

Bulk density, water content, dry matter and organic matter (equivalent to volatile solids) were determined in triplicate according to the standard procedures (The US Composting Council, 2001). Fat, protein and carbohydrates content in the initial and final mixtures (after 135 days) were determined according to official methods in Spain (Spanish Ministry of Environment, 2009). No replications were available for these analyses.

2.4. Statistical methods

Anova test was performed to compare different treatments. If Anova test resulted in statistically significant differences, Tukey test was performed in pairwise comparisons. 95% of confidence level was selected for all statistical comparisons. Statistical tests were conducted with SPSS 15.0.1 (SPSS Inc., USA).

3. Results and discussion

3.1. Methane production yields

The general characterization of the inoculum, OFMSW and co-substrates is shown in Table 1. All the values reported are in agreement with usual characterizations of these materials (Neves et al., 2009; Alatriste-Mondragón et al., 2006; Fernández et al., 2005; Zhang et al., 2008).

Methane cumulative productions for all the mixtures were continuously monitored and compared with the control test (OFMSW:inoculum ratio 1:2) during the entire experiment. As mentioned above, the experiment finished when no significant methane production was detected. As a result the ultimate methane production (UMP), which means the maximum methane potential, was obtained for all the mixtures and expressed as (Nl CH_4 kg VS_{loaded}^{-1}). Total solids reduction was 4.5% in the control test and 18% in the VO experiment while it was practically negligible in the rest of experiments. The inhibition of the methanogenic stage by volatile acid accumulation was not detected in any case as demonstrated by methane concentration in biogas that was always higher than 55%. Furthermore ammonia inhibition was not detected when using protein as co-substrate.

Table 1. Initial OFMSW, inoculum and co-substrates characteristics.

Parameter	OFMSW	Inoculum	Vegetable oil	Animal fat	Cellulose	Protein
Dry matter (%)	29.0	7.0	>99	>98	>99	>99
Organic matter (% dry basis)	77.0	65.4	>99	>99	>99	>99
Fat content (% dry basis)	11.52	7.86	>99	>99	0.0	0.0
N-Kjeldahl (% dry basis)	1.83	2.89	< 0.02	< 0.02	0.0	14
C/N ratio	14.09	37.45	> 4000	> 4000	> 4000	-

The UMP results obtained are reported and compared in Table 2. As observed, UMP of the mixtures increased significantly when using fats as co-substrates. Specifically UMP increased 83.1% and 33.0% for VO and AF respectively compared to control UMP. The opposite trend was observed when using cellulose and protein as co-substrates since UMP decreased around 30% in these experiments. This could mean that using fats as co-substrates and increasing 20% the total solids ratio, higher VS degradations were obtained, since more carbon from the volatile fraction was converted to methane and carbon dioxide. Accordingly, it could be concluded that fats could be suitable co-substrates for anaerobic digestion of OFMSW that improve the VS degradation and increase the biogas production. In addition, considering these results, it could be also stated that cellulose and protein are not suitable for anaerobic co-digestion with OFMSW.

Table 2. Ultimate methane potential obtained in co-digestion experiments. For each parameter, values followed by different letters in brackets are statistically different.

Mixture	UMP (Nl CH_4 kgVS^{-1})	UMP' (Nl CH_4 l^{-1})
Control (OFMSW)	382 ± 23 (a)	5.2 ± 0.3 (a)
OFMSW:Vegetable Oil	699 ± 6 (b)	19.6 ± 0.2 (b)
OFMSW:Animal Fat	508 ± 16 (c)	14.4 ± 0.5 (c)
OFMSW:Cellulose	254 ± 10 (d)	7.0 ± 0.4 (d)
OFMSW:Protein	288 ± 7 (d)	8.0 ± 0.2 (e)

However, these results need to be carefully interpreted. The amount of total solids was increased 20% in the co-digestion experiments and consequently the amount of VS treated in the same working volume was also increased. Therefore the use of different units to express the UMP has to be considered. UMP was normalized by the initial VS concentration (kg VS l^{-1}) in the mixture to obtain the specific volumetric yield. UMP values expressed as Nl CH_4 l^{-1} (UMP') are also shown in Table 2. In this case, it can be observed that the addition of all four types of co-substrates significantly increased UMP' in 35.2%, 54.4%, 176.9% and 276.2% for cellulose, protein, AF and VO respectively. These results indicate that the reactor yield in terms of methane (or biogas) produced increases when adding any co-substrate. However, the organic matter (VS) degradation is not always improved and, in consequence, when using cellulose or protein wastes as co-substrates, a more intensive post-treatment for the end-product of anaerobic digestion (e.g. composting) might be necessary.

3.2. Kinetic modeling and biological methane potential validation

Evolutions of methane cumulative production for vegetable oil and animal fat and for cellulose and protein experiments are shown in Figure 1 and Figure 2 respectively. Control test evolution is also represented in both Figures to permit comparison.

The Gompertz model was used to describe the methane production in the different experiments. The fitting of Gompertz equation to the experimental cumulative methane production is also shown in Figures 1 and 2 for all the co-digestion experiments as well as for the control test. Table 3 shows the model parameters for the Gompertz model (Eq. 1) determined for the co-digestion experiments and the control test. The values obtained for P were similar to the UMP experimentally obtained (Table 2). This confirms that the experimental cumulative methane production evolution followed the theoretical trend in all the cases, as it is also confirmed by the wellness of the fitting of the Gompertz model to the experimental data ($p < 0.001$ in all cases).

Lag phase was almost negligible and statistically equivalent for the control test and the cellulose and protein experiments. However, when adding fats as co-substrates a lag phase of around 9 days was detected (Table 3). This could be explained by the fact that the inoculum used was not acclimatized to the higher organic load or the different biochemical nature of fats (Fernández et al., 2005). In continuous experiments or in real digesters, this lag phase would disappear after an inoculum acclimation period.

R_{max}, expressed as Nl CH_4 $kgVS_{loaded}^{-1}$ d^{-1}, was statistically higher for control test and protein experiment than for VO, AF and cellulose co-digestion experiments, which again highlights the importance of the inoculum acclimation and the effect of increasing the organic load.

Figure 1: Evolution of Cumulative Methane Production during 135 days for Control test, Vegetable Oil (VO) and Animal Fat (AF) co-digestion experiments.

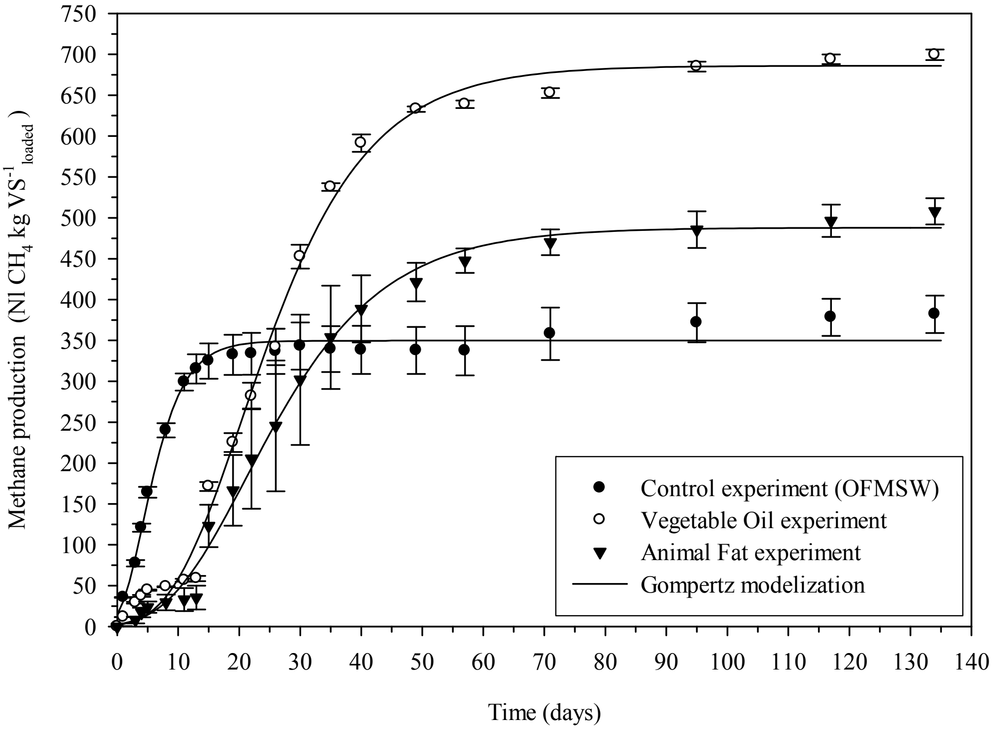
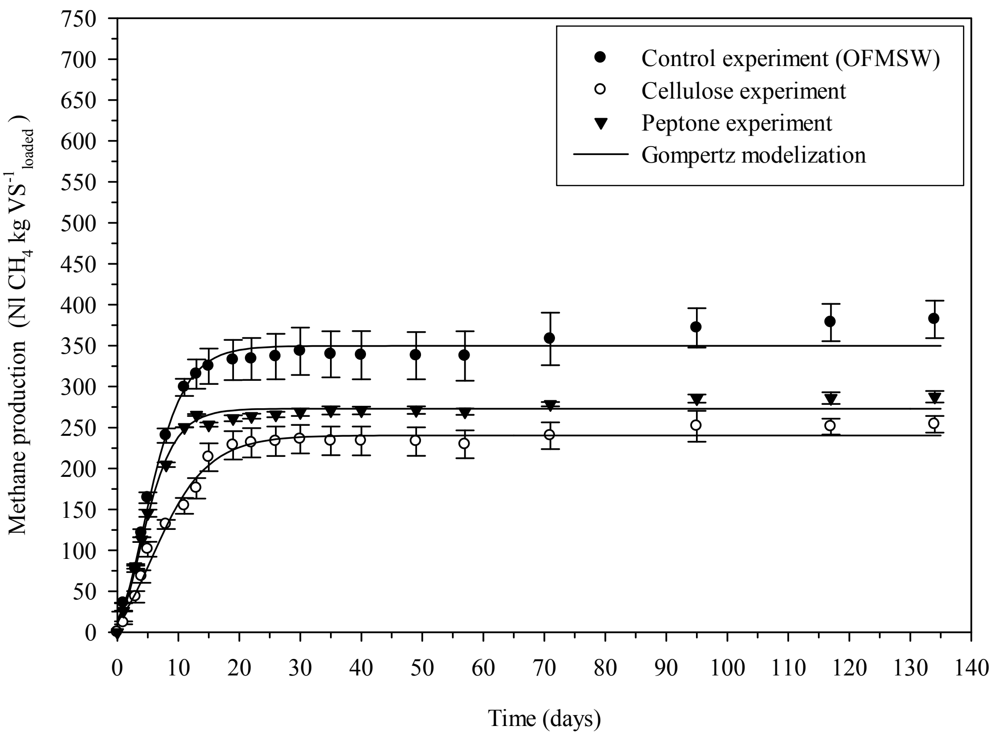


Figure 2: Evolution of Cumulative Methane Production during 135 days for Control test, Cellulose and Protein co-digestion experiments.



Considering the Gompertz data fitting, it can be noted that the cumulative methane production for the control test and for the cellulose and peptone experiments reached the maximum before 21 days. This is in accordance with the operational HRT of the real digester where the inoculum was obtained. However, for fats co-digestion experiments, and assuming that the lag phase would disappear in continuous operation, the maximum methane production would be reached after approximately 60 days of operation, which is similar to that found in other studies with complex wastes (Cuetos et al., 2008). This is related to the different biochemical nature and biodegradability of the co-substrates used, as well as to the higher energy content of fats compared to protein and cellulose (Ruggieri et al., 2008).

Taking into consideration the control test individually, where the ratio OFMSW:inoculum at industrial scale was maintained, it could be stated that the real digester was working at the optimum HRT because the maximum methane potential for OFMSW was reached in 21 days.

Considering the cumulative methane potential at 21 days of operation for all the experiments, interesting conclusions can be obtained. For the control test, the cellulose and peptone co-digestion experiments, the values corresponded to P (ultimate methane potential) from Gompertz fitting. However, for fat co-digestion experiments 21 days were insufficient to reach the ultimate or maximum methane production. The M values obtained at this point were close to 450 and 300 Nl CH_4 $kgVS_{loaded}^{-1}$ for VO and AF respectively. Comparing these co-digestion results for VO with the control test results (Table 3) an improvement over 25% is observed.

Table 3. Summary of the estimated parameters from Gompertz equation for digestion and co-digestion experiments. For each parameter, values followed by different letters in brackets are statistically different.

Mixture	P (Nl CH_4 $kgVS^{-1}$)	R_{max} (Nl CH_4 $kgVS^{-1}$ d^{-1})	λ (days)	P' (Nl CH_4 l^{-1})	R'_{max} (Nl CH_4 l^{-1} d^{-1})
Control (OFMSW)	350±27 (a)	35±1 (a)	0.6±0.1 (a)	4.7±0.4 (a)	0.47±0.01 (a)
OFMSW:Vegetable Oil	686±7 (b)	21.9±0.7 (b)	8.9±0.2 (b)	19.2±0.2 (b)	0.61±0.02 (b)
OFMSW:Animal Fat	490±26 (c)	14±1 (c)	9.1±0.1 (b)	12.9±0.8 (c)	0.38±0.04 (a)
OFMSW:Cellulose	240±16 (d)	17±2 (d)	0.37±0.05 (a)	6.6±0.6 (d)	0.47±0.05 (a)
OFMSW:Protein	269±3 (d)	32.0±0.7 (a)	0.50±0.07 (a)	7.53±0.06 (d)	0.90±0.02 (c)

Table 4. Co-substrates specific degradation analysis.

	Initial (0 days)			Final (after 135 days)			Elimination		
Mixture	Total Fats (%ww)	Total Sugars (%ww)	Total Protein (%ww)	Total Fats (%ww)	Total Sugars (%ww)	Total Protein (%ww)	Fats (%)	Sugars (%)	Protein (%)
Control (OFMSW)	0.71	0.69	4.37	0.44	0.14	4.93	40.86	59.71	4.41
OFMSW:Vegetable Oil	2.08	0.33	4.86	0.44	0.15	3.63	80.00	56.67	29.37
OFMSW:Animal Fat	2.12	0.33	4.86	0.55	0.41	4.16	75.64	0.00	19.62
OFMSW:Cellulose	0.70	1.71	4.86	0.54	0.14	3.42	27.72	92.31	33.94
OFMSW:Protein	0.70	0.33	6.24	0.55	0.18	6.24	24.65	47.27	3.23

ww: wet weight

Again these results need to be carefully interpreted because the yield per unit of reactor volume should be also considered. The results obtained after normalizing the P and R_{max} parameters with the VS concentration of the initial mixture and expressed as Nl CH_4 l^{-1} (P') and Nl CH_4 l^{-1} d^{-1} (R'_{max}) are also reported in Table 3. P' values are similar to the results obtained for UMP' (Tables 2 and 3), therefore the discussion already done for UMP' can be extended to P'. Nevertheless R'_{max} results must be separately discussed. In this case, the control test, AF and cellulose co-digestion experiments presented a non-statistically different R'_{max}. However, higher maximum methane production rates were obtained for VO (29.8% higher) and protein (91.5% higher) co-digestion experiments compared to control test. In terms of maximum methane or biogas production rate per unit of volume, protein seemed to be the most suitable co-substrate although vegetable oil could be also recommended. On the contrary, when adding AF as co-substrate the maximum methane rate was lower per unit of VS loaded as well as per unit of volume (Table 3). In the cellulose co-digestion experiments, R_{max} value decreased 51.2% while R'_{max} value coincided with the control test result (0.47 Nl CH_4 l^{-1} d^{-1}).

Finally, an individual analysis for each co-substrate used can be done. Considering the above results, it could be established that VO is the most suitable waste that can be used as co-substrate in anaerobic digesters, since it allowed increasing the organic load more than 20%. In addition UMP, UMP' and R'_{max} increased 83.1, 276.2 and 29.8% respectively as well as it occurred with the cumulative methane potential at 21 days that increased 28.6%. Consequently, higher VS degradation was also obtained after 21 and 135 days. Additionally, methane concentration in biogas was always up than 85% after 25 days while the higher value for the control test was 68%. All these results would indicate that the anaerobic digestion was completely improved in all aspects. Moreover a previous work demonstrated that VO is an excellent co-substrate for a simulated OFMSW when operating under continuous conditions (Fernández et al., 2005) showing no LCFA inhibition or cellular washout. In addition LCFA were completely degraded in the process.

When using AF a different behavior was observed compared to VO. UMP and UMP' values increased 33.0 and 176.9% respectively while R_{max} decreased 61.1% and R'_{max} was not statistically different. Additionally, although the UMP was notably increased, the low methane production rate led to a low cumulative methane production at 21 days (16.7% lower than control test). The feasibility of using AF as co-substrate needs to be evaluated in economical terms and considering possible destabilization due to the presence of fats (Rincón et al., 2008). Higher methane (and biogas) production per unit of digester volume would be obtained when increasing HRT over 21 days, but a lower organic matter stabilization (degradation) would take place. This means that other organic matter stabilization process, such as composting, must be intensively applied to the digested material. In economical terms it would mean that for an HRT of 21 days more energy can be obtained per volume unit of reactor while less energy is obtained per kg of VS loaded, and consequently more energy must be used in other post-treatment to stabilize the organic matter.

Results obtained for cellulose and protein experiments were similar; therefore the same analysis can apply for both. UMP and R_{max} values did not increase in any case, which means that the cumulative methane and biogas production at 21 days was lower than in control experiments, specifically 31.3 and 22.9% lower for cellulose and protein assays respectively. Accordingly, organic matter degradation was also lower, which means that, as in the case of using AF as co-substrate, other intensive post-treatment would be necessary to stabilize the remaining organic matter. However, when results are expressed in a volume basis (UMP' and R'_{max}), trends changed completely. UMP' increased 39.9 and 58.2% for cellulose and protein experiments respectively. R'_{max} became higher (91.5%) when using protein as co-substrate while it was maintained constant when using cellulose. Again, these results should be analyzed from an economical point of view. Higher reactor yields in terms of Nl CH_4 l^{-1} would be obtained while less organic matter would be degraded into biogas.

3.3. Co-substrates specific degradation

In order to know the amount of co-substrate that had been degraded in co-digestion experiments, fat, sugars and protein analysis were carried out. The initial and final (after 135 days of experiment) mixtures compositions are reported in Table 4 as well as the calculated reduction for each fraction.

The results showed that fats were more degraded when using fats as co-substrate since it became the main substrate for anaerobic bacteria in detriment of sugars or protein. The same behavior was detected for cellulose experiments but not for protein.

When using VO and AF as co-substrates fat degradation values were similar. However sugars and protein degradations were much higher for VO experiment. This would explain its higher UMP, UMP' (and its theoretical equivalent P and P'), R_{max} and R'_{max} values. When using AF as co-substrate, sugar degradation seemed to be inhibited and protein degradation decreased significantly (33%).

When using cellulose as co-substrate, high degradation of sugars was achieved together with the highest protein degradation. It can be concluded that cellulose is a good co-substrate since it allows the simultaneous anaerobic degradation of the other organic components.

3.4. Assessment of biodegradable organic matter fractions through anaerobic biodegradation kinetics modeling

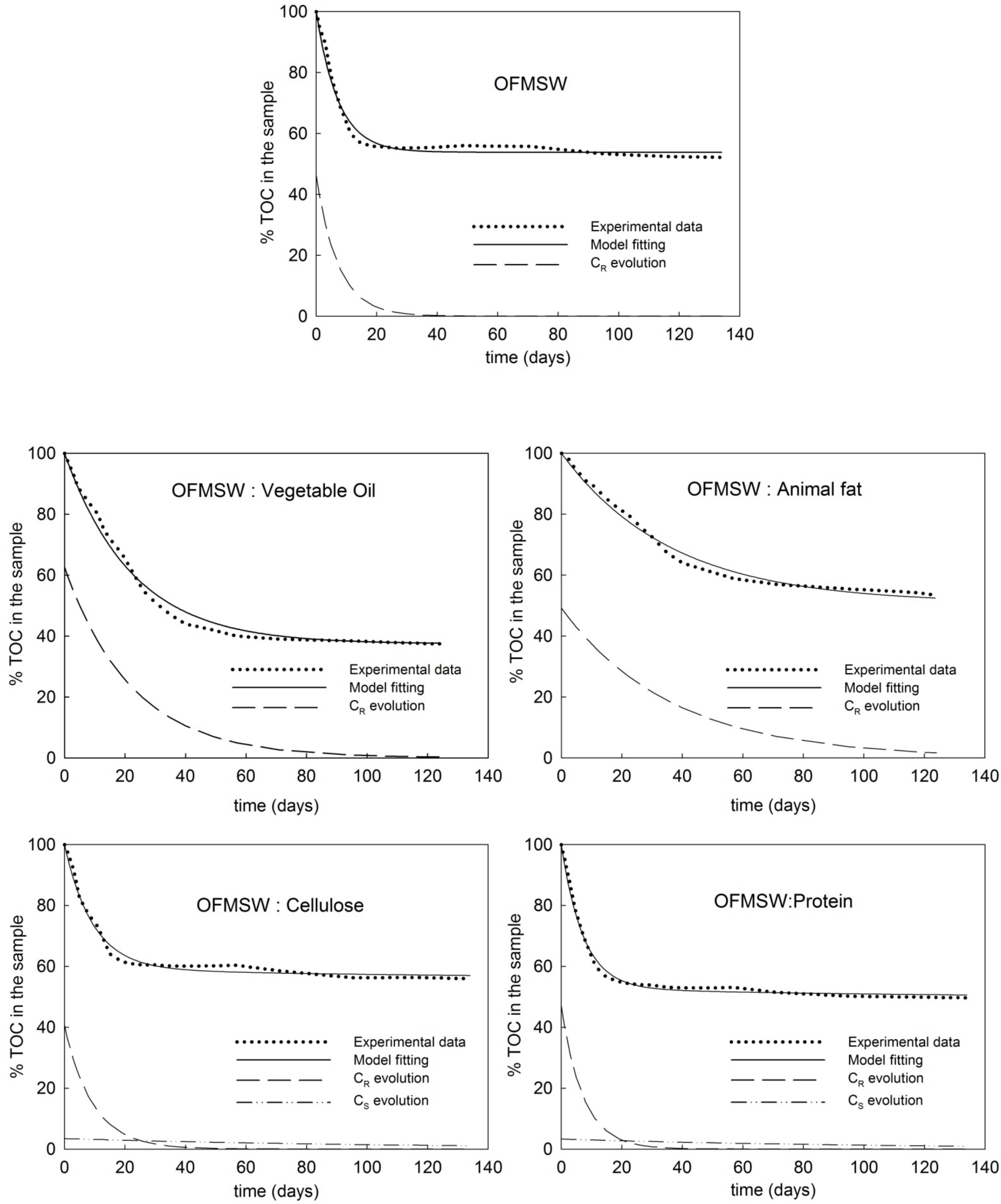
All data from the co-digestion experiments was fit to the new model proposed and the results obtained are shown in Table 5 while model fittings and the evolution of C_R and C_S are plotted in Figure 3.

Table 5. Kinetic parameters for new model developed.

	TOC (%)	C_R (%)	C_S (%)	C_I (%)	k_R (day^{-1})	k_S (day^{-1})
OFMSW (control)	44.2	46.2	---	53.8	0.138	---
OFMSW:VO	57.5	62.6	---	37.4	0.045	---
OFMSW:AF	58.9	49.2	---	50.8	0.027	---
OFMSW:C	44.3	40.6	3.4	55.9	0.107	0.009
OFMSW:P	44.8	47.1	3.3	49.7	0.139	0.009

After fitting experimental data to the model, it can be stated that this model undoubtedly permits the determination of three carbon or organic matter fractions (C_R, C_S and C_I) and the two biodegradation rate constants (k_R and k_S). This method is more reliable than those proposed by Tosun, since the consideration of non biodegradable carbon as part of the total organic carbon is unquestionably necessary for a complete waste characterization. In addition it is also confirmed by the wellness of the model fitting to the experimental data ($p<0.001$ in all cases) and by the correlation coefficients ($R^2>0.98$ in all cases). It has to be mentioned that lag phase data was subtracted from OFMSW:VO and OFMSW:AF co-digestion experiments previous to fitting the data to the new model.

Figure 3: Evolution of carbon remaining in the sample, kinetic model~~s~~ fittings, evolution of C_R degradation and evolution of C_S degradation



Although not reflected in Table 5, for OFMSW (control), OFMSW:VO and OFMSW:AF the model proposed gives values for both C_R and C_S. However, the resultant kinetic constants k_R and k_S are exactly the same and consequently the organic matter mathematically included in C_R and C_S fractions is equivalent. The organic matter contained in OFMSW can be entirely considered as rapidly anaerobically biodegradable, but when OFMSW is co-digested with VO or AF, biodegradation kinetic rate decreases significantly (67% and 80% respectively) and consequently organic matter is slowly biodegraded.

On the contrary, when OFMSW is co-digested with cellulose and protein, different kinetic rate constants are obtained for C_R and C_S with k_R values similar to those obtained for the control experiment. Particularly when OFMSW is co-digested with cellulose k_R decreases a 22% while it is maintained at the same value when is co-digested with protein. In spite of this, C_S values are really low compared to C_R and therefore they can be considered negligible. The biodegradability of the OFMSW and its comparison with co-digestion mixtures can be evaluated when comparing C_R values and including also C_S results. In this sense, C_R approximately ranges from 40% to 50% in all the mixtures studied except when adding VO as co-substrate. If VO is co-digested with OFMSW C_R increases up to 63% what would be in accordance with results obtained from the Gompertz model. In addition, if comparing the rate of biodegradability after 21 days (equivalent to the HRT of the real digester) with the control results, the values are similar and close to 40%. This would mean that in both experiments (control and OFMSW:VO) after 21 days of anaerobic biodegradation process 40% of the initial TOC would have been converted to biogas. Furthermore, when VO is added the methane content in biogas increases a 25% what gives an additional economical benefit to the process.

When OFMSW is co-digested with AF, cellulose or protein waste, the percentage of organic matter converted to biogas is similar (C_I values range from 50-55%) while the initial loading rate is increased. That would imply, as was also suggested from the Gompertz model results, an intensive post-treatment after anaerobic digestion process that allows for the required stabilization of the organic matter.

Finally, it is important to point out that this model allows for the evaluation of carbon degradation kinetics, related to the efficiency of the process in terms of organic matter biodegradation, while Gompertz model allows for the evaluation of methane production kinetics and therefore a complete economical analysis of the process.

4. Conclusions

The main conclusions that can be extracted from this work are listed next:

1) The co-substrates used, vegetable oil, animal fat, cellulose and protein, seem to be adequate for anaerobic co-digestion because all four led to some operative improvements. However the implementation of a real full scale co-digestion process using these co-substrates needs a rigorous economical and technical analysis according to local factors.

2) It has been demonstrated that VO is the most suitable co-substrate to be anaerobically digested with OFMSW since all the parameters evaluated with Gompertz model (UMP, UMP', R and R' and total solids reduction) are extremely improved compared to the control experiment. In addition, when assessing the biodegradable organic matter biodegradation, VO is also the most suitable co-substrate because C_R is clearly increased while biodegradation rate is maintained close to 40% after 21 days of process and despite 20% of increasing in the initial loading rate. When individual co-substrate degradations are considered, VO is again the more feasible waste to be used as co-

substrate. The use of the rest of co-substrates (AF, cellulose and peptone) needs an economical and technical evaluation since they improve some anaerobic digestion aspects as ultimate methane production but their initial production rate is lower than that of control and rates of biodegradability are not improved.

3) The experimental data obtained in all the co-digestion experiments correctly fitted the Gompertz model.

4) The way to express a yield in anaerobic digestion, based on reactor volume or volatile solid fed in the reactor may lead to different observations. Both forms are to be considered when evaluating a new co-substrate in a specific situation.

5) The new model proposed and based on that described by Tosun, can appropriately predict the biodegradable fractions of a sample as well as the biodegradation kinetic rates. In addition the total rate of biodegradability is provided by the model.

6) Future work on the use of co-substrates in anaerobic digestion at industrial scale should be based on real tests at full scale with an accurate operational, economical, logistical and environmental analysis.

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Article VII

Development of a simple model for the determination of the biodegredable organic fractions in several organic wastes

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DEVELOPMENT OF A SIMPLE MODEL FOR THE DETERMINATION OF THE BIODEGRADABLE ORGANIC FRACTIONS IN SEVERAL ORGANIC WASTES

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Abstract

Several organic wastes of major production in the world (municipal solid wastes, wastewater sludge, manures and bulking agents) and some already treated organic wastes have been investigated to determine the partition among the several fractions that compose them and their kinetics of biodegradation. Different literature models have been explored for their suitability to predict the behaviour in respiration studies of these wastes. All the models presented limitations related to their simplicity or their excessive complicity, which makes them unsuitable for reliable and fast studies at real scale. A new model based on the rapid, the slowly and the inert organic fractions has been tested for all the wastes, showing excellent correlations with actual respiration activity. This model is proposed as a rapid tool to determine the biodegradability of a given waste. Finally, the kinetic parameters for this model in its application to all the wastes studied are presented.

Keywords: Biodegradation kinetics; Organic matter characterization; Biodegradability; Respirometry; Composting.

1. Introduction

In recent years, the increasing amounts of organic solid wastes generated by municipalities, industries or agricultural activities have become a worldwide problem. Among the available technologies to treat and recycle organic wastes, composting is presented as one of the most useful options to recycle organic materials into valuable organic fertilizer popularly known as compost.

The characteristics of the waste or material that is going to be composted are of especial interest to perform the process in a favorable way to finally obtain the desirable compost quality. The aerobic biodegradation potential, what means the organic carbon content that is susceptible to be biodegraded and transformed to carbon dioxide, is a key parameter to take into consideration to optimally design the composting process. The total organic carbon (TOC) is not a reliable measure for this purpose since the recalcitrant carbon fraction can be sometimes greater than the biodegradable organic carbon (BOC) fraction of the sample. In addition, the knowledge of the kinetic parameters regarding aerobic biodegradation reactions would be extremely helpful for determining the time required for a properly stabilization of the material (Lasaridi and Stentiford, 1998).

The initial C/N ratio is one of the most important factors affecting the composting process and the compost quality (Epstein, 1997; Zhu, 2007). Therefore, the C/N ratio is generally used in the composting industry as a feedstock recipe, since an optimal C/N ratio is required to appropriately perform the process, but also as final product quality guideline (Haug, 1993; Larsen and McCartney, 2000). Traditionally, the assessment of the C/N ratio in solid samples has been determined on total organic fractions through the determination of total organic carbon (TOC) and total nitrogen (N). Specifically, TOC has been performed following two procedures:

dichromatometric oxidation (Walkley and Black, 1934) and direct determination by dry combustion in a C-analyser. When using the first mentioned, only the oxidizable carbon (OXC) is obtained. Generally, the OXC values determined are within 75 and 85% of the TOC values (Navarro et al., 1991). Several studies have indirectly deduced the TOC from the organic matter (OM) content, applying a suitable factor of transformation (Iglesias et al., 1991; Navarro et al., 1991; Haug, 1993; Bisutti et al., 2004). Thus, the C/N ratio as an indicator of the composting process has been determined assuming that both nutrient sources are fully biodegradables (Eiland et al., 2001; Huang et al., 2004; Zhu, 2007). However, only a percentage of the carbon is really biodegradable (BOC) and only a fraction of the BOC will be susceptible of biodegradation during the time restricted of a real biological process. The present study will be focused on the determination of BOC and the rapidly biodegradable (C_R) and slowly biodegradable (C_S) fractions under aerobic conditions on which BOC can be classified. C_R and N values would be the most appropriate for more reliable determinations of C/N ratios.

There are many publications regarding biodegradation potentials and kinetic analysis, being the most recent and significant: Adani et al., 2004; Tremier et al., 2005; Komilis, 2006; Tosun et al., 2008; Bueno et al., 2008; de Guardia et al., 2010, among others. In all of them, except in Tosun et al., complex models are developed and checked to describe the aerobic biodegradation of wastes, obtaining the biodegradation kinetic rate constants and the different fractions in which organic matter (or organic carbon) can be classified depending on the biodegradation rate. However, although these models provide valuable scientific information, in terms of applicability, they are not easy to implement, since many analysis, including physical, chemical and biological analysis, and process monitoring are required. Moreover, they are not valid for all the wastes subjected to composting because some kinetic parameters are only defined for specific types of wastes such as sewage sludge. On the constrast, Tosun et al. (2008) reports some simple models, easy to apply. However they have not been proved with a wide range of different wastes with different biochemical composition.

The objectives of this study are: 1) to test the already proposed models for biodegradable organic matter content assessment; and 2) to develop a respirometric methodology and an easily applicable mathematical model able to characterize the initial organic carbon composition of the waste, as C_R, C_S and non-biodegradable or inert (C_I) fractions and the kinetic rate constants associated to each fraction in order to provide valuable information for composting processes management and design.

2. Materials and Methods

2.1. Organic Wastes

Ten organic samples of different origins and at different stages of biodegradation were used in this work. Raw wastes were: mixed municipal solid waste (MSW), the organic fraction of municipal solid waste (OFMSW), raw sludge (RS) and digested sludge (DS) from wastewater treatment plants, pruning waste (PW), solid fraction of pig slurry (PM) and cow manure (CM). Processed and already biologically treated wastes were: digested and composted OFMSW (C-OFMSW), mature and refined C-OFMSW, which means final product (F-OFMSW) and composted sludge (CS).

All municipal organic samples, MSW, OFMSW, C-OFMSW and F-OFMSW, were collected from a MBT plant previously described elsewhere (Ponsá et al., 2008), which main processing steps are mechanical pre-treatment, anaerobic digestion and composting, in this order. RS and DS were obtained from Besòs (Barcelona) and Sabadell (Barcelona) wastewater treatment plants, respectively. CS came from the Olot (Barcelona) composting plant. PM and CM samples were selected as typical farm wastes around Barcelona province and they were collected from a farm in Vic (Barcelona). Finally, a sample of PW from La Selva (Girona) composting plant was also studied since this is a typical waste used as a bulking agent.

After collection, MSW and OFMSW samples were grinded to 15 mm particle size to obtain more representative samples but also to increase the available surface and maintain enough porosity and matrix structure. In the laboratory each sample was vigorously mixed and representative samples of about 1 kg were frozen and conserved at -18 °C. Before analysis, the samples were thawed at room temperature for 24 h.

2.2 Respirometric tests

Microbial respiration was measured as O2 consumption and CO2 production in the dynamic respirometer built and started-up by Ponsá et al. (2010) based in the methodology described by Adani et al. (2006).

Briefly, a 150 g organic sample was placed in a 500 mL Erlenmeyer flask that was introduced in a water bath at 37 °C. A constant airflow was supplied to the sample and on-line O_2 and CO_2 contents in the exhaust gases were measured and monitored. From the curves of oxygen concentration vs. time and carbon dioxide vs. time, two Dynamic Respirometric Indices (DRI_{24h}, measured as the average DRI in the 24 hours of maximum activity) related to O_2 consumption and CO_2 production were obtained from each sample. All measurements were undertaken in duplicate. Low porosity samples were mixed with an inert bulking agent. This is formed by small pieces (20 x 10 mm) of the inert material (Spontex, Iberica) in 1:10 wet weight ratio (Sample:Spontex).

The DRI_{24h} represents the average oxygen uptake rate during the 24 hours of maximum biological activity observed along the respirometric assay and it reports the stability degree (Adani et al., 2004; Ponsá et al., 2010). It is expressed in mg of O_2 consumed per g of dry matter and per hour. However, to achieve the objectives of this paper, the DRI_{24h} is required to be also expressed in mg of CO_2 produced per g of dry matter and per hour.

2.3 Biodegradable Organic Carbon

Based in the methodology presented by Ponsá et al. (2010) to determine the cumulative oxygen consumption for a specific time, the cumulative CO_2 production was calculated in order to know the total BOC content for each sample.

A time increase of the performed respirometric test allowed determining the total cumulative CO_2 production. The time required depended on the biostability of each sample i.e., the determination was concluded when the CO_2 production rate was negligible. It is assumed that the assay can be finished when the measure of oxygen uptake rate (OUR) is below the 5 % of the maximum OUR achieved. At that moment, it can be considered that all the readily and almost all the slowly biodegradable carbon have been consumed. A first reference to the approach of a direct determination of the biodegradable organic carbon in solid wastes was proposed by Sánchez (2007) in his discussion about the cumulative CO_2 production data presented by Komilis (2006).

The aim of this methodology is to determine the biodegradable organic carbon under composting conditions. Consequently, nor inoculum neither additional nutrients were added.

As it is well known, during the aerobic degradation of organic matter, the biodegradable organic carbon is transformed by oxidation to CO_2. Thus, the total CO_2 production measured by the respirometric test is an indirect BOC measure of the sample, since this is all the carbon produced by biological activity. From these data, and knowing that one mol of CO_2 equals to one mol of C, the BOC can be calculated as a dry weight percentage from the final cumulative CO_2 production and the molecular weight ratio between Carbon Dioxide and Carbon (44/12), as shown in equation 1.

$$BOC(\%, db) = final\ cumulative\ CO_2\ production \left[\frac{mg\, CO_2}{g\, DM} \right] \cdot \frac{12}{44} \cdot \frac{100}{1000} \qquad \text{Equation (1)}$$

where BOC is the biodegradable organic carbon; the cumulative CO_2 production (or carbon mineralized) is in mg CO_2 g DM^{-1}; 12 and 44 are the molecular weight of C and CO_2, respectively; 1000 is the conversion factor from mg to g and 100 is to express BOC as percentage.

2.4. Analytical methods

Water content, dry matter (DM), organic matter (OM) content and Total Organic Carbon Content (TOC), were determined according to the standard procedures (The U.S. Department of Agriculture and The U.S. Composting Council, 2001). Three replicates were analyzed for each sample.

2.5 Asessment of biodegradable organic matter fractions through biodegradation kinetics modeling

In order to initially characterize the biodegradable organic matter content of a given waste by means of quantitative measures of the easily and slowly biodegradable organic matter and biodegradation kinetic rate constants, the data of cumulative CO_2 produced or mineralized was fitted to the four models described by Tosun et al. (2008), which were considered as a first approach since they were simple and easy to apply. The four models are described below:

- First-zero-order kinetic model:

The first-zero-order kinetic model is expressed as:

$$C = C_R(1 - \exp(-k_R t)) + C_S k_s t \qquad \text{Equation 2}$$

where, C is cumulative CO_2–C mineralized (or produced) (%) at time t (days), C_R, C_S are the percentages of rapidly and slowly mineralizable fractions, respectively, and k_R and k_S are the rapid and slow rate constants (day^{-1}), respectively.

- First-first-order kinetic model:

The first-first-order kinetic model is expressed as:

$$C = C_R(1 - \exp(-k_R t)) + C_S(1 - \exp(-k_s t)) \qquad \text{Equation 3}$$

- Chen and Hashimoto's kinetic model:

The model is expressed by the following equation as suggested by Tosun et al. (2008):

$$C = 100 - 100 \times (R + (1 - R)K / (\mu_m t - 1 + K)) \qquad \text{Equation 4}$$

where R is the refractory coefficient, K is Chen and Hashimoto dimensionless kinetic constant, and μ_m is maximum specific growth rate of microorganisms, day^{-1}.

- Levi-Minzi kinetic model:

Levi-Minzi model expresses net mineralization with an exponential kinetic:

$$C = kt^m \qquad \text{Equation 5}$$

where k is a constant that characterizes the units used for the variables and m is a constant that characterizes the shape of the curve.

3. Results and discussion

3.1 Physico-chemical characteristics

The main properties of the samples studied are reported in Table 1. In general, dry matter content was higher and organic matter content were lower in final products than in raw materials. Most raw wastes presented a TOC content around 45 % which was higher than those of final products. F-OFMSW presented higher organic matter and TOC contents than C-OFMSW since inert materials and bulking agents were removed after final product post-treatment (Ruggieri et al., 2008).

3.2 Dynamic respiration index (DRI_{24h})

Table 1 shows the DRI_{24h} based on CO_2 production and O_2 consumption in order to know the maximum carbon degradation rate and the stability degree, respectively. It is assumed that 1 mg O_2 g OM^{-1} h^{-1} is the maximum DRI_{24h} threshold for biological stability (Adani et al., 2004; Baffi et al., 2007). Only C-OFMSW, CS and PW were below this limit and therefore, they were considered stabilized samples with minor biodegradable organic matter content. On the contrary, higher stability indices were found for RS, CM, OFMSW, MSW and DS. Recently, Ponsá et al. (2010) has presented a qualitative classification of wastes in three categories based on the material typology and its stability indices. According to this classification, RS, PM and OFMSW are highly biodegradable wastes because they present an stability index higher than 5 mg O_2 g DM^{-1} h^{-1}; MSW, DS and CM can be classified as moderately biodegradable wastes since they present a DRI_{24h} between 2 to 5 mg O_2 g DM^{-1} h^{-1} and the rest of the materials are wastes of low biodegradability, which have a DRI_{24h} below 2 mg O_2 g DM^{-1} h^{-1}.

Table 1. Characterizations of the different wastes used for the assessment of biodegradable organic matter fractions.

	DM (%, wb)	OM (%, db)	TOC (%, db)	BOC (%, db)	DRI_{24h}-O_2 (mg O_2·g DM^{-1}·h^{-1})	DRI_{24h}-CO_2 (mg CO_2·g DM^{-1}·h^{-1})
MSW	62 ± 6	38 ± 6	34 ± 3	12.6 ± 0.1	1.50 ± 0.09	1.70 ± 0.00
OFMSW	29 ± 3	77 ± 3	44 ± 3	23.4 ± 0.2	4.10 ± 0.06	5.5 ± 0.6
C-OFMSW	65 ± 2	28 ± 3	16 ± 1	1.8 ± 0.2	0.22 ± 0.06	0.26 ± 0.01
F-OFMSW	50.2 ± 0.8	33.3 ± 0.9	38 ± 3	3.7 ± 0.4	0.55 ± 0.07	0.70 ± 0.08
Raw Sludge	29.4 ± 0.8	77.1 ± 0.9	45 ± 3	17.7 ± 0.2	6.1 ± 0.9	6.57 ± 0.03
Digested Sludge	19.6 ± 0.1	54.8 ± 0.1	29 ± 2	11 ± 3	3.2 ± 0.2	2.9 ± 0.3
Composted Sludge	57.4 ± 0.4	65 ± 2	38 ± 4	2.19 ± 0.04	0.14 ± 0.02	0.20 ± 0.01
Cow Manure	23.5 ± 0.2	84.9 ± 0.9	47 ± 3	23.1 ± 0.4	2.69 ± 0.02	3.03 ± 0.08
Pig Manure	12.7 ± 0.3	85.1 ± 0.4	67 ± 4	22 ± 3	5.3 ± 0.2	6.4 ± 0.6
Pruning Waste	60.4 ± 1.1	92 ± 1	42 ± 1	19 ± 4	0.82 ± 0.09	1.1 ± 0.2

wb: wet basis. db: dry basis. OFMSW: Organic Fraction of Municipal Solid Waste. C-OFMSW: Digested and Composted OFMSW. F-OFMSW: Mature C-OFMSW. OM: Organic Matter. DM: Dry Matter. TOC: Total Organic Carbon. BOC: Biodegradable Organic Carbon. DRI: Dynamic Respiration Rate (referred to O_2 consumption or CO_2 production).

3.3. Biodegradable Organic Carbon (BOC)

Total BOC content for the samples analyzed is presented in percentage on dry matter and reported in Table 1. BOC correlated well with OM (R^2=0.825, p<0.001) and was the 29.4 % of OM as average. The BOC determination was undertaken during the respirometric test, therefore the evolution of BOC cumulative consumption can be determined and will be used in next section. Each sample had a different assay-time according to the threshold established to finish the process. Only the pruning waste assay was stopped before the limit because it is a really slowly biodegradable material and it was considered that in 90 days the assay was enough for a proper biodegradable carbon determination. Essentially, the DRI obtained for the PW assay was 0.82 mg O_2 gDM^{-1} h^{-1}, which was the lowest value observed for different raw wastes. Additionally, it must be pointed out that real aerobic biological processes longer than 90 days are not expected.

As expected, most of the samples obtained after an anaerobic digestion and/or composting treatment had lower BOC values than raw materials since in both biological treatments the BOC is degraded. According to these results, the total BOC could be directly related to the biological stability degree, which was measured as DRI_{24h} and it is reported in Table 1. It could be observed for all the samples a similar trend between DRI_{24h} values and BOC content (i.e., more BOC at higher DRI_{24h} while less BOC at lower DRI_{24h}). However, no significant correlation could be established. Basically, two different samples could present a similar BOC and very different DRI_{24h} depending on their biochemical composition. For instance, PW and RS presented a similar BOC, around 18 % on dry basis, while the DRI_{24h} of PW was much lower, according to the lower rate of decomposition of fibers. In this sense, the characterization of BOC into easily and slowly degradable fractions would be of interest (Tremier et al., 2005).

3.4 Assessment of biodegradable organic matter fractions through biodegradation kinetics modeling

In order to provide a quantitative measure of the different fractions of biodegradable organic matter of which the organic wastes are composed, data of CO_2

produced or mineralized was fitted to different models. The objective was to assess the differently biodegradable organic fractions by means of a simple model, rapidly and easily applicable. Therefore, the percentage of carbon mineralized was calculated as the amount of cumulative C-CO_2 produced at a given time on the basis of the initial total organic carbon, that is the BOC/TOC ratio for a given time. The discussion and evaluation of the biodegradable organic matter fractions will be carried out on carbon basis assuming the equivalence between organic matter and carbon biodegradation.

The four models described by Tosun et al. (2008) were fitted to experimental data obtained for the ten different wastes studied. Figure 1 shows the percentage of carbon mineralized with time and the fitting of the four models considered for one of the MSW replicates. Similar behavior was observed for all the wastes, except for CS, since any of the tested models provided a good fitting for CS data.

The kinetic parameters obtained when fitting experimental data to the models are presented in Table 2. Levi-Minzi model did not fit experimental data. Chen & Hashimoto model fitting was mathematically acceptable but resulting parameters did not offer reliable information, with K ranging from 1 to 10^{+16} and μ_{max} ranging from 1.7 to 10^{+13} depending on the waste considered. Consequently both models were discarded for posterior discussion.

First-zero-order and first-first-order models fitted well to experimental data but the best fitting results were observed for the first-first-order kinetic model, with correlation coefficients always up to 0.99.

Higher values for C_R were obtained for F-OFMSW (16.19%) than C-OFMSW (6.06%), which can be explained by the organic matter concentration occurred in the MBT post-treatment, where the material, after being composted, is subjected to bulking agent separation and inorganic material removal.

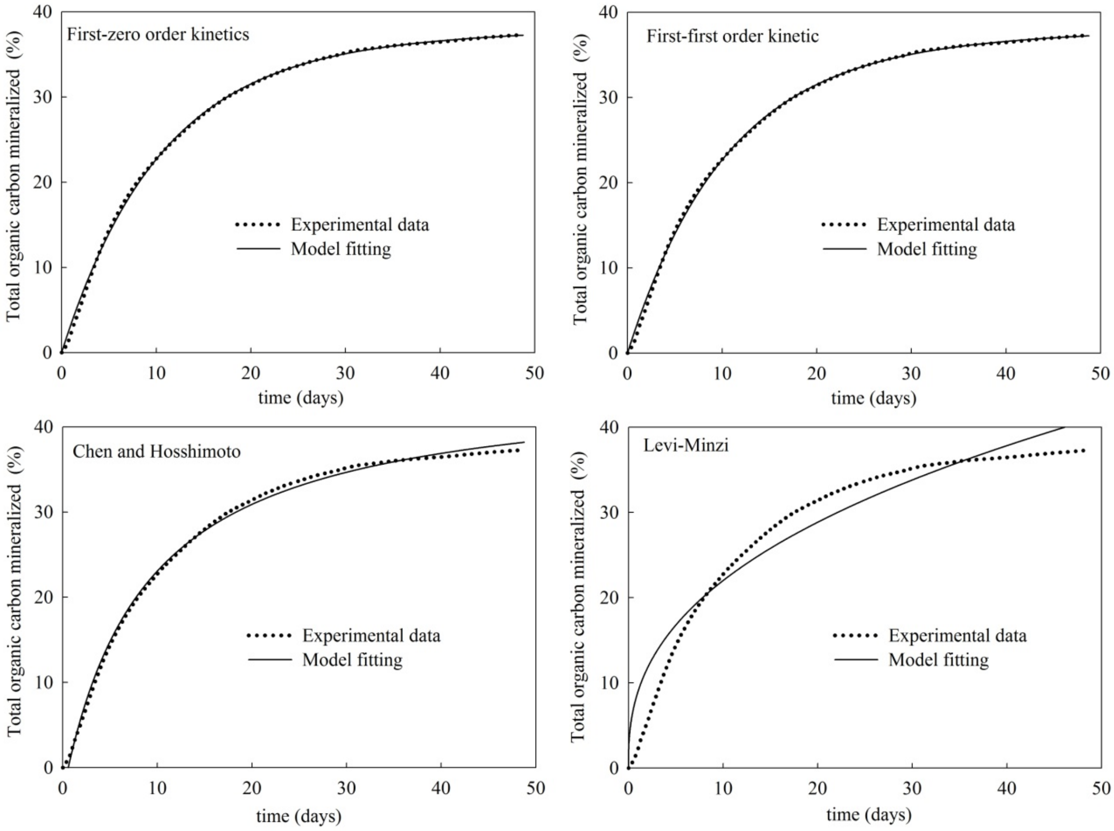

Figure 1. Evolution of carbon mineralized with time and kinetic models fittings for one of the replicates of Municipal Solid Waste.

As expected from DRI_{24h} data, the lowest rapidly mineralizable fraction, C_R, was obtained for C-OFMSW and PW and, in general, wastes with high DRI_{24h} presented high C_R. However, no significant relationship was found between C_R or k_R and DRI_{24h}.

Data on Table 2 confirmed the lower rapidly (or easily) biodegradable organic carbon content (or equivalent biodegradable organic matter content) on treated samples and in pruning waste. On the contrary, fresh samples presented an easily degradable content over 24%. In the case of pig manure, although the first-first-order model fitting highlighted a relatively small fraction of highly biodegradable carbon (9.67%), the high kinetic constant k_R 0.547 $days^{-1}$ would make sense to the results and they would be in agreement with the high DRI_{24h} observed (Table 1).

Table 2. Kinetic parameters for different models analyzed fitted to experimental BOC evolution determined in this work.

Kinetic model	Model parameter	MSW	OFMSW	C-OFMSW	F-OFMSW	RS	DS	CM	PM	PW	CS
First-zero-order	C_R (%)	33.70	33.96	6.06	16.19	25.06	16.01	50.66	9.62	13.41	0.097
	C_S (%)	66.30	66.04	93.94	83.81	74.94	83.99	49.34	90.39	86.59	99.90
	k_R(day^{-1})	0.10	0.193	0.161	0.127	0.229	0.415	0.095	0.69	0.062	2.786
	k_S(day^{-1})	0.001	0.009	0.002	0.000	0.007	0.001	0.000	0.01	0.004	0.002
First-first-order	C_R (%)	33.57	31.66	5.92	16.18	24.24	16.00	50.58	9.67	7.90	0.068
	C_S (%)	66.43	68.34	94.08	83.82	75.76	84.00	49.42	90.33	92.10	99.93
	k_R(day^{-1})	0.10	0.202	0.165	0.127	0.234	0.416	0.096	0.547	0.182	4.51
	k_S(day^{-1})	0.001	0.011	0.002	0.000	0.008	0.001	0.000	0.006	0.005	0.002
Chen and Hashimoto	R	0.551	0.125	0.822	0.783	0.537	-0.086	0.410	0.006	0.164	-0.256
	K	17.72	1773.7	2.61E+11	29.43	12.06	8.17E+15	14.19	1.006	6.11E+14	1.14E+4
	μ_{max}(day^{-1})	850.5	63.07	1.20E+10	3.66	1.96	5.14E+13	1.736	2.006	5.64E+12	23.02
Levi-Minzi	k	48942	11.85	1.672	4.135	9.141	8.843	13.59	3.006	2.221	0.262
	m	0.394	0.439	0.564	0.431	0.453	0.225	0.348	4.006	0.657	0.975

OFMSW: Organic Fraction of Municipal Solid Waste. C-OFMSW: Digested and Composted OFMSW. F-OFMSW: Mature C-OFMSW. RS: Raw Sludge. DS: Digested Sludge. PW: Pruning Waste. PM: Solid Fraction of Pig Slurry. CM: Cow Manure. PW: Pruning Waste. CS: Composted Sludge. C_R: rapidly biodegradable carbon fraction on initial TOC. C_S: slowly biodegradable carbon fraction on initial TOC. k_R: rapid rate constant. k_S: slow rate constant. R: refractory coefficient. K: Chen and Hashimoto dimensionless kinetic constant. μ_m : maximum specific growth rate of microorganisms. k: model constant. m: model constant.

When analyzing and discussing these results, it is important to consider the limitations that this methodology entails. The first-zero-order and first-first-order models permit the classification of the carbon contained in a given sample into two different categories: easily and slowly biodegradable fractions. However it does not necessarily means that, for example, the characteristics of the easily organic matter contained in a sample of the OFMSW are comparable to the same fraction in a sample of pig manure. The unique equivalent meaning for all samples is the next: the easily biodegradable fraction of a given waste has a biodegradation rate constant much higher than the slowly biodegradable fraction. In this sense, it is very important to consider simultaneously both parameters, the percentage of easily biodegradable carbon and the biodegradation rate constant. The higher the rate constant is, the more easily biodegradable the waste fraction will be. To sum up, it can be established a classification of the different fractions in which a sample can be divided. From first-first-order model fitting results, it can be considered that a sample or a fraction is easily biodegradable if the biodegradation constant rate ranges from 0.096 to 0.6 days^{-1}. On the contrary, to be considered as a slowly biodegradable fraction, the biodegradation constant rate may range between 0.001 and 0.011 days^{-1}. When biodegradation constant rates equal to 0 or lower than 0.001 days^{-1} are obtained, the corresponding organic or carbon fraction or the whole sample may be considered as inert organic matter. Similar conclusions can be obtained from data presented by Tosun et al. (2008). According to results in Komilis (2006) kinetic study, the threshold between both fractions will be for biodegradation constant rates of 0.05 d^{-1}.

However, the most important limitation when using first-zero-order and first-first-order models is the consideration of the non-biodegradable organic matter or organic carbon as slowly biodegradable fraction that obviously leads to non completely reliable results.

Two additional models that permit the characterization of easily and slowly biodegradable organic matter fractions were considered. Model suggested by Komilis (2006) was found more complete than those described by Tosun et al. (2008) but it requires additional chemical analysis (final TOC and initial DOC) so it was discarded in this first assessment. Model suggested by Tremier et al. (2005) was also fitted to experimental data. This model had been optimized for a sludge:bulking agent mixtures and provided good results for sludge experimental data in this work (data not shown). However, the model did not properly adjust to the respirometric profile of the rest of wastes. Tremier model requires five kinetics parameters and two stoichiometric parameters to estimate the three active compounds on substrate: biomass, easily and slowly biodegradable fraction. The seven parameters required vary according to biochemical composition of substrate, as demonstrated from Tosun models fitting. Consequently, model optimization would be necessary for each waste prior to its use. For this reason Tremier's model was discarded for this study.

Trying to sort out the limitations of the first-zero-order and first-first-order models described by Tosun, a new simple model was developed to obtain the three different fractions in which organic matter or carbon can be classified after fitting the data: C_R, C_S and inert fraction (C_I).

If keeping the concept of the Tosun model, the mathematical expression is unable to predict the inert fraction. However, instead of considering the evolution of the carbon emitted in form of CO_2, the carbon that has not still been degraded can be also followed, assuming that the initial TOC corresponds to the 100% of the carbon in the sample and subtracting the carbon emitted from this initial value. The remaining carbon in the sample can be expressed as percentage of the initial TOC and some profiles are shown in Figure 2.

The mathematical modeling of these data would correspond to the following expression:

$$C_W = C_R \times \exp(-k_R t) + C_S \times \exp(-k_S t) + C_I \qquad \text{Equation 6}$$

where, C_W is the remaining carbon in the sample (%) at time t (days), C_R and C_S are the percentages of rapidly and slowly mineralizable fractions respectively, C_I is the inert fraction, and k_R and k_S are rapid and slow rate constants (day^{-1}), respectively. This expression consists of two exponential decay terms (first order kinetics) and an independent and constant term.

Although it is not always necessary, when fitting the model it is recommendable to add the restriction of the equivalency of the total biodegradable carbon fractions (C_R plus C_S) to the total BOC degraded, otherwise the model could lead to wrong results since all matter in the sample would be considered as potentially biodegradable. That implies the previous chemical analysis of TOC but also the biological analysis of BOC for all samples studied.

All data from the wastes analyzed were fit to this model and results obtained are shown in Table 3. The model fittings and the evolution of C_R, C_S and evolution of organic matter degradation when no distinction between C_R and C_S is provided by the model (C_{BIO}) are plotted in Figure 2 for all wastes analyzed.

After fitting experimental data to the model, it can be stated that this model undoubtedly permits the determination of three carbon or organic matter fractions (C_R, C_S and C_I) and the two biodegradation rate constants (k_R and k_S). This method is more reliable than those proposed by Tosun, since the consideration of non biodegradable

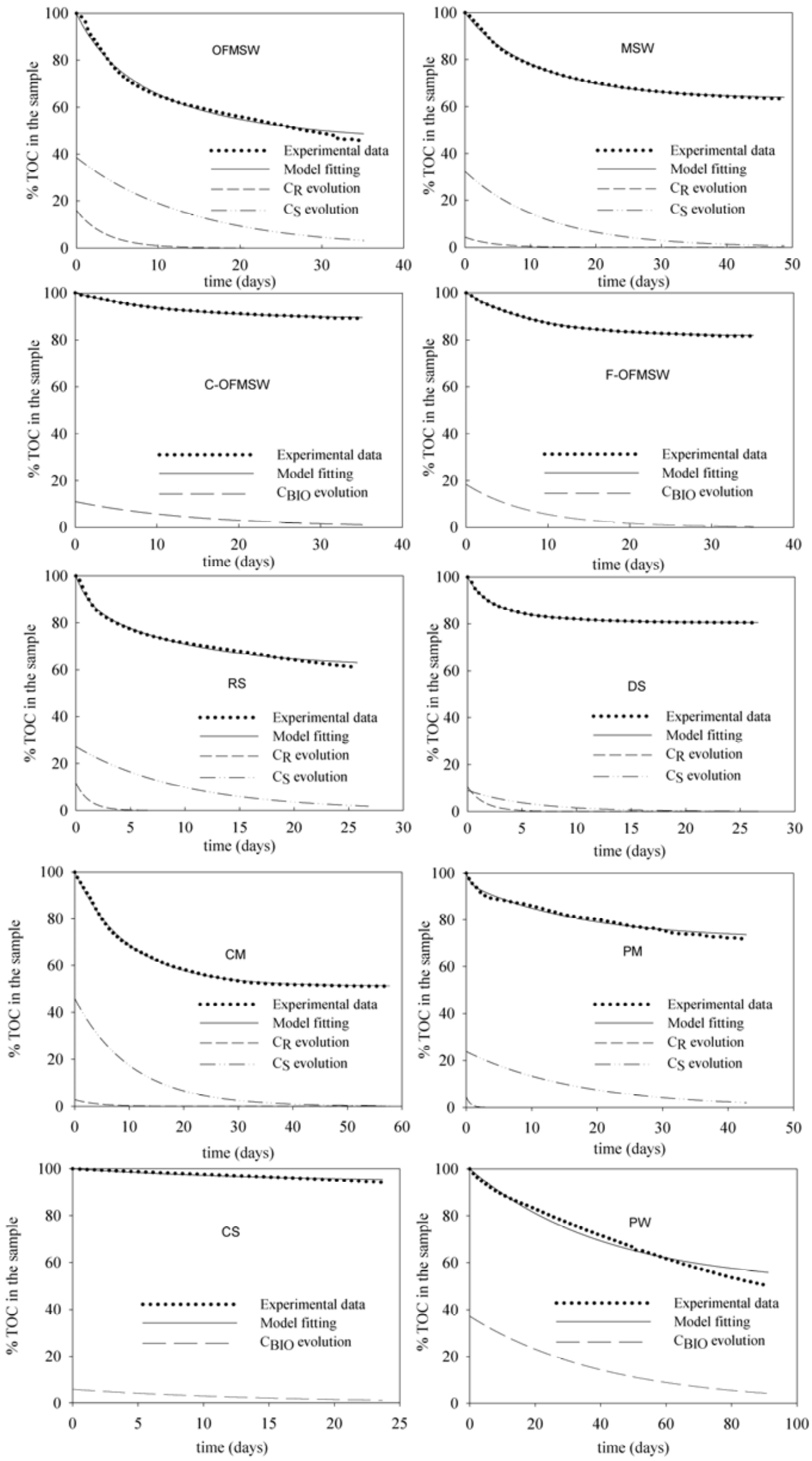

Figure 2. Evolution of carbon remaining in the sample, kinetic models fitting, evolution of C_R and C_S degradation and evolution of organic matter degradation when no distinction between C_R and C_S is provided by the model (C_{BIO}) for one the replicates of each waste sample.

carbon as part of the total organic carbon is unquestionably necessary for a complete waste characterization. In this sense values of C_R and C_S and the new C_I are different from those obtained from Tosun models. In addition it is also confirmed by the wellness of the model fitting to the experimental data ($p<0.001$ in all cases) and by the correlation coefficients ($R^2>0.94$ in all cases).

Table 3. Kinetic parameters for new model developed in this work.

New kinetic model developed					
Model parameter	C_R(%)	C_S(%)	C_I (%)	k_R (day^{-1})	k_S (day^{-1})
MSW	4.2 ± 0.4	32.34 ± 0.06	63.0 ± 0.9	0.25 ± 0.01	0.08 ± 0.01
OFMSW	13 ± 3	40 ± 2	46.0 ± 0.7	0.30 ± 0.03	0.08 ± 0.01
C-OFMSW	---	12 ± 1	87 ± 1	---	0.08 ± 0.01
F-OFMSW	---	16 ± 2	82 ± 1	---	0.120 ± 0.002
Raw Sludge	12.5 ± 0.9	26.6 ± 0.7	60.9 ± 0.2	0.77 ± 0.07	0.100 ± 0.003
Digested Sludge	10 ± 1	7 ± 1	81 ± 2	0.65 ± 0.01	0.12 ± 0.04
Cow Manure	3.2 ± 0.2	45 ± 1	51 ± 1	0.24 ± 0.05	0.094 ± 0.004
Pig Manure	4.3 ± 0.4	23 ± 1	73 ± 1	1.5 ± 0.2	0.05 ± 0.01
Pruning Waste	---	49 ± 2	50 ± 2	---	0.024 ± 0.003
Compost Sludge	---	5.8 ± 0.1	94.2 ± 0.1	---	0.068 ± 0.001

OFMSW: Organic Fraction of Municipal Solid Waste. C-OFMSW: Digested and Composted OFMSW. F-OFMSW: Mature C-OFMSW. C_R: rapidly biodegradable carbon fraction on initial TOC. C_S: slowly biodegradable carbon fraction on initial TOC. k_R: rapid rate constant. k_S: slow rate constant.

Although not reflected in Table 3 for C-OFMSW, F-OFMSW, PW and CS, the proposed model gives values for both C_R and C_S. However, the kinetic constants k_R and k_S present exactly the same numeric value and consequently the organic matter mathematically included in C_R and C_S fractions is equivalent. Therefore, considering the values of the kinetic rate constants, it can be established that already exhaustive biologically treated wastes and those wastes in which low biodegradation potential is expected, such as pruning waste, present only one type of organic matter which can be classified as slowly biodegradable organic matter, with kinetic rate constants always lower than 0.12 days^{-1}. DS is an exception, because although the sample has been already biologically treated, anaerobic digestion cannot be considered as a final treatment, since not all biodegradable organic matter under aerobic conditions can be anaerobically biodegraded.

On the contrast, two different fractions of organic matter with different biodegradation rate constants are obtained for all fresh samples with a low standard deviation between the replicates analyzed. The difference between the biodegradation rate constants is always up to 61% meaning that C_R and C_S have clearly different characteristics. From these results, the threshold between easily and slowly biodegradable carbon rate constants would be somewhere between 0.12 and 0.24 $days^{-1}$. Additional experiments with other wastes are required to accurately establish this limit.

All samples have a percentage of organic matter which is non biodegradable (C_I) and this value is directly given by the model fitting. The already treated wastes are those that present a higher percentage of non biodegradable carbon, ranging from 94% (for CS) to 82% (for C-OFMSW). Nevertheless, fresh samples always present a percentage of C_I lower than 73%, except DS with C_I values close to 80%. DS is an especial case, since it presents a C_R value around 10% but the total biodegradable organic carbon is similar to those wastes with a low biodegradation potential. Probably this would be due to the presence of hydrolyzed organic matter that does not have been degraded by methanogenic bacteria during anaerobic digestion and that is easily biodegradable under aerobic conditions.

The wastes with the highest biodegradable organic matter percentages are the OFMSW (54%) and CM (49%). All fresh samples have a low percentage of C_R except the OFMSW and RS with values around 13%. The highest k_R (1.5 $days^{-1}$) has been obtained for PM waste while lowest k_S value has been obtained for PW, which indicates that this waste is the slowest biodegradable but not the least biodegradable, since C_I represents only a 50% of the initial TOC.

If comparing the values obtained from this new model with values obtained from Tosun models, it is clearly obvious that values differ significantly, since initial considerations are also diverse. In this new model, the k_R is never lower than 0.24 $days^{-1}$ while in Tosun models, carbon was considered as rapidly biodegradable when k_R was over 0.096 $days^{-1}$, what means a difference between the two k_R of 60%. In fact k_R values from Tosun model are similar than k_S values from new model, what manifestly indicates that the results from Tosun models can not be considered reliable.

Finally, it can be considered that a sample or a fraction is rapidly biodegradable when biodegradation constant rate ranges from 0.25 to 1.5 $days^{-1}$ and it can be considered as a slowly biodegradable when biodegradation constant rate ranges between 0.001 and 0.10 $days^{-1}$. When biodegradation constant rates equal to 0 or lower than 0.001 $days^{-1}$ are obtained, the corresponding organic or carbon fraction or the whole sample may be considered as inert organic matter. These results are not in accordance to those obtained by Komilis (2006) and establish a new classification and methodology to discern between different biodegradation potentials of wastes and consistently characterize the organic matter of these wastes.

DRI_{24h} results can not be directly related to a single parameter of the model. High values on DRI_{24h} would be consequence of high C_R values with a moderate k_R or moderate values of C_R with high values of k_R. This would be in accordance to Ponsa et al., (2010) who established that DRI_{24h} can not be used as single parameter to determine the aerobic biodegradability potential and, in consecuence, longer and cumulative aerobic respirometric indices need to be used.

4. Conclusions

The present work establishes a new respirometric methodology that allows for a complete organic matter characterization by adjusting experimental data to a simple and applicable mathematical model based on organic carbon depletion monitoring. This new model overcomes the limitations, complexity and considerable chemical-physical analysis demanded at present in the already proposed methodologies and models.

Different raw and already biologically treated wastes have been completely characterized in terms of C_R, C_S, C_I, k_R and k_S allowing for a new classification on their biodegradation rates.

Anyone of the results from the model is not directly related to DRI_{24h}, which indicates, as suggested in Ponsá et al. (2010), that organic matter can not be characterized by an unique parameter. Therefore the different organic matter fractions and biodegradation rates must be considered together for a reliable characterization.

This methodology also allows for correct determinations of BOC, which should be used instead the traditionally used mesures of TOC for C/N determinations.

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Protocol per a la determinació de l'estabilitat biològica mitjançant l'Índex Respiromètric Dinàmic (IRD) en mostres de residus urbans orgànics

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Presented to Agència de Residus de Catalunya (ARC)

Protocol per a la determinació de l'estabilitat biològica mitjançant l'Índex Respiromètric Dinàmic (IRD) en mostres de residus urbans orgànics

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Índex

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1. Introducció a la respirometria i a la metodologia experimental

L'estabilitat biològica es defineix com la mesura del grau de descomposició de la matèria orgànica fàcilment biodegradable continguda en una matriu [1]. En el conjunt de les metodologies publicades recentment, tant en bibliografia científica com en normatives estatals o esborranys de directives europees [2], es conclou que la mesura de l'activitat respiratòria (test respiròmetric) d'una matriu orgànica és, sens dubte, el paràmetre més significatiu per determinar la seva estabilitat biològica.

En un ambient eminentment aerobi, els microorganismes fan servir la matèria orgànica del substrat (matriu orgànica) com a font d'energia i com a font de nutrients, consumint oxigen (O_2) per oxidar la matèria orgànica i conseqüentment produir diòxid de carboni (CO_2). Aquest metabolisme aerobi és més intens quant més alta és la presencia de compostos orgànics fàcilment biodegradables en la matriu orgànica analitzada (matriu amb una baixa estabilitat biològica) mentre que, de forma anàloga, es veu atenuat quan la concentració d'aquests compostos és més baixa (matriu amb una alta estabilitat biològica).

Per altra banda, la mesura de l'activitat biològica d'una matriu orgànica es pot considerar, a més d'una mesura d'estabilitat, una mesura de la biodegradabilitat aeròbia d'aquesta matriu, dada que pot ser utilitzada per calcular rendiments de transformació (o estabilització) de matèria orgànica, per establir quin és el tractament biològic més adient per a un determinat residu o com a paràmetre de disseny de les diferents tecnologies basades en processos biològics [3,4].

En relació a la metodologia, i donada l'aparent disparitat de mètodes que es proposen actualment a les normatives dels diferents estats europeus, és convenient assenyalar que els criteris d'estabilitat per a materials de sortida de planta (compost de FORM, bioestabilitzat de Resta o rebuigs) que algunes administracions catalanes i espanyoles estan adoptant en l'actualitat són els proposats en el segon esborrany de "Directiva Biowaste" proposat per la Comissió Europea fa uns anys (*Working document-biological treatment of biowaste, 2nd draft, European Commission*, 2001). Aquesta normativa proposava dos possibles mètodes respiromètrics dinàmics, l'Índex Respiromètric Dinàmic (IRD) i el consum acumulat d'oxigen a 4 dies (AT_4).

Els mètodes dinàmics es basen en la mesura de la velocitat de consum d'oxigen utilitzat per l'oxidació bioquímica dels compostos fàcilment biodegradables continguts en una matriu orgànica, en condicions d'aeració forçada i contínua d'una mostra que es troba confinada en un recipient condicionat amb aquesta finalitat. Com a resultat d'aquests tests s'obté l'índex respiromètric dinàmic (IRD), en les seves diferents expressions proposades per Adani i col·laboradors [5]:

- IRD puntual ($IRD_{puntual}$), calculat en un instant de temps concret.
- IRD màxim (IRD_{max}), que correspon a l'$IRD_{puntual}$ màxim al llarg de tota la determinació.
- IRD mitjà durant l'hora de màxim consum (IRD_{1h}).
- IRD mitjà durant les 24 hores de màxim consum (IRD_{24h}).

A més, aquest sistema també permetria calcular, a partir de la mateixa anàlisi i allargant el temps de mesura, el consum d'oxigen acumulat al llarg del temps, de tal forma que es pot obtenir l'AT_4, índex respiròmetric contemplat en algunes de les normatives actuals (per exemple, Alemanya i Anglaterra).

Aquests mètodes tendeixen a reproduir les condicions de màxima activitat aeròbia en les que la matriu orgànica es pogués trobar en qualsevol operació biològica que s'adoptés per al tractament del material. D'aquesta manera es pot establir, de forma fidedigna, quina seria l'estabilitat del material abans i després del/s corresponent/s tractament/s biològic/s i determinar quina és la seva màxima biodegradabilitat aeròbia a la vegada que es pot determinar quin seria el seu impacte ambiental una vegada s'apliqués al sòl per a una valoració agronòmica o en activitats de restauració, o es disposés com a combustible derivat de residus o en abocador controlat.

L'objectiu del present document és definir de forma detallada el protocol tècnic i metodològic per a la determinació de l'índex respiròmetric dinàmic (IRD) exclusivament en mostres de residus urbans orgànics.

2. Termes i definicions

Compostos fàcilment biodegradables: Materials orgànics que poden ser metabolitzats per microorganismes aerobis en les condicions naturals de la biosfera en un breu període de temps (CEN/TC 343, 2004).

Estabilitat biològica: Mesura del grau de descomposició dels compostos fàcilment biodegradables continguts en una matriu orgànica.

Fase de latència: Interval de temps necessari per a l'aclimatació i/o reactivació de la flora microbiana en unes condicions d'assaig determinades.

Fracció biodegradable: Porció de la matriu que pot ser degradada pels microorganismes, tenint en compte les condicions d'assaig, el tipus de microorganismes presents, les característiques fisicoquímiques i el temps disponible (CEN/TC 343,2004).

Índex respiromètric: Velocitat de consum d'oxigen expressada com mil·ligrams d'O_2 per kilogram de sòlids totals i hora, és a dir, mg $O_2 \cdot$ kg $ST^{-1} \cdot h^{-1}$.

Índex respiromètric dinàmic (IRD): Velocitat de consum d'oxigen expressada com mil·ligrams d'O_2 per kilogram de sòlids totals i hora, és a dir, mg $O_2 \cdot$ kg $ST^{-1} \cdot h^{-1}$. Al ser una determinació dinàmica, ha de ser realitzada en condicions d'aeració forçada i contínua.

Matriu orgànica: material d'origen biològic, excloent els combustibles fòssils i els seus derivats.

Respiròmetre: Conjunt d'instrumentació necessària per dur a terme un test respiromètric.

Sòlids totals: Fracció solida residual d'una mostra que resta desprès de la determinació de la humitat (normalment després d'assecatge a 105°C fins a pes constant).

Test respiròmetric dinàmic: Assaig biològic per a la mesura del consum d'oxigen utilitzat en l'oxidació bioquímica dels compostos fàcilment biodegradables continguts en una matriu orgànica per part dels microorganismes aerobis autòctons, en condicions d'aeració forçada i contínua de la biomassa.

3. Metodologia

3.1 Principi i objectiu del mètode

El mètode per a la determinació de l'índex d'activitat microbiològica aeròbia especificat en el present document tècnic està basat en la mesura de la velocitat de consum d'oxigen per part dels microorganismes autòctons al degradar la matèria orgànica fàcilment biodegradable de la pròpia mostra sota unes condicions d'aeració forçada i temperatura determinades i conegudes.

El resultat de l'anàlisi respiromètrica dinàmica proporciona una mesura de l'estabilitat d'un material o el que és el mateix, la seva biodegradabilitat aeròbia, en unitats de mg $O_2 \cdot kg\ ST^{-1} \cdot h^{-1}$.

3.2 Camp d'aplicació

El mètode pot ser aplicat indistintament per a la mesura de l'estabilitat o biodegradabilitat aeròbia de qualsevol tipus de residu orgànic de procedència municipal, com ara fracció orgànica de recollida selectiva, fracció resta de residus municipals, rebuigs de les plantes de tractament de residus, compost, material bioestabilitzat, etc. La seva aplicació a residus orgànics no porosos com ara fangs de depuradora o certs residus agrícoles i ramaders necessita d'un ajust inicial de la porositat i d'unes condicions específiques d'assaig que es recullen en detall a l'Annex I d'aquest protocol.

3.3 Interferències i causes de possibles errors

Les interferències o els possibles errors poden estar provocats per la presència de determinades substancies tòxiques que puguin condicionar o fins i tot inhibir l'activitat metabòlica dels microorganismes aerobis. Altres factors més comuns d'inhibició poden venir provocats per una anaerobiosi inicial del material, que són solucionats durant l'aclimatació de la mostra i queden reflectits a la fase de latència.

De totes formes, en la llarga experiència del Grup de compostatge de residus orgànics, no s'han detectat mai aquest tipus d'interferències en mostres procedents de residus municipals.

3.4 Mostreig i conservació de la mostra

El procediment de mostreig és diferent en funció de les característiques del material o residu a estudiar. El principi bàsic en què es basa la metodologia de mostreig és el de tenir una mostra el més representativa possible del material que es vol estudiar. Per a mostres on es disposa d'una quantitat superior als 2000 kg, es farà servir el protocol estandarditzat de presa de mostra proposat per l'ARC (Agencia de Residus de Catalunya) per a la caracterització de la Fracció Orgànica dels Residus Municipals. Per a mostres de les que es disposa de menys quantitat o en les que no és possible aplicar aquest protocol (per exemple, piles de material), la mostra final s'obtindrà mitjançant la suma de submostres d'un volum no inferior a 5 litres agafades en diferents punts equidistants de la matriu de material (amb un mínim de 5 punts). Per altra banda, alguns tipus de materials molt específics, com per exemple sortides de digestors anaerobis en unitats de metanització, que són de més difícil manipulació degut a les seves característiques inherents, han de ser tractats de forma específica, agafant diferents submostres en instants de temps diferents per tal de poder aconseguir una mostra final representativa. Alternativament, es podran realitzar altres procediments normalitzats de mostreig en residus sòlids [6]. En aquest cas, s'haurà d'especificar quina ha estat la metodologia utilitzada.

En qualsevol dels casos, la quantitat de mostra total a recollir ha de ser com a mínim de 15 kg. Aquesta mostra, que es considera representativa del material, ha de ser triturada en la seva totalitat fins a tenir un mida de partícula inferior als 15 mm. En algunes mostres (per exemple, compost), pot no ser necessària aquesta trituració, ja que la mostra pot tenir una grandària inferior als 15 mm. De la mostra triturada (si ha estat necessari) se'n prendrà una submostra de 5 kg, que serà la que es processarà als assajos respiromètrics.

L'assaig respiromètric s'ha de dur a terme en el termini de les 48 hores següents a la presa de mostra. Durant aquestes 48 hores, cal mantenir la mostra a 4°C. En cap cas la mostra pot estar més de 12 hores a una temperatura superior a 4°C, per tal d'evitar la biodegradació no quantificada de la matèria orgànica fàcilment biodegradable (fracció més làbil). Si no és possible seguir aquest procediment, la mostra haurà que ser separada en almenys 5 alíquotes de 1000 g i congelada (a una temperatura igual o inferior a -18°C) durant les 12 hores següents al mostreig. Per condicionar la mostra congelada abans de ser analitzada, es deixarà descongelar a temperatura ambient, durant no més de 24 hores i mai sobrepassant els 25°C de temperatura.

3.5 Caracterització de la mostra

Per a cada mostra i abans de realitzar el test respiromètric és necessari determinar el seu contingut en humitat, en percentatge respecte el pes total de mostra (per conèixer el contingut en matèria seca o sòlids totals). També es pot analitzar com a mesura complementària el contingut en matèria orgànica total (equivalent al contingut en sòlids volàtils determinat per calcinació de la mostra).

3.6 Reactor

El test es duu a terme en un flascó Erlenmeyer o recipient de geometria cilíndrica de 500 ml on s'introdueix una malla de niló a la part inferior per tal de permetre la circulació d'aire per sota i a través de la mostra. El reactor es complementa amb un tap de cautxú que tanca de forma hermètica el flascó i que té incorporades dues conduccions que s'introdueixen al reactor (entrada i sortida d'aire) (Figura 1).

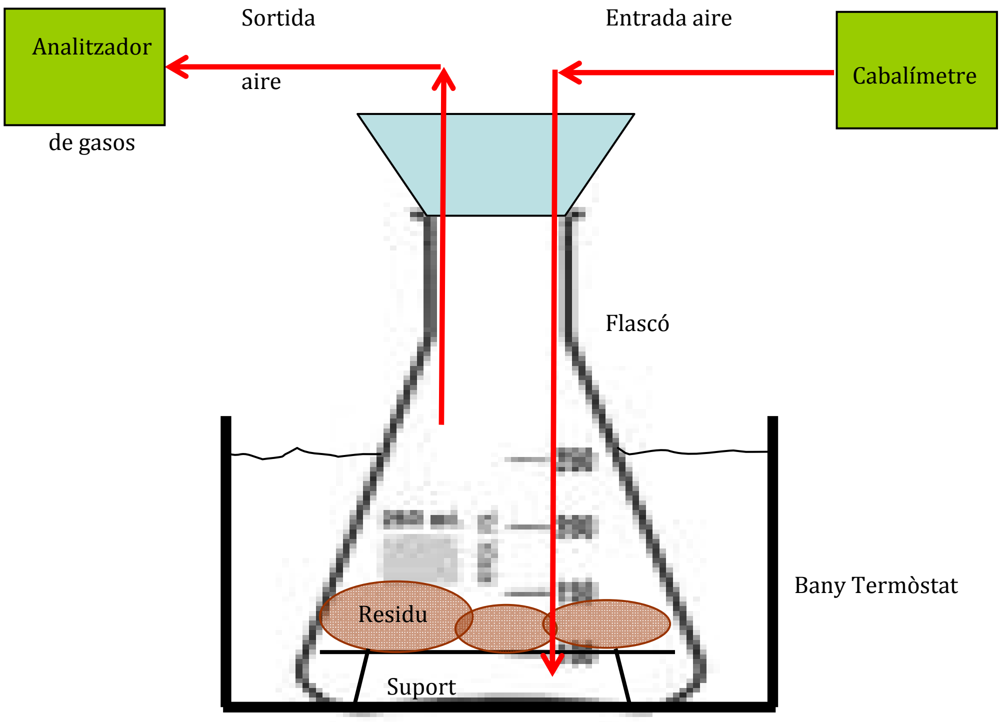

Figura 1: Esquema del reactor.

3.7 Nombre de replicats

El test s'ha de dur a terme realitzant, com a mínim, dos assajos en paral·lel, podent ser necessària la realització de tres assajos (veure punt 3.14).

3.8 Tractament de l'aire

Per tal d'evitar l'assecament de la mostra durant l'experiment, l'aire ha d'estar saturat d'humitat a la temperatura d'operació abans d'entrar al flascó Erlenmeyer, per evitar l'assecament de la mostra durant l'assaig. Una possibilitat, que és altament recomanable, és fer bombollejar l'aire per un flascó previ ple d'aigua a la temperatura d'operació (Figura 2).

Per altra banda, normalment és necessari eliminar la humitat de l'aire de sortida, abans d'enviar-lo als analitzadors de gasos, mitjançant un assecador, que pot utilitzar diferents materials absorbents de la humitat (gel de sílice, tamisos moleculars, etc.) (Figura 2).

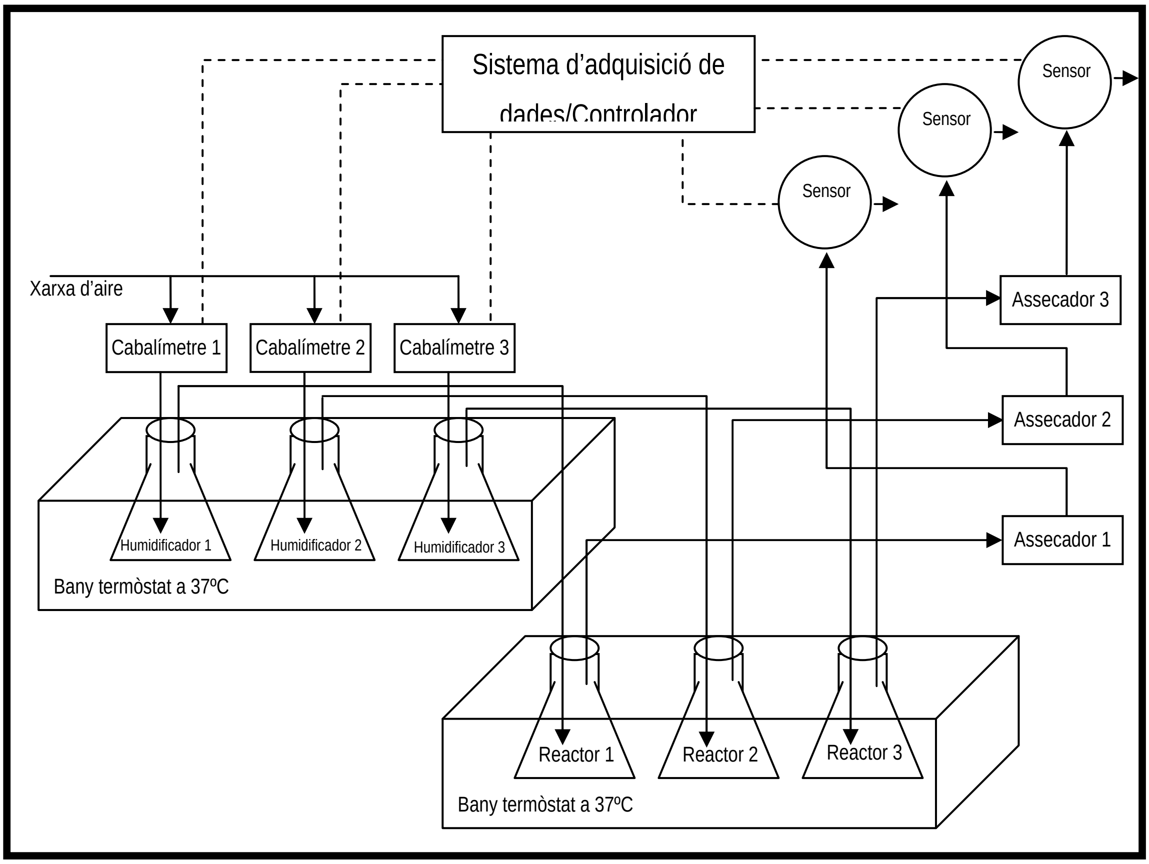

Figura 2: Esquema d'un respiròmetre dinàmic.

3.9 Regulació del cabal d'aire

El cabal d'aire ha d'estar regulat de forma molt precisa mitjançant cabalímetres o equips similars que assegurin una precisió mínima de ± 0,2 ml/min. A més, és necessari assegurar que el sistema de conduccions, connexions i instrumentació és totalment estanc. El cabal d'aire subministrat és una mesura necessària i imprescindible per al càlcul de l'índex respiromètric i per tant, ha de ser monitorat i enregistrat en continu durant tot l'assaig (Figura 2).

3.10 Temperatura d'assaig

L'assaig es duu a terme a una temperatura constant de 37°C, que s'ha d'assegurar mitjançant banys termòstats o altres dispositius (Figura 2). A aquesta temperatura s'assegura la màxima activitat biològica.

3.11 Instrumentació

Aquest test respiromètric es basa en la mesura del consum d'oxigen. Aquesta mesura indirecta es realitza mitjançant dues mesures directes: el cabal d'aire alimentat en continu i la concentració d'oxigen a la sortida del reactor. Per tant, és necessària la implantació d'un sensor d'oxigen amb una alta sensibilitat que sigui capaç de mesurar la concentració d'oxigen d'un corrent continu d'aire.

En qualsevol cas, mitjançant el sistema d'adquisició de dades s'han de registrar les dades de:

i. Cabal d'aire alimentat
ii. Concentració d'oxigen a la sortida del reactor

També és necessari conèixer amb exactitud la concentració de l'aire a l'entrada del reactor, que normalment serà la típica de l'aire atmosfèric.

3.12 Procediment experimental

3.12.1 Preparació de la mostra

Abans d'iniciar el test, és necessari assegurar una humitat mínima de la mostra del 50%. Per tal d'assolir aquesta humitat s'afegirà aigua destil·lada al material quan sigui necessari, integrant i homogeneïtzant l'aigua en el material. En mostres procedents de residus municipals, no és necessari un ajust de la porositat; de totes formes, cal assegurar que en la manipulació del material no es provoquin compactacions excessives que provoquin una pèrdua significativa de la porositat del material. En el cas que les mostres presentin una mancança important de porositat (cas típic de fangs i digestats) cal seguir el procediment d'ajust d'aquest paràmetre explicat a l'Annex I d'aquest protocol.

3.12.2 Inici del test respiròmetric

3.12.2.1 Verificació de la instrumentació

Efectuar una verificació de la instrumentació abans de començar el test:

i. Assegurar una pressió mínima de l'aire de xarxa (que asseguri el cabal d'aire necessari al reactor), d'acord amb l'equip utilitzat i els seus requeriments específics.
ii. Comprovar el correcte funcionament del cabalímetre de mesura del cabal d'aire subministrat al reactor.
iii. Realitzar el calibrat del sensor d'oxigen (mitjançant patrons estàndard) amb la periodicitat corresponent (segons especificacions de l'equip).
iv. Assegurar l'estanqueïtat del sistema.

3.12.2.2 Càrrega del reactor

Introduir en el flascó Erlenmeyer, amb la malla de niló incorporada, una quantitat de mostra coneguda i prèviament identificada entre 100 i 150 g (en pes humit i després de la correcció de la humitat). La mostra no es pot pressionar ni comprimir a l'introduir-la al reactor, de cara a que la seva porositat es mantingui en un nivell adequat per a la realització de l'assaig. La càrrega del reactor ha de ser gradual (en petites quantitats) i en forma de partícules disgregades.

3.12.2.3 Posada en marxa

Adaptar el tap de cautxú al reactor i iniciar l'aeració de la mostra amb un cabal d'aire inicial de 0,3 L·kg mostra^{-1}·min^{-1}. El cabal d'aeració ha de ser continu i pot haver-se de regular durant el test per tal d'assegurar una concentració mínima del 10% d'oxigen (v/v) a la sortida del reactor. Els cabals utilitzats tampoc han de ser excessius de forma que es mantingui una diferència significativa entre els valors de concentració d'oxigen a l'entrada i la sortida del material. Simultàniament s'ha d'iniciar el sistema d'adquisició de dades.

3.12.3 Evolució i durada de l'assaig

L'evolució típica de la corba de l'índex respiromètric dinàmic es mostra a la Figura 3. A la figura estan representats els valors de l'índex IRD expressat com mitjana dels valors enregistrats durant les 24 hores de màxima activitat. Aquesta mitjana de valors es considera mòbil, ja que es calcula com la mitjana dels valors que donin la màxima activitat al llarg de 24 hores i centrada en el punt de màxima activitat, independentment de en quin temps tingui lloc aquesta activitat, aspecte que serà funció del tipus de residu.

Com evolució típica, es pot dir que normalment apareix una fase inicial que s'anomena fase de latència (Fase A), la durada de la qual és variable i funció del tipus de mostra i del tractament previ que ha rebut (emmagatzematge mitjançant congelació o a 4°C). Aquesta fase de latència pot durar des d'unes poques hores fins al voltant d'un dia. En algunes ocasions (especialment en mostres analitzades en el termini de les 48 hores següents a la presa de mostra), aquest temps de latència pot arribar a ser inapreciable, degut a que la mostra està en les condicions òptimes per a l'anàlisi (els microorganismes estan aclimatats a les condicions d'assaig i actius).

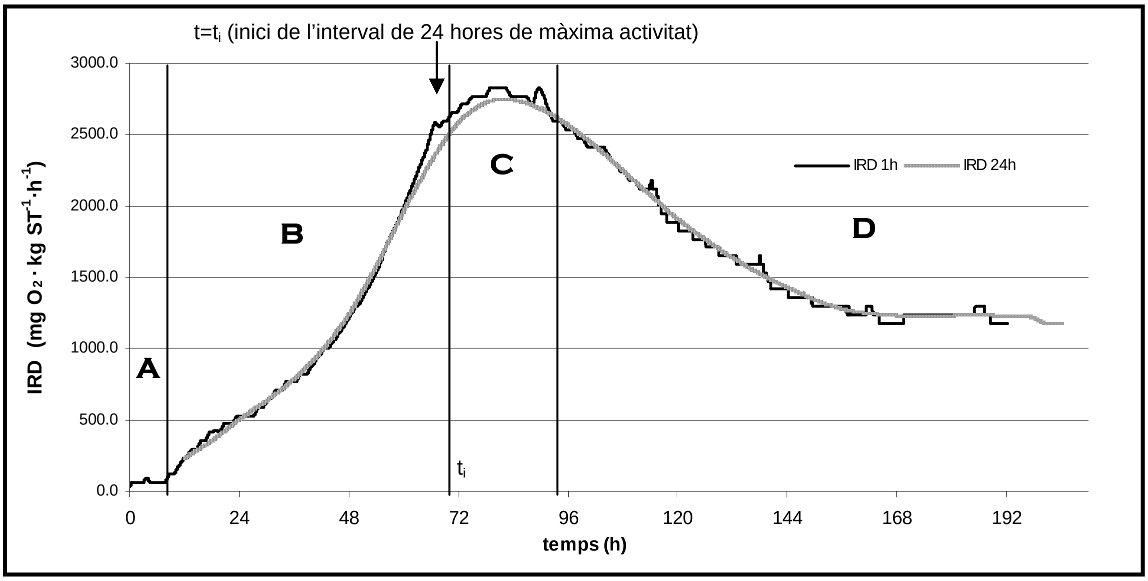

Figura 3: Corba d'evolució típica de l'índex respiromètric.

A mesura que avança l'assaig, les condicions fisicoquímiques de la matriu orgànica afavoreixen el desenvolupament de les poblacions microbianes i, en conseqüència, l'evolució de la corba esdevé de tipus exponencial (Fase B).

La tercera fase (Fase C) s'inicia amb la progressiva disminució de la presència dels compostos fàcilment biodegradables (compostos làbils). Aquesta reducció es veu reflectida en un alentiment de l'activitat de degradació microbiològica i en l'establiment d'una situació on els factors de multiplicació i inactivació dels microorganismes es troben en equilibri entre ells. En aquesta fase, que és on es troba el t_i (temps d'inici de l'interval de 24 hores de màxima activitat), l'IRD canvia la tendència creixent inicial per una decreixent, i presenta uns valors gairebé constants.

Finalment la quarta i última fase (Fase D) descriu una progressiva disminució del valor de l'IRD, evidenciant l'atenuació de l'activitat microbiològica a conseqüència de la reducció dels compostos fàcilment biodegradables.

La durada total del test és variable i depèn de diversos condicionants que poden afectar la dinàmica de l'assaig, alentint-lo o afavorint-lo. Aquests condicionants són, per exemple, el tractament de la mostra per a la seva conservació previ a l'assaig, ja que la congelació de la mostra suposa una major durada de la fase de latència, i les característiques intrínseques de la mostra, com la seva procedència, edat, composició bioquímica, etc.

De forma general, i en mostres procedents de residus municipals, el valor de l'IRD màxim s'hauria d'obtenir en tots els casos abans de les 120 hores d'assaig. Encara que temps d'assaig més llargs són admissibles, és necessari considerar que aquest fet pot significar que la mostra no està condicionada de forma correcta i, per tant, la màxima activitat biològica mesurada (que reflectirà la biodegradabilitat o l'estabilitat del material) no es correspon amb la que s'obtindria en les condicions òptimes d'assaig. El motiu principal d'un excessiu temps d'assaig sol ser la manca d'estructura del material i, per tant, d'una baixa porositat, que dificulta una difusió deficient de l'oxigen en la matriu (veure Annex I a aquest protocol).

3.13 Càlcul de l'Índex Respiromètric Dinàmic

El valor final de l'IRD s'obté seguint la següent seqüència de càlculs:

i. Càlcul de l'IRD puntual a l'instant de l'adquisició discreta de les dades (Equació 1)

$$IRD_{puntual} = \frac{(O_{2,i} - O_{2,o}) \times Q_L \times 31{,}98 \times 60 \times 1000^a}{1000^b \times 22{,}4 \times ST} \qquad \text{Equació 1}$$

On:

- $IRD_{puntual}$: Índex respiròmetric dinàmic expressat en mg O_2 · kg $ST^{-1} \cdot h^{-1}$
- $(O_{2,i} - O_{2,o})$: Diferència de concentració d'oxigen entre l'entrada i la sortida del reactor expressada en tant per u
- Q_L: Cabal d'aire (ml/min) mesurat en condicions normals (1 atm i 273 K) (si no es troba en aquestes condicions cal fer la correcció pertinent)
- 31,98: Pes molecular de l'oxigen
- 60: Factor de conversió (minuts a hores)
- 1000^a: Factor de conversió (g a mg)
- 1000^b: Factor de conversió (ml a l)
- 22,4: Volum en litres que ocupa un mol d'un gas ideal en condicions normals
- ST: Quantitat de sòlids totals de mostra carregats al reactor (kg)

ii. Càlcul de l'IRD_{24h} al llarg de l'experiment (Equació 2)

$$IRD_{24h} = \frac{\sum_{t=ti}^{ti+24h} IRD_{puntual}}{m} \qquad \text{Equació 2}$$

On:

- IRD_{24h}: Índex respiròmetric dinàmic mitjà durant les 24 hores de màxim consum expressat en mg $O_2 \cdot$ kg $ST^{-1} \cdot h^{-1}$
- $\sum_{t=ti}^{ti+24h} IRD_{puntual}$: Sumatori dels valors d'$IRD_{puntual}$ mesurats durant les 24 hores de màxim consum (t_i és el temps a partir del qual es computen les 24 hores de màxima activitat)
- m: Nombre de valors d'$IRD_{puntual}$ calculats durant les 24 hores de màxim consum. Aquest valor estarà determinat per la freqüència amb la que el sistema d'adquisició de dades registri les diferents variables mesurades (una freqüència d'un valor cada 5 minuts es considera adequada per a la realització dels càlculs).

3.14 Expressió dels resultats

Es considera que el valor més adequat i representatiu per definir l'estabilitat o activitat d'un residu municipal és l'IRD_{24h}. El resultat s'ha d'expressar en mg $O_2 \cdot$kg $ST^{-1} \cdot h^{-1}$, com a mitjana de, com a mínim, dos replicats i amb la corresponent desviació estàndard. En el cas que la desviació dels dos replicats sigui superior al 20%, aleshores caldrà afegir un tercer replicat.

La presentació final dels resultats ha d'incloure:

1) **Descripció de la mostra**: procedència, data de presa de mostra, edat de la mostra, tipus de mostra i descripció.
2) **Contingut en matèria seca**: d'acord amb els procediments estandarditzats.
3) **Valor de l'IRD_{24h}**: expressat en mg $O_2 \cdot$kg $ST^{-1} \cdot h^{-1}$.
4) **Nombre de replicats i desviació estàndard**.

5) Opcionalment, altres propietats de la mostra com el contingut en sòlids volàtils, contingut en nitrogen i altres propietats que es considerin rellevants, i que puguin tenir relació amb l'estabilitat de la mostra.

4. Referències

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5. Annexos

5.1 Annex I:

Procediment per a la determinació de l'estabilitat biològica mitjançant l'índex respiromètric dinàmic (IRD) en mostres de fangs procedents d'estacions depuradores d'aigües residuals (EDARs) i altres residus de baixa porositat

Modificacions al protocol original

A) Modificació del punt "3.12.1 Preparació de la mostra".

3.12 (b) Procediment experimental

3.12.1 (b) Preparació de la mostra

En mostres amb elevada humitat (70-80%) i una porositat molt baixa és necessari un ajust d'aquesta última per tal d'assegurar una bona difusió del aire en la matriu orgànica. Per augmentar la porositat es mescla la mostra a analitzar amb un agent estructurant, que actua com un material inert durant el temps d'assaig considerat, mitjançant el següent procediment:

3.12.1.1 (b) Preparació de l'agent estructurant
Com estructurant es fa servir petits trossos d'un material inert, concretament baietes absorbents (Spontex Iberica) amb una llargada de 2 cm i una amplada màxima de 1 cm.

3.12.1.2 (b) Preparació de la mescla
Posteriorment, en un recipient prèviament tarat, es realitzarà la mescla del material amb una relació estructurant:fang de 1:10 en pes. Els pesos recomanats aproximats són: 10 grams d'estructurant i 100 grams de fang.

B) Modificació del punt "3.12.2.2 Càrrega del reactor"

3.12b Procediment experimental

3.12.2b Inici del test respiròmetric

3.12.2.2b Carga del reactor

Introduir en el flascó Erlenmeyer, amb la malla de niló incorporada, la totalitat de la mescla fang:estructurant realitzada. Al tractar-se de mostres de difícil manipulació, és possible que part del fang es quedi enganxat a les parets del recipient original i no pugui ser introduït al reactor (no succeeix el mateix amb l'agent estructurant, el qual cal assegurar que s'hagi introduït completament). Cal per tant, quantificar de forma exacta el fang que no ha pogut ser introduït al reactor mitjançant la diferencia amb la tara del recipient buit original, i tenir el pes real del material amb el qual es realitza l'assaig respiromètric.

C) Modificació del punt "3.13 Càlcul de l'Índex Respiromètric"

3.13 Càlcul de l'Índex Respiromètric Dinàmic

El valor final de l'IRD s'obté seguint la següent seqüència de càlculs:

i. Càlcul de l'IRD puntual a l'instant de l'adquisició discreta de les dades (Equació 1)

$$IRD_{puntual} = \frac{(O_{2,i} - O_{2,o}) \times Q_L \times 31{,}98 \times 60 \times 1000^a}{1000^b \times 22{,}4 \times ST} \qquad \text{Equació 1}$$

On:

- $IRD_{puntual}$: Índex respiròmetric dinàmic expressat en mg $O_2 \cdot$ kg $ST^{-1} \cdot h^{-1}$
- $(O_{2,i} - O_{2,o})$: Diferència de concentració d'oxigen entre l'entrada i la sortida del reactor expressada en tant per u
- Q_L: Cabal d'aire (ml/min) mesurat en condicions normals (1 atm i 273 K) (si no es troba en aquestes condicions cal fer la correcció pertinent)
- 31,98: Pes molecular de l'oxigen

- 60: Factor de conversió (minuts a hores)
- 1000^a: Factor de conversió (g a mg)
- 1000^b: Factor de conversió (ml a l)
- 22,4: Volum en litres que ocupa un mol d'un gas ideal en condicions normals
- ST: Quantitat de sòlids totals de mostra (sense tenir en compte la part corresponent a l'agent estructurant) carregats al reactor (kg)

ii. Càlcul de l'IRD_{24h} al llarg de l'experiment (Equació 2)

$$IRD_{24h} = \frac{\sum_{t=ti}^{ti+24h} IRD_{puntual}}{m} \qquad \text{Equació 2}$$

On:

- *IRD_{24h}*: Índex respiròmetric dinàmic mitjà durant les 24 hores de màxim consum expressat en mg $O_2 \cdot kg\ ST^{-1} \cdot h^{-1}$
- $\sum_{t=ti}^{ti+24h} IRD_{puntual}$: Sumatori dels valors d'$IRD_{puntual}$ mesurats durant les 24 hores de màxim consum (t_i és el temps a partir del qual es computen les 24 hores de màxima activitat)
- m: Nombre de valors d'$IRD_{puntual}$ calculats durant les 24 hores de màxim consum. Aquest valor estarà determinat per la freqüència amb la que el sistema d'adquisició de dades registri les diferents variables mesurades (una freqüència d'un valor cada 5 minuts es considera adequada per a la realització dels càlculs).