UNIVERSITAT DE
BARCELONA

Nutrient recovery and improvement of anaerobic digestion process by low grade magnesium oxide application

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Programa de Ingeniería y tecnologías avanzadas

Línea – Biotecnología Ambiental

Tesis Doctoral

Nutrient recovery and improvement of anaerobic digestion process by low grade magnesium oxide application

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Barcelona 2015

Index

Annexes

INTRODUCCIÓN GENERAL

Problemática de los purines de cerdo

La actividad agrícola ha sido tradicionalmente una actividad familiar que ha combinado la explotación de cultivos y la ganadería, donde las deyecciones ganaderas eran utilizadas como fertilizantes. Sin embargo, a finales del siglo XX las exigencias del mercado, el desarrollo de material genético y equipo agrícola y la disponibilidad de pienso animal barato causo la especialización de los agricultores y ganaderos. En consecuencia, el número de granjas y el número de animales en ellas aumentó considerablemente dando lugar a la ganadería intensiva. En este sentido, la producción porcina en los países de la UE-27, se ha incrementado de manera importante las últimas dos décadas, alcanzando, en 2006, las 22 millones de toneladas de carne [1]; que generaron casi 300 millones de toneladas de purines de cerdo (ver Tabla 1.1). Consecuentemente, la cantidad de purines es excedentaria en muchas regiones, donde las explotaciones ganaderas se han desvinculado de las agrícolas, de modo que no se dispone de terrenos de cultivo suficiente para reutilizar las deyecciones ganaderas como fertilizante; es decir, se ha superado la capacidad de aceptación del medio [2].

De manera ilustrativa la Figura 1.1 muestra el proceso de digestión de los alimentos por parte de los cerdos, en esta se observa que en el proceso los cerdos no metabolizan todos los nutrientes, de modo que una parte muy significativa se excreta en las deyecciones [1]. Las características físicas del purín de cerdo, así como su composición, presentan variaciones importantes en función de la especie de producción, el tipo de explotación, el tipo de alimentación y el grado de dilución de las deyecciones en agua [4]. Por otro lado, la problemática ambiental ocasionada por su acumulación y/o mala gestión se debe a las siguientes propiedades de los purines de cerdo: (i) alto contenido de materia orgánica, (ii) alto contenido de nitrógeno, (iii) generación de gases contaminantes y (iv) presencia de metales pesados [5].

Tabla 1.1 Cantidad estimada de estiércol animal producida en EU-27 (adaptada de Holm-Nielsen y col. [3]).

País	**Cerdos (1000 Cabezas)**	**Ganadería (1000 granjas)**	**Purín (10^6 toneladas)**
Austria	3,125	261	6
Bélgica	6,332	529	12
R. Checa	2,877	240	5
Dinamarca	13,466	1124	25
Francia	15,020	1254	28
Alemania	26,858	2242	49
Grecia	1,000	83	2
Hungría	4,059	339	7
Irlanda	1,758	147	3
Italia	9,272	774	17
Holanda	11,153	931	20
Polonia	18,112	1512	33
Portugal	2,348	196	4
Rumania	6,589	550	12
Eslovaquia	1,300	109	2
España	25,250	2107	46
suiza	1,823	152	3
Reino Unido	4,851	405	9
Otros	5,337	458	12
UE-27	160,53	13,399	295

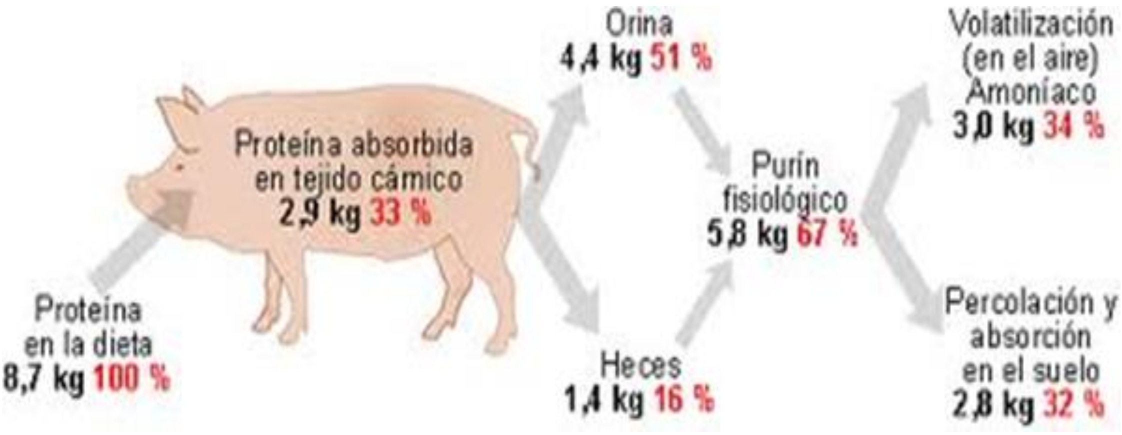

Figure 1.1 Consumo, utilización y pérdidas de proteínas en la producción de cerdo con peso vivo final de 108 kg [6].

La Tabla 1.2 muestra los principales efectos que pueden originarse y deben tenerse en consideración en relación con la actividad ganadera intensiva. En este sentido, la gran problemática ambiental generada por la producción y acumulación de purines de cerdo ha hecho desarrollar múltiples tecnologías para reducir el impacto ambiental de estos [7–9]. La idoneidad de un determinado proceso de tratamiento dependerá de la zona geográfica, la legislación vigente, la aceptación social, la calidad del producto obtenido y los costes económicos asociados [10]. En todos los casos, el objetivo principal es aumentar la capacidad de gestión y tratamiento de residuos.

Tabla 1.2 Contaminación originada por exceso de purines (adaptada de Danés y col. [2]).

	Causa	Consecuencia
Contaminación del medio acuático	• Abono de campos en épocas no óptimas para los cultivos • Lixiviación • Vertidos incontrolados	• Eutrofización • Enfermedades como la metahemoglobina o mal azúcar. • Cáncer de estómago por nitratos presentes en las aguas.
Contaminación del suelo	• Vertidos incontrolados en exceso	• Desequilibrio por acumulación de nutrientes (N,P) y/o metales pesados. • Disminución de la producción agrícola. • Fitotoxicidad. • Perdida de nutrientes por evaporación o filtración.
Contaminación del aire	• Evaporación de NH_3, NO_x, H_2S, COVs*.	• Malos Olores. • Lluvia ácida. • Efecto invernadero.

*COVs : compuestos orgánicos Volátiles.

Las características básicas de las tecnologías más utilizadas y/o investigadas para tratar los purines se resumen en la Tabla 1.3. Siempre teniendo en cuenta que la elevada cantidad de agua del purín, y los efectos que esta tiene en el incremento de los costes de transporte, obligan a que la planta de tratamiento deba situarse cerca del punto de generación.

Tabla 1.3 Operaciones aplicables al tratamiento de purines de cerdo (Flotats y col. [11])

Proceso	Fracción	Objetivo
Balsas de homogeneización, estercoleros	T, S, L*	• Regular la producción continua al consumo estacional de cultivos. • Regular entradas discontinuas a las plantas de tratamiento. • Reducir patógenos.
Separación de fases	T	• Separar para proporcionar específicas de tratamiento, transporte o aplicación a la fracción S o L resultante.
Aplicación de encimas y bacterias a balsas	T	• Aumentar la concentración de sólidos. • Transformar N amoniacal a orgánico.
Nitrificación	L	• Oxidar N amoniacal a nitrito/nitrato.
Des-nitrificación	L	• Transformar N nitrito/nitrato a N2. • Eliminar materia orgánica fácilmente biodegradable.
Descomposición aeróbica heterótrofa	L, T	• Eliminar materia orgánica.
Digestión anaeróbica	T, L, S	• Producir biogás. • Eliminar materia orgánica. • Higienizar.
Compostaje	S	• Eliminar/estabilizar materia orgánica. • Higienizar. • Obtener abono orgánico de calidad.
Reducción biológica del fósforo	L	• Transferir P soluble a fase biológica sedimentable. • Eliminar materia orgánica fácilmente degradable.
Precipitación química	L	• Transferir algunos componentes a fase sedimentable. • Separar P (apatitas, estruvita).
Evaporación/ Peletización	S	• Separar agua. • Reducir volumen.
Evaporación/ Concentración	L	• Separar agua. • Reducir volumen.
Stripping/ Absorción	L	• Recuperar N amoniacal.
Higienización térmica	T	• Eliminar y/o inactivar patógenos. • Hidrólisis térmica.
Dosificación de aditivos	T, S, L	• Modificar la composición para adecuarla a cultivo o posibilitar otros procesos.
Ozonización	L	• Oxidación de compuestos orgánicos recalcitrantes.
Filtración en membrana/ ósmosis inversa	L	• Separar sales y reducir la conductividad.

***T:** residuo íntegro**; S:** fracción sólida**; L:** fracción líquida

Indistintamente de la zona de actuación, la gestión y tratamiento de residuos tiene actualmente el siguiente orden jerárquico [12]:

- La minimización de generación de residuos y de su peligrosidad.
- La reutilización de los residuos.
- El reciclaje y la valorización energética del residuo.
- La disposición en vertedero.

La digestión anaeróbica destaca entre todos las tecnologías, debido a que es un proceso biológico capaz de estabilizar parcialmente la materia orgánica, reducir la cantidad de patógenos, reducir los malos olores y disminuir las emisiones de gases efecto invernadero, a la vez que se produce biogás como fuente de energía renovable (aproximadamente 21.945 kJ m^{-3}) y un digerido más apto para ser aplicado como fertilizante [13].

En este aspecto cabe mencionar que, la utilización del biogás como fuente de energía va aumentando día a día, según se va dando mayor importancia a las energías renovables como alternativa a las fuentes tradicionales de energía [14,15]. El biogás puede utilizarse en prácticamente las mismas aplicaciones energéticas desarrolladas para el gas natural, como la generación de calor mediante combustión, generación de electricidad, integración en la red de gas natural, combustible para vehículos y combustible en fuel cells, etc. [16,17]. A modo de ejemplo, la Figura 1.2 muestra un esquema básico de una planta de digestión anaerobia para deyecciones ganaderas.

En el informe “EurObserv´ER, 2009” se estimaba que en el año 2009 se produjeron en Europa 7.5 millones de toneladas equivalentes de petróleo (tep) procedentes del biogás [18]. Siendo la energía producida en plantas descentralizadas de tratamiento de residuos agropecuarios, de residuos municipales y centralizadas de co-digestión, las que presentaron un aumento más significativo en el periodo 2006-2008.

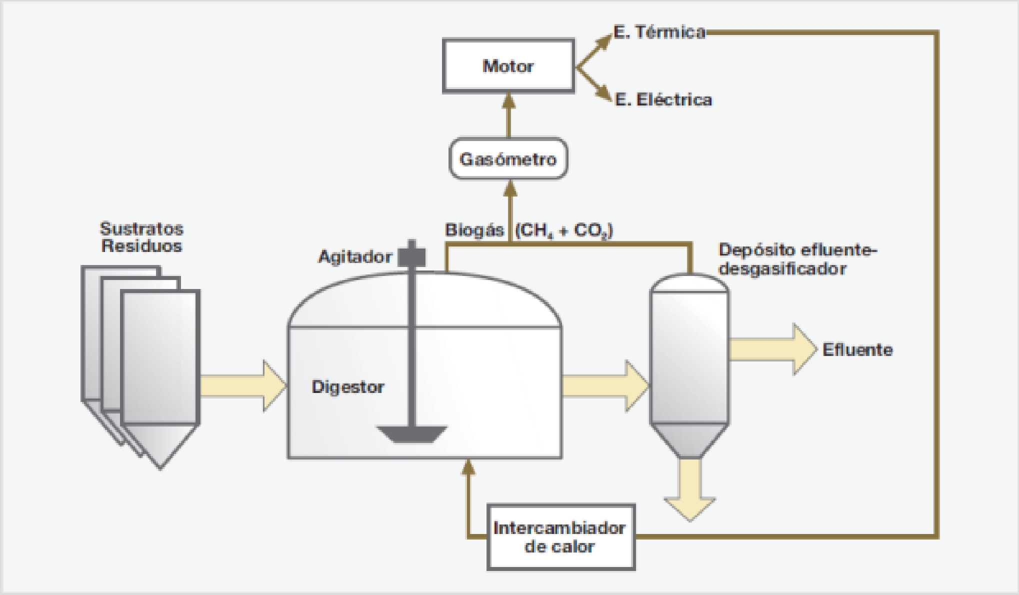

Figura 1.2 Esquema de una instalación de digestión anaeróbica para residuos ganaderos (www.arc-cat.net).

Digestión anaeróbica

La digestión anaeróbica es una tecnología que permite estabilizar todos aquellos residuos con un elevado contenido de materia orgánica biodegradable: agrícolas, ganaderos, aguas residuales urbanas e industriales, fangos procedentes de estaciones depuradoras o la fracción orgánica de los residuos municipales entre otros [19]. Concretamente, el proceso anaeróbico consiste en la descomposición, en ausencia de oxígeno, de la materia orgánica como consecuencia de las interacciones metabólicas entre distintos grupos de microorganismos [20]. Los productos finales que se obtienen son un residuo digerido estabilizado y biogás, formado principalmente por metano (CH_4), dióxido de carbono (CO_2) y otros gases, en menor proporción, como ácido sulfhídrico (H_2S), amoniaco (NH_3) e hidrógeno (H_2). Las ventajas de incluir un proceso de digestión anaeróbica en el proceso de tratamiento del purín se citan brevemente en la Tabla 1.4.

Tabla 1.4 Ventajas del proceso de digestión anaerobia (adaptada de Flotats y col. [11])

FACTOR	VENTAJAS DE LA DIGESTION ANAEROBIA
Variabilidad de la composición	Homogenización de la composición, más intensa cuan mayor es el tiempo de retención hidráulico.
Malos olores y COVs	Eliminación de ácidos grasos volátiles (AGV) y otros compuestos fácilmente degradables. La materia orgánica resultante es lentamente o difícilmente degradable, los purines digeridos no presentan olor desagradable y son un producto más estable.
Reducción de la materia orgánica total, mineralización	Reducción de la materia orgánica degradable y mantenimiento de las condiciones de nutrientes. Transformación de N orgánico en amoniacal.
Distribución de partículas y de fracción soluble	Homogenización en la distribución de partículas, lo que favorece el diseño y la aplicación de procesos posteriores al de secado. Hidrólisis de partículas pequeñas y coloidales, y reducción de orgánicos solubles, con lo cual se facilita la separación entre fases solubles y en suspensión.
Consistencia	Consistencia pastosa de la fracción sólida del purín digerido, lo que favorece su manipulación y peletización.
Alcalinidad	Disminución significativa de la relación de alcalinidad. Aportación de alcalinidad para favorecer un proceso posterior de nitrificación. A su vez, y debido a la reducción de materia orgánica, el consumo energético en este proceso será inferior al de la nitrificación de la fracción líquida de purines frescos.
Balance Energético	Balance energético positivo y proceso productor neto de energía renovable. Contribuye a disminuir las necesidades externas de energía para procesos térmicos posteriores. Permite el tratamiento de mezclas con otros residuos para optimizar la producción energética (co-digestión), y facilitar la gestión integral de residuos orgánicos en la zona de aplicación del plan (cogestión).
Emisión de gases efecto invernadero	El proceso contribuye a la disminución en la generación de gases de efecto invernadero si el metano producido sustituye una fuente no renovable de energía.

Etapas del proceso

El proceso de digestión se puede representar esquemáticamente de acuerdo con la siguiente reacción química (Ec. 1.1),

$$C_mH_nO_p \rightarrow r\ CH_4 + s\ CO_2 + H_2O \qquad \text{(Ec. 1.1)}$$

donde r + s=m (Baraza y col. [21]). Esta ecuación simplifica una serie de etapas en serie-paralelo donde pueden participar más de 300 especies bacterianas y cuyo esquema se muestra en la Figura 1.3:

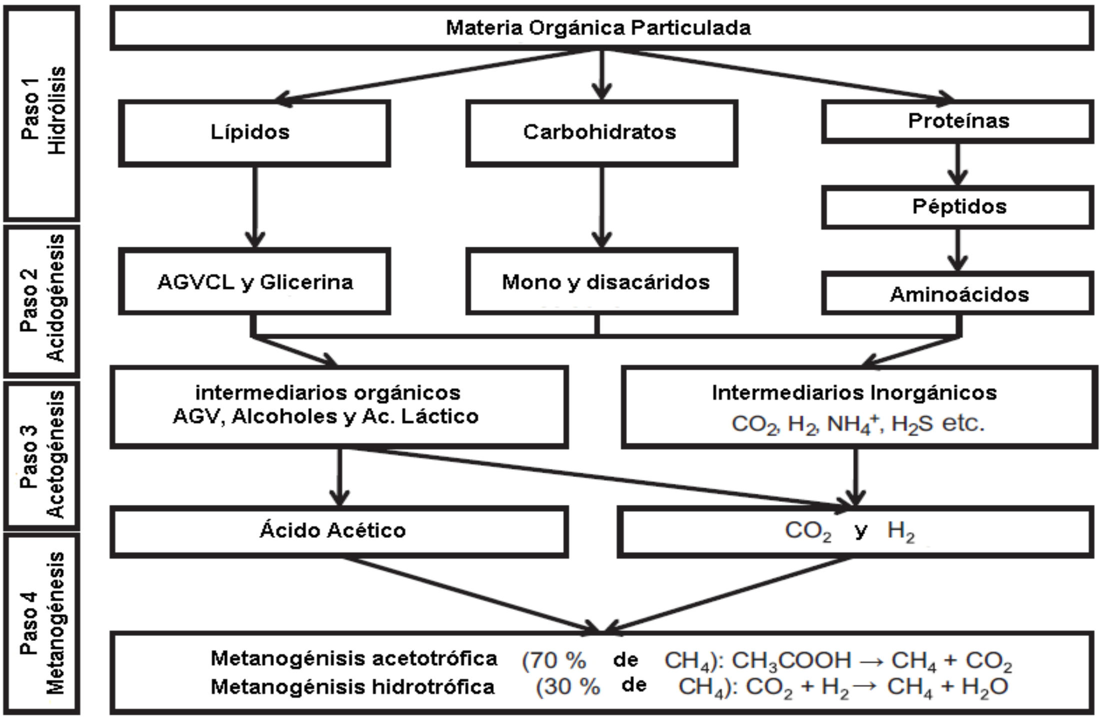

Figura 1.3 Esquema de los diferentes procesos de la conversión anaeróbica de residuos orgánicos (adaptado de Madsen y col. [22]).

El proceso se inicia con la desintegración de las moléculas complejas de sustratos a inertes y partículas de carbohidratos, proteínas y lípidos, gracias a procesos físicos y a las enzimas extracelulares producidas por los microorganismos facultativos [23]. A continuación, tiene lugar la hidrólisis enzimática de las partículas de carbohidratos, proteínas y lípidos a azúcares, aminoácidos y ácidos grasos de cadena larga (AGCL) respectivamente; compuestos solubles, que posteriormente serán metabolizados por las bacterias en el interior de la célula. La degradación de los azúcares y los aminoácidos por microorganismos acidógenos produce ácidos grasos volátiles (AGV), hidrógeno y dióxido de carbono. Los AGV y los AGCL son convertidos por los microorganismos acetogénicos en ácido acético (CH_3COOH), H_2 y CO_2. Finalmente, el H_2 y CO_2 producidos a lo largo del proceso son usados por los microorganismos metanógenos hidrogenotróficos para producir CH_4, mientras que el CH_3COOH es usado por metanógenos acetoclásticos para producir CH_4 y CO_2 [24]. Como se puede observar la digestión anaeróbica es un proceso complejo donde existen muchas variables que pueden afectar al proceso; a continuación se explican de forma resumida los principales parámetros que afectan la producción de biogás, el porcentaje de CH_4 y el porcentaje de materia orgánica degradada.

Factores físicos

- *Tiempo de residencia hidráulico y velocidad de carga orgánica*

El tiempo de residencia hidráulico (TRH) se define como la relación del volumen del reactor con el caudal diario efectivo. TRH altos implican flujos bajos pero una elevada degradación de la fracción orgánica, mientras que TRH muy bajos provocan el arrastre de las bacterias metanogénicas que son las de más lento crecimiento, provocando la acumulación de AGV, lo cual inhibiría el proceso de metanización. Por otro lado, la velocidad de carga orgánica es la cantidad de materia orgánica por unidad volumétrica de reactor y unidad de tiempo; una alta carga orgánica en ausencia de inhibidores genera una alta producción de biogás, pero a la vez esto puede generar acumulación de AGV y desestabilización del sistema.

- *Temperatura*

Los rangos de trabajo se definen como psicrófilo (por debajo de 25ºC), mesófilo (entre 25 y 45 ºC) y termófilo (entre 45 y 60 ºC). De forma general, a elevadas temperaturas las tasas de reacciones químicas y biológicas son más rápidas que a bajas temperaturas. La cinética de la reacción de los procesos biológicos depende de la velocidad de crecimiento de los microorganismos responsables, que a su vez es dependiente de la temperatura.

- *Agitación*

Esta puede ser mecánica, hidráulica o neumática. El objetivo de la agitación es poner en contacto el residuo y productos de la degradación con la flora bacteriana, favorecer la salida de gases, prevenir la formación de espuma, evitar la formación de zonas muertas y mantener la temperatura uniforme en el reactor.

- *Características del sustrato*

La velocidad de conversión del proceso dependerá de las concentraciones de sustrato y de biomasa activa, siendo las características fisicoquímicas del substrato a metanizar las que determinaran la elección de la tecnología y del tipo de digestor a utilizar; cabe destacar parámetros como la solubilidad, granulometría, humedad, biodegradabilidad, concentración de substrato en la corriente de entrada al digestor, estructura y composición química.

Factores Químicos

- *pH y alcalinidad*

Para que el proceso anaeróbico se desarrolle de forma satisfactoria, el pH debe estar alrededor de 7, presentando problemas importantes si el pH está por debajo de 6 o por encima de 9. La alcalinidad es una medida de la capacidad tapón del medio; las principales especias con capacidad *buffer* en el sistema de digestión anaerobia son los Ácidos Grasos Volátiles (AGV) y el bicarbonato. La alcalinidad total (TA) es determinada como la medida de titulación a un pH final de 4.3. Esta incluye ambas especies, pero este no puede ser considerado un parámetro de control ya que la inestabilidad del proceso puede incrementar los AGV y disminuir la concentración de bicarbonato, lo cual resulta en un valor constante de TA, por lo cual es necesario determinar la alcalinidad parcial (PA) como medida de la titulación a un pH final de 5.75, la cual indica la carga de bicarbonato presente [25].

- *Ácidos grasos volátiles (AGV)*

Los AGV son un factor clave en la digestión anaerobia ya que son los compuestos intermediarios del proceso, los AGV son oxidados por la bacterias acetogénicas a acetato (HAc), hidrogeno molecular y dióxido de carbono que son utilizados como sustratos por las bacterias metanogénicas. Por lo tanto existe una relación entre la concentración de los AGV con el rendimiento del digestor. Así, es conocido que los AGV a elevadas concentraciones generan estrés microbial, reducción en el pH y por ende disminución de la actividad microbiana en el digestor [26].

- *Nutrientes*

La composición del medio afecta considerablemente a la velocidad de crecimiento de los microorganismos, de forma que en un medio con el contenido de carbono y macro y micronutrientes idóneo, presenta una velocidad de crecimiento celular superior a la de un medio no equilibrado en estas substancias [27].

- *Tóxicos e inhibidores*

Se entiende por toxicidad la disfunción total de la actividad microbiana; mientras que por inhibición el descenso de esta actividad. Así mismo, antagonismo es una reducción de la toxicidad de un substrato en presencia de otro y sinergismo es el aumento del efecto tóxico de una sustancia causada por la presencia de otra. En este aspecto el nitrógeno amoniacal es un importante nutriente para el crecimiento de los microorganismos, cuya carencia hace inviable el proceso, aunque por otro lado, una concentración elevada puede limitar el crecimiento bacteriano. La forma química con mayor efecto inhibidor por amoniaco es el amoníaco libre (NH_3) ya que el efecto inhibidor del amonio parece aumentar a pH alcalinos y a elevadas temperaturas [28].

Inhibición por amoniaco

El amoniaco es producido por la degradación biológica de la materia nitrogenada presente en el sustrato, mayoritariamente en forma de proteínas y aminoácidos. Teóricamente, y partiendo de la composición elemental del residuo, la cantidad de amoniaco que puede ser generada de la biodegradación anaeróbica de un sustrato puede ser estimado mediante la ecuación 1.2:

$$C_aH_bO_cN_d + \frac{4a-b-2c+3d}{4}H_2O \rightarrow \frac{4a+b-2c-3d}{8}CH_4 + \frac{4a-b+2c+3d}{8}CO_2 + dNH_3 \quad \text{(Ec. 1.2)}$$

Donde N_d es la cantidad de nitrógeno presente en el alimento y d NH_3 la cantidad de amoniaco producido. En otras palabras, todo el nitrógeno orgánico degradado será convertido a amonio/amoniaco. El mecanismo de inhibición a los microorganismos ocurre a partir de los componentes de ión amonio y amoníaco, los cuales se engloban en el denominado nitrógeno amoniacal ($N\text{-}NH_4^+$) y coexisten en soluciones acuosas según la ecuación 1.3.

$$NH_{3\ (14C)} + H_2O \leftrightarrow NH_4^+ + OH^- \qquad \text{(Ec. 1.3)}$$

No obstante, la presencia de nitrógeno amoniacal total (NAT = amonio + amoniaco) en determinadas concentraciones puede tener diferentes efectos sobre las bacterias metanogénicas como muestra la Tabla 1.5. Sin embargo, se observa que los factores determinantes son la concentración de nitrógeno inicial, temperatura de proceso, pH, velocidad de carga orgánica y aclimatación del inoculo, todos ellos con un efecto directo o indirecto sobre las concentraciones de inhibición [29].

Tabla 1.5 Inhibición por TAN y FAN en digestión anaeróbica (Adaptada de Yenigün y Demirel [29])

Sustrato	**Tipo de reactor**	**Carga Orgánica**	**Temperatura (ºC)**	**pH**	**Concentración critica**		**Inhibición (%)**	**Aclimatación**	**Ref.**
					NAT (mg L^{-1})	**FAN (mg L^{-1})**			
Lodos	Batch	-	30	7.2 – 7.4	>5000	-		Si	[30]
Purín de cerdo	Batch	-	30	7.2 – 7.4	>3075			Si	[30]
RSU/lodos	Semi-continuo	-	39	8.0	2800	-		No	[31]
Sintético	UASB	1.2 kg COD m^{-3} d^{-1}	35	7.7 – 8.1	6000	800		Si	[32]
Residuos de matadero y RSU	CSTR	3.2 kg VS m^{-3} d^{-1}	34	7.5	4100	337		Si	[33]
lodos	Semi-continuo	2.0 kg VS m^{-3} d^{-1}	35	8.0	3000	400		Si	[34]
Purín bovino	CSTR	-	45	7.4-7.9	6000	700		Si	[35]
Fracción orgánica de RSU	Reactor de alto contenido de sólidos	6.5 g VS kg^{-1} d^{-1}	55	7.0	2500	-	100	Si	[36]
Suero lácteo	CSTR	4 g COD L^{-1} d^{-1}	55	6.5-8.0	5770	-	64	Si	[37]
Purín de cerdo	CSTR	9.4 g VS L^{-1} d^{-1}	51	8.0	11000	1450	50	Si	[38]
Fracción orgánica de RSU	Batch	-	Meso - Thermo			215-468	50	Si	[39]

NAT = Nitrógeno amoniacal total

FAN = Nitrógeno amoniacal libre (NH_3)

RSU = Residuo sólido urbano

Por otra parte, el rendimiento y operación de los reactores está altamente influenciada por las poblaciones microbianas que lo componen, las comunidades microbianas anaeróbicas pueden ser clasificadas en dos grupos dominantes, denominados bacteria y *Archaea* [40]. Una mezcla de comunidades bacterianas facilita la hidrolisis, acidogenisis y acetogénesis, mientras que las *Archaea* convierten los productos metabólicos de las reacciones previas en metano. Como se mencionó previamente, el metano puede ser producido a través de dos vías: i) metanogénesis acetoclastica (acetato produce metano y dióxido de carbono), la cual en digestores convencionales proporciona aproximadamente un 70% del metano producido, y ii) metanogénesis hidrogenotrofica (combinación de hidrogeno y dióxido de carbono para formar metano y agua). Una vía alternativa para la metanogénesis vía oxidación de acetato hacia dióxido de carbono e hidrogeno se encuentra emergiendo en importancia [41], pero esta no es distinguible en la práctica como la metanogénesis acetoclastica [42]. Cuando se comparan los grupos tróficos en la comunidades presentes en la digestión anaeróbica. Los metanogenos acetoclasticos son considerados generalmente como los más sensitivos a los cambios ambientales, condiciones del proceso y presencia de inhibidores como el NAT [28]. La Tabla 1.6 muestra el impacto del NAT sobre diferentes *Archaeas*.

La Figura 1.3 muestra las diferentes vías inhibidoras por NAT [36], estas son: i) el efecto directo del ión amonio sobre la enzima sintetizadora de CH_4 y ii) la difusión pasiva del amoníaco al interior de la célula causando un desequilibrio protónico y/o una deficiencia de potasio.

Tabla 1.6 Impacto del NAT y FAN sobre *Archaea* en digestión anaeróbica (adaptada de Yenigün y Demirel [29])

Sustrato	Temperatura (°C)	pH	Concentración critica		observación	Organismos	Técnica molecular aplicada	Ref.
			NAT (mg L^{-1})	FAN (mg L^{-1})		Afectados/presentes		
-	38	-	4000		100% inhibición	*Methanobacterium formicicum*	-	[43]
-	-	6.5	4200		50% inhibición	*Methanospirillum hungatei*	-	[44]
-	60	6.9	4000			*Methanobacterium*		[45]
		7.0	6000		50% inhibición	*Thermoformicucum* (presente)		
Purín de cerdo	25	-	>3500			*Methanomicrobiales*	16S rRNA gene análisis	[46]
Sintético	35	8.0	6000	>700	100% inhibición	*Methanosarcina*	FISH/DGGE	[47]
Sintético	35	7.7	-	>100	100% inhibición	*Methanosaeta*-especies relacionadas	FISH/DGGE	[48]
Acetato de sodio	-	-	7000 5000		Aclimatado No-aclimatado	*Methanosarcinaceae spp.* *Methanococcales spp.*	FISH	[49]
Purín bovino y residuos de molienda de olivas	37/55	-				*Methanosarcina*	16S rRNA gene análisis	[50]

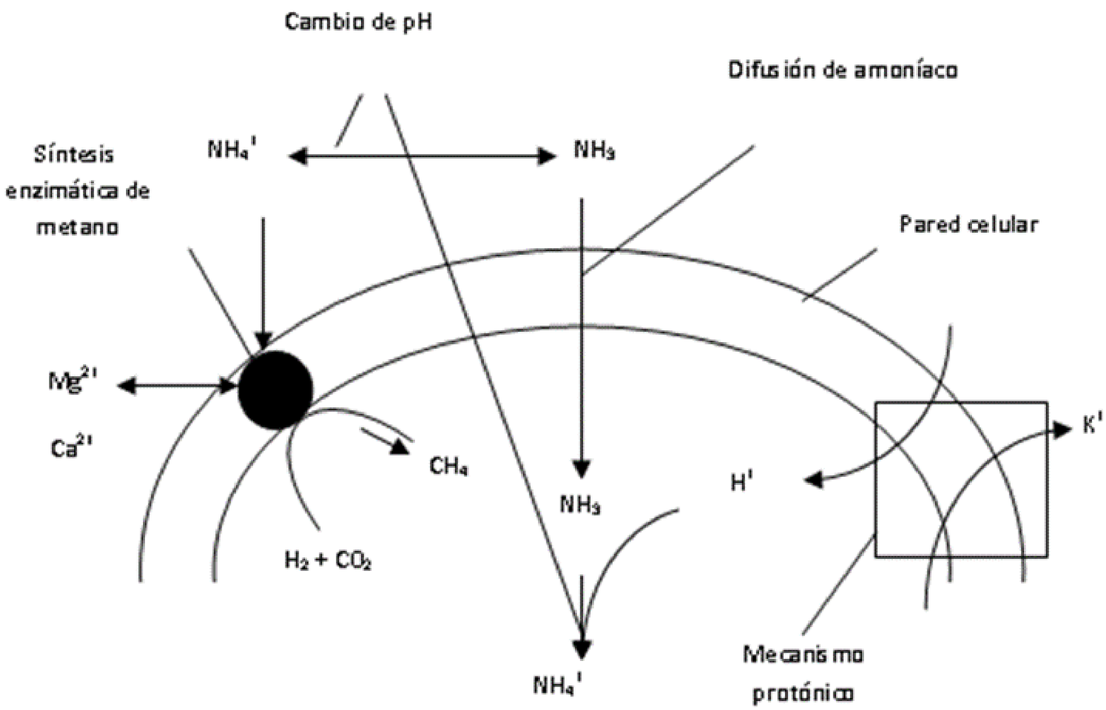

Figura 1.3. Mecanismo de inhibición de la bacteria metanogénica (Adaptado Sprott y Patel. [66])

Debido a la problemática del NAT se han desarrollado muchas técnicas para disminuir el $N\text{-}NH_3$ presente en las deyecciones ganaderas. Entre ellas, cabe destacar las siguientes: (1) disminuir la cantidad de proteínas en la dieta, (2) separar la orina de las heces, (3) reducir el pH para desplazar el equilibrio hacia el ión amonio, (4) convertir biológicamente el NH_3 a nitrógeno gas (N_2) mediante procesos de nitrificación/des-nitrificación, (5) proceso anammox y (6) precipitación de estruvita [51]. Algunas de estas técnicas se han utilizado como pre-tratamiento de la digestión anaerobia de purines de cerdo con el fin de disminuir el efecto del TAN en el proceso, ó como pos-tratamientos para disminuir el efecto del TAN en el medio ambiente, sin embargo este planteamiento representa un incremento muy grande en los costes de explotación [52]. Sin embargo, diferentes estudios han mostrado la capacidad de las comunidades microbianas a ser aclimatadas gradualmente a elevados niveles de NAT, mostrando que los digestores pueden ser operados a elevadas concentraciones de NAT sin poner en riesgo su operación.

Por otra parte, si el proceso es inhibido diversas técnicas han sido propuestas para recuperar la actividad microbiana, entre ellas se encuentran la dilución del substrato, dilución del contenido del reactor, ajustar el pH o la relación de C:N en el sustrato, así como la adición de sólidos tipo zeolitas, glauconita y carbón activo [29].

Estruvita

Uno de los procedimientos que más interés ha despertado para la recuperación de amonio de corrientes residuales es la precipitación de este mediante la formación de estruvita [53], según la Ec. 1.4.

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O_{(S)} \qquad \text{(Ec.1.4)}$$

Precipitación de la Estruvita

La Estruvita se caracteriza por ser un buen fertilizante, ya que ésta, una vez es aplicada en el suelo, libera nitrógeno y fosfatos lentamente (*slow release fertilizer*) [54]. La Estruvita puede obtenerse de diferentes fuentes, aunque la utilización de aguas residuales y/o deyecciones ganaderas permite obtenerla económicamente [55]. La tecnología a emplear para la formación del compuesto depende de la composición de la corriente residual y su precipitación puede ser usada para eliminar el amonio y/o fosfato de aguas residuales. La Tabla 1.7 presenta el resultado de los estudios más relevantes que se han encontrado en la bibliografía. Es importante remarcar que la cristalización de estruvita ocurre de forma natural, pudiendo causar serios problemas en las plantas de tratamiento, generando una pérdida de la capacidad hidráulica, un aumento de bombeo e incremento en los costos de producción y mantenimiento; sin embargo también proporciona la vía para la recuperación de P y N. La formación de estruvita se produce con relativa rapidez debido a la sobresaturación en el líquido, como resultado de la reacción química de magnesio con fosfato en presencia de amonio, la estruvita cuenta con un pK_{ps} optimo entre 12-13 que se da a un pH entre 8.5 - 9 y una relación molar de 1:1:1 para PO_4^{-3}:Mg^{2+}:NH_4^{+} [56].

Tabla 1.7 Datos de remoción de NH_4^+ y PO_4^{3-} por precipitación de estruvita de diferentes residuos (adaptada de Uludag-Demirer y col. [57]).

Tipo de residuo	Sustancia adicionada	Cantidad de sustancia adicionada	Concentración inicial		Remoción (%)		pH Optimo	Referencia
			NH_4^+	PO_4^{3-}	NH_4^+	PO_4^{3-}		
Aguas residuales del sector bovino y de fábricas curtidoras de piel.	$MgCl_2.2H_2O$	Mg:N:P = 1:1:1	200	4.1	82	NI	9.0	[58]
Lodos de aguas secundarias de digestión anaerobia para remoción de fósforo en EDAR.	Na_2HPO_4 $Mg(OH)_2$	mezcla 55 % (w/w) $Mg(OH)_2$ Mg:P = 1:1.3	760	61 (ortho-P)	6	94 (ortho-P)	8.5 (Mg(OH)2 mezcla)	[59]
Residuos de cerdo.	$MgCl_2.2H_2O$	Mg:TP=1.6:1	NI	572 (SP)	NI	91 (SP)	9.0 (1M NaOH)	[60]
Sobrenadante anaerobio de la sección de centrifugación de lodos de depuradora.	no hay adición		1090	58,2	NI	80	8.78 (por aireación)	[61]
Efluente del tratamiento (UASBR) biológico de aguas residuales de alcaloide opio	$MgCl_2.6H_2O$ Na_2HPO_4	Mg:N:P = 1:1:1	98	0.3	65	NI	9.2	[62]
Efluente de tratamiento anaerobio de la industria de levadura para panadería.	$MgCl_2.6H_2O$ Na_2HPO_4	Mg:N:P = 1:1:1	735	5.8	84	NI	9.2	[62]
Efluentes de tratamiento anaerobio de aguas residuales domesticas + 2% de lixiviados.	$MgCl_2.6H_2O$ $Na_2HPO_4.2H_2O$	Mg:N:P = 1:1:1	60-92	8.2	77	NI	9.2	[62]
Efluentes de tratamiento anaerobio de lixiviados de rellenos sanitario.	$MgCl_2.6H_2O$ $Na_2HPO_4.2H_2O$	Mg:N:P = 1:1:1	2240	11.2	85	NI	9.2	[62]
Aguas residuales de cochinillas.	MgO de bajo grado	24 g/L	2320	3490	89	100	8.5-9 (MgO)	[63]
Supernadante de digestión anaerobia de planta de tratamiento de lodos.	$MgSO_4.7H_2O$	Mg:P=1.1:1	441-602	198-242	NI	92	8.4-8.5	[64]

TP: fosforo total; SP: fosforo soluble; EDAR: Estación depuradoras de Aguas Residuales; NI: no investigado.

Como se puede observar todas las investigaciones muestran una disminución en la concentración de amonio y fósforo, en etapas previas o posteriores a la digestión anaerobia y siempre con el fin de adecuar los efluentes de digestión o aguas residuales a condiciones óptimas para su utilización como fertilizantes.

Dependiendo del origen y las características del agua residual, la precipitación de estruvita es usada para la remoción de amonio (NH_4^+), fosfato (PO_4^{3-}) o ambos. En general es utilizada la adición de Mg^{2+}, ya que este actúa como agente limitante en la formación de estruvita, entre las fuentes de Mg^{2+} utilizadas se encuentran el $Mg(OH)_2$, $MgCl_2.6H_2O$ y MgO. En ocasiones donde la concentración de fosfato es baja, este se adiciona conjuntamente al Mg^{2+} con el fin de no limitar la formación de estruvita e incrementar el rendimiento del proceso.

Fixasol

El uso de estruvita para la eliminación y la recuperación de los fosfatos y amonio es técnicamente factible para los tratamientos de aguas residuales, pero este no es aplicado debido al alto costo de los compuestos de magnesio. Sin embargo, el óxido de magnesio de bajo contenido (LG-MgO) se convierte en una opción económicamente viable. El LG-MgO ha sido usado para la recuperación de amonio y fosfatos de aguas residuales de la extracción de cochinilla, donde la adición de 24 g de LG-MgO L^{-1} de agua residual presenta una reducción de 99% de fosfatos y 89 % de amonio [63]. Aunque la utilización de LG-MgO puede ser efectiva en el tratamiento de aguas residuales con alto contenido de fosfatos y amonio, en el caso de las deyecciones ganaderas (en especial purines de cerdo) la alta concentración a amonio y baja concentración de fosfatos (debida a que la mayoría de los fosfatos se encuentran contenidos en la fase sólida del purín, formando productos insolubles) hacen que el tratamiento de estos requieran la adición de fosfatos en el proceso para incrementar el rendimiento. Con el fin de ofrecer una solución comercial que incluya el magnesio y los fosfatos, el grupo de investigación DIOPMA desarrolló para el tratamiento de purines y efluentes residuales con un alto contenido en $N\text{-}NH_4^+$ un producto denominado *Fixasol*. Según la patente (PCT/ES 2009/000406), el *Fixasol* consiste en partículas sólidas que comprenden P y Mg y que tiene como objetivo reducir la concentración de amonio en deyecciones de explotaciones ganaderas, así como el uso del producto obtenido en el tratamiento de deyecciones ganaderas como fertilizante, ya que el *Fixasol* fija el nitrógeno amoniacal en forma de estruvita. El producto desarrollado es un formulado obtenido a partir de LG-MgO, es inocuo, de fácil manipulación, no agresivo y de bajo coste. Ensayos realizados para el tratamiento de purín fresco ($N\text{-}NH_4^+$: 895 mg L^{-1}), así como ensayos de los efluentes procedentes de la digestión anaerobia de deyecciones porcinas ($N\text{-}NH_4^+$: 3546 mg L^{-1}) muestran que la concentración de $N\text{-}NH_4^+$ en ambos casos, tienen tiempos de reacción inferiores a 24 h y el contenido de $N\text{-}NH_4^+$ de las deyecciones tratadas alcanza valores inferiores a 50 mg L^{-1} y 100 mg L^{-1} respectivamente. El *Fixasol* permite obtener, con un coste en reactivos de aproximadamente 1-3 € m^{-1} de deyecciones ganadera del sector porcino, un compuesto de baja solubilidad y lenta asimilación que puede ser empleado como fertilizante mineral u órgano-mineral. El producto resultante contendrá el amonio y gran parte del fósforo y el potasio contenidos en las deyecciones ganaderas, así como otras fases minerales presentes en el producto desarrollado que no ha reaccionado [65].

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OBJETIVES

According with an extensive bibliography revision and different expert opinions, the anaerobic digestion can be considered a completely mature technology. However, since economic feasibility of anaerobic digestion plants is directly linked with the biogas potential and the treated waste, many research efforts have been made in order to improve biogas yields, process stability, mitigate inhibitory mechanisms and generate by-products with value added. In this regard, controlled struvite formation has been attracting increasing attention as a near mature technology to recover nutrient from anaerobic digestion. However, struvite recovery feasibility is generally limited by the high cost of magnesium chemical reagent. To solve this problem some researchers have proposed to use magnesium by-products as raw materials and reduce the struvite processing cost by coupling anaerobic digestion and struvite precipitation in the same reactor.

These considerations are the motivation of the present thesis, which deals with the evaluation of: (i) nutrient recovery by struvite precipitation using low cost reagent precursors (MgO by-products) and (ii) evaluate the feasibility of coupling anaerobic digestion and struvite precipitation using low cost reagent precursors (MgO by-products). In order to develop these objectives the main specific objectives are:

- Use of experiments and equilibrium model simulations to examined inorganic nitrogen removal from pig manure via struvite precipitation promoted by non pre-treated and acid phosphoric pre-treated (called stabilization agent) magnesium low cost reagents addition.

- Evaluate the effects of different magnesium sources on anaerobic digestion as well as struvite precipitation capacity through a series biomethane potential test.

- Evaluate the effects of coupling anaerobic digestion and struvite precipitation in the same reactor using stabilization agent addition.

CHAPTER 1. Nutrients recovery

1.1 Nutrient recovery technologies for anaerobic digestion systems: An overview

Nutrient recovery technologies for anaerobic digestion systems: An overview

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Submitted on "*Revista ION*"

Abstract

Anaerobic digestion is a worldwide technology to treat organic waste streams, primarily due to its capacity to produce methane as renewable energy. However, there is an increasing interest on nutrient recovery (N and P), which from both environmental and economic reasons have been identified as key feature in anaerobic digestion plants. The present manuscript presents a comprehensive overview on recent advances in nutrient recovery technologies applicable for anaerobic digestion systems. The review focus on N and P recovery through the use of digestates as fertilizers, struvite precipitation and biological systems such as phycoremediation (i.e. algae cultivation) and polyphosphates accumulating organisms.

1. Introduction

Anaerobic digestion (AD) stands as an important technology in the emerging green energy economy [1]. Advantages of AD over other technologies are: (i) cost-effective organic wastes treatment for municipal wastewater and solid waste streams, and (ii) energy/economy alternative in rural sector through the digestion of agro-wastes and/or energy crops [2,3]. Today, most AD plants are energy focused, while lower attention has been paid to nutrient recovery. Nevertheless, the continuous increase in fertilizer prices (mainly formed of N, P and K) has raised interest on nutrient recovery from waste streams. Batstone and Virdis [4] clearly stated that new wastewater treatment plants have to: (i) achieve existing public health and environmental goals, (ii) recover maximal energy from wastewater, and (iii) preserve and recover nutrients for reuse. Recent advances on nutrient recovery from wastes streams propose a three-steps framework in order to achieve the best outcomes: (i) nutrient accumulation, (ii) nutrient release and (iii) nutrient extraction [5]. Nutrient accumulation can be achieved via plants, microorganisms and physicochemical mechanism (e.g. microalgae and polyphosphates accumulating organisms). Nutrient release can occur by biochemical (e.g. AD) and thermochemical treatment; while nutrient extraction can occur via physicochemical mechanism, mostly precipitation [5]. Besides renewable energy, AD of organic wastes produces a digestate which is a mixture of partially degraded organic matter, anaerobic biomass and inorganic matter (including nutrients).

AD facilitates the mobilization of nutrients from the organic matter to the liquid phase. N is converted into ammonium and organic P is hydrolyzed to soluble P, where the extent is dependent on the operational conditions and waste properties [5,6]. Today, using AD digestates as organic fertilizer or soil conditioner seems to be the best option for its recycling [3,6,7]. Table 1 shows the heavy metals, micro- and macro-nutrients composition of different AD digestates, which have been grouped in five categories [3,8]: (i) sewage sludge (SS); (ii) animal manures; (iii) food industry wastes; (iv) energy crops and harvesting residues; and (v) organic fraction of municipal solid waste (OFMSW). It can observe that element concentrations are highly variable and substrate type dependent. For instance, pig manure and sewage sludge digestates present a relatively high P concentration while slaughterhouse waste digestates present a high N concentration. Additionally, digestates are also evaluated in terms of heavy metal content (specially Cu and Zn), salinity, remaining biodegradable organic matter, phytotoxicity and pathogens abundance [9,10]. Such facts determine the need for applying substrate specific pre- or post-treatment to increase digestate quality until acceptable levels [11].

2. Digestate post-treatment

Rural centralised biogas plants co-treat animal manure collected from several farms and other suitable organic residues [3], whereas in urban areas AD plants mostly treat sewage sludge and OFMSW [24–27]. AD plants are usually of large scale, with digester capacities ranging from few hundreds m^3 up to several thousand m^3 [28]. The quality management of digested implies control of the three main components of the anaerobic digestion system: (i) the feedstock, (ii) the digester design and operational conditions, and (iii) digestate post-treatment [29]. As an example, Figure 1 illustrates the most common OFMSW AD plant configurations.

Table 1. AD digestates composition (adapted and expanded from Zirkler et al. [12])

Feed	Reactor size	pH	TS	TOC	N	P	K	S	Ca	Mg	Fe	Mn	Zn	Cu	Pb	Cd	Ni	Mo	Se	Ref.
			(g kg^{-1})*									(mg kg^{-1})*								
Animal manure and energy crops																				
CM	F	8.6	52	274	22	1	17		20											[13]
CM	L	8.5		500	42	9	13	3.6	20	6	2.0	164	137	44						[14]
CM	L	7.7	92	355	43	7	47			18										[15]
PM	L	7.3		551	43	20	18	4.6	34	12	1.0	245	1304	121						[14]
Poultry manure	L	7.8		452	67	24	24	5.3	92	6	1.8	663	578	105						[14]
Horse manure	L												43	14	3.2	0.3	3.8			[16]
Maize	L												34	29	1.3	0.05	5			[16]
AcoD using manure as principal substrate																				
CM + 4% glycerol	L	5.6	38	465	49	13	47	4.6	40	7	3.0	358	473	282						[11]
CM + 6% glycerol	L	7.4	73	587	32	5	22	3.6	24	5	2.3	235	388	178						[11]
CM + 5% orange peel residues	L	7.9	24	385	59	8	45	4.6	41	11	1.2	246	316	115						[11]
PM + 0.6% SHW + 6.5%biodiesel wastewater	L	8.0	21	276	138	24	105	10	38	15	2.4	543	4019	681						[11]
PM + 1% SHW + 6.5 % biodiesel wastewater	F	8.2	20	303	205	10	103	35	11	3	1.1	149	1779	206						[11]
CM + 4.3% CM + 11.6% maize oat silage	F	7.5	90	374	44	9	34	5	45	8	3.3	305	307	120						[11]
PM + 1% SHW + 6.5% biodiesel wastewater	F	8.3	19	247	200	6	52		26	10	1	158	1158	211	2	0.5	0.5			[17]
PM + 24% milk serum + 14% CM + 10% maize silage + 4% rice residues	F		40	483	93	11	13.5													[18]
PM + 20% blood industry residues + 15% maize silage	F		60	488	88	12	28													[18]
Rabbit manure and SS + 17% fat + 8% duck SHW	F		200	365	25	14														[19]
CM + 7% manure + 3% garden wastes + 17% fruits and vegetables	F		240	330	20	8														[19]
25 different mixtures of PM and/or CM , maize and/or grass silage	F							4.4			2.6						6.2	3	0.5	[19]
OFMSW																				
Source-selected OFMSW	F		440	274	14	6														[20]
OFMSW	L												77	25	5	0	50			[21]
Source-separated OFMSW	F	8	15		152	16	78	7	50	10		<0.7	79	13						[22]
OFMSW + 20% PM	F		40	481	144	5.4	23													[20]
Sewage sludge																				
SS	F		19		2.8	0.43	0.1		0.04	0.03			0.1	0.15		0.12	0.16			[23]
SS	F		200	291	42	32														[20]

L = Lab-scale reactor
F = Full-scale reactor
PM = Pig manure
CM = Cattle manure
SHW = Slaughterhouse waste
SS = Sewage sludge
*Data expressed on dry basis

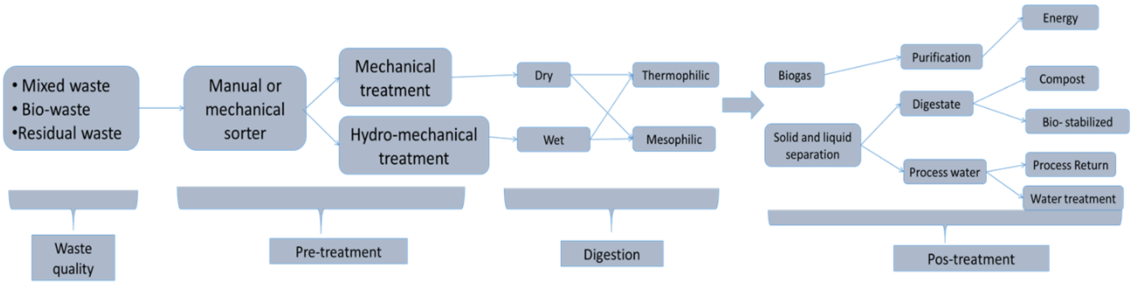


Figure 1. Current OFMSW AD plant schemes

One of the simplest digestate post-treatment methods is the separation of the solid and a liquid fraction (digestate dewatering). This step is mainly performed by a centrifuge or a belt press together with flocculating agents. The main objetives of solid and liquid separation are: (i) increase the possibilities of digestates management as by-product; (ii) avoid uncontrolled decomposition process; (iii) reduce transport cost (solid fraction). In general, solid fractions are further stabilized by aerobic treatments (e.g. compost and bio-stabilization) and liquids fractions are return to the process [30] or treated by aerobic wastewater treatment process [31]. In manures digestates, the dry matter content of the solid fraction is typically 25-35%, containing 60-80% of the dry matter and phosphorus content of the original slurry, but only 20 – 25% on the nitrogen and 10-15% of the potassium [29].

3. Use of digestate as fertilizer

The use of AD digestates as fertilizer allow to recycle nutrients and reduce the use of chemical fertilizers [32]. Nonetheless, the quality of the digestate must be carefully evaluated prior to use [7]. From an agricultural point of view, the main parameters to take into consideration are pH, salinity, nutrients, pathogens and heavy metals [3,6,33]. Other environmental concerns are inappropriate handling, storage and application, which may led to ammonia emissions, nitrate leaching and phosphorous overdoses [34]. Another risk is the application of unstable digestates (i.e digestates with large amounts of non-degraded organic matter), which may exert negative impacts on organic matter mineralization and nutrient turn-over in the plant soil system [6,35,36]. This type of digestates can be obtained from digesters operated on intense or unstable conditions due to short hydraulic retention time, high organic loading rates, co-substrate addition based on random or heuristic decisions [3]. Enlarging digestion time can decrease the amount of labile compounds in digestates; however it may reduce the biogas production of digesters as well as require a higher investment (larger vessel). Aerobic post-treatment can be used to decrease the phytotoxic impact of digestates without affecting AD feasibility as well as improve pathogens destruction. In this regard, Abdullahi et al. [36] found that the seed germination increase with dilution and incubation time, suggesting that lower application rates and longer lag periods between application of aerobically treated digestates and planting can reduce the occurrence of phytotoxicity. Abubaker et al. [37], who studied bacterial community structure and microbial activity in different soils amended with digestates and untreated cattle slurry, observed that differences in microbial community structure induced by the digestate appeared to be smaller than those induced by cattle slurry, and those changes did not translate into altered microbial functioning.

4. Nitrogen

The fertilizing potential of digestates is mainly associated with their content of ammonium [38]. Today, nitrogen treatment technologies are mainly focus on its elimination rather than on its recovery. However, conventional TAN removal methods are being recognised as wasteful. For instance, the conventional nitrification-denitrification process, where nitrogen is converted to elemental nitrogen gas through, requires a high both electrical and chemical energy [4]. In this regard, Anammox, adsorption and membrane technologies have been present as alternative nitrogen treatment and recovery from digestates.

Anammox

Anaerobic ammonium oxidation (Anammox) is growing on importance as an alternative technology for biological nitrogen removal form wastewater, due to its lower energy, oxygen and carbon requirements [39]. The optimal operational conditions for Anammox have been reported at pH=7-8.5; C/N ration 0.6:1; hydraulic retention time of 1 day and temperature 30-37 ºC [40]. However, Anammox reactors have already been operated at psychrophilic temperatures [41,42]. The Anammox process consist on ammonia oxidation in the absence of oxygen but in the presence of nitrite/nitrate (Eq. 1) [43,44]. Therefore, a pre-requisite of the Anammox process is a partial nitration unit where about 50% of the ammonium is converted to nitrite concentration appropriate to the stoichiometry for the Anammox reaction as shown in Eq. 1 [45].

$$NH_4^+ + 1.32NO_2^- + 0.066HCO_3^- + 0.13H^+ \rightarrow$$

$$1.02N_2 + 0.26NO_3^- + 0.066CH_2O_{0.65}N_{0.15} + 2.03H_2O \quad \text{(Eq.1)}$$

Adsortion

Ammonium plays a vital role as a buffer agent in the AD process [46–48]. However, high ammonium concentrations are inhibitory for anaerobic biomass, especially aceticlastics methanogens [49]. Consequently, several research efforts have been made to reduce the ammonium concentration in the digester medium [9,49–51]. On the one hand, chemical adsorptions use new reactors configuration to capture the TAN in a solid or liquid medium. Serna-Maza et al. [52] propose a side-stream ammonium stripping using thermal alkaline treatment, in this method the digestate and biogas are treated in the stripping column and the biogas leaving the stripping column is passed though acid (0.25 N H_2SO_4) traps to remove ammonia, while the biogas and digestate return to the reactor. Sun et al. [53] proposed reduce ammonia during thermophilic anaerobic digestion of protein rich stillage at a higher organic loading rate (7 g $L^{-1}d^{-1}$) by biogas recirculation on water-washed (4.5 L water tank) biogas system. On these instances the biogas recirculation, temperature and pH are the determining columns factors by ammonia absorption. Moreover, Acidic gel cation exchange resin column were tested to remove ammonium by ion exchange after filtration and reverse osmosis from full scale AD system digestate. Resin shows 99% of ammonium removal (27.6 g NH_4^+-N L^{-1} resin) and present also a regeneration with 3 bed volumes of 2 M HCl, recovering 91.7% of the original cation exchange capacity [54].

Membrane

Membrane technology has acquired significant relevance. This technology allows a gaseous transfer between two liquid phases. To accomplish this mass transfer, a microporous hydrophobic membrane separates the two liquid phases, which are an NH_3 rich feed and an acidic adsorption solution. The gas filled pores of the membrane are the transfer area. The difference in the NH_3 partial pressure between the two liquid phases is the driving force for the mass transfer. Hollow fiber membrane contactors can remove NH_3 from anaerobic digestate [55] and also directly from an operating AD reactor [56]. Other uses of membranes in nutrient recovery of anaerobic digestion system are associate to bio-electrochemical systems (BES). The representative system includes microbial fuel cells (MFCs), microbial electrolysis cells (MECs) and microbial desalination cells (MDCs) [57]. The foundation for realizing ammonia recovery in a BES is the fact that ammonium ions can move across ion exchange membrane via either current-driven migration or diffusion [57]. It was found that an MFC could achieve 100% TAN recovery in efficiency and reduce TAN inhibition on anaerobic digestion

[57,58]. The theoretical analysis of energy consumption and production suggested that TAN recovery in an MFC had significant energy advantage (with a positive energy balance) [57,59]. One of the key factors in TAN recovery is the high pH of cathode, which can drive ammonium to ammonia gas [60].

Although the use of chemical fixation and adsorption is a fast and reliable method for ammonium removal from digestates. The posterior ammonium recovery require chemical or/and energy cost. In this regard, some alternative methods have been applied. For instance, struvite precipitation and algae cultivation, which will be discusses in the following sections.

5. Struvite

Struvite precipitation has been attracting an increased interest as a technique to recover N and/or P, since struvite has a high nutrient value per unit weight (low transport cost) and is highly effective as a slow-release fertilizer [61,62]. Struvite is a crystalline solid phase consisting of magnesium, ammonium and phosphorus in equal molar concentrations and its precipitation naturally occurs, as for Eq. 1, when the combined concentration exceeds the solubility product [63,64].

$$Mg^{2+} + NH_4^{+} + HPO_4^{2-} + 7H_2O \rightarrow MgNH_4PO_4{\cdot}6H_2O + H_3O^{+} \qquad \text{(Eq. 1)}$$

The struvite crystal development occurs in two chemical phases: nucleation (crystal birth) and crystal growth [61]. Several physicochemical parameters influence these mechanisms such as pH [65], super-saturation [66], mixing energy [67], temperature and presence of foreign ions [68]. Taking account these factors, several struvite crystalliser reactors have been development, mostly continuous flow reactors [61,68–70].

The precipitation of struvite AD from digestates normally requires the addition magnesium since their concentration is very low with relation to NH_4^+ and PO_4^{3-} concentration [71]. Nevertheless, although the use of struvite for recovering NH_4^+ and PO_4^{3-} from wastewaters is technically feasible, it is not widely adopted because of the high costs of magnesium chemical compounds ($MgCl_2{\cdot}H_2O$, $Mg(OH)_2$ and MgO) [63,72]. Several authors have evaluated the utilisation of alternative magnesium sources such as bittern [73], sea water and brine [74], magnesite [75], magnesite pyrolysate [76], struvite pyrolysate recycling [77] and electrochemical magnesium dosage [78]. Table 2 summarises the removal of NH_4^+ and PO_4^{3-} by struvite precipitation from different wastewater and digestates using different magnesium source. Rich-magnesium by-products from the calcination of magnesite have shown good results in struvite precipitation and some advantages in comparison with other Mg sources [63,79,80]. In this topic, Quintana et al. (2008) observed that the origin and the pre-treatment of the by-products have a considerable influence over the reaction time as well as on the quantity and quality of the struvite obtained.

Coupling anaerobic digestion and struvite precipitation in the same reactor have been presented as an alternative approach to reduce operation cost and, additionally, mitigate ammonium inhibition on anaerobic digestion systems. This approach have been trialed by some researchers on continuous reactors without any negative impact on AD performance and high nutrient recovery (N <50%; P<90%) [82–84]. However, continued dosing of Mg can led to inhibitory phenomena by extreme pH or cation toxicity as well as high operation costs associated with Mg reagents purchasing [63]. Romero-Güiza et al. [85] found that the use of stabilizing agent (mainly formed of newberyite ($MgPO_4{\cdot}3H_2O$)) formulated with low-grade magnesium oxide by-product, can reduce the ammonium concentration up to 70% and increase the specific biogas production by 40% with a long-term stability.

Table 2. Removal of NH_4^+ and PO_4^{3-} by struvite precipitation from different wastewaters and digestates using different magnesium source (expanded and expanded from Uludag-Demirer et al., [71])

Waste water	Chemicals added		Mg:N:P	Initial concentrations (mg L^{-1})		Removal (%)		Optimum pH	Ref.
	Mg^{2+}	PO_4^{3-}		$N\text{-}NH_4^+$	$P\text{-}PO_4^{3-}$	$N\text{-}NH_4^+$	$P\text{-}PO_4^{3-}$		
Activated sludge	$MgCl_2{\cdot}H_2O$		1.4:1.1:1	60	120	53	75	9.1 - 10.2	[38]
	Seawater					54	81	10	
	bittern					39	76	9.6	
Landfill leachate	$MgCl_2$	H_3PO_4	1:1:1	2700	43	97		8.6-9.4	[63]
	$MgCO_3$					91			
Pigglery waste waters	Struvite pyrolysate		2.5:1:1	985	161	80	96	8.6	[73]
Urine	Mg (Electrochemical)		Mg:P (1.5:1)	2540	197		100	8.9	[75]
Cochineal insects processing	LG-MgO		3.7:1.5:1	2320	3490		100	8.5-9	[76]
Sewage	LGMgO		Mg:P (1.6:1)	322	64		80	8.4-8.5	[78]
	LGMgO Pretreated (1)						70		
	LGMgO Pretreated (2)						90		
Municipal wasate water	MgO		Mg:P (1.5:1)	630	54	82	92	8.8	[80]
	LG-MgO		Mg:P (3.6:1)			89	96	8.7	
Calf manure digestate	Bittern	bone meal	1.3:1:1.3	1060	450	91	99	9	[81]
source-sepatated urine	wood ash		(Mg+Ca):P (1.5:1)	2720	187		99	8.5-8.7	[86]
Molasses	Struvite Mg^{2+} and PO_4^{3-} recycled (3)		1.2:1:1.2	1400	24	92		8.5	[87]
Leachate municipal landfill	MgO	H_3PO_4	1:1:1	2600	27	67		9	[88]
			2:1:1			95			

(1) Pretreated correspond to suspension at a concentration of 3g of LGMgO L^{-1} of tap water
(2) Pretreated correspond to supernatant after settling for 4h after 28h aeration
(3) Distillation with NaOH
LG-MgO = Low grade magnesium oxide

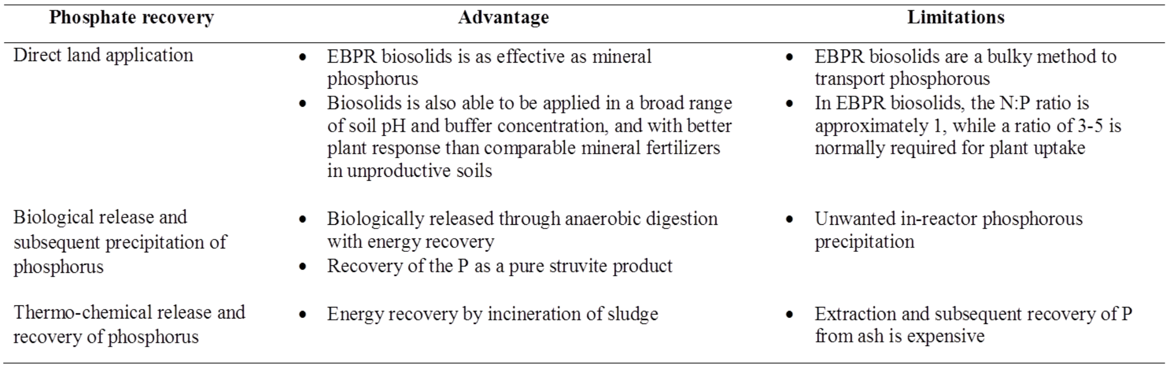
Struvite has been successfully used as fertilizer on different crops. Moreover, struvite is the preferable fertilizer for crops that needs magnesium, like sugar beet [89]. Other favorable aspects of struvite are its low leaching rate (release nutrients slowly during the plant growing season) and that does not burn the roots like traditional ammonium-phosphate fertilizer [61]. However, in some cases struvite obtained from anaerobic digestates may contain some heavy metals, which are incorporated into the struvite crystalline network not only by nucleation, but also during the crystal growth process [75,90–92].

6. Phosphorus

Phosphorus is typically present in wastewaters, industrial streams, and anaerobic digestates at low concentrations (10-100 mg P L^{-1}). Recovery of phosphates through precipitation with aluminium, iron, calcium and magnesium is technically possible; however aluminium and iron sources are expensive and makes phosphorus unavailable to plants [93]. Calcium phosphates are a poorer fertilizer (particularly in alkaline soils) [94,95], while recovery as struvite requires a higher P concentration in the solution [96]. To solve this problem enhanced biological phosphorus removal (EBPR) is suggested as technology to concentrate phosphorus in order to make phosphorus recovery and reuse feasible. EBPR sludge contains 5-7% phosphorus in contrast with normal activated sludge, ranging 1 and 2% (dry weight) [97]. EBPR relies on polyphosphates accumulating organisms (PAOs) to take up phosphorus form wastewater streams and thus concentrating P in the biomass, which can be either directly applied to land or solubilized to recover P as struvite [98].

Yuan et al., [97] review, describe and discuss EBPR. According to the author the main factors involving the EBRP technology are: (i) biochemical transformations performed by PAOs, (ii) process design and operation, and (iii) phosphorus recovery form EBRP sludge. The EBPR system requires alternating anaerobic and aerobic/anoxic conditions. In continues system this is achieved by spatially dividing the bioreactor into anaerobic, anoxic and aerobic zones, while sequencing batch reactors provide anaerobic, anoxic and aerobic periods in a single vessel. Table 3 summarise the different ways to phosphorous recovery from EBPR sludges.

Table 3. Routes for the utilization of phosphates in EBPR sludges (adapted and expanded from Yuan et al. [97])



Phosphate recovery	Advantage	Limitations
Direct land application	• EBPR biosolids is as effective as mineral phosphorus • Biosolids is also able to be applied in a broad range of soil pH and buffer concentration, and with better plant response than comparable mineral fertilizers in unproductive soils	• EBPR biosolids are a bulky method to transport phosphorous • In EBPR biosolids, the N:P ratio is approximately 1, while a ratio of 3-5 is normally required for plant uptake
Biological release and subsequent precipitation of phosphorus	• Biologically released through anaerobic digestion with energy recovery • Recovery of the P as a pure struvite product	• Unwanted in-reactor phosphorous precipitation
Thermo-chemical release and recovery of phosphorus	• Energy recovery by incineration of sludge	• Extraction and subsequent recovery of P from ash is expensive

7. Phycoremediation

Algal biomass has emerged as a potential feedstock for fuels production (e.g. bio-ethanol, biodiesel, and biogas) [99]. Advantages of algae include: (i) the capacity to grow on fresh, brackish, saline and wastewater streams (including AD supernatants); (ii) tolerance to a wide variety of environmental conditions; (iii) an ability to be cultivated on land not suitable for food production, and (iv) algae can be produced all year round [100]. However, the high cost of algae biofuel production has constrained the development of industrialized production [101]. A large quantity of water is consumed during algae cultivation, representing 10-20% of the total cost of algae production [102,103]. Hence, combining algae biomass production with digestates nutrient recovery can mitigate cost in algae-oriented biofuel industry [104]. Nitrogen and phosphorus are considered as essential nutrients for algal cultivation. Nitrogen is directly associated with the primary metabolism of algae as it is the main constituent of nucleic acid and proteins [105]. Phosphorus needs to be supplied as phosphates because phosphorus in other forms may combine with metal ions and get precipitated, thus becoming unavailable to the algae [105]. Algae cultivation in AD supernatants is limited by the free ammonia (toxic for most strains of algae) and light limitation [106]. In fact, only a few species of algae has been found able to grow in anaerobic digestion supernatant (e.g. *Chlorella* sp. and *Scenedesmus* sp.) [104]. Table 4 shows different nutrient removal experiences from anaerobic digestion supernatant. In addition to nitrogen and phosphorous, algae also require trace amount of micro-nutrients such as metals (Na, Mg, Ca, Mn, Zn, Cu, Fe and Mo) and vitamins for effective growth [107]. Algae can also be used as biosorbents to remove heavy metal ions (e.g. Cu, Pb, Cr, and Sr) [108]. Biosortion applied on digestates using algae has several advantages over conventional methods (e.g. chemical reduction, ion exchange, precipitation and membrane separation): (i) low operating cost, (ii) high efficiency in detoxifying heavy metals in low concentration streams, and (iii) no nutrient requirements [109].

Table 4. Comparison of major nutrient removal rates by microalgae cultivation in various anaerobic digestion wastewater conditions (adapted and expanded from Ji et al. [104])

Anaerobic digestion wastewater	**Gas source**	**Microalgae species**	**Cultivation period (d)**	**Initial nutrient (mg L^{-1})**	**Nutrient removal (mg $L^{-1}d^{-1}$)**	**Dry cell weight (g $L^{-1}d^{-1}$)**	**References**
Digested dairy manure (20x dilution)	CO_2	*Chlorella* sp.	21	NH_4-N = 89.1 TNK= 172.8 TP= 12.5	4.28 6.24 0.20	0.0814	[71]
Digested dairy manure (50x dilution)	2-3% CO_2	*Neochloris oleoabundans*	16	NH_4-N = 42	6.48	0.0883	[121]
Digested pig manure (10x dilution)		*Scenedesmus accuminatus*	10	NH_4-N = 120	5.20	0.0458	[122]
Anaerobic Digestete (6x dilution)	Biogas	*Chlorella* sp.	6	NH_4-N = 59.6 TP= 6.21	8.33 0.83	0.1026	[123]
Digested cattle manure (20x dilution)	CO_2	*Chlorella vulgaris*	21	NH_4-N = 81.7 PO_4^{3-}-P= 3.65	5.2 0.19	0.25	[124]
Anaerobic Digestate	3% air	*Synechocystis* sp.	10	TN = 80 NH_4-N = 6.8 TP= 1.143	0.15	0.1509	[125]

Conclusions

Apply anaerobic digestion digestates as organic fertilizer or soil conditioner seem to be the best option for its nutrient recycling. However, most digestates are not suitable to be directly applied on land, as they might create several environmental phenomena, i.e. ammonia emissions, nitrate leaching and phosphorous overdoses. Separation of the solid and liquid fraction is, due to its simplicity, the most widespread digestate post-treatment method. However, adequate liquid and solid fraction treatment is necessary for the correct management of digestates. Nitrogen treatment technologies for AD supernatants are mainly focused on ammonium removal rather than recovery, aiming to reduce the ammonium concentration/inhibition on AD, particularly on thus AD plants with water-process recirculation. Contrariwise, phosphorous recovery has been identified as key a feature in full-scale treatment plants. In this later aspect, most efforts have been made in concentrating phosphorous in polyphosphates accumulating organisms. Struvite precipitation is a useful process for both N and P recovery, where research is made to investigate the feasibility of magnesium by-products. Finally, the integration of anaerobic supernatant treatment and algae cultivation could be a viable ways to reduce the risk of nitrogen and phosphorus pollution form anaerobic digestion; however further research is required to overcome limiting factors.

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1.2 Reagent use efficiency with removal of nitrogen from pig slurry via struvite: A study on magnesium oxide and related by-products

Reagent use efficiency with removal of nitrogen from pig slurry via struvite: A study on magnesium oxide and related by-products

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Submitted on Water Research

Abstract

Controlled struvite formation has been attracting increasing attention as a near mature technology to recover nutrients from wastewater. However, struvite feasibility is generally limited by the high cost of chemical reagents. With the aim to understand and control reagent use efficiency, experiments and equilibrium model simulations examined inorganic nitrogen (TAN) removal from pig manure via struvite with added magnesium and phosphate reagents. Four industrial magnesium oxide (MgO), a commercial product and three by-products from magnesite calcination, were tested with phosphate added as a highly soluble potassium salt. TAN removal extents with the MgOs ranged from 47 to 72%, with the highest grade MgO providing the greatest extent of TAN removal. However, model analysis showed that all the MgO reagents were poorly soluble (only about 40% of added magnesium actually dissolved). The model results suggested that this poor dissolution was due to kinetic limitations, not solubility constraints. A further set of additional reagents (termed stabilization agents) were prepared by pre-treating the MgO reagents with phosphoric acid, and were tested separately as a source of both magnesium and phosphate. Results showed that acid pre-treatment of moderate to highly reactive MgOs (soft to medium-burnt) primarily formed bobierrite as the stabilizing agent, whereas the pre-treatment of very low reactivity MgOs (dead-burnt) mostly formed newberyite. The newberyite stabilizing agents achieved very high TAN removal extents of about 80%, which is significant, considering that these were formed from dead-burnt/low-grade MgOs. However, the bobierrite stabilizing agents achieved a substantially lower TAN removal extent than their medium-to-high reactivity precursor MgOs. Again, model analysis showed that the bobierrite stabilizing agents were poorly soluble, due to kinetic limitations, not solubility constraints. In contrast, the model suggested that the newberyite stabilizing agents almost completely dissolved to very effectively form struvite. A mechanism was proposed by which conditions near a dissolving reagent particle surface causes unwanted struvite nucleation onto and overgrowth of the reagent particle, inhibiting further dissolution and markedly reducing reagent efficiency. The findings of the study could have implications for reagent efficiency with struvite using other solid reagents, such as magnesium hydroxide or other MgOs.

1. Introduction

Nitrogen and phosphorus recovery from wastewaters has become increasingly important due to environmental concerns about nutrients discharged to the environment (e.g. eutrophication and land nutrient overload) (Kumar and Pal, 2013; Liu et al., 2012; Wang and Wang, 2009). During recent years, several technologies have been developed to recover nitrogen and phosphorus (Mehta et al., 2015). Of these, controlled struvite formation has been attracting particular interest as a mature technology which produces a concentrated saleable slow-release fertiliser (Rahman et al., 2014; Uysal et al., 2010). Unfortunately, the equimolar composition of struvite (magnesium, ammonium and phosphate, $MgNH_4PO_4{\cdot}6H_2O$) often requires magnesium addition for phosphate removal, and both magnesium and phosphate (PO_4^{3-}) addition for total ammonia nitrogen (TAN) removal. This is because many wastewaters have a large molar excess of TAN. With only magnesium added, PO_4^{3-} removal can be good at over 60%, but TAN removal is typically poor at 30% or less (Le Corre et al., 2007; Münch and Barr, 2001; Quintana et al., 2008). With magnesium and PO_4^{3-} addition (as phosphoric acid or a soluble phosphate salt), phosphorus is still sequestered, and TAN removal is also high at up to 99% (Le Corre et al., 2007).

Because the economic feasibility of struvite is heavily influenced by reagent cost (Chimenos et al., 2003, Giesen, 1999), several authors have trialled lower-cost magnesium sources such as bittern (Lee et al., 2003), sea water and brine (Liu et al., 2013), magnesite (Gunay et al., 2008), magnesite pyrolysate (Huang et al., 2011), struvite pyrolysate recycling (Yu et al., 2012), and the cyclone dust collected in the air pollution control system of the natural magnesite calcination process (Chimenos et al., 2003; Quintana et al., 2008). Commercial high-grade magnesium sources include (listed in order of typical decreasing cost): magnesium chloride ($MgCl_2{\cdot}6H_2O$), magnesium sulphate ($MgSO_4{\cdot}7H_2O$), magnesium hydroxide ($Mg(OH)_2$), and magnesium oxide (MgO), while PO_4^{3-} reagents include phosphoric acid and potassium or sodium salts (Huang et al., 2011). Importantly, the magnesium reagents are sold as solid reagents which have to dissolve to release magnesium for struvite formation. This dissolution step may dictate the kinetics of the struvite precipitation process (Münch and Barr, 2001), as also supported by studies that have observed faster struvite precipitation for milled MgO as compared to un-milled MgO of the same composition (Quintana et al., 2008). This is in line with obvious efforts by industry to reduce particle size in magnesium hydroxide suspensions (increased surface-to-volume ratio) for faster neutralization reactions. However, Santinelli et al. (2013) also significantly noted a mild-to-strong effect of the order of reagent addition on TAN removal efficiency. They trialled MgO addition to the wastewater followed by phosphoric acid addition, and MgO pre-mixed with phosphoric acid before combined addition to the wastewater, and generally achieved better TAN removal with the MgO pre-mixed with phosphoric acid. These effects may be partly explained by observations of Romero-Guiza et al. (2014, 2015), who observed a struvite coating over phosphoric acid-pretreated low-grade MgO in pig manure. Specifically, a higher localised pH and magnesium concentration near the interface of dissolving MgO particles could induce struvite nucleation onto the MgO surface, restricting further reagent dissolution. Such a phenomenon could be critical when using solid reagents such as MgO and $Mg(OH)_2$, because poor dissolution would not only slow down struvite formation kinetics, but would also require large excesses of reagent to achieve a particular TAN removal. Such a large excess could negate the cost benefits of using a less expensive solid reagent.

Studies to date on struvite precipitation with MgO have largely focused on the aqueous phase, with little attention given to the preceeding MgO dissolution. However, the observations noted above suggest that there may be opportunity to better understand, intervene and improve dissolution and access to MgO. The present study uses experiments and chemistry modelling to evaluate and better understand TAN removal from pig manure using MgO. Tests were performed with four industrial magnesium oxide (MgO) from natural magnesite calcination: a commercial high grade MgO (HGMgO) as well as a number of low-grade MgO (LGMgOs) by-products. All these MgO reagents were also pre-treated with phosphoric acid and tested separately after pre-treatment. The study focussed on the underlying chemistry to show how reactivity and dissolution of the various magnesium by-products influenced struvite precipitation and TAN removal performance.

2. Materials and methods

2.1 Pig slurry and reagents

Pig slurry was collected from a centralised AD plant located in Lleida (Spain). It was stored at 4ºC prior to use. An aliquot of slurry sample was centrifuged at 4,000 rpm for 5 minutes, the supernatant was recovered and filtered at 0.45 µm. The ion content of the supernatant (Cl^-, PO_4^{3-}, SO_4^{2-}, K^+, Ca^{2+}, Mg^{2+} and NH_4^+) was determined by ion chromatography (see analysis techniques). Characterisation results are given in Table 1. K_2HPO_4 was provided by Panreac Quimica, S.A. (Barcelona, Spain).

The commercial HGMgO was provided by Premier Magnesia, LLC (Nevada, USA). It is calcined from magnesia ore in a multiple-hearth furnace and used for wastewater treatment and soil fertilization, among other industrial applications. The three industrial by-products rich in magnesium oxide were provided by Magnesitas Navarras, S.A. (Navarra, Spain), which calcines natural magnesite in two rotary kilns at 1100 ºC and 1800 ºC, to obtain caustic calcined magnesia (CCM) or dead-burned magnesia (DBM), respectively. According to MgO concentration, the three industrial by-products were classified as low-grade MgO (LGMgO) samples and were labelled as PC8, PCC and Caustica P. The PC8 and PCC were dust samples collected from the fabric filters of the air pollution control system from both the DBM and CCM furnaces, respectively. The Caustica P is the finest fraction (< 500 µm) of the caustic calcined magnesia taken at the outlet of the CCM kiln after sieving. These MgO reagents were analysed for their further loss on ignition at 1100 ºC, citric acid reactivity and their mineral content. The latter included MgO, calcium oxide, sulphite, iron oxide and silica (see analysis techniques). The characterisation results are shown in Table 2.

Table 1 - Pig slurry characterization (elemental concentrations are as measured for the aqueous phase).

Measure	Units	Experimental value	Model value
Total solids	g L^{-1}	25.4 ± 0.1	-
Volatile solids	g L^{-1}	16.1 ± 0.1	-
pH	-	7.44 ± 0.12	7.44
Alkalinity	g CO_3 L^{-1}	9.46 ± 0.47	11.0 *
Na^+	mg L^{-1}	433 ± 7	433
K^+	mg L^{-1}	1,760 ± 10	1,760
Ca^{2+}	mg L^{-1}	163 ± 8	163
Mg^{2+}	mg L^{-1}	45.1 ± 4.0	45
$N\text{-}NH_4^+$	mg L^{-1}	2,110 ± 118	2,110
$P\text{-}PO_4^{3-}$	mg L^{-1}	53.1 ± 2.0	53
SO_4^{2-}	mg L^{-1}	32.1 ± 1.0	32
Cl^-	mg L^{-1}	1,460 ± 10	1,460
Total inorganic carbon	mg L^{-1}	-	2,290*

* Estimated from model Step 1, Figure 1.

A number of additional reagents were also formed by pre-treating the LGMgOs and HGMgO with phosphoric acid. This pre-treatment was expected to form magnesium phosphate minerals with unique properties for TAN and PO_4^{3-} removal. These pre-treated reagents were called stabilizing agents (SAs) throughout the rest of this paper. During the pre-treatment step, phosphoric acid was slowly added to an aqueous slurry of each of the magnesium source reagents at a high solid-to-liquid ratio (Romero-Güiza et al., 2014). The stabilizing agents were dried (<60ºC), crushed to a particle size of about 500 µm and then labelled SA-HGMgO, SA-PC8, SA-PCC and SA-Caustica P according to their source reagents. The stabilizing agents were analysed for loss on ignition and mineral content as for their MgO predecessors (Table 2).

Table 2 - Semi-quantitative characterisation reagents

MgO reagents

	Units	HGMgO	PC8	Caustica P	PCC
MgO	%	89.8	68.6	79.4	61.1
P_2O_5	%	-[#]	-	-	-
CaO	%	1.5	9.0	9.9	9.8
SO_3	%	0.0	8.1	0.0	4.7
Fe_2O_3	%	0.0	2.7	2.9	2.3
SiO_2	%	0.0	2.5	3.8	2.3
LOI (1100 °C)	%	8.7	8.7	8.7	19.5
Reactivity*	s	90	445	2655	2725

Stabilizing agents

		SA-HGMgO	SA-PC8	SA-Caustica P	SA-PCC
MgO	%	27.4	25.3	25.8	25.9
P_2O_5	%	39.7	28.8	36.5	27.0
CaO	%	0.4	3.0	2.3	3.6
SO_3	%	0.0	0.0	0.0	0.0
Fe_2O_3	%	0.0	0.9	0.9	0.9
SiO_2	%	0.0	1.2	1.3	2.0
LOI (1100 °C)	%	32.4	40.0	33.0	40.2

* Using the citric acid reactivity test

[#] “-“ means not measured/not relevant

2.2 Analysis techniques

The measure of pH, total solids (TS) and volatile solids (VS) were performed according to standard methods procedures (Eaton et al., 2005). Ion contents (Cl^-, PO_4^{3-}, SO_4^{2-}, K^+, Ca^{2+}, Mg^{2+} and NH_4^+) were determined by ion chromatography using an 863 Advanced Compact IC Metrohm ionic chromatographer using Metrosep columns (Astals et al., 2013). The major and minor components of the magnesium sources and the loss of ignition (LOI) at 1100°C were determined by X-ray fluorescence (XRF) using a Philips PW2400X-ray sequential spectrophotometer. Particular crystal mineral phases were identified by X-ray diffraction (XRD) using a Bragg-Brentano Siemens D-500 powder diffractometer with CuK radiation. The reactivity of HGMgO and LGMgO samples was determined by the citric acid test, which measures the time required by 2.0 g of powdered sample in 100 mL of 0.4 N citric acid solution to reach pH 8.2 (Strydom et al., 2005). Accordingly, the MgO reagents were classed as; highly reactive/soft burnt (acid neutralization times <60 s), medium reactive (acid neutralization times of 180 to 300 s), low reactivity/hard-burnt (acid neutralization times >600 s) and dead burnt (acid neutralization times >900 s).

2.3 Ammonia nitrogen removal experiments

The TAN removal experiments were performed at 25 ºC in a Jar-Test device (Flocculator 2000, Kemira) containing 1.0 L of pig slurry (used as received) and the added magnesium and PO_4^{3-} source reagents. The reactors were continuously stirred at 20 min^{-1} during 4 hours and pH, TAN and PO_4^{3-} were measured at 0, 0.5, 1, 1.5, 2, 3 and 4 hours. For TAN and PO_4^{3-} measurements an aliquot of the jar-tester contents was centrifuged (4,000 rpm for 5 minutes) and filtered (0.45 µm), and the supernatant was analysed. TAN removal was calculated according to Equation (1), where C_0 is the concentration of TAN (mg N L^{-1}) in the aqueous phase at the beginning of each experiment and C is the concentration of TAN (mg N L^{-1}) at a specific experimental time.

$$\%\,TAN\ Removal = \left(\frac{C_0 - C}{C_0}\right) \times 100 \qquad (1)$$

When the MgOs were used, PO_4^{3-} was added as K_2HPO_4 (highly soluble). Whereas, when stabilizing agents were added, these contained both magnesium and PO_4^{3-}, so no additional reagents were added. Calculated N:P:Mg ratios (including added reagents, but not solids contributed by the pig slurry) were 1:1:1.6 for all the MgOs and 1:1:1.3, 1:1:1.6, 1:1:1.3 and 1:1:1.8 for SA-MgO, SA-PC8, SA-Caustica P and SA-PCC, respectively.

2.4 Chemistry modelling

Chemistry modelling was performed with the software package PhreeqC Version 3. PhreeqC calculates conditions that satisfy thermodynamic equilibrium within the aqueous phase and between the aqueous phase and added mineral phases. Fig. 1 illustrates the model steps. The Minteq V.4 database was used, which contained the solubility product constants (K_{sp}) for brucite, dolomite, magnesite, bobierrite, newberyite, periclase and many other relevant minerals involved. A solubility product constant for struvite ($MgNH_4PO_4 \cdot 6H_2O$) of $10^{-13.26}$ was added to the model database (Ohlinger et al., 1998).

In the model, the initial pH and composition of the pig slurry aqueous phase was set to the experimentally measured values before reagent addition, and then an ion charge balance was used to calculate total inorganic carbon (the only major ion that was not measured).

With the MgO reagents, a known amount of K_2HPO_4 was added to the model as a highly soluble equilibrium phase (with arbitrarily large K_{sp}). Periclase was then added to the model in progressively increasing amounts (always fully dissolved, never reached solubility constraints) until the model prediction matched the experimentally measured TAN removal and pH at 4 hours experimental time. This amount of periclase (for which experimental performance equalled modelled performance) was then assumed to reflect the extent of dissolution of reagent in the experiment. This extent of dissolution (in the model) was then converted to an equivalent amount of magnesium and compared to the actual amount of magnesium added as reagent to the experiment. From this comparison a magnesium (elemental) use efficiency was calculated.

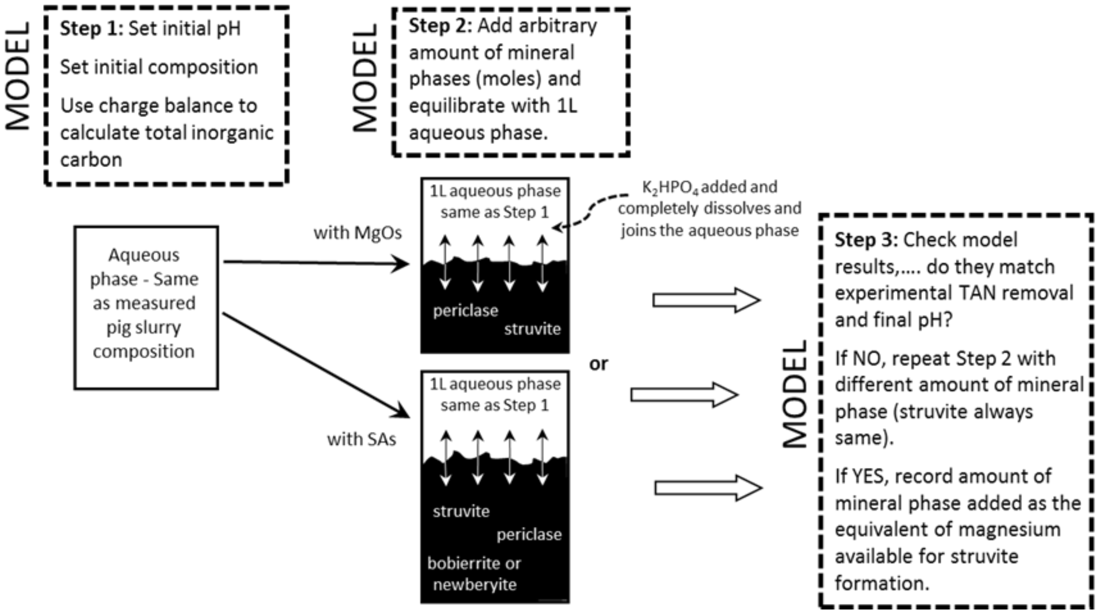

Fig. 1 - Equilibrium modelling approach.

A similar modelling approach was used for the stabilizing agents, but instead periclase plus either bobierrite or newberyite (depending on the dominant form of the stabilizing agents as measured by XRD) were added to the model. All the minerals added to the model always fully dissolved and never reached solubility constraints. The relative amounts of periclase vs. bobierrite or newberyite added to the model, depended on desired model pH and TAN removal to match experimental results. Magnesium and phosphate use efficiencies were then calculated by comparing the amounts of both PO_4^{3-} and magnesium added to the models and to the experiments.

Saturation index (*SI*) values were calculated in accordance with Equation (2); where *IAP* is the ion activity product and a_x is the activity of a respective ion. Equation (2) also illustrates an example for struvite:

$$SI_{\text{struvite}} = \log_{10}\left(\frac{IAP}{K_{\text{sp}}}\right) = \log_{10}\left(\frac{a_{\text{Mg}^{+2}} \times a_{\text{NH}_4^+} \times a_{\text{PO}_4^{-3}}}{K_{\text{sp}}}\right) \quad (2)$$

The SI value of a mineral indicates how likely it is that it would precipitate at particular aqueous phase conditions, with $SI<0$ indicating undersaturated or dissolving conditions, $SI=0$ indicating equilibrium, and $SI>0$ indicating supersaturated or potentially precipitating conditions. Table 3 shows SI values for the pig slurry prior to any reagent addition.

Table 3 - Saturation indices (*SI*) values for the raw pig slurry aqueous phase

Measure		Model value
Periclase	MgO	-10.18
Brucite	$Mg(OH)_2$	-5.44
$Mg(OH)_2$ (active)	$Mg(OH)_2$	-7.39
Newberyite	$MgHPO_4 \cdot 3H_2O$	-1.18
Bobierrite	$Mg_3(PO_4)_2$	-4.00
Magnesite	$MgCO_3$	0.21
Struvite	$MgNH_4PO_4$	0.36
Calcium phosphate (beta)	$Ca_3(PO_4)_2$	2.37
Dolomite (disordered)	$CaMg(CO_3)_2$	2.28
Aragonite	$CaCO_3$	1.29

3. Results and Discussion

3.1 Pig slurry and magnesium reagent properties

Table 2 presents composition and characterisation results for all the magnesium reagents and shows that all the MgOs were predominantly magnesium. Table 2 also shows that pre-treatment with phosphoric acid did form phosphate-based minerals as a significant constituent in the stabilizing agents. Fig. 2 presents XRD patterns for the respective reagents and indicates that all the MgOs contained predominantly periclase, and that PC8 and PCC also contained magnesite and dolomite (Fig. 2a). Fig. 2b suggests that phosphoric acid dissolved periclase and predominantly formed newberyite in the case of SA-PCC and SA-Caustica P, and bobierrite in the case of SA-HGMgO and SA-PC8. These differences in composition of the stabilizing agents correlated with the relative reactivities of their precursor MgOs (Table 2). That is, HGMgO and PC8 were the reagents with highest reactivity (shortest citric acid test time, corresponding to medium and low reactivity, respectively, according to Strydom et al., 2005), while PCC and

Caustica P were the reagents with lowest reactivity (longest citric acid test time, both dead burnt according to Strydom et al., 2005). Newberyite is said to be thermodynamically stable at a pH between 6.4 and 7.7, while bobierrite is said to be stable at a more alkaline pH (Bhuiyan et al., 2008). The compounds with highest reactivity (HGMgO and PC8) could have maintained alkaline conditions via rapid release, despite the added phosphoric acid. Such alkaline pH conditions could have favoured bobierrite formation. Whereas, slow hydrolysis of PCC and Caustica P could have led to near neutral pH conditions which are more conducive to newberyite. Unreacted periclase was detected in all the stabilizing agents (Fig. 2b).

Tables 1 and 3 summarise results from model Step 1 (Fig. 1) and show that there was good agreement between modelled and measured alkalinity (Table 1), indicating that the estimation of total inorganic carbon (TIC) was reliable and that all major ions were accounted for in the model. Negative SI values in Table 3 suggested that the pig slurry was undersaturated with respect to periclase, $Mg(OH)_2$, newberyite and bobierrite, so that these minerals could dissolve (i.e. no solubility constraints). Magnesite and struvite were near equilibrium (slightly positive SI values). This is expected, because these minerals can occur naturally in pig slurry (Ekama et al., 2006). Positive SI values in Table 3 indicated that dolomite and amorphous calcium phosphate could also precipitate in the pig slurry.

In a set of TAN removal experiments, MgOs and K_2HPO_4 were added to supply magnesium and PO_4^{-3}, respectively. The added K_2HPO_4 dissolved rapidly and completely, as confirmed by measurements of dissolved potassium (data not shown). In general, the capacity of an MgO to hydrate and convert to $Mg(OH)_2$ is said to be influenced by MgO concentration, mineral of origin and calcining conditions (del Valle-Zermeño et al., 2012, Strydom et al. 2005). The hydration and dissolution of MgO releases hydroxyls which increases pH. Thus, the dissolution of MgO is reflected in Fig. 3a by the observed sharp increase in measured pH over the first 30 minutes of experimental time. For the remainder of the experimental time, pH rise was gradual (PC8, PCC and Caustica P) or pH stayed essentially constant (HGMgO). The calculated TAN removal extents (Fig. 3d) mirrored the trends in measured pH (Fig. 3a), which suggested that MgO dissolution was releasing magnesium for struvite to remove TAN. TAN removal extents ranged from 47 to 72%, and HGMgO performed the best. As expected, the struvite that formed also sequestered a large proportion of the added PO_4^{3-} (Fig. 3c).

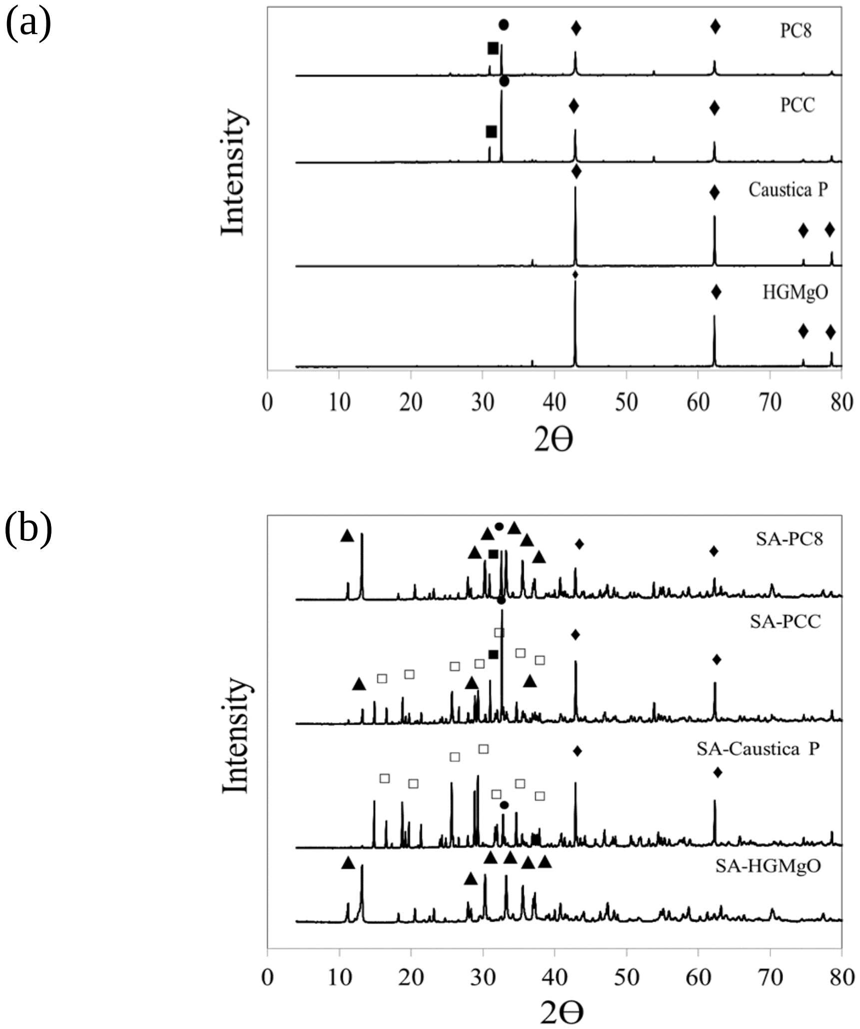

Fig. 2 - Results from XRD analysis of the (a) HGMgO, LG-MgOs and (b) their respective stabilizing agents (SAs), indicating standard peak positions for periclase (♦), magnesite (●), dolomite (■), bobierrite (▲) and newberyite (□).

3.2 Ammonia nitrogen removal using MgO reagents

Model analysis and results in Fig. 3b clearly showed that TAN removal was limited by magnesium supply. Additional TAN would have precipitated as struvite, if more magnesium was available in the aqueous phase. In fact, the model suggested that TAN remained in large excess and would only have become the limiting reagent for struvite at about 10-80 mg N L^{-1} over the relevant pH range 7.0-9.5. Further, the model indicated that all the MgO reagents were poorly dissolved, with only 31-45% of added magnesium being available for struvite formation (see magnesium use efficiencies, Table 4). Note that the calculated efficiencies considered all elemental magnesium in the added reagents, including that of impurities such as magnesite or dolomite which were expected to poorly soluble due to poor reactivity and positive *SI* values (Table 3).

While the magnesium use efficiencies in Table 4 correlated somewhat with reactivities of MgOs in Table 2, the relationship was not as strong as that observed between MgO hydration extents and reactivity (Strydom et al., 2005). Further, a wide range of hydration extents (0.79-76.3%) has been reported over a relevant range of reactivities (Strydom et al., 2005), which does not compare well with the narrow band of magnesium use efficiencies observed in the present study (31-45%). These differences indicated that the extent of conversion of added MgO reagents to struvite (i.e. magnesium use efficiencies, Table 4) was only partly dictated by relative reactivity.

An alternative explanation for the observed poor magnesium use efficiencies is proposed. A high localised pH in close vicinity to dissolving MgO particles could have caused a high localised supersaturation for struvite and induced nucleation and overgrowth of struvite onto the MgO reagent particles. Consequently, eventhough the thermodynamic solubility of periclase and brucite was not constrained (negative SI values, Table 4), a struvite coating layer could have kinetically limited/prevented further

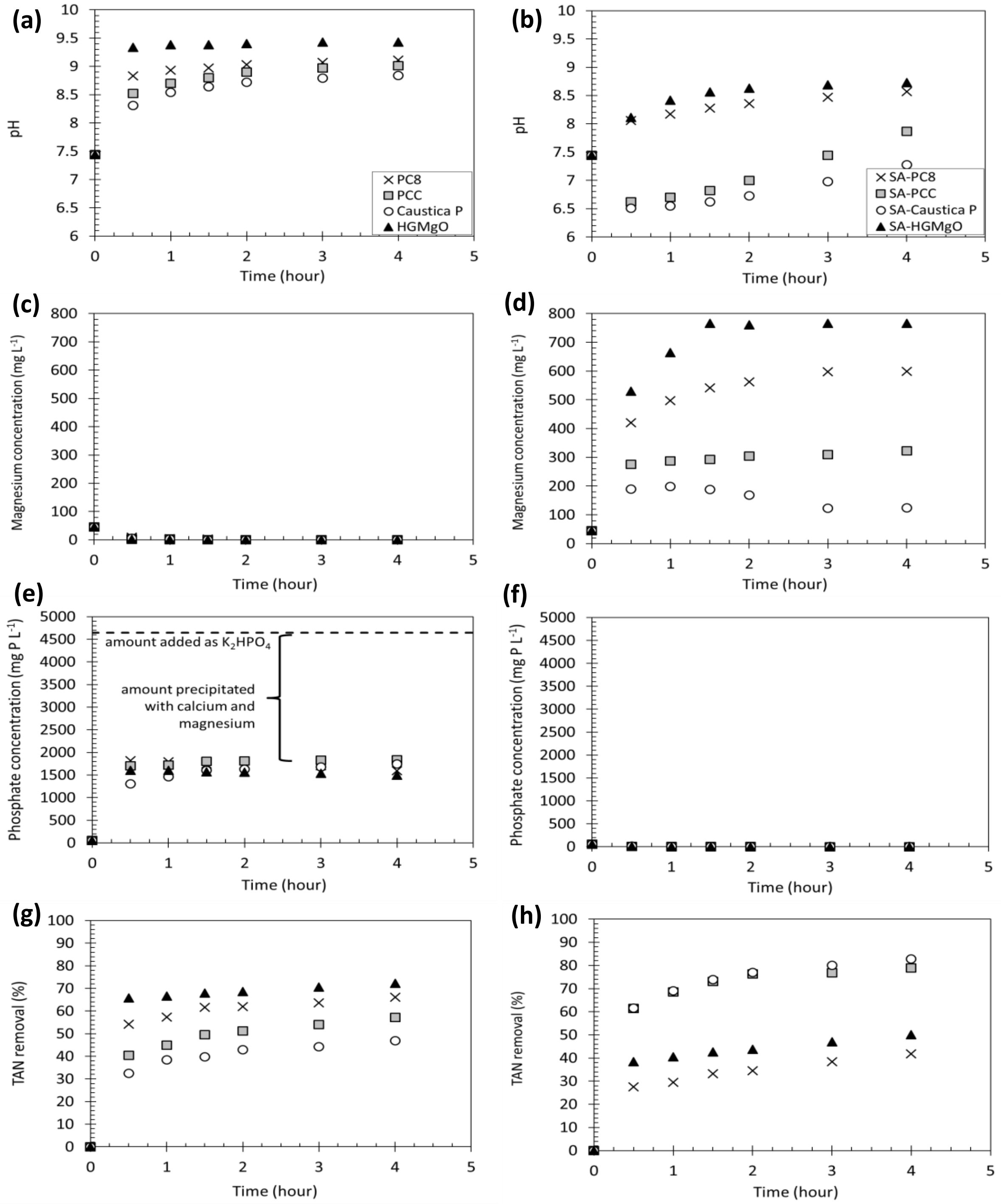

Fig. 3 - Results from the TAN removal experiments showing measured pH, dissolved magnesium and phosphate concentrations, and percentage TAN removal for (a, b, c, d) tests using the MgO reagents and (e, f, g, h) tests using the stabilizing agents (SAs). The legend provided in (a) also applies to (b, c, and d) and that in (e) also applies to (f, g and h).

dissolution. Romero-Guiza et al. (2014, 2015) and Chimenos et al. (2003) observed such struvite coatings over stabilizing agents added to anaerobically digested pig manure and cochineal extraction wastewater, respectively. Accordingly, the leveling off in measured pH, PO_4^{-3} and TAN (Figs. 3a-d) could have been caused by a kinetically limited reagent dissolution. The test series with stabilizing agents provided further corroborating evidence of such phenomena.

Table 4 - Comparison of model results from Steps 1-3 with experimental measurements at 4 hours sampling time using MgO reagents and K_2HPO_4.

	HGMgO		PC8		Caustica P		PCC	
	Exp.[a]	Model [b]	Exp.[a]	Model [b]	Exp.[a]	Model [b]	Exp.[a]	Model [b]
pH	9.43	9.55	9.11	9.41	8.84	9.16	9.01	9.31
Mg (mg L^{-1})	0	0.23	0	0.18	0	0.13	0	0.16
Ca (mg L^{-1})	588	163	328	163	520	163	298	163
TAN (mg N L^{-1})	585	700 [c]	715	860	1,121	1,126	903	981
PO_4^{3-} (mg P L^{-1})	1,498	1,495	1,599	1,604	1,742	2,192	1,833	1,868
Amount of periclase (MgO) added to the model (mM) [e]	- [d]	100	-	88	-	69	-	80
Equivalent magnesium added as MgO reagent to experiment (mM)	223	-	223	-	223	-	223	-
Magnesium use efficiency [e]	-	45%	-	39%	-	31%	-	36%
Saturation indices values								
Periclase (MgO)	-	-8.9	-	-9.2	-	-9.8	-	-9.5
Brucite ($Mg(OH)_2$)	-	-4.1	-	-4.5	-	-5.1	-	-4.7
Magnesite ($MgCO_3$)	-	-0.7	-	-0.9	-	-1.2	-	-1.0
Dolomite (disordered, $CaMg(CO_3)_2$)	-	2.3	-	2.1	-	1.7	-	1.9
Struvite ($MgNH_4PO_4$)	-	0	-	0	-	0	-	0

[a] The values measured at 4 hours were used in this case (assumed to have reached equilibrium)

[b] the result of model Steps 1-3, Fig. 1

[c] TAN calculated by the model may be slightly higher than TAN measured in the experiment, because the model did not include ammonia stripping.

[d] “-“ means not relevant

[e] Percentage of added magnesium that is available for struvite. This was calculated by comparing the known amount of magnesium added as MgO reagent to each experiment, with the amount of periclase required by the model to satisfy the mass balance and match the final measured aqueous phase composition.

3.3 Ammonia nitrogen removal using stabilizing agents

A separate test series used stabilizing agents (SAs) as a source of both magnesium and PO_4^{3-}. The experimental response (Figs. 3e-h) correlated with overall differences in the composition of the SAs (see Section 3.1). That is, results with SA-PCC and SA-Caustica

P (prevalent newberyite) were similar, and results with SA-PC8 and SA-HGMgO (prevalent bobierrite) were similar. With SA-PCC and SA-Caustica P (prevalent newberyite), there was an initial pH decrease to about 6.5 (Fig. 3e), probably due to the release of protons by struvite precipitation. From 30 minutes onwards, the measured pH gradually increased, likely due to the dissolution of residual newberyite (up to pH 7.5) and/or residual periclase. Although PO_4^{3-} in the aqueous phase was barely measurable (Fig. 3g), model analysis showed that SA-Caustica P and SA-PCC were very efficiently supplying PO_4^{3-} for struvite precipitation. In fact, 78-82% of the PO_4^{3-} added as SA-Caustica P or SA-PCC was available to form struvite (see phosphate use efficiencies, Table 5). These high PO_4^{3-} efficiencies translated into high TAN removal extents of 79-83% (Fig. 3h), which is significant, considering that TAN removal extents for the low-grade MgO precursors (Caustica P and PCC) were relatively poor (45-58%, Fig. 3d). These results indicated that pretreatment with phosphoric acid could potentially upgrade low-grade MgOs for TAN removal. With tests using SA-HGMgO and SA-PC8 (prevalent bobierrite), measured pH progressively increased (Fig. 3e), likely due to the rapid dissolution of bobierrite (up to pH 7.7) and/or residual periclase. There was also a substantial magnesium release in the first 30 minutes (Fig. 3f) and struvite did form, but the resulting TAN removal extents were substantially lower for SA-HGMgO and SA-PC8 than for SA-PCC and SA-Caustica P (Fig. 3h). The release of PO_4^{3-} by SA-HGMgO and SA-PC8 appeared to limit TAN removal extents, as indicated by low phosphate use efficiencies of 41-49% (Table 5). Also significantly, SA-HGMgO and SA-PC8 showed inferior TAN removal performance as compared to their precursor MgOs (HGMgO and PC8), so pretreatment with phosphoric acid did not improve performance in this case.

The tests with SAs were mass balance limited by PO_4^{3-} supply, albeit that the PO_4^{3-} efficiencies of SA-PCC and SA-Caustica P were arguably approaching a maximum.

Negative SI values for newberyite and bobierrite (Table 5) indicated that further dissolution was not equilibrium-constrained, and the model also suggested that TAN remained in large excess. Therefore, dissolution of SA reagent was being kinetically limited, similar to the tests using MgOs. The implications of these findings are further discussed below. It is noted here that the magnesium efficiency for SA-HGMgO was unexpectedly high at 75% (mismatch with PO_4^{3-} efficiency, Table 5). This discrepancy could have been caused by a questionable XRF result for SA-HGMgO, which suggested an unexpectedly high PO_4^{3-} content (compared to bobierrite). Sensitivity analysis indicated that this disparity for this particular SA did not significantly influence the overall interpretation of test results.

Table 5 - Comparison of model results from Steps 1-3 with experimental measurements at 4 hours sampling time using stabilizing agents.

	SA-HGMgO		SA-PC8		SA-Caustica P		SA-PCC	
	Exp.	Model	Exp.	Model	Exp.	Model	Exp.	Model
pH [a]	8.73	8.73	8.57	8.57	7.28	7.28	7.87	7.85
Mg (mg L^{-1})	766	1,558	600	1,267	125	1,485	323	1,574
Ca (mg L^{-1})	74	164	91	164	211	163	214	163
TAN (mg N L^{-1})	1,054	1,059	1,228	1,227	361	363	446	456
PO_4^{3-} (mg P L^{-1})	0.1	0.21	0	0.26	1.6	14	0	2.8
Amount of periclase (MgO) added to the model (mM)	-	27	-	21	-	61	-	65
Amount of newberyite added to the model (mM)	-	-	-	-	-	124	-	117
Amount of bobierrite added to the model (mM)	-	37	-	31	-	-	-	-
Magnesium use efficiency	-	75%	-	49%	-	99%	-	72%
Phosphate use efficiency [b]	-	49%	-	41%	-	82%	-	78%
Saturation Indices – *SI* values								
Periclase (MgO)	-	-6.2	-	-6.6	-	-9.0	-	-7.8
Bobierrite ($Mg_3(PO4)_2$)	-	-2.5	-	-2.8	-	-1.6	-	-1.8
Newberyite ($MgHPO_4.3H_2O$)	-	-2.4	-	-2.4	-	-0.6	-	-1.3
Brucite ($Mg(OH)_2$)	-	-1.4	-	-1.8	-	-4.2	-	-3.1
Magnesite ($MgCO_3$)	-	2.8	-	2.7	-	1.5	-	2.1
Dolomite (disordered, $CaMg(CO_3)_2$)	-	5.9	-	5.7	-	3.4	-	4.6
Struvite ($MgNH_4PO_4$)	-	0	-	0	-	0	-	0

[a] Similar meanings are identical to that in Table 3

[b] Same principles as calculation of magnesium use efficiency, but instead considering the phosphate that was added with the stabilizing agents.

3.4 Implications, reagent use efficiency, strategies

An appealing and direct outcome from observations above, was an apparent ability to use phosphoric acid pre-treatment to upgrade low-grade/low-cost MgOs for TAN removal via struvite (compare Sections 3.2 and 3.3). The resulting stabilizing agents are safe, easy to handle, non-invasive and would be relatively low-cost as compared to separate addition of MgOs and PO_4^{-3}. However, acid pretreatment did not improve the TAN removal in every case (compare Sections 3.2 and 3.3 for PC8 and SA-HGMgO). This variable success of acid pretreatment agrees with observations by Santinelli et al. (2013) who found that premixing with phosphoric acid only improved TAN removal for some sources of MgO, and not for others. The present section deals with the underlying precipitation/dissolution chemistry that could cause the variable TAN removal success. It may be possible to understand and perhaps dictate magnesium/phosphate use efficiency with solid reagents such as $Mg(OH)_2$, MgO and SAs. The paragraphs that follow consider a number of possible explanations for the observations noted above, and conclude with a stated alternative hypothesis that appears to be more generally applicable.

Could poor reagent use efficiency of MgOs be explained by differences in composition and reactivity? The MgOs used in the present study had a range of reactivities and differed significantly in composition (Table 2). However, as noted in Section 3.2, magnesium use efficiencies (Table 4) were markedly similar (31-45%), considering that achievable hydration extents were expected to be quite different based on differences in measured reactivities (after Strydom et al., 2005). From these observations, Section 3.2 concluded that reagent use efficiency for struvite was only partly influenced by reactivity.

Further, reagent use efficiency for struvite appears to be only weakly influenced by reagent purity. For instance, TAN removal was only marginally better for HGMgO as compared to LGMgOs (Figure 3), despite a significantly higher purity of the HGMgO

(Table 2). In fact, the improvement in performance by pretreating Caustica P and PCC with phosphoric acid, far exceeded any performance benefits of using the higher purity HGMgO (Section 3.2). For comparison, a study by Di Iaconi et al. (2010) achieved moderate magnesium use efficiencies of 66% or less for a technical grade fine powder MgO (efficiencies were determined in the present study by model analysis of their published data), and a study by Santinelli et al. (2013) was able to achieve very high TAN removal extents with a low purity industrial grade MgO (85% purity). Interestingly, in the study of Santinelli et al. (2013), the measured TAN removal was generally less for a high purity MgO than for the industrial grade MgO. Overall, such observations suggest that reagent use efficiency for struvite is only weakly influenced by MgO purity and that a high TAN removal can also be achieved with a lower purity MgO added at comparable stoichiometric amounts (Santinelli et al. (2013), SAs in Table 5).

Could solubility constraints be limiting reagent dissolution and thus reagent use efficiency? SI values of the pig slurry were negative for the dominant minerals periclase, bobierrite and newberyite throughout all the experiments (Tables 3, 4 and 5). Thus, the pig slurry was always undersaturated with respect to these minerals, and dissolution was not constrained by thermodynamic equilibrium/solubility. Albeit that some mineral (minor) impurities such as magnesite and dolomite were expected to be poorly soluble, due to poor reactivity and positive *SI* values (Table 3). For comparison, model analysis of the data of Santinelli et al. (2013) showed undersaturated conditions with respect to periclase in 22 of their 24 experiments. This was also the case with landfill leachate in the study of Di Iaconi et al. (2010). Overall, such observations suggest that reagent dissolution of MgO is largely kinetically limited, not equilibrium limited.

A more generally applicable explanation: The observations of the present study and other relevant studies, appear to be more generally explained by an alternative hypothesis.

That is, that conditions near a dissolving reagent particle surface can cause unwanted struvite nucleation onto and overgrowth of the reagent particle, restricting further dissolution and markedly reducing reagent use efficiency. Romero-Guiza et al. (2015) observed such struvite coating layers on acid-pretreated LGMgO added to pig manure. In order for struvite to heterogeneously nucleate onto a reagent particle surface, a sufficiently high level of supersaturation must exist near the particle surface to induce such nucleation. In this regard, a high pH (e.g. by hydrolysis), a rapid release of magnesium/PO_4^{-3} by the reagent particle, and a high wastewater strength could all contribute to a high supersaturation near the reagent particle surface. To illustrate, Santinelli et al. (2013) trialled two wastewaters of differing TAN concentration and found that the wastewater with lower TAN content consistently achieved higher TAN removal with MgO. By simple mass balance, a higher yield of TAN would be expected from a higher starting concentration of TAN in a wastewater, however, this was not observed by Santinelli et al. (2013). Instead, if struvite overgrowth was influential, it could have been more prominent in the more concentrated wastewater with a higher starting supersaturation, and this was indeed observed by Santinelli et al. (2013). MgOs could also produce a high localized pH near the dissolving reagent particle surface (pH up to 10-11), which can increase struvite supersaturation. This may have contributed to the similarly poor reagent use efficiencies for all the MgOs (31-45%, Table 4). Also of relevance, an initial decrease in pH was observed with two SAs (SA-PCC and SA-Caustica P) and this depressed pH would have resulted in a reduced level of supersaturation for struvite. Such conditions could suppress struvite nucleation and overgrowth, and it is therefore not surprising that these SAs were the reagents with highest reagent use efficiency. Lastly, a less reactive or less pure reagent could dissolve/release magnesium or PO_4^{3-} at a slower rate, thus leading to a lower supersaturation near the reagent particle surface interface. Thus, a less reactive/less pure reagent could be less prone to struvite overgrowth. This is indeed what is observed by previous studies (Borojovich et al. 2010, Santinelli et al. 2013) who have observed higher TAN removal extents with less pure MgOs added at comparable stoichiometric amounts.

In general, a high reagent use efficiency would reduce requirements for excess reagent. This is important in order to keep operating costs down and maintain feasibility for struvite. Also, a high efficiency (low or no excess of reagent) would reduce residual unreacted reagent in the struvite product, which is important to ensure a consistent and adequate product quality (Di Iaconi et al. 2010).

Conclusions

A commercial high-grade MgO and three MgO-rich industrial by-products from the calcination of natural magnesite have been examined for use in struvite precipitation. Four additional reagents (called stabilizing agents) were prepared by pretreating the MgOs with phosphoric acid. This pretreatment led to a stabilizing agent rich in newberyite or bobierrite depending on the reactivity of the precursor MgOs. The MgOs achieved total ammonia nitrogen removal extents ranging between 47 and 72%. The stabilizing agents with predominantly newberyite performed better (79-83% TAN removal) than their precursor MgOs. These results were significant because they suggested that it may be possible to use phosphoric acid pretreatment to upgrade low-grade MgOs for struvite precipitation. Unfortunately, the stabilizing agents with predominantly bobierrite performed worse than their precursor MgOs, highlighting a need to better understand the underlying chemistry. Model analysis showed that struvite formation was limited by magnesium or phosphate reagent dissolution, and that this was not caused by solubility constraints, but rather kinetic limitations. A mechanism was proposed by which conditions near a dissolving reagent particle surface causes unwanted struvite nucleation onto and overgrowth of the reagent particle, inhibiting further dissolution and markedly reducing reagent efficiency. The findings of the study could have implications for reagent use efficiency with other solid reagents, such as magnesium hydroxide or other MgOs.

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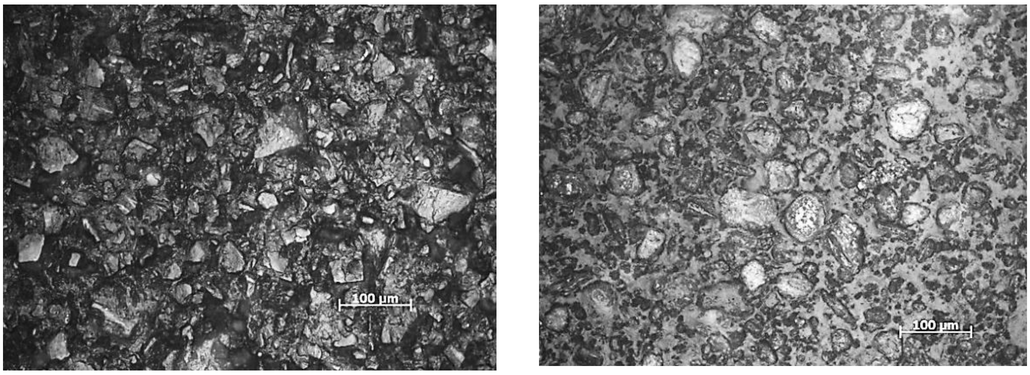

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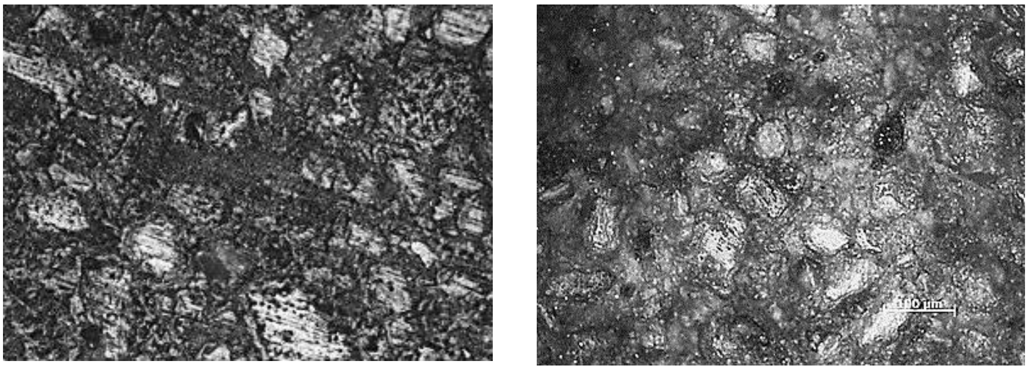
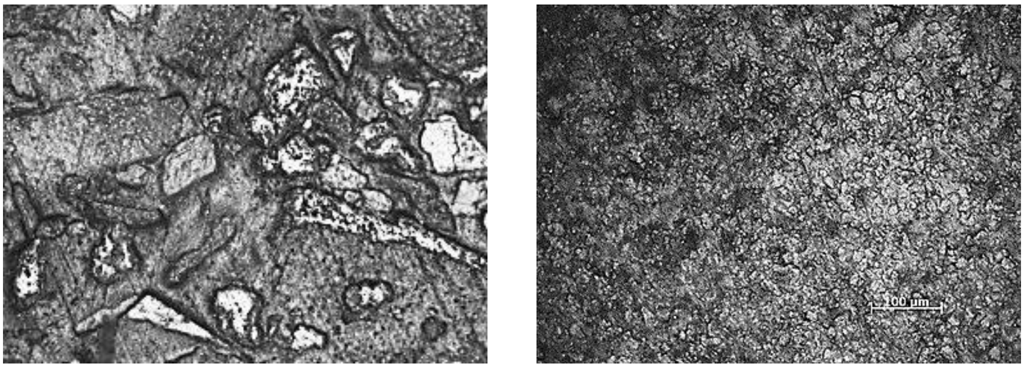
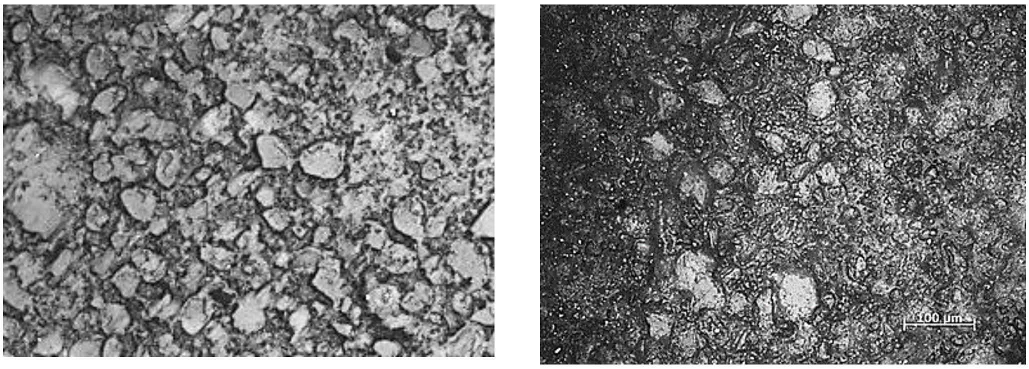


PCC SA-PCC



Caustica-P SA-Caustica-P



HGMgO SA-HGMgO

Fig. S1 - Micrographs of the HGMgO and LG-MgOs and their stabilizing agents (scale bar is identical in all the images). Note that the stabilizing agents appear to show a large amount of fines, which are likely to be mineral products from the phosphoric acid pretreatment.

CHAPTER 2. Coupling anaerobic digestion and struvite precipitation

2.1 The role of additives on anaerobic digestion: a review

The role of additives on anaerobic digestion: a review

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Submitted on Renewable & Sustainable Energy Review

Abstract

Anaerobic digestion is a worldwide technology for the treatment of organic waste streams with clear environmental benefits including generation of methane as renewable energy. However, the need to improve process feasibility of existing applications as well as to expand anaerobic digestion to a range of new substrates has raised interest on several intensifications techniques. Among them, the supplementation of inorganic and biological additives has shown good results at improving digesters methane yields and/or process stability. This manuscript presents a comprehensive review about recent advances in the utilization of inorganic and biological additives. On the one hand, reviewed inorganic additives comprise: (i) macro (e.g. P, N and S) and micro (e.g. Fe, Ni, Mo, Co, W and Se) nutrients supplements, (ii) ashes from waste incineration, (iii) compounds able to mitigate ammonia inhibition, and (iv) substances with high biomass immobilization capacity. Among them, iron additives ($Fe^0$and Fe(III)) have shown particularly promising results, which have been mainly related to

their action as electron donors/acceptors and cofactors of many key enzymatic activities. On the other hand, reviewed biological additives include: (i) the dosage of microbial inocula with high hydrolytic or methanogenic activity (bioaugmentation), and (ii) the addition of enzymes able to facilitate particulate organic matter solubilization.

1. Introduction

Anaerobic digestion (AD) is a widespread technology able to treat organic waste streams, which implementation has been steadily increasing over the last years [1,2]. Digesters design, operation and performance as well as process drawbacks are linked to the nature/origin of the organic residue [3], which can be grouped in five different categories [4,5]: (i) sewage sludge (SS); (ii) animal manures; (iii) food industry wastes, including slaughterhouse waste; (iv) energy crops and harvesting residues, including algae; and (v) organic fraction of municipal solid waste (OFMSW). Nonetheless, digesters configuration is less diverse since most AD plants are either continuous stirred tank reactor (CSTR) or upflow anaerobic sludge blanket (UASB) reactor, which are utilized for particulate and soluble organic streams, respectively [6–8]. Despite these facts, the need to improve the economic feasibility of AD plants, directly linked to biogas yields, has raised attention in process intensification techniques. Different approaches have been applied to enhance digesters biogas production such as (i) co-digestion to increase the digester organic loading rate (OLR); (ii) pre-treatments to increase the bioavailability of the waste; (iii) improvement of the reactor configuration and operation conditions; and (iv) dose of additives to stimulate microbial activity and/or reduce the concentration of inhibitory agents. Several bibliographic reviews addressing these techniques already exist in the literature [4,9–15]; however these publications are mainly devoted to pre-treatments and anaerobic co-digestion, while less attention has been paid to the introduction of additives to the digester medium.

The present paper presents a comprehensive review about the recent advances in the utilization of inorganic and biological additives, a topic of increasing interest in anaerobic digestion due to their capacity to promote microbial activity. On the one hand, inorganic additives comprise chemical reagents, minerals and waste sources able to provide micronutrients or support to immobilize biomass. On the other hand, biological additives include bioaugmentation, typically the dosage of microbial inoculum with high methanogenic activity, and the addition of enzymes able to facilitate particulate organic matter solubilization.

2. Micro- and macro-nutrients supplements

Supply of micro- and macro-nutrient supplements (NS) has become an important topic for agricultural biogas mono-digestion plants (i.e. energy crops, animal manures, and crop residues), since the lack of some micro-nutrients has been identified to be the main reason behind poor process performance [16–18]. Several studies concluded that dosing NS can stimulate methane production as well as improve process stability (e.g. keep pH within optimum values by avoiding volatile fatty acids accumulation and/or providing a minimum alkalinity level) [18–20]. Macro-nutrients (e.g. P, N and S) are indispensable constituents of biomass but also play a necessary role as buffering agents, while micro-nutrients (e.g. Fe, Ni, Mo, Co, W, and Se) are crucial cofactors in numerous enzymatic reactions involved in the biochemistry of methane formation [17,21]. However, excessive concentrations of some macro- and micro-nutrient can led to inhibition of the AD process [22].

Table 1 shows the reported stimulatory and inhibitory concentrations of some metals and their role in methanogenesis. The concentrations varied significantly from one study to another, which has been related to a number of factors, including: (i) the abundance, structure and adaptation periods of the anaerobic niche; (ii) the chemical form of the metals (dependant on pH, redox potential and presence of chelating compounds), which may change their bioavailability for stimulatory and inhibitory purposes; and (iii) the antagonistic and synergistic effects between elements [1,23,24].

Table 1. Reported stimulatory and inhibitory concentrations of metals on anaerobic biomass and their role in methanogenesis (expanded from Lo et al. [25] and Schattauer et al. [17])

Metal	**Stimulatory concentration (mg L^{-1})**	**Inhibitory concentration (mg L^{-1})**	**Role in Methanogenesis**	**References**
Al		1000<Al<2500		[24]
Ca	100<Ca<1035	300<Ca<8000		[24-27]
Cd	<1.6	36<Cd<3400		[28-30]
Co	0.03<Co<19	35<Co<950	• Methyltransferase	[31-36]
Cr	0.01<Cr<15	27<Cr<2500		[28, 29,36]
Cu	0.03<Cu<2.4	12.5<Cu<350		[28,29,34,36]
Fe	<0.3		• Formyl-MF-dehydrogenase • CODH, ACS • Hydrogenases	[35]
K	<400	400<K<28934		[24,27]
Mg	<720			[24]
Mn	<0.027			[35]
Mo	<0.05		• Format-dehydrogenase • Formyl-MF-dehydrogenase	[35]
Na	100<Na<350	3500<Na<8000		[24]
Ni	0.03<Ni<27	35<Ni<1600	• CODH • Methylreductase • Hydrogenases	[28,29,31-34]
Pb	<0.2	67.2<Pb<8000		[26-28]
S			• CODH • Hydrogenases	
Se	<0.04		• Format-dehydrogenase • Formyl-MF-dehydrogenase • CODH/ACS	[35]
W	<0.04			[35]
Zn	0.03<Zn<2	7.5<Zn<1500		[28,29,31,34,35]

CODH: carbon monoxide dehydrogenase; SODM: superoxide dismutase; ACS: acetyl-CoA synthesis; FDH: formate dehydrogenase

Process stability is a major concern in commercial full-scale AD plants, since poor process stability normally leads to unsteady methane productions. Even more, prolonged instability episodes may result in process failure. Accordingly, several research efforts have been carried out to overcome source of AD instability [37–40]. Table 2 shows some experiences with macro- and micro-nutrients addition that improved methane production and/or process stability. For instance, Nges and

Björnsson [18] observed that the addition of a concentrated solution of micro- and macro-nutrients stimulated and stabilized a digester fed with a mixture of energy crops. NS addition also allowed to reach higher methane yields at relatively short hydraulic retention times (HRT, 30 – 40 days). Similarly, Zhang et al. [19] concluded that the micro-nutrients provided by a piggery wastewater were the main reason behind the improved methane yield of a food waste digester, whose control (without piggery wastewater addition) presented low methane yields and high levels of volatile fatty acids (VFA). Table 2 summarizes research experiences demonstrating the beneficial effect of NS addition on methane production and process stability.

Ni, Co and Fe are the most studied NS, since they are essential cofactors of carbon monoxide dehydrogenase, acetyl-CoA decarbonylase, methyl-H_4SPT:HS-CoM methyltransferase, methyl-CoM reductase and other enzymes involved in the acetoclastic methanogenesis pathway [33,44]. Furthermore, these metals have also shown to be essential for the acetotrophic pathway of methanogenesis (acetate oxidation to carbon dioxide and hydrogen), which is currently emerging in importance [45–47]. Pobeheim et al. [48], who digested maize silage at mesophilic conditions, reported that Ni and Co deficit (<0.1 mg Ni^{2+} kg^{-1} and <0.02 mgCo^{2+} kg^{-1} in wet-basis) had a negative impact on process stability (i.e. accumulation VFA) at OLR above 2.6 g TS L^{-1} d^{-1}. However, enhancing Ni and Co levels to 0.6 and 0.05 mg kg^{-1} respectively, allowed stable digester performances until the system reached an OLR of 4.3 g TS L^{-1} d^{-1}. Contrariwise, Zandvoort et al. [49], who analyzed the impact of Fe, Ni and Co on a methanol UASB reactor, noted that only Fe had significant effect on the methanol degradation rate. Specifically, increasing influent Fe concentration from 0.056 mg L^{-1} to 0.56 mg L^{-1} allowed improving the methanogenic activity from 152 mg CH_4-COD g VSS^{-1} d^{-1} to 291 CH_4-COD g VSS^{-1} d^{-1}, respectively.

Table 2. Experiences with macro- and micro-nutrients addition that improved methane production and/or process stability.

Waste	Inoculum	Assay conditions			Nutrient addition		SMP			Stability period		Reference
		Reactor	OLR ($kg^a\ m^{-3}d^{-1}$)	T (°C)	Solid add	($mg^b\ L^{-1}$)	Control	Sample	($m^3CH_4\ kg^{-1c}$)	HRT (d)	Operation time (d)	
OFMSW	SS digestate	CSTR		37	Ni/Co/Fe	0.13/3.5/817	0.38 - 0.1	0.35	VS	30	140	[41]
				55		0.22/3.49/896	0.38 - 0.1	0.3	VS	30	140	
FVW (x2)	FVW digestate	CSTR	3.0 (TS)	37	NS^e		412*	383	TS	30	100	[18]
FVW (x2)	FVW digestate	CSTR	3.0 (TS)	37	NS^e		391*	371	TS	40	100	
FVW (x4)	FVW digestate	CSTR	3.0 (TS)	37	NS^e		403*	360	TS	40	100	
OFMSW	PM digestate	Semi-CSTR	6.3 (COD)	37	NS^f		0.4-0.5	0.35-0.5	VS	20	92	[19]
			3.2 (COD)		NS^f		0.4-0.6	0.35-0.6	VS	40	62	
			4.3 (COD)		NS^f		0.3-Fail	0.35-0.5	VS	30	73	
			6.3 (COD)		NS^f		Fail	0.35-0.5	VS	20	113	
FVW	FVW digestate	BMP		22	KH_2PO_4	155 (P)	0.28	0.29	VS	-	-	[42]
						465 (P)	0.28	0.27	VS	-	-	
						755 (P)	0.28	0.27	VS	-	-	
OFMSW	OFMSW digestate	CSTR	5 (VS)	37	Se/Co	0.2/1.0	0.7-Fail**	0.6-0.8	VS^g	n.d.***	300	[38]

x#: number of different FVW substrates used

[a] OLR organic basis units in brackets

[b] Concentration nutrients basis units in brackets

[c] SMP organic basis units

[d] m^3 biogas

[e] Nutrient supplement composed by N, P, S, Fe, Ni, Co, Mo

[f] Nutrient supplement composed by Co, Mo, Ni, Fe

[g] SMP expressed in biogas instead of CH_4

* obtained by BMP assay

** control working at an OLR of 2 kgVS $m^{-3}d^{-1}$

***n.d. non-determined

Coates et al. [50] showed that adding amorphous Fe_2O_3 at a concentration of 16 g L^{-1} diminished the concentration of malodorous compounds (H_2S and VFA) and enhanced the methane production of a pig manure digester. The positive effect of Fe(III) supplementation was attributed to the Fe(III)-reducing capacity, which favors redox processes alleviating the thermodynamic limitations on VFA degradation. Furthermore, Fe(III) can precipitate H_2S minimizing related inhibition phenomena [51]. In a full-scale OFMSW digester, Romero-Güiza et al. [52] observed that reducing the H_2S concentration from 1900 to 50 mg L^{-1} through a $FeCl_3$ solution (2.5 kg of $FeCl_3$ per ton of organic matter fed), led to a prompt reduction of the propionate concentration.

Schmidt et al. [37] individually studied the influence of Fe, Ni, Co, Mo and W depletion on five wheat stillage digesters operated at a high OLR (10 g VS L^{-1} d^{-1}) and HRT of 7-8 days. It was found that Fe and Ni deficiency affected digester performance after 14 days, whereas more than 50 days were required to detect an adverse effect linked to Co or W deficiency. Fe deficiency led to the accumulation of propionic acid (7.0 g L^{-1}), whereas Ni deficiency resulted in the accumulation of 1.5 g L^{-1} of acetic and propionic acids. The authors concluded that Fe deficiency did not only affect methanogenic archaea but also propionate oxidizing bacteria. Actually, both groups are known to utilize hydrogenases which contain Fe and Ni as cofactors. Nonetheless, Fe is required in higher concentrations and therefore its deficiency causes a greater impact on process performance compared to Ni [35,53]. Banks et al. [38] identified Se and Co as critical micro-nutrients when an OFMSW AD was operated at high OLR (3-5 g VS L^{-1} d^{-1}) and high ammonia concentration (4.7 g NH_4^+-N L^{-1}). Microbial analysis of the methanogenic community revealed that the acetotrophic pathway (acetate oxidation followed by hydrogenotropic methanogenesis) was the predominant methanogenic pathway rather than acetoclastic methanogenesis. The authors linked this fact to the different trace elements requirement (i.e. 0.2 mg Se L^{-1} and 1.0 mg Co L^{-1}).

Digester temperature is known to play a key role in determining the microbial community structure [54,55] and degradation pathways [56]; consequently, different micro-nutrient requirements are expected under different temperature conditions. Higher micro-nutrient requirements have been reported for thermophilic systems in respect to mesophilic systems [57,58]. This phenomenon has been related to a decrease in nutrient bioavailability and/or an increased nutrient requirement under thermophilic conditions [59]. Comparing the micro-nutrient (i.e. Ni, Co, Fe) requirements to obtain an stable performance of a mesophilic and a thermophilic OFMSW digester, Uemura [42] observed that they were slightly higher in thermophilic (Ni/Co/Fe: 0.20/3.5/896 mg L^{-1}) than in mesophilic conditions (Ni/Co/Fe: 0.13/3.5/817 mg L^{-1}). Similarly, Zitomer et al. [60] studied the impact of Ni, Co and Fe (25 mg L^{-1}) supplementation on thermophilic and mesophilic communities taken from 5 full-scale sewage sludge digesters. Specifically, anaerobic biomass was obtained from four temperature-phased anaerobic digesters (thermophilic followed by mesophilic) and one single-phased thermophilic digester. The results showed that propionate and acetate uptake rates increased at different extent after micro-nutrient addition (either individually or all three micro-nutrients together). As a general trend, propionate utilization rates were more frequently stimulated by micro-nutrient addition than those of acetate, and especially in thermophilic systems.

2.1 Ashes from waste incineration

Municipal solid waste incineration (MSWI) is a widespread technology to treat municipal solid waste (MSW) as it produces energy and reduces MSW volume up to

90% [61]. However, MSWI generates two types of solid ash: (i) bottom ash (BA), and (ii) fly ash (FA), the latter is also known as air pollution control residue. BA, classified as a non-hazardous waste, is generally rich in calcium oxide and silica with a low heavy metals content, while FA, classified as a hazardous waste, is mainly composed of heavy metals, soluble salts, chlorinated organic compounds and lime [62]. The addition of BA and/or FA to an anaerobic digester might increase metals concentration resulting in beneficial or detrimental effects on the AD process [63–65]. The beneficial impact of MSWI ashes on AD performance has been mainly related to alkalis and trace metals, able to leach out from the ash under AD pH values (6.5-8.0). For instance, under this pH range, CaO provides alkalinity to the system. Moreover, at reasonable dosing rates, it is unlikely that light metal ions would reach inhibitory levels when adding MSWI ashes into anaerobic digesters [64,65]. Table 3 summarises the results of research studies that added MSWI ashes to AD systems.

Lo et al. [27] studied the effect of ashes particle size on MSW anaerobic digestion through a series of biomethane potential test (BMP). Specifically, different doses of milled BA (68% 0.4-106 nm; 32% 1110-10000 nm), milled FA (75% 0.4-106 nm; 25% 1110-10000 nm) as well as non-milled BA and FA were tested. Results clearly indicated that both BA and FA (milled and not-milled) were able to improve biogas yields of OFMSW digestion (controls seemed inhibited as pH values around 6 were recorded during the test). Regarding particle size, milled BA and FA showed slightly better performance than non-milled ashes, this was related to their higher capacity to immobilize microorganisms. The authors concluded that the improvement of digester performance was mainly related to the increased levels of alkali metals, heavy metals and trace metals (i.e. Ca, Mg, K, Na, Fe, Si, Mn, B, Al, Ta, Ba and W).

Table 3. Impact of MSWI ashes addition on anaerobic digesters biogas production.

Waste	Inoculum	Assay conditions			Ashes addition		Gas production			Reference
		Reactor	**OLR (kg[a] m^{-3} d^{-1})**	**T (°C)**	**Ash**	**Concen. (g x^{-1}[b])**	**Control**	**Sample**	**(m^{3}biogas kg^{-1}[c])**	
MSW	SS full-scale plant Digested	CSTR	2 (VS)	35	BA	12 (d)	< 0.2	> 0.2	VS	[21]
					BA	24 (d)		> 0.2	VS	
MSW	SS full-scale plant Digested	BMP		35	BA	100 (L)	0.209	0.124	VS	[63]
					FA	20 (L)		0.222	VS	
MSW	SS full-scale plant Digested	CSTR	2.5 (VS)	35	BA	15 (L)	0.05-0.20	0.15-0.30	VS	[65]
						30 (L)		0.20-0.35	VS	
MSW	SS full-scale plant Digested	BMP		35	FA	30 (gVS)	0.065	0.134	VS	[27]
					MNFA	18 (gVS)		0.160	VS	
					BA	120 (gVS)		0.175	VS	
					MNBA	120 (gVS)		0.195	VS	
Synthetic MSW	SS full-scale plant Digested	CSTR	2.5 (VS)	35	BA	1:4[d]	1200	800	(mg L^{-1})[e]	[64]
						1:2[d]		500	(mg L^{-1})[e]	
Synthetic MSW	SS full-scale plant Digested	Four layers arrangement UASB	n.d.	35	FA	10 (L)	0.211	0.167	VS	[66]

[a] OLR organic basis units in brackets

[b] Concentration ash basis units in brackets

[c] Gas production on organic basis units in brackets

[d] BA:MSW ratio

[e] TOC effluent

In a subsequent study, Lo et al. [21] analyzed the effect of two BA (12 and 24 g d^{-1}) and two FA (1 and 3 g d^{-1}) additions on OFMSW continuous digesters (5 L), each operated at four different hydraulic retention times (i.e. 40, 20, 10 and 5 days). Results showed that, after an adaptation period, both BA dosing allowed to improve digesters performance (stability and biogas yields), but only when operated at high HRT (20 and 40 days). FA (1 g d^{-1}) also led to minor biogas production improvements. This phenomenon was again related to the released levels of alkalis (i.e. Ca, K, Na and Mg) and other metals (i.e. Co, Mo and W) [21].

2.2 Iron

Iron has become one of the most prominent additives to improve anaerobic digestion performance owing to its conductive properties and low price [67–69]. Reported iron advantage also include: (i) its capacity to decrease oxidative-reductive potential (ORP) of the anaerobic digestion media and therefore provide a more favorable environment for anaerobic digestion [70]; and (ii) its role as a cofactor of several key enzymatic activities, such as pyruvate-ferrodoxin oxidoreductase, which contains Fe-S clusters and plays a key role in fermentation [71]. Different iron forms have been reported to stimulate the anaerobic digestion. On the one hand, Fe(III) reduction is a favorable process to directly oxidize organics into simple compounds [71–73]. Nonetheless, Fe(III) reduction can limit the conversion of organics to methane as Fe(III) reduction is more thermodynamically favorable than methanogenesis [74]. On the other hand, Zero valent iron (ZVI) has been found able to accelerate the hydrolysis and fermentation stages due to its action as electron donor [75]. Table 4 summaries the impact of iron addition in AD systems.

As can be observed in Table 4, different iron forms have led to important methane production improvements. For instance, Zhang et al. [78] studied the impact of adding Fe powder or scraps (clean scrap or rusty scrap) in a waste activated sludge AD. Enhanced methane yields were reported for all Fe additions, being rusty scrap the iron source that led to a higher improvement (30%). According to the authors, the reduction of the Fe(III) oxides on the surface of the rusty scrap promoted microbial hydrolysis-acidification of complex matters, and therefore provided more organic matter for methanogenesis. Schmidt [80], who studied the effects of an iron additive (composed of 37% iron and other macro and trace elements) on the anaerobic digestion of *Jatropha curca* press cake (0.059 g iron additive gTS^{-1}), observed that the increase of the OLR from 1.3 to 3.2 gVS L^{-1} d^{-1} led to a decrease in biogas yield. However, biogas yield decline was less pronounced in the presence of the iron additive. This different behavior was explained by the reduction of the H_2S concentration in the biogas and digester media caused by the iron additive, which smoothed the inhibition of the anaerobic biomass as well as kept biogas quality.

Focusing on the utilization of ZVI, Zhang et al. [77] showed that the use of a ZVI bed in a UASB reactor allowed a good performance with a COD/SO_4^{2-} ratio of 4.5. The authors claimed that ZVI could act both as an additional electron donor and buffering agent to decrease the un-dissociated H_2S concentration, thereby diminishing its negative impact on the anaerobic process. Regarding the microbial community, a clear stratification was observed within the reactor. Most sulfate reduction occurred in the bottom of the reactor while a more efficient methanogenesis occurred in the upper layer.

Table 4. Impact of iron addition to anaerobic digester

Waste	Inoculum	Assay conditions			Fe addition		SMP			Reference
		Reactor	OLR (kg^a m^{-3} d^{-1})	T (ºC)	Fe add	Concen. (g L^{-1})	control	sample	(m^{3}CH$_4$ kg^{-1b})	
Waste water textile factory	Lab-digester digestate	UASB	(HRT 24h)	25	ZVI	200	0.87	2.11	(L d^{-1})^c	[76]
Synthetic	MSW digestate	UASB	(HRT 24h)	35	ZVI		5.6	10.5	(L d^{-1})^c	[77]
Wastewater treatment plant	SS digestate	BMP		35	Clean scrap	10	0.166	0.201	VSS	[78]
					Rusty scrap	10		0.215	VSS	
Synthetic (Cellulose)	OFMSW digestate	BMP		37	Fe-NPs	18	0.471	0.519	TS^d	[79]
Jatropha press cake	Lab-digester processing JPC digestate	CSTR	2.6 (VS)	38	Iron additive	0.059^e	0.355	0.368	VS	[80]
							0.086	0.282	VS	

[a] OLR organic basis units in brackets
[b] SMP organic basis units
[c] Methane production rate, units in brackets
[d] SMP expressed in biogas instead of CH_4
[e] Concentration in g gTS^{-1}

The inhibition in anaerobic digestion reactors by high sulfate concentrations (influent COD/SO_4^{2-} ratio <10) can be explained by the activity of sulfate reducing bacteria (SRB) which compete with methanogens for electron utilization and produce sulfide, highly toxic for a number of anaerobic microorganisms [24,81]. In a subsequent study, where azo dye wastewater was treated in a UASB reactor, Zhang et al. [76] found that ZVI promoted the growth of methanogens. Such properties enabled the UASB reactor to operate well at low temperatures (35 to 25 ºC) and HRTs (24 to 12 h). Later on, Liu et al. [70] studied the application of ZVI in combination with an electric field in an UASB reactor. Applying a voltage of 1.4V, allowed to sped up sludge granulation (granule size rapidly increased from 151 µm to 695 µm in 38 days) and improve reactor chemical oxygen demand (COD) removal (from 60% to 91% in 4 days). According to the authors, the electric field combined with ZVI created a favorable environment for the growth of methanogens through reducing the ORP (-270 to -370 mV) and increasing the buffer capacity of the system [70].

Liu et al. [71] studied in the acidogenic reactor of a two-stage sewage sludge digester the impact of ZVI power dosage (20 g L^{-1}) at two HRTs (2 and 6 h). The ZVI dosed reactor presented a lower concentration of VFA and a higher COD removal efficiency than the control at both HRTs, highlighting ZVI capacity to facilitate hydrolysis and fermentation. ZVI powder supplementation also change VFA distribution, since the ZVI dosed reactor presented a lower percentage of propionate and a higher percentage of butyrate and acetate than control. The authors related the difference on VFA distribution to the reducibility of ZVI powder. Finally, fluorescence in situ hybridization (FISH) images showed that the ZVI dosed reactor present a higher abundance of acidogenic and acetogenic bacteria compared to the control reactor. These results are in agreement with the observations made by Meng et al. [73], who reported that ZVI power addition into an acidogenic reactor enhanced the enzymatic activity 2-34 times, and increased propionate degradation rates in comparison to the control. In addition, microbial analysis results showed an increased diversity and relative abundance of homoacetogenic and propionate-utilizing bacteria in the presence of ZVI [73].

3. Additives to mitigate ammonia inhibition through struvite formation

Many research efforts have been carried out to mitigate ammonia nitrogen inhibition in AD systems. Among them, the addition of material with ion exchange capacity (bentonite, glauconite, phosphorite and zeolites) or inorganic absorbent materials (clay, manganese oxides or zeolites) have shown good results [82–84]. In the recent years, the possibility of coupling AD and struvite precipitation in the same reactor has attracted some attention (Table 5), as struvite ($MgNH_4PO_4 \cdot 6H_2O$) is a valuable slow-releasing fertilizer [85–88]. Struvite precipitation naturally occurs when the combined concentrations of Mg^{2+}, NH_4^+ and PO_4^{3-} exceed the struvite solubility product [89]. Therefore, the precipitation of struvite in many AD systems requires the addition of chemical compounds since the concentrations of Mg^{2+} and PO_4^{3-} are typically low in relation to that of NH_4^+ [90]. For this purpose, several magnesium ($MgSO_4$, $Mg(OH)_2$, $MgCl_2$, MgO) and phosphate (H_3PO_4, phosphates salts) sources have been applied [91]. Uludag-Demirer et al. [92], who investigated the effect of adding $MgCl_2$, $Mg(OH)_2$ and Na_2HPO_4 in batch manure digesters, did not observe any improvement on the methane production despite the lower ammonia nitrogen concentration. The authors observed that the digesters supplied with $Mg(OH)_2$ and Na_2HPO_4 suffered cation (Na^+ and Mg^{2+}) and pH inhibition (pH above 8.5 were obtained at the end of the assay), while the digesters supplied with $MgCl_2$ and

Na_2HPO_4, which presented final pH values similar to those of the control assays, had only cation inhibition. Contrariwise, Lee et al. [93] satisfactorily operated a continuous food waste digester with struvite precipitation, where $MgCl_2$ was added to reach a Mg:P molar ratio of 1:1 and pH was adjusted between 7.7 and 8.3. The authors concluded that the 50% methane production improvement was due to the reduction of ammonia nitrogen concentration from 6.0 to 2.0 g N L^{-1}. Demirer et al. [94] demonstrated that the addition of $MgCl_2$ (0.92 and 1.87 g Mg^{2+} L^{-1}) to a SS anaerobic digester with an initial concentration of 1.4 g NH_4-N L^{-1} and 0.06 g PO_4^{3-}-P L^{-1} allowed to recover 50% of the nutrients (N and P) in the form of struvite. Moreover, the authors claimed no significant impact on the methane yield and the acetate-utilizing methanogens population [94]. However, continued dosing of Mg reagents (e.g. $MgCl_2$ or $Mg(OH)_2$) in excess can led to inhibitory phenomena by extreme pH or cation toxicit as well as high operation costs associated with Mg reagents purchasing [89]. In this regard, Romero-Güiza et al. [95] found that the use of stabilizing agent (composed mainly of $MgPO_4 \cdot 3H_2O$) formulated with low-grade magnesium oxide by-product, can reduce the ammonium concentration up to 70% and increase the specific biogas production by 40% with a long-term stability. The authors attributed the increase in biogas production to the reduction in ammonia concentration, and the increase of magnesium and particles concentration in the digester medium.

Table 5. Mitigation of ammonia inhibition by combining anaerobic digestion and struvite precipitation in the same reactor.

Waste	Inoculum	Assay conditions			Solid addition		NH_4^+ removal (%)	Biogas production			Reference
		Reactor	OLR (kg^a m^{-3} d^{-1})	T (ºC)	Solid add	Concen. (g L^{-1})		control	sample	(units)	
Synthetic	Winery wastewater sludge digestate	Batch		35	Magnesic Zeolite*	0.005	n.d.**	0.75	1.22	g COD-CH_4 g $VSS^{-1}d^{-1}$	[96]
SS	SS digestate	Lab-scale batch		35	$MgCl_2$*	0.266	n.d.**	215	208.2	mL biogas^b	[41]
						0.533	n.d.**		218.9	mL biogas^b	
						0.800	n.d.**		211.2	mL biogas^b	
CM	CM full-scale digestate	BMP		35	$Mg(OH)_2$	4.0	n.d.**	101.1	-87.4	mL biogas^b	[92]
					$Mg(OH)_2$	2.0	n.d.**		-92.8	mL biogas	
					$Mg(OH)_2$	1.0	n.d.**		-74.6	mL biogas^b	
					$MgCl_2 \cdot 6H_2O$	7.0	13		71.2	mL biogas^b	
					$MgCl_2 \cdot 6H_2O$	3.5	17		72.6	mL biogas^b	
					$MgCl_2 \cdot 6H_2O$	1.8	11		88.3	mL biogas^b	
SS	SS full-scale digestate	BMP		35	$MgCl_2 \cdot 6H_2O$*	0.0009	n.d.**	140	140	mL CH_4	[94]
						0.0019	n.d.**		140	mL CH_4	
SS		CSTR	0.050 (COD)			0.0033	<50	3300-4500	1000-4400	mL CH_4 d^{-1}	
						0.0021	<30		2600-4300	mL CH_4 d^{-1}	
PM	PM digested	CSTR	1.1 (VS)	37	$MgPO_4.3H_2O$	5	4.5	0.13	0.17	m^3CH_4 kg^{-1}	[95]
						30	77		0.19	m^3CH_4 kg^{-1}	

[a] OLR organic basis units in brackets

[b] Net biogas production

*Concentration expressed as Mg^{2+}

**n.d. non-determined

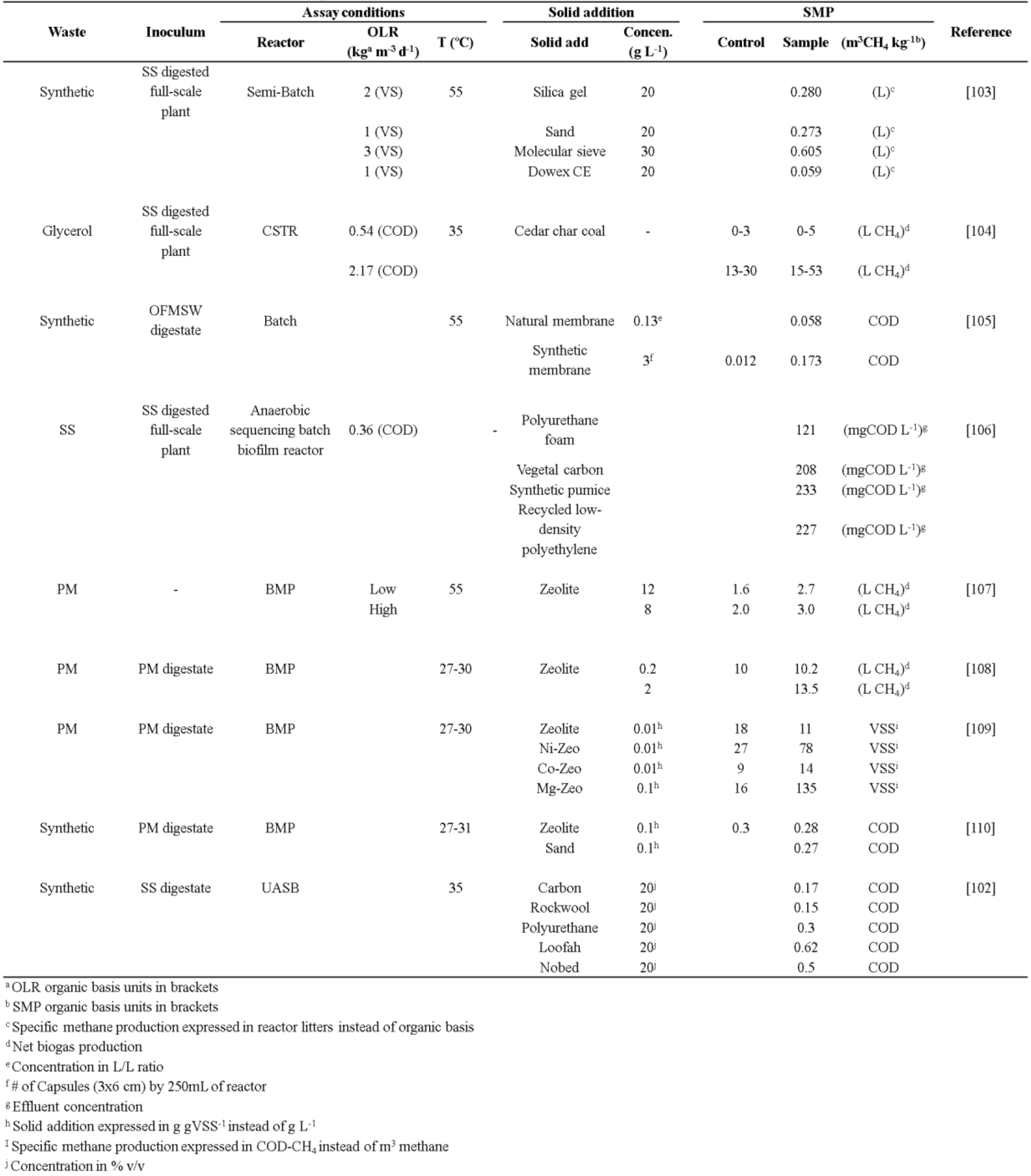
4. Additives to promote biomass immobilization

One of the main constrains in AD systems is biomass washout, specifically when treating low-medium COD wastewaters [97,98]. The use of supports to retain the biomass in the digester allow to operate digesters at a lower HRT and at a higher OLR [82]. Furthermore, biomass immobilization, particularly methanogens, may result in an improvement of process robustness [84,99–101]. The rate of biofilm formation (microbial attachment) on these supports media has been reported to be influenced by several factors, such as specific surface area, porosity, pore size and surface roughness [102]. Table 6 summarizes research outcomes of supports utilized in AD systems.

Watanabe et al. [104] placed cedar charcoal (pore size = 50 µm) in a continuous mixed digester co-digesting sewage sludge and crude glycerol at three OLRs, where OLR increments were reached by adding more glycerol to the feeding. At the highest OLR (2.17 g COD $L^{-1}d^{-1}$), results clearly illustrated that cedar charcoal addition was able to enhance the propionate degradation rate and thus avoid its accumulation, which has been identified as the main disrupting phenomena when using glycerol as co-substrate [111]. Additionally, the charcoal-containing reactor showed methane productions 1.6 times higher than control. Scanning electron microscopy (SEM) imaging revealed microbial attachment to the pores of the charcoal, while the examination of the microbial community revealed a high presence of hydrogenotrophic methanogens. The authors concluded that the presence of charcoal in the digester facilitated the abundance hydrogenotrophic methanogens (H_2-utilizing methanogen) and consequently the conversion of glycerol to methane. The effectiveness of charcoal as support material was also reported by Lima de Oliveira et al. [112], which used two immobilized biomass anaerobic reactors (a charcoal bed and a mixed bed of expanded clay and polyurethane foam) to treat synthetic wastewater with 14 mg L^{-1} of linear alkylbenzene sulfonates (LAS). Lima de Oliveira et al. [112] determined that the reactor with biomass immobilized on charcoal presented higher kinetic degradation coefficient than the biomass on the mixed bed. The authors concluded that the support materials influenced the development of the microbial community, since they selected some microorganisms in detriment to others. In this particular case, archaea was favored when the support material was charcoal, while both supports allowed the growth of different groups of bacteria (including SRB biomass), which were probably responsible for LAS degradation.

Zeolites have also been reported as a capable microbial support in AD system for different types of wastewater [109] (Table 6). Besides its biomass immobilizing capacity, advantages of zeolites have also been related to being a cost-effective ammonia sequestrating agent [82,84]. Even more, zeolites can be modified to increase their ionic exchange capacity or supply micronutrients (e.g. Ni, Co, Mg) [108]. Nonetheless, high amounts of zeolite can lead to toxic phenomena due to the accumulation of heavy metals [110]. Fernandez et al. [113] studied the microbial communities immobilized on zeolite (particle size distribution 0.25 – 0.50 and 0.50-0.80 mm) in an anaerobic fluidized bed reactors treating distillery wastewater at mesophilic conditions. Scanning electron micrographic (SEM) images revealed the high level of colonization on both the interior of the ruggedness and in the superficial zones.

Table 6. Solids added to AD reactors to promote biomass immobilization.



Waste	Inoculum	Assay conditions			Solid addition		SMP			Reference
		Reactor	OLR (kg^{a} m^{-3} d^{-1})	T (ºC)	Solid add	Concen. (g L^{-1})	Control	Sample	(m^{3}CH$_4$ kg^{-1b})	
Synthetic	SS digested full-scale plant	Semi-Batch	2 (VS)	55	Silica gel	20		0.280	(L)^{c}	[103]
			1 (VS)		Sand	20		0.273	(L)^{c}	
			3 (VS)		Molecular sieve	30		0.605	(L)^{c}	
			1 (VS)		Dowex CE	20		0.059	(L)^{c}	
Glycerol	SS digested full-scale plant	CSTR	0.54 (COD)	35	Cedar char coal	-	0-3	0-5	(L CH$_4$)^{d}	[104]
			2.17 (COD)				13-30	15-53	(L CH$_4$)^{d}	
Synthetic	OFMSW digestate	Batch		55	Natural membrane	0.13^{e}		0.058	COD	[105]
					Synthetic membrane	3^{f}	0.012	0.173	COD	
SS	SS digested full-scale plant	Anaerobic sequencing batch biofilm reactor	0.36 (COD)	-	Polyurethane foam			121	(mgCOD L^{-1})^{g}	[106]
					Vegetal carbon			208	(mgCOD L^{-1})^{g}	
					Synthetic pumice			233	(mgCOD L^{-1})^{g}	
					Recycled low-density polyethylene			227	(mgCOD L^{-1})^{g}	
PM	-	BMP	Low	55	Zeolite	12	1.6	2.7	(L CH$_4$)^{d}	[107]
			High			8	2.0	3.0	(L CH$_4$)^{d}	
PM	PM digestate	BMP		27-30	Zeolite	0.2	10	10.2	(L CH$_4$)^{d}	[108]
						2		13.5	(L CH$_4$)^{d}	
PM	PM digestate	BMP		27-30	Zeolite	0.01^{h}	18	11	VSS^{i}	[109]
					Ni-Zeo	0.01^{h}	27	78	VSS^{i}	
					Co-Zeo	0.01^{h}	9	14	VSS^{i}	
					Mg-Zeo	0.1^{h}	16	135	VSS^{i}	
Synthetic	PM digestate	BMP		27-31	Zeolite	0.1^{h}	0.3	0.28	COD	[110]
					Sand	0.1^{h}		0.27	COD	
Synthetic	SS digestate	UASB		35	Carbon	20^{j}		0.17	COD	[102]
					Rockwool	20^{j}		0.15	COD	
					Polyurethane	20^{j}		0.3	COD	
					Loofah	20^{j}		0.62	COD	
					Nobed	20^{j}		0.5	COD	

[a] OLR organic basis units in brackets
[b] SMP organic basis units in brackets
[c] Specific methane production expressed in reactor litters instead of organic basis
[d] Net biogas production
[e] Concentration in L/L ratio
[f] # of Capsules (3x6 cm) by 250mL of reactor
[g] Effluent concentration
[h] Solid addition expressed in g gVSS^{-1} instead of g L^{-1}
[I] Specific methane production expressed in COD-CH$_4$ instead of m^3 methane
[j] Concentration in % v/v

5. Nanomaterials

The use of nanoparticles (NP) in commercial products and industrial applications has increased greatly in recent years. Consequently, the transport of these nanoparticles to the environment as well as their impact of the waste and wastewater treatment processes is raising concerns [79,114]. In this matter, several researchers have evaluated the effects of NPs on AD performance, either as a supplement or as an intrinsic compound in waste material (Table 7).

Mu et al. [115] studied the effect of metal oxide nanoparticles (i.e. TiO, Al_2O_3, SiO_2, ZnO) on anaerobic digestion of SS in doses up to 150 mg $gTSS^{-1}$. The authors concluded that TiO_2, Al_2O_3, and SiO_2 did not present any beneficial or inhibitory effect on biogas production, while 30 and 150 mg g TSS^{-1} of ZnO caused reduction of 23 and 81%, respectively. In a subsequent study, Mu et al. [116] showed that high doses of ZnO-NP (30 to 150 mg $gTSS^{-1}$) led to inhibitory effects on both hydrolytic and methanogenic biomass. The inhibitory impact was attributed to the release of Zn^{2+} from the NP (12 to 18 mg L^{-1} respectively), which caused a decrease in the activities of proteases and coenzyme F_{420} as well as in the abundance of methanogenic biomass. Yang et al. [118] detected that Ag-NP at 1 mg $kgST^{-1}$ have minimal impact on AD. However, a negative strong impact on methanogenic community and, therefore, on the biogas production was observed when Ag-NP was doses at 10 mg $kgTS^{-1}$ or higher. The potential toxicity (EC_{50}) of bulk (1 – 5 µm) and CuO-NP and ZnO-NP (30 – 70 nm) on methane production was evaluated by Luna del Risco et al. [119]. Results indicated that dosing metal oxides as NPs decrease (more inhibitory) the EC_{50} by 10 and 2-folds for CuO and ZnO, respectively. The authors related the higher inhibitory effect of the NPs to the higher solubility and therefore higher concentration of Cu and Zn ions in the digester medium. Nyberg et al. [120] studied the potential inhibitory effect of fullerene (C_{60}); however, they did not observe any significant changes either on biogas production or on the microbial community structure over an exposure period of five months [120].

Table 7. Reported impact of nanoparticles on AD systems

Waste	Inoculum	Assay conditions			NP		SMP			Reference
		Reactor	OLR (kg[a] m^{-3} d^{-1})	T (ºC)	Element or compound	Concen. (g L^{-1})	Control	Sample	(m^3CH_4 kg^{-1}[b])	
SS	SS Digestate	BMP	-	35	TiO	0.03[c]	0.129	0.135	VSS	[115]
						0.15[c]		0.120	VSS	
					Al_2O_3	0.03[c]		0.135	VSS	
						0.15[c]		0.125	VSS	
					SiO_2	0.15[c]		0.135	VSS	
					ZnO	0.006[c]		0.120	VSS	
						0.15[c]		0.025	VSS	
SS	SS Digestate	CSTR	HRT (20 d)	35	ZnO	0.001[c]		0	VSS	[116]
						0.030[c]		-0.018	VSS	
SS + Glucose	SS Digestate	BMP	-		Ag	0.010	0.179	0.196	(L CH_4)[d]	[117]
						0.040		0.185	(L CH_4)[d]	
Cellulose	OFMSW digestate	BMP	-	37	Ag	0.016	0.471	0.474	TS[e]	[79]
					Fe	0.018		0.519	TS[e]	
					Au	0.010		0.509	TS[e]	

[a] OLR organic basis units in brackets

[b] SMP organic basis units

[c] Solid addition expressed in g $gTSS^{-1}$ instead of gL^{-1}

[d] Net biogas production

[e] Specific methane production expressed in biogas instead of methane

6. Biological additives

The supplementation of enzymes or microorganisms has been widely studied as an alternative to physicochemical pretreatments of wastes before AD [121]; however, their direct introduction into the digester has received less attention. The improvement of AD systems by adding biological additives have been achieved by: (i) increasing the microbial diversity, which leads to a better process performance (bioaugmentation); and (ii) adding enzymes to facilitate hydrolysis of the particulate compounds. Table 8 summarizes some studies about microbial inocula or enzyme addition to AD systems.

6.1 Bioaugmentation

Since AD is performed by microbial communities, a correlation exists between the population of microorganisms and the behavior of AD systems [5,128]. Therefore, improvements in AD performance could be potentially accomplished by the enhancement, selection or manipulation of particular groups of microorganisms within anaerobic digesters [119]. One of the main causes leading to process failure in AD systems is the microbial community shift occurring during transitional phases or in response to stress conditions [131]. Bioaugmentation has been suggested as a mechanism to recover systems efficiency or increase the performance of AD, since a higher microbial diversity is to be expected [132], and the introduction of new microorganisms may result in the appearance of novel capabilities [133]. However, it should be undertaken by selecting the appropriate inocula and dosage based on the specific microbial communities present on operating reactors. In this regard, Traversi et al. [134] pointed out that the diversity and abundance of methanogenic bacteria should be the key factor for an appropriate biogas production performance. Pandey et al. [135]

and Romero-Guiza et al. [52] showed that the start-up as the most crucial phase of AD, because a proper microbial community has not been established yet, and thus it is highly susceptible to imbalances. For this reason, several bioaugmentation assays have been directed to enhance the methanogenic community during the initial stages of AD. For example, Lins et al. [136] pointed out that inoculation with communities enriched in members of the robust *Methanosarcina* might improve the overall process in acetate-rich systems, but especially during the start-up phase. The success of bioaugmentation may be further improved by the addition of immobilized microbial cultures, therefore different supporting materials have been studied. A trace metal activated zeolite was used by Weiss et al. [121] to apply hemicellulolytic bacteria to an AD reactor treating hemicellulose rich agricultural residues. In the presence of the inoculum, a 53% increase in methane production yields was observed in respect to non-inoculated controls. Youngsukkasem et al. [122] encapsulated methanogenic bacteria using Durapore® membrane filters, exhibiting a higher stability in the digester than with alginate-based capsules. The use of capsule membrane during the digesting process might have permitted that both, dissolved substrates penetrated through the capsule membrane and biogas produced inside the capsules escaped by diffusion.

Addition of anaerobic hydrolytic microorganisms can be an alternative to enhance hydrolysis-fermentation process when treating partly biodegradable wastes, such as lignocellulosic materials [137]. Tuesorn et al. [126] showed that the use of a lignocellulolytic microbial consortium to enhance biogas production from fiber-rich swine manure showed promising results, increasing cellulose and hemicelluloses removal efficiencies from 15% to 30-62% and 23% to 31-75%, respectively when compared to controls. Considering the capacity of rumen microbes to digest cellulose and hemicelluloses, the use of rumen fluid in MSW has also been successfully tested as inoculum to enhance the hydrolytic step [138]. Moreover, the addition of pure bacterial cultures with broad hydrolytic capacities has been also assayed. In a two-phases AD system (mesophilic/thermophilic), Lü et al. [123] demonstrated that the inoculation of a strain of *Coprothermobacter proteolyticus* accelerated the hydrolysis and fermentation of proteins and polysaccharides remaining in the digestate during the early stage of the thermophilic step, and stimulated methane production by syntrophic cooperation with methanogenic granular sludge.

As previously stated, one of the most common problems in full-scale AD plants is ammonia inhibition. It has been observed that ammonia has a strong impact on anaerobic microbial communities [24], but especially on aceticlastic methanogens [139]. Fotidis et al. [140] presented a recent transcriptomic analysis of a pure culture of *Methanosaeta* submitted to ammonia stress, and related their susceptibility with the inhibition of expression of their methanogenic pathway. The study demonstrated the higher robustness of the syntrophic acetate oxidation (SAO) pathway followed by hydrogenotrophic methanogenesis compared to aceticlastic methanogenesis. This would be in agreement with the predominance of this pathway in anaerobic digesters working under high ammonia concentrations and other stress conditions [47,56]. Thus, the supplementation of ammonia tolerant SAO methanogenic consortia [122], but especially of fast growing hydrogenotrophic methanogens (e.g. *Methanoculleus bourgensis*), could provide a new solution to alleviate the ammonia inhibitory effect in AD processes [141]. For instance, in a CSTR operating under inhibited steady-state at high ammonia levels (5 g NH_4^+-N L^{-1}), bioaugmentation with *Methanoculleus bourgensis* resulted in a 31% increase in methane production yield [141]. Microbial community analysis, directly related this effect on methane production to bioaugmentation, revealing a 5-fold increase in the relative abundance of members of

Methanoculleus in the inoculated reactors. However, due to its economic uncertainties and risks, bioaugmentation has almost exclusively been investigated in lab-scale digesters [135], being its application in full-scale plants still rare. Reuter et al. [142] and Schmack and Reuter [143] reported that bioaugmentation of full-scale biogas plants, either with the H_2-consuming *Methanoculleus bourgensis* or the H_2-producing *Clostridium sartagoformum* resulted in increased biogas production under mesophilic conditions. These two inocula are commercially available, and their producer recommends an initial inoculation as a boost, followed by a daily or weekly application interval, based on the digester volume and cell counts.

6.1 Enzymes supplementation

A number of authors have reported significant improvement in biogas production when crude and commercial enzymes are used in the pretreatment of complex organic matter, such as lignocellulosic and lipid-rich materials [13,121,144,145]. However, enzymes can also be directly dosed into AD systems, since [121,146]: (i) enzymes are capable of acting in the presence of various toxic and recalcitrant substrates and under a wide range of environmental conditions (e.g. pH, temperature, and salinity) remaining active even if these conditions quickly change; (ii) enzymes can work in presence of microorganisms, predators, and inhibitors of microbial metabolism, avoiding the adverse effects actually occurring on living biomass; (iii) enzymes due to their smaller size, higher solubility and mobility, have easier access to the substrates than microbes do. As example, the inoculation of lipases (0.33 % v/v) in an AD system treating grease trap (5% VS_{FED}^{-1}) and sewage sludge improved notably the methane production (from 365 to 452 mL CH_4 gVS^{-1}) [124]. However, it is observe that enzyme dose of 0.25% (v/v) present a not clear effect on degradation kinetic. The use of small quantities of lipases can generate low yields due 0.25% is a too low concentration in order to overcome the mass transfer limitation for the lipase can access to the lipids present in the grease trap [124].

Table 8. Effect of bioaugmentation with microbial inocula or enzyme addition to AD systems.

Waste	Inoculum	Assay conditions			Microorganisms or enzyme		SMP			Reference
		Reactor	OLR (kg^a m^{-3} d^{-1})	T (ºC)	Add	Concen. (% ^{b})	Control	Sample	(m^3CH_4 kg^{-1c})	
Synthetic	Anaerobic granules from full-scale UASB	UASB	0.5 (g Glc) 0.26 (g N-NH_4^+)	37	-		0.350		VS	[122]
			0.5 (g Glc) 5 (g N-NH_4^+)				0.260	0.260	VS	
			0.5 (g Glc) 5 (g N-NH_4^+)		SAO co-culture (*C. ultunense* + *Methanocullreus*)^d		0.260	0.260	VS	
Mesophilic SS digestate	SS digestate	BMP		55	*C. proteolyticus*	10 (V/V)	6.26	6.42	VSS^e	[123]
					C. proteolyticus & methanogenic granular sludge	10 & 1.1 (V/V)	6.25	7.00	VSS^e	
GT (2%) and SS	SS digestete	BMP		35	Enzime-lipase (Biolipase L)	0.25 (V/V)	0.140	0.322	VS	[124]
GT (5%) and SS						0.25 (V/V)	0.161	0.365	VS	
GT (10%) and SS						0.25 (V/V)	0.243	0.434	VS	
GT (5%) and SS						0.83 (V/V)		0.470	VS	
Mashed sugar beet	SS digestate	BMP		40	Compost	1 (VS)		0-6	(%)^f	[125]
				60		1 (VS)		26.5	(%)^f	
Fibre rich swine manure	Lignocellulosic biomass digestate	BMP		37	LMC:SM	13 (mgVSS/gVS)	0.110	0.125	VS^g	[126]
				37		75 (mgVSS/gVS)		0.185	VS^g	
				37		85 (mgVSS/gVS)		0.175	VS^g	
				50		80 (mgVSS/gVS)		0.145	VS^g	
Xylene	Maize silage digestate	BMP		35	Hemicellulolytic bacteria immobilised on activated zeolite	0.2 (Wzeo/V)	0.150	0.210	VS	[127]

[a] OLR organic basis units in brackets

[b] Concentration in percentage based on the units in brackets

[c] SMP organic basis units

[d] bioaugmentation with 20% (V/V_{feed}) with SAO co-culture inoculum (OD_{600}=0.3-0.4) per day

[e] SMP expressed in mol of CH_4

[f] % of net biogas production over control

[g] SMP expressed in kg of CH_4

Conclusions

The use of inorganic and biological additives in anaerobic digestion systems has become an important topic due to its capacity to increase reactors performance in terms of process stability and biogas production. However, research experiences also show that additives can also lead to inhibitory phenomena, mainly as a result of high cation concentration in the digester media.

Macro- and micro-nutrient supplements have been successfully used to overcome anaerobic digestion instability through primarily the improvement of system buffer capacity and anaerobic biomass activity. The latter has been mainly related to the role of micro-nutrients as cofactors in numerous enzymatic reactions involved in the biochemistry of methane formation. Ni, Co and Fe are the most investigated nutrients. Especially promising are the results reported for Fe which together with its low cost makes it a promising supplement in anaerobic digesters. Other reported inorganic additives comprise substances able to mitigate ammonia nitrogen inhibition and/or to immobilize anaerobic biomass; both approaches targeting the creation of more favorable conditions for their microbial activity, especially for methanogens. Finally, an increased interest on using nanoparticles on anaerobic digesters has been observed, although current results are still not as promising as expected.

Regarding biological additives, the inoculation of microbial cultures (bioaugmentation) has been more studied than the supplementation of enzymes with hydrolytic capacity. Results clearly indicate that bioaugmentation is a useful tool to improve digester performance; especially when the digester is subjected to stress conditions (e.g. start-up, inhibitory concentrations). However, its application in full-scale plants is still scarce due to its economic uncertainties and risks.

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2.2 Feasibility of coupling anaerobic digestion and struvite precipitation in the same reactor: evaluation of different magnesium sources

Feasibility of coupling anaerobic digestion and struvite precipitation in the same reactor: evaluation of different magnesium sources

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Chemical Engineering Journal, vol. 270 (2015) 524-528

Abstract

The feasibility of coupling anaerobic digestion and struvite precipitation in the same reactor was evaluated to enhance manure anaerobic digestion methane yields through ammonia inhibition mitigation. Five different magnesium sources were tested as struvite (ammonia sequestration agent) precursor, i.e. $MgCl_2$, $Mg(OH)_2$, two industrial by-products rich in MgO but with different reactivity, and a stabilizing agent. The latter was formulated in advance with the low reactivity industrial by-product and phosphoric acid. The effect of each magnesium source on anaerobic digestion as well as its struvite precipitation capacity was evaluated through a series biomethane potential test. Results indicated that all magnesium sources were able to reduce ammonia concentration in different extents. However, the stabilizing agent was the unique magnesium source that did not inhibit the anaerobic digestion process. The avoidance of adding a phosphate source directly into the digester medium and the high newberyite content were the advantages of the stabilizing agent over the other magnesium sources. Finally, a series of experiments indicated that if anaerobic digestion and struvite

precipitation are combined in a single reactor, stabilizing agent addition should be carried out through several small additions rather than few large additions.

1. Introduction

The capacity to mineralise organic matter, reduce greenhouse gases emissions, produce an effluent with good fertilising qualities and, overall, recover energy through methane production have made anaerobic digestion (AD) a widely used technology to treat animal manure [1,2]. However, a wide variety of factors have been reported as inhibitors of the AD process and, therefore, to reduce its methane yield [3]. Among all inhibitors, ammonia nitrogen is especially distinct when digesting animal manure [4,5]. Ammonia nitrogen is produced by the biological degradation of nitrogenous organic matter in the acidogenesis step and it remains in the digester medium in two forms, NH_4^+ and NH_3, which are in equilibrium depending mainly on temperature and pH [6,7]. Although both forms have been reported as inhibitors of methanogenic activity, the capacity to diffuse into the cell, causing proton imbalance and/or potassium deficiency makes NH_3 the most harmful form [8–10].

Many research efforts have been made to mitigate ammonia nitrogen inhibition in AD. Among them, the addition of material with ion exchange capacity (e.g. bentonite, glauconite, phosphorite and zeolites) or inorganic absorbent materials (e.g. clay, manganese oxides and zeolites) have shown good results [9,11–15]. Likewise, struvite ($MgNH_4PO_4 \cdot 6H_2O$) precipitation prior or after AD has taken great interest since it is very valuable as slow-releasing fertiliser [16]. Struvite precipitation naturally occurs when the combined concentration of Mg^{2+}, NH_4^+ and PO_4^{3-} exceed the struvite solubility product [17,18]. Therefore, the precipitation of struvite in manures requires the addition of chemical compounds since the concentration of Mg^{2+} and PO_4^{3-} are very low in relation to NH_4^+ concentration [19]. Several magnesium ($MgSO_4$, $Mg(OH)_2$, $MgCl_2$, MgO) and phosphate (H_3PO_4, phosphates salts) sources have been successfully applied to facilitate struvite precipitation [20–22]; nonetheless, the high cost of the pure or high-grade magnesium compounds has limited its full-scale implementation [23]. In this vein, the use of industrial magnesium by-products seems to be a cost-effective alternative to overcome this problem [2,24,25]. Another option to minimise struvite precipitation cost is to combine struvite precipitation and AD in the same reactor; however, this approach has been barely studied. Uludag-Demirer et al. [27] who investigated the effect of $MgCl_2$, $Mg(OH)_2$ and Na_2HPO_4 in batch manure digesters, did not observe any improvement on the methane yield. The authors concluded that the digesters supplied with $Mg(OH)_2$ and Na_2HPO_4 suffered cation (Na^+ and Mg^{2+}) and pH inhibition, while the digesters supplied with $MgCl_2$ and Na_2HPO_4 had only cation inhibition. Contrariwise, Lee et al. [29] satisfactorily operated a continuous biowaste digester combined with struvite precipitation, where $MgCl_2$ was added to reach a Mg:P molar ratio of 1:1 and pH was adjusted between 7.7 and 8.3. The authors concluded that the 50% methane production improvement was due to the reduction of NH_3 concentration from 6.0 to 2.0 g $N \cdot L^{-1}$. Similarly, Romero-Güiza et al., [30] recorded a 25% and 40% methane production improvement when dosing 5 and 30 $g \cdot L^{-1}$ of a stabilizing agent formulated with low-grade magnesium oxide, respectively, in a continuous pig manure digester. The authors related the methane yield improvement to the reduction of the ammonia concentrations, the increase of magnesium concentration, and the presence of particles in the digester medium. Even though the literature is scarce, the disparity between studies suggest that there are aspects from the magnesium sources that have not been considered (e.g. cation availability, reagent solubility and reactivity) but which might have a significant role on the feasibility of this promising approach.

The main goal of this study was to compare the performance of five different magnesium sources (i.e. $MgCl_2$, $Mg(OH)_2$, high-grade MgO, low-grade MgO and a stabilizing agent) in reactors coupling anaerobic digestion and struvite precipitation. The study also aims to identify the factors that may limit the applicability of combining both processes in a single reactor.

2. Materials and methods

2.1 Analytical methods

The major and minor components of the magnesium sources and the loss of ignition (LOI) were determined by X-ray fluorescence (XRF) using a Philips PW2400 X-ray sequential spectrophotometer. X-ray diffraction patterns were performed in a Bragg-Brentano Siemens D-500 powder diffractometer with CuK_α radiation to obtain information about the crystalline phases. Scanning electronic micrographs were obtained with a SEM Quanta 200 FEI analyser equipped with an energy dispersive spectrometer analyser. The reactivity of the MgO samples was determined using the citric acid method, which measures the time required by 2.0 g of powdered MgO in 100 mL of 0.4 N citric acid solution to reach pH 8.2 [31]. The specific surface area of the MgO samples was determined using the BET single point method with a Micromeritics Tristar 3000 porosimeter.

Total solids (TS) and volatile solids (VS) were determined following the guidelines given by the standard methods 2540G [32] with minor modifications [33]. Inorganic carbon (IC) were measured by means of a Shimadzu 5055 TOC-VCSN TOC analyser. Individual volatile fatty acids (VFAs; acetate, propionate, butyrate and valerate) were analysed by a HP 5890-Serie II chromatograph as for Astals et al. [34]. Anions (Cl^- and PO_4^{3-}) and cations (NH_4^+, K^+, Ca^{2+} and Mg^{2+}) were determined in an 863 Advanced Compact IC Metrohm ionic chromatographer using Metrosep columns [35]. Total ammonia nitrogen (TAN) comprises both forms NH_4^+ and NH_3, while total phosphate (TP) is the sum of $H_2PO_4^-$ and HPO_4^{2-} (main phosphate species under assay pH conditions). Biogas composition was analysed by a Shimadzu GC-2010+ gas chromatograph equipped with a capillary column (Carboxen® - 1010 PLOT) and a thermal conductivity detector [2].

2.2 Pig manure, inoculum and chemical reagents origin

Pig manure and digested pig manure, used as inoculum, were collected from a centralized mesophilic anaerobic digestion plant, which treats around 100000 tons of pig manure per year. After collection, both samples were stored at 4 ºC. Prior to commencement of the biomethane potential (BMP) tests inoculum was degassed at 37 ºC for one week. Pig manure and the inoculum characterisation is given in Table 1.

Table 1. Pig manure and inoculum characterization

	Units	**Pig manure**	**Inoculum**
TS	$g\cdot L^{-1}$	32.1	47.2
VS	$g\cdot L^{-1}$	21.0	29.9
pH	-	7.5	8.0
TAN	$mg\ N\cdot L^{-1}$	1785	2490
TP	$mg\ P\cdot L^{-1}$	36	33
Mg^{2+}	$mg\cdot L^{-1}$	37	36

Analytical grade $MgCl_2$, $Mg(OH)_2$, and K_2HPO_4 were purchased from Panreac Quimica, S.A. (Barcelona, Spain). The two industrial by-products, named as high-grade magnesium oxide (HG-MgO) and low-grade magnesium oxide (LG-MgO) according to their MgO content, were provided by Magnesitas Navarras, S.A. (Navarra, Spain). HG-MgO and LG-MgO were obtained from the calcination of natural magnesite in rotary kiln at 1100 ºC to obtain caustic calcined magnesia. HG-MgO is the finest fraction (<1 mm) of the calcined magnesia collected at the bottom of the furnace, while LG-MgO is a by-product collected as cyclone dust in the fabric filters from the air pollution control system. The stabilizing agent (SA) was formulated with LG-MgO and phosphoric acid following Romero-Güiza et al. [30]. Briefly, phosphoric acid was slowly added to an aqueous slurry of LG-MgO with a high solid-to-liquid ratio. The exothermic acid-base reaction generated a solid with a high content of newberyite ($MgHPO_4 \cdot 3H_2O$) and other magnesium phosphate compounds, which inner core did not react on the basis of the shrinking core model and remained as LG-MgO. Then, the compound was dried and crushed to a particle size of about 500 µm. The chemical composition of HG-MgO, LG-MgO and SA is shown in Table 2.

Table 2. Semi-quantitative characterisation of HG-MgO, LG-MgO and SA

	Units	**HG-MgO**	**LG-MgO**	**SA**
MgO	%	89.8	63.4	31.8
P_2O_5	%	-	-	32.8
CaO	%	1.5	8.7	4.7
SO_3	%	-	3.8	1.1
Fe_2O_3	%	-	2.4	1.2
SiO_2	%	-	3.2	0.9
V_2O_5	%	-	0.3	0.3
MnO	%	-	0.1	0.1
LOI (1100ºC)	%	3.3	8.9	24.7
Reactivity	s	90	2280	>3000
BET surface area	$m^2 \cdot g^{-1}$	8.83	10.87	11.94

2.3 Biomethane potential test

BMP tests were carried out following the stages defined by Angelidaki et al. [37] in 115 mL serum bottles at mesophilic conditions. The bottles were filled with: (i) 40 mL of inoculum; (ii) the amount of pig manure that met an inoculum to substrate ratio of 2 (VS-basis) (30 mL); (iii) deionised water, used to adjust the same effective volume for all tests (80 mL); and (iv) varying amounts of $MgCl_2$, $Mg(OH)_2$, HG-MgO, LG-MgO, SA and K_2HPO_4. The amount of reagent/s added in each assay is provided in Table 3. A control assay containing inoculum and pig manure was used to determine pig manure specific methane potential, while a blank test containing inoculum and no substrate was used to correct for background methane potential in the inoculum. Bottles headspace were flushed with N_2 for one minute ($3\ L\cdot min^{-1}$), sealed with a PTFE/Butyl septum retained with an aluminium crimp cap and placed in a water bath set at 37 ºC. Tests were mixed by swirling once a day. All tests were carried out in triplicate, and all error bars indicate 95% confidence in the average of the triplicate. Biogas production during the running test was measured with a vacumeter (Ebro – VAM 320). Biogas composition was analysed with a GC analyser after each sample event. Accumulated volumetric methane production in time was calculated considering the biogas produced, once converted at standard temperature and pressure conditions (i.e. 0 ºC and 1 bar), and the methane composition in the biogas.

Eleven different Mg doses were tested, i.e. $MgCl_2$, $Mg(OH)_2$, three SA doses, three HG-MgO doses and three LG-MgO doses. Note that SA supplied both Mg and P, while K_2HPO_4 was added for the rest of Mg sources as P source (Table 3). $MgCl_2$ and $Mg(OH)_2$ were tested individually, reagents dosage was adjusted to obtain a N:P:Mg molar ratio of 1:1:1 according to pig manure TAN concentration. The three SA additions were selected considering the results obtained in a previous study by the author Romero-Güiza et al. [30]. The tested SA additions were 5, 15 and 30 g SA·L^{-1} which gave a N:P:Mg molar ratio of 6:1:1.7, 2:1:1.7 and 1:1:1.7 respectively (tests were named as SA(1), SA(2) and SA(3) respectively). HG-MgO and LG-MgO along with K_2HPO_4 doses were performed considering the Mg and P additions in the SA assays. Both MgO by-products experiments were labelled as MgO(1), MgO(2) and MgO(3) as solid dose increased (Table 3).

Table 3. Magnesium and phosphate add for each assay

	Mg^{2+} (g·L^{-1})	**TP (g·L^{-1})**	**N:P:Mg**
Control	-	-	-
$MgCl_2$	3.30	0.42	1:1:1
$Mg(OH)_2$	3.30	0.42	1:1:1
SA(1)	1.00	0.07	6:1:1.7
SA(2)	2.87	0.21	2:1:1.7
SA(3)	5.75	0.42	1:1:1.7
HG-MgO(1)	1.00	0.07	6:1:1.7
HG-MgO(2)	2.87	0.21	2:1:1.7
HG-MgO(3)	5.75	0.42	1:1:1.7
LG-MgO(1)	1.00	0.07	6:1:1.7
LG-MgO(2)	2.87	0.21	2:1:1.7
LG-MgO(3)	5.75	0.42	1:1:1.7

2.4 Struvite precipitation with SA in batch experiments

Struvite precipitation batch experiments were performed in a Jar-Test device (Flocculator 2000, Kemira) at 37 ºC. All reactors had 0.6 L of pig manure, and four SA doses were tested (i.e. 5, 10, 15 and 30 g SA·L^{-1}). Reactors were continuously stirred at 15 min^{-1} to ensure particles were maintained in suspension in the slurry, providing the reaction. The process was monitored by means of pH, IC, TAN, Mg^{2+} and TP, measured for each experimental trial at 0, 0.25, 0.5, 1, 2 and 4 hours.

3. Results and discussion

3.1 Effect of the magnesium source on anaerobic digestion

The utilisation of analytical grade Mg sources, $MgCl_2$ and $Mg(OH)_2$, as struvite precursors caused a significant reduction of pig manure methane yield when compared to control ($p= 0.0001$, $p<0.0001$), which is in agreement with those results published by Uludag-Demirer et al. [27]. $MgCl_2$ addition reduced pig manure methane yield from 148 to 61 mL $CH_4 \cdot g^{-1}$ VS, whereas $Mg(OH)_2$ addition led to a complete breakdown of the AD process (Fig. 1a). Regarding the $MgCl_2$ assay, the low VFA concentration at the end of the BMP indicates that the inhibitory agent had a toxic effect on acid-forming microorganisms rather than on methanogenic biomass. This statement is fulfilled by the mechanisms reported for potassium inhibition [3], which is the cation supplied by the phosphate source (K_2HPO_4). Potassium concentration in the $MgCl_2$ digester was 14 $g \cdot L^{-1}$ (Table 4), which is within the potassium threshold concentration (6 – 29 $g \cdot L^{-1}$) found by other authors [3,38]. Hence, it is most likely that potassium was the compound partially inhibiting the AD process. Additionally, the minor accumulation of acetate at the end of the BMP dismisses magnesium as source of inhibition, since it has been reported as inhibitor of the acetate-consuming methanogens [3,39,40]. Contrariwise, the VFA distribution at the end of the $Mg(OH)_2$ BMP (i.e. high concentration of propionate, butyrate and valerate together with the relatively low concentration of acetate) may suggest that hydrogen-utilising methanogens were more inhibited than acetate-utilising methanogens and acid-forming bacteria by $Mg(OH)_2$ test conditions. Actually, $Mg(OH)_2$ assay produced less methane than the blank assay, thus giving negative accumulated methane values throughout the test. The detrimental impact of $Mg(OH)_2$

test conditions on AD performance might be linked to two different factors: (i) $Mg(OH)_2$ basic property, which made digester pH rose to 8.5, and (ii) the high concentration of potassium in the digester medium.

The use of industrial by-products (HG-MgO and LG-MgO) as magnesium source also led to a lower manure methane yield (Fig. 1b,c). However, the extent of it varied with the by-product concentration. Low magnesium doses (HG-MgO(1) and LG-MgO(1)) presented similar behaviours than the observed for $MgCl_2$, i.e. partial reduction of the methane yield, neutral pH and no accumulation of VFA at the end of the BMP (Table 4). Although K^+ concentration was lower than observed in $MgCl_2$ test, K^+ can still be identified as the inhibitory agent of both tests. The HG-MgO medium dose (HG-MgO (2)) test, which AD process was completely breakdown, presented a similar pH and VFA distribution at the end of the BMP than the recorded for $Mg(OH)_2$. Accordingly, pH increase and K^+ concentration were the two potential inhibitory phenomena. However, the higher VFA concentration at the end of the HG-MgO(2) assay in a half K^+ concentration, when compare with $Mg(OH)_2$, indicates that pH increase was more detrimental to hydrogen-utilising methanogens than K^+ concentration. The high HG-MgO dose (HG-MgO(3)) as well as the medium and high LG-MgO doses (LG-MgO(2) and LG-MgO(3)) also resulted in a complete breakdown of the AD process (Fig. 1b,c). Nevertheless, the high pH values (>9) and the fact that acetate was the main VFA at the end of the assays suggest that both hydrogenotrophic and acetoclastic methanogens were inhibited under this pH condition.

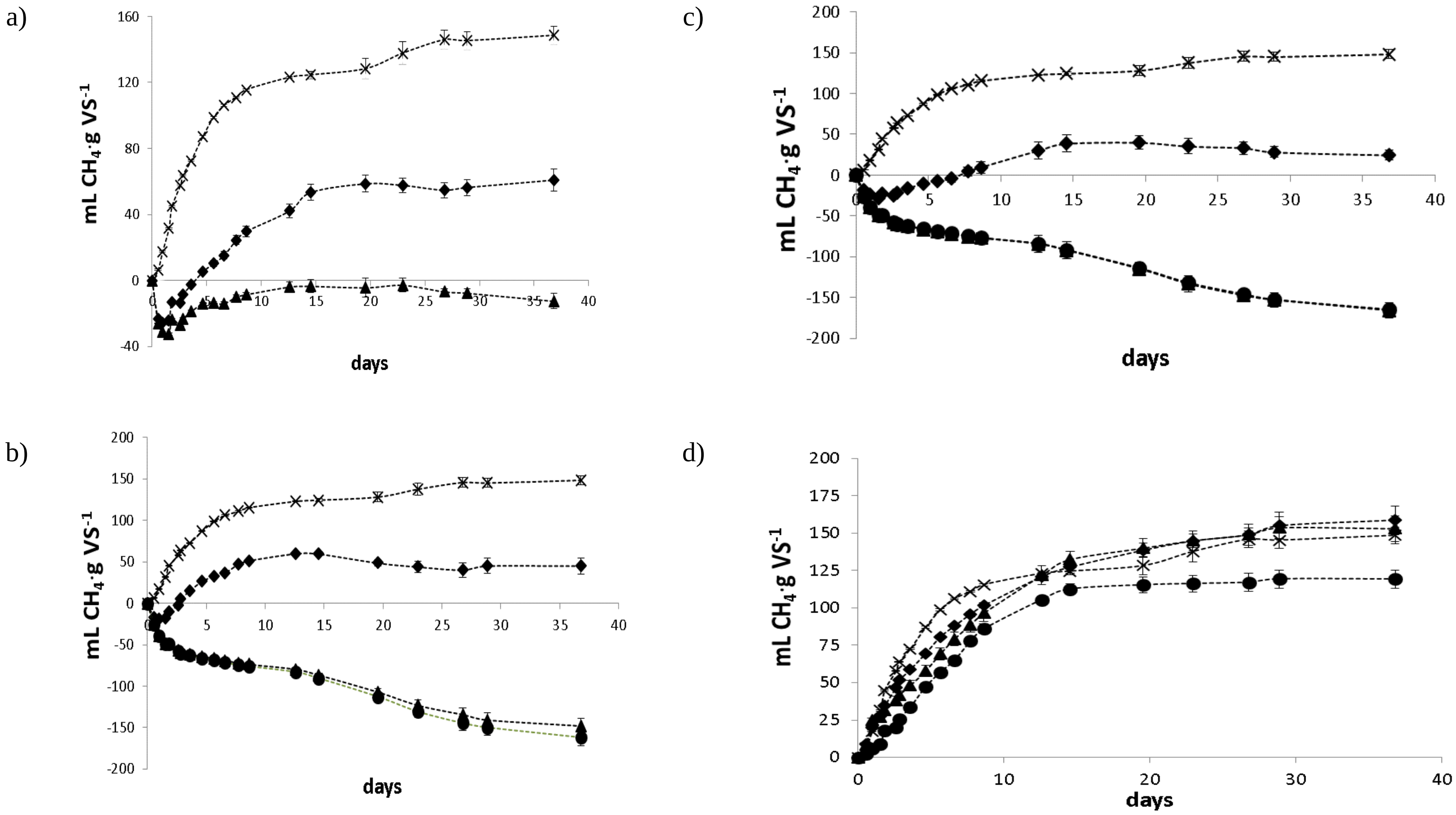

Fig. 1. Cumulative methane production curve of pig manure (×) and; (a) (♦) $MgCl_2$ and (▲) MgOH; (b) (♦) HG-MgO(1), (▲) HG-MgO(2) and (●) HG-MgO(3); (c) (♦) LG-MgO(1), (▲) LG-MgO(2) and (●) LG-MgO(3); (d) each SA addition (♦) 5 mg L^{-1}, (▲) 15 mg L^{-1} and (●) 30 mg L^{-1}.

The SA additions presented a completely different trend than the other magnesium sources since no severe inhibition phenomena were recorded. Low and medium SA doses (SA(1) and SA(2)) showed the same methane potential than control, while the high SA dose (SA(3)) presented a slight reduction of manure methane potential (from 148 to 127 mL CH4·g^{-1} VS) (Fig. 1d). The capability of fixing TAN, different extents, without a negative effect on AD performance shows the suitability of SA as a reagent able to couple anaerobic digestion and struvite precipitation in a single reactor. The main advantage of the SA over the other magnesium sources is the avoidance of adding the phosphate source directly into the digester medium. Note that phosphoric acid direct addition may cause a lot of foam (effervescences) due to the displacement of the IC equilibrium as well as pH problems, while the required concentration of cation (Na^+ or K^+) supplied by the phosphate salt has been identified as inhibitor of the AD process in the present study and by Uludag-Demirer et al. [27]. Moreover, the low impact of SA on AD performance might also be related to its high newberyite content, since newberyite has a low reactivity (Table 2) and is non-toxic for biological systems [41]. Finally, it should be noted that the equal and the reduction of the methane yield for SA(1) and SA(3) (5 and 30 g SA L^{-1}) are in disagreement with the methane production increase (25% and 40% respectively) reported in our previous study when dosing the same amount of SA into a continuous pig manure digester [2]. This fact may be related to the stirring and feeding difference between batch and continuous systems. In the continuous experiment SA concentration was added gradually and diluted (1/20) once introduced in the digester, while in BMP SA concentration is not diluted. Therefore, BMP reactors had a higher ion concentration and less adaptation time for the anaerobic biomass.

Table 4. Characterisation of the BMP tests at the end of the assay

	Units	Control	$MgCl_2$	$Mg(OH)_2$	HG-MgO(1)	HG-MgO(2)	HG-MgO(3)	LG-MgO(1)	LG-MgO(2)	LG-MgO(3)	SA(1)	SA(2)	SA(3)
pH	-	7.31	6.72	8.46	7.57	8.51	9.21	7.73	9.05	10.38	7.29	7.18	7.00
TP	$mg \cdot L^{-1}$	551	510	1310	440	214	1319	346	1039	1815	498	493	1041
TAN	$mg \cdot L^{-1}$	2498	954	1699	2553	1968	1512	2472	1775	1171	2406	1529	567
Mg^{2+}	$mg \cdot L^{-1}$	41	1086	288	831	674	514	770	707	534	715	1198	1836
K^+	$mg \cdot L^{-1}$	2067	13917	15418	4273	7351	12526	4276	7413	11881	2382	2226	2032
VFA	$mg \cdot L^{-1}$	115	190	1984	117	4664	17574	130	13143	18847	199	166	159
Acetate	$mg \cdot L^{-1}$	99	115	327	93	317	14899	130	10715	15696	159	137	134
Propionate	$mg \cdot L^{-1}$	-	44	895	-	1587	1095	-	868	1333	12	-	-
Butyrate	$mg \cdot L^{-1}$	17	32	280	24	290	770	-	701	841	28	29	25
Valerate	$mg \cdot L^{-1}$	-	-	459	-	2471	758	-	719	724	-	-	-

3.2 Struvite precipitation with stabilizing agent in batch experiments

To better comprehend the effect of SA addition on pig manure, the evolution of pH, TAN, IC, TP and Mg^{2+} were followed when four different SA doses (5, 10, 15 and 30 $g \cdot L^{-1}$) were added to pig manure.

As shown in Fig. 2a, all SA additions caused a reduction of pH during the first 30 minutes and then pH increased progressively, which is similar to the behaviour observed in our previous publication [2]. Accordingly, pH reduction can be related to the reaction mechanisms involved during the struvite precipitation: (i) the proton released by the displacement of the P equilibrium and (ii) TAN fixation (Fig. 2b,d). With the expectation of 30 g $SA \cdot L^{-1}$, struvite precipitation (directly related to TAN removal (Fig. 2d)) took place during the first 60 minutes of the assays, since from then on TAN concentration remained constant over time. The lower pH drop at low SA doses together with the short reaction time suggest that, when combining AD and struvite precipitation, SA addition should be carried out through several small additions rather than few large doses. This strategy would also allow to reach higher SA doses without affecting the AD process, since struvite precipitation extent increased as SA dose increased; where 5, 10, 15 and 30 g $SA \cdot L^{-1}$ additions led to TAN removals of 35, 41, 52 and 76% respectively. Likewise, the IC (CO_2/HCO_3^-) abatement during the first stages of the process (Fig. 2e) was due to the precipitation of calcium carbonates, promoted by the lime content in SA (Table 2), and the liberation of protons during the struvite precipitation, which together with system operational conditions (constant agitation and open to the atmosphere) facilitated CO_2 stripping. For a second time, small SA doses will help to avoid pH changes in the digestion medium and diminish CO_2 stripping. In this matter, the pH evolution of 5, 10 and 15 g $SA \cdot L^{-1}$ pH evolution was mostly a result of the concentration of IC and TAN (NH_4^+/NH_3) in the digester medium, while for 30 g SA L^{-1} the TP ($H_2PO_4^-/HPO_4^{2-}$) concentration also had an important role. The increase of TP and Mg^{2+} concentration at the beginning of the assay indicated the total and/or partial solubilisation of some SA particles, where TP came mainly from newberyite solubilisation while Mg^{2+} came from both newberyite solubilisation and magnesium oxide hydrolysis (Fig. 2b,c). Furthermore, the profile of the TP and Mg^{2+} concentration confirmed the coexistence of the two struvite precipitation mechanisms suggested by Romero-Güiza et al. (2014): (i) the reaction of the TAN with the newberyite present in the SA particle (eq. 1) and (ii) the reaction of the TAN with the TP and Mg^{2+}, released by the newberyite and/or magnesium oxide, in the liquid phase (eq. 2) (Fig. 3).

$$MgHPO_4 \cdot 3H_2O_{(S)} + NH_4^+{}_{(aq)} + 4H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O_{(S)} + H_3O^+{}_{(aq)} \qquad \text{(eq. 1)}$$

$$Mg^{2+}{}_{(aq)} + HPO_4^{2-}{}_{(aq)} + NH_4^+{}_{(aq)} + 7H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O_{(S)} + H_3O^+{}_{(aq)} \qquad \text{(eq. 2)}$$

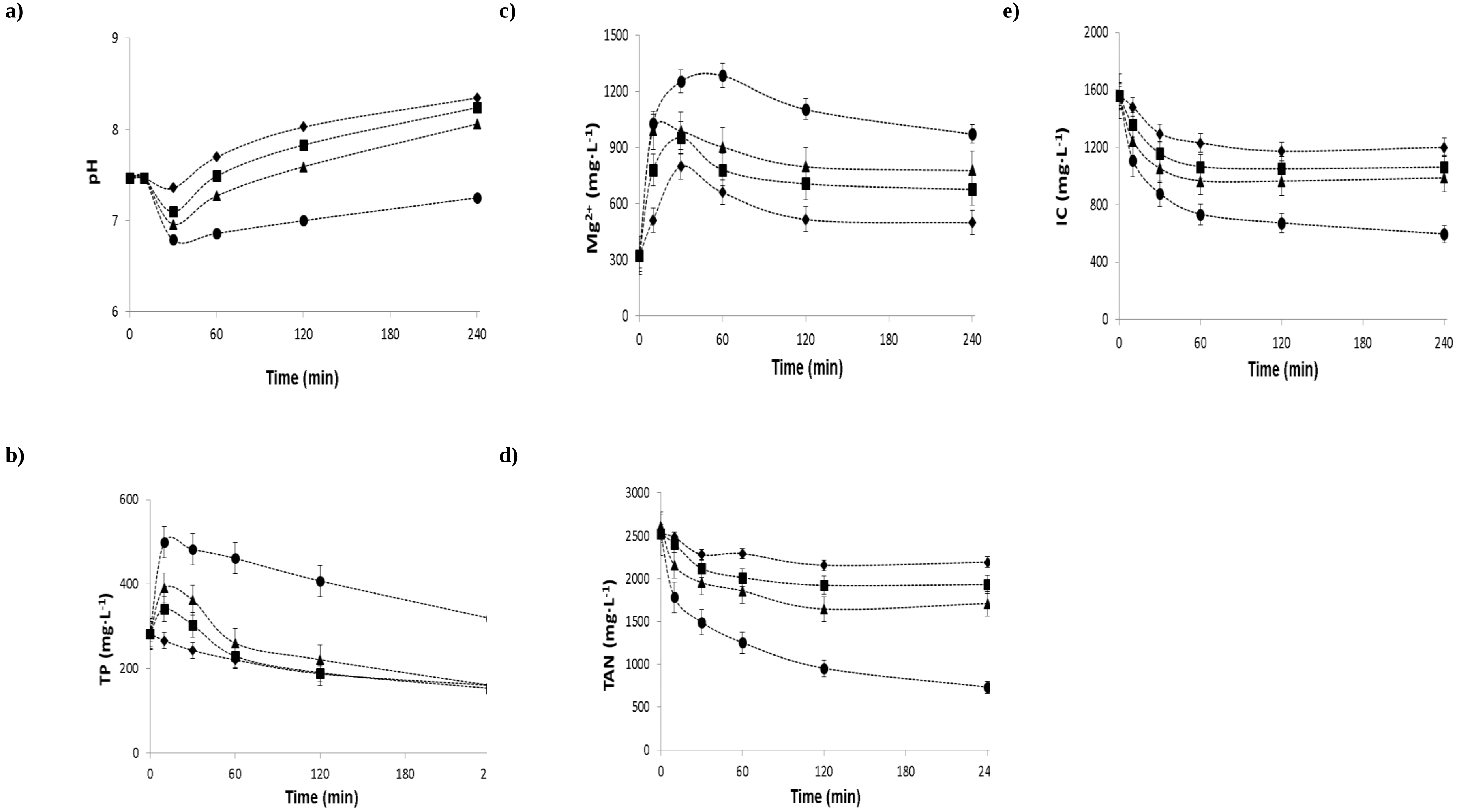

Fig. 2. (a) pH, (b) P-PO_4^{3-}, (c) Mg^{2+}, (d) TAN, and (e) IC evolution in the course of time for the different SA additions, i.e. (♦) 5 mg·L^{-1}, (■)

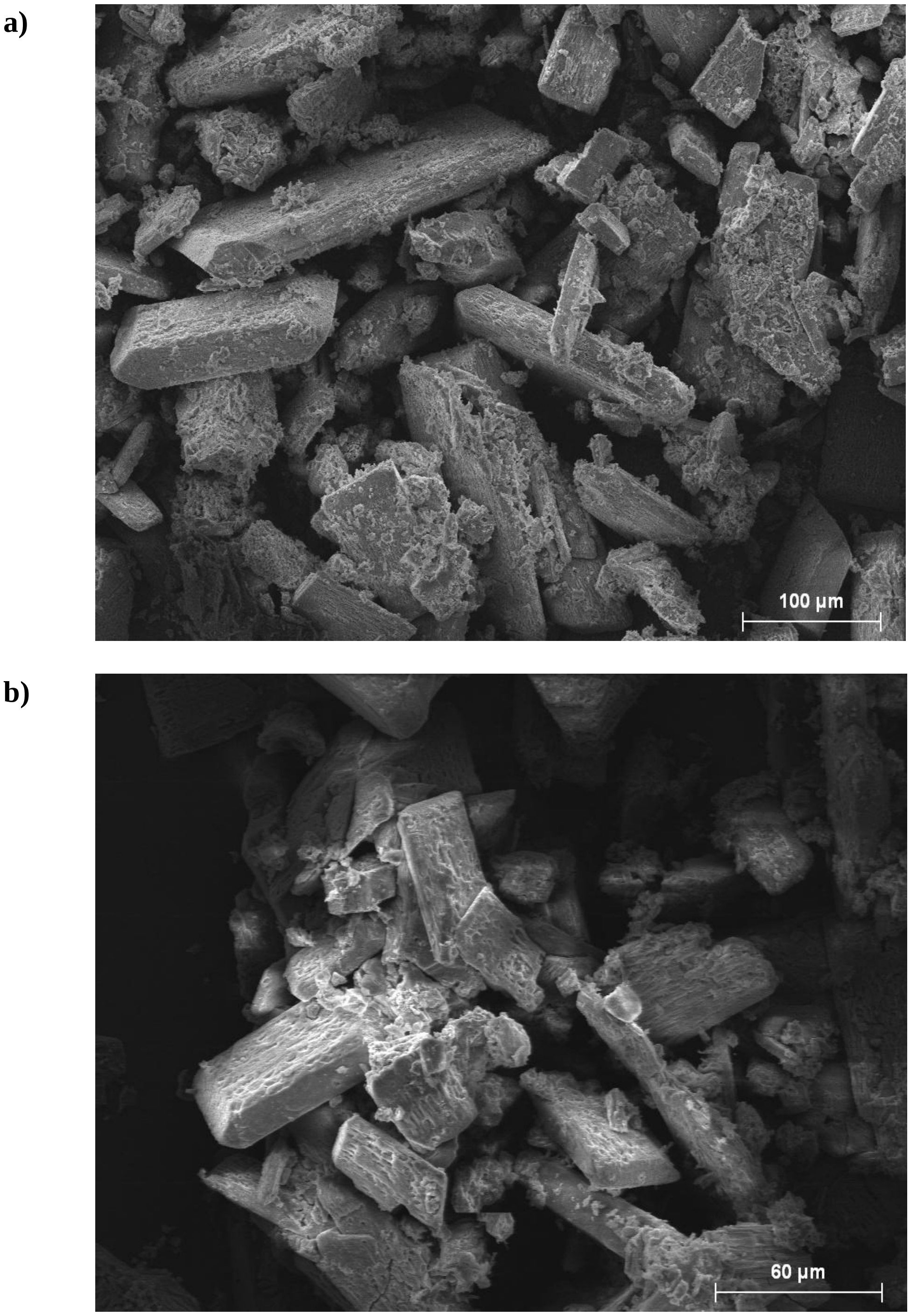

Fig. 3. Scanning electron micrograph of (a) struvite particles growth in the digester medium and (b) struvite particles growth in the surface of the stabilizing agent.

Conclusions

The present study evaluated the feasibility of combining anaerobic digestion and struvite precipitation in the same reactor through five different magnesium sources. The addition of $Mg(OH)_2$ as well as the higher dose of the two industrial by-products rich in MgO resulted in a complete breakdown of the anaerobic digestion process; likely due to the increased pH and K^+ concentration, supplied by phosphate source (K_2HPO_4), in the digester medium. $MgCl_2$ and the lower dose of both industrial by-products showed a significant reduction of the methane yield when compared to pig manure (control), but pH remained within neutral values. The latter assays were possibly only inhibited by the increased K^+ concentration. In contrast, no relevant inhibition phenomenon was recorded when the stabilizing agent assays was used as struvite precursor. Results showed the capacity of the stabilizing agent to promote struvite precipitation without causing a significant pH change and/or being inhibitory for anaerobic biomass. The stabilizing agent presented two main advantages over the other magnesium sources: (i) the avoidance of adding the phosphate source directly into the digester medium, and (ii) a low reactivity due to its high content in newberyite. A final series of experiments suggested that when AD and struvite precipitation are combined in a single reactor, stabilizing agent addition should be carried out through several small additions rather than few large doses.

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2.3 Improving Anaerobic Digestion of Pig Manure by Adding in the Same Reactor a Stabilizing Agent Formulated with Low-Grade Magnesium Oxide

Improving anaerobic digestion of pig manure by adding in the same reactor a stabilizing agent formulated with low-grade magnesium oxide

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Biomass and Bioenergy, vol. 67 (2014) 243-251

Abstract

Struvite precipitation and pig manure anaerobic digestion were coupled in the same reactor in order to mitigate the inhibitory effect of free ammonia and avoid precipitator costs. The stabilizing agent used to facilitate struvite precipitation was formulated with low-grade magnesium oxide by-product; an approach that would notably reduce struvite processing costs. The interaction between pig manure and stabilizing agent was analyzed in batch experiments, on a wide range of stabilizing agent additions from 5 to 100 kg m^{-3}. The monitoring of the pH and ammonia removal during 24 hours showed the high capacity of the stabilizing agent to remove ammonia; removal efficiencies above 80% were obtained from 40 kg m^{-3}. However, a long term anaerobic digester operation was required to assess the feasibility of the process and to ensure that the stabilizing agent does not introduce any harmful compound for the anaerobic biomass. In this vein, the addition of 5 and 30 kg m^{-3} of the stabilizing agent in a pig manure continuous digester resulted in a 25% (0.17 m^3 kg^{-1}) and a 40% (0.19 m^3 kg^{-1}) increase in methane production per mass of volatile solid, respectively, when compared with the reference digester (0.13 m^3 kg^{-1}). Moreover, the stability of the process during four hydraulic retention times guarantees that the stabilizing agent did not exert a negative effect on the consortium of microorganisms. Finally, scanning electron microscopy and X-ray diffraction analysis confirmed the presence of struvite as well as two precipitation mechanisms, struvite precipitation on the stabilizing agent surface and in the bulk solution.

1. Introduction

Today, in most countries, intensive pig farming is concentrated in certain regions. There, the high production of pig manure linked to the insufficient amount of available land makes pig manure management and treatment important to minimize its contaminant potential [1,2]. Amongst all the treatment options, anaerobic digestion (AD) is a technology that is widely used since: (i) avoid volatile organic compound emissions, (ii) stabilize organic matter and (iii) recover energy through methane production [3]. However, pig manure AD regularly presents low efficiencies due to the high concentration of ammonia and its low hydrolysis rate [3,4].

In AD a wide range of inhibiting total ammonia nitrogen (TAN) concentrations have been reported, varying from 1.5 to 14 kilogram of nitrogen per cubic meter, where differences can be attributed to the characteristics of the substrates and the inoculum, the environmental conditions (mainly temperature and pH) and the adaptation periods [5,6]. TAN in anaerobic reactors has two forms: unionized or free ammonia (NH_3) and ionized ammonia or ammonium (NH_4^+). Although both forms have been reported as inhibitors of methanogenic activity NH_3 is the most toxic form. NH_3 concentration depends basically on three parameters, i.e. TAN concentration, temperature and pH [7,8]. In order to mitigate the inhibitory effects of NH_3 many successful research efforts have been carried out before AD like air stripping, zeolite addition, clay addition and struvite precipitation [9-14]. However, these technologies would involve the construction and operation of another unit, which would be, in most cases, unfeasible for small and medium biogas plants.

High TAN removal efficiencies have been obtained for several waste streams by adding magnesium (Mg^{2+}) and phosphate (PO_4^{3-}) to precipitate struvite ($MgNH_4PO_4 \cdot 6H_20$), which is a valuable slow-release fertilizer [15-17]. The addition of magnesium and phosphate is necessary to ensure the formation of struvite, since usually the amount of them in waste streams, like in pig manure, is not high enough to remove all NH_4^+ [12,17,18]. Nevertheless, the high price of raw materials and the large quantities of phosphate and magnesium required to achieve high ammonia removal efficiencies might cause a significant increase in processing costs, making struvite precipitation unfeasible [19,20]. To solve this problem some researchers have used magnesium by-products as raw materials [18-21]. Another option to reduce the struvite processing cost is to couple anaerobic digestion and struvite precipitation in the same reactor. This approach has only been studied by Lee et al. [22] in a continuous food waste digester with $MgCl_2$ addition and by Uludag-Demirer et al. [23] in batch manure digesters with $MgCl_2$ and $Mg(OH)_2$ addition. However, to our knowledge, no references have been found evaluating the utilization of magnesium by-products within the reactor to precipitate struvite during anaerobic digestion. The introduction of inhibitory and/or toxic compounds for the anaerobic biomass is the main drawback when an industrial by-product wants to be introduced in an anaerobic digester [1]. Therefore, in addition to the ammonium removal potential of the by-product, a long term digester operation is required to assess the viability of the process.

The main objective of the present study is to couple anaerobic digestion and struvite precipitation in the same reactor where a stabilizing agent, formulated with magnesium oxide by-product, is used to facilitate struvite precipitation. To achieve this goal the research sought to: (i) determine the ammonium removal efficiency when different doses of stabilizing agent are added to pig manure; (ii) compare the long term operation performance of a pig manure anaerobic digester with and without the addition of a stabilizing agent; and (iii) identify the struvite precipitation mechanisms.

2. Materials and Methods

2.1. Source of the low-grade magnesium oxide and pig manure

Low-grade magnesium oxide (LG-MgO) powder was supplied by Magnesitas Navarras, S.A. (Navarra, Spain). LG-MgO was generated during the calcination of natural magnesite in a rotary kiln at 1100 ºC to obtain caustic calcined magnesia and then was collected in the fabric filters of the air pollution control system. Table 1 sets out the chemical composition of the major elements shown by X-ray diffraction (XRD) to be the most stable corresponding oxides as well as the other physicochemical parameters.

Pig manure (PM, see Table 2 for its characterization) and digested pig manure, used as inoculum, were collected from a centralized anaerobic digestion plant. The facility digests at mesophilic conditions around 100,000 metric tons of pig manure per year utilizing the VALPUREN® process [2]. After collection, the pig manure was stored at 4 ºC until it was used.

Table 1. X-ray diffraction characterization of the LG-MgO and the stabilizing agent

	LG-MgO	**SA**
Oxides composition		
MgO (%)	63.7	31.8
CaO (%)	9.9	4.7
SO_3 (%)	4.1	1.1
Fe_2O_3 (%)	2.4	1.2
SiO_2 (%)	2.0	0.9
K_2O (%)	0.3	< 0.1
Al_2O_3 (%)	0.2	< 0.1
V_2O_5 (%)	0.1	0.26
MnO (%)	0.1	0.1
P_2O_5 (%)	< 0.1	32.8
Physicochemical parameters		
Loss of ignition (1100 ºC) (%)	16.7	27.4
Density (kg m^{-3})	3,200	
Specific surface (m^2 kg^{-1})	10,400	

2.2. Formulation of the stabilizing agent

The stabilizing agent (SA) was formulated according to the procedure described in the patent [24]. Briefly, phosphoric acid was added slowly to an aqueous slurry of LG-MgO with a high solid-to-liquid ratio. The exothermic acid-base reaction generated a mixture with a high content of newberyite ($MgHPO_4 \cdot 3H_2O$) and other magnesium phosphate compounds, such as magnesium phosphate tribasic ($Mg_3(PO_4)_2$) and magnesium phosphate dibasic ($MgHPO_4$), which coated the particles of LG-MgO that did not react on the basis of the shrinking core model [25,26]. Then, the compound was dried and crushed to a particle size of about 500 µm.

As a result, instead of adding LG-MgO and phosphoric acid directly into the reactor, the stabilizing agent was formulated in advance obtaining a solid product in powder form, non-toxic or aggressive and easy to handle [24]. Table 1 presents the chemical composition of the major elements shown by XRD to be the most stable corresponding oxides as well as the other physicochemical parameters. Moreover, the scanning electronic microscopy (SEM) shows that the stabilizing agent has an amorphous morphology with a particle size below 200 μm (Fig. 1a).

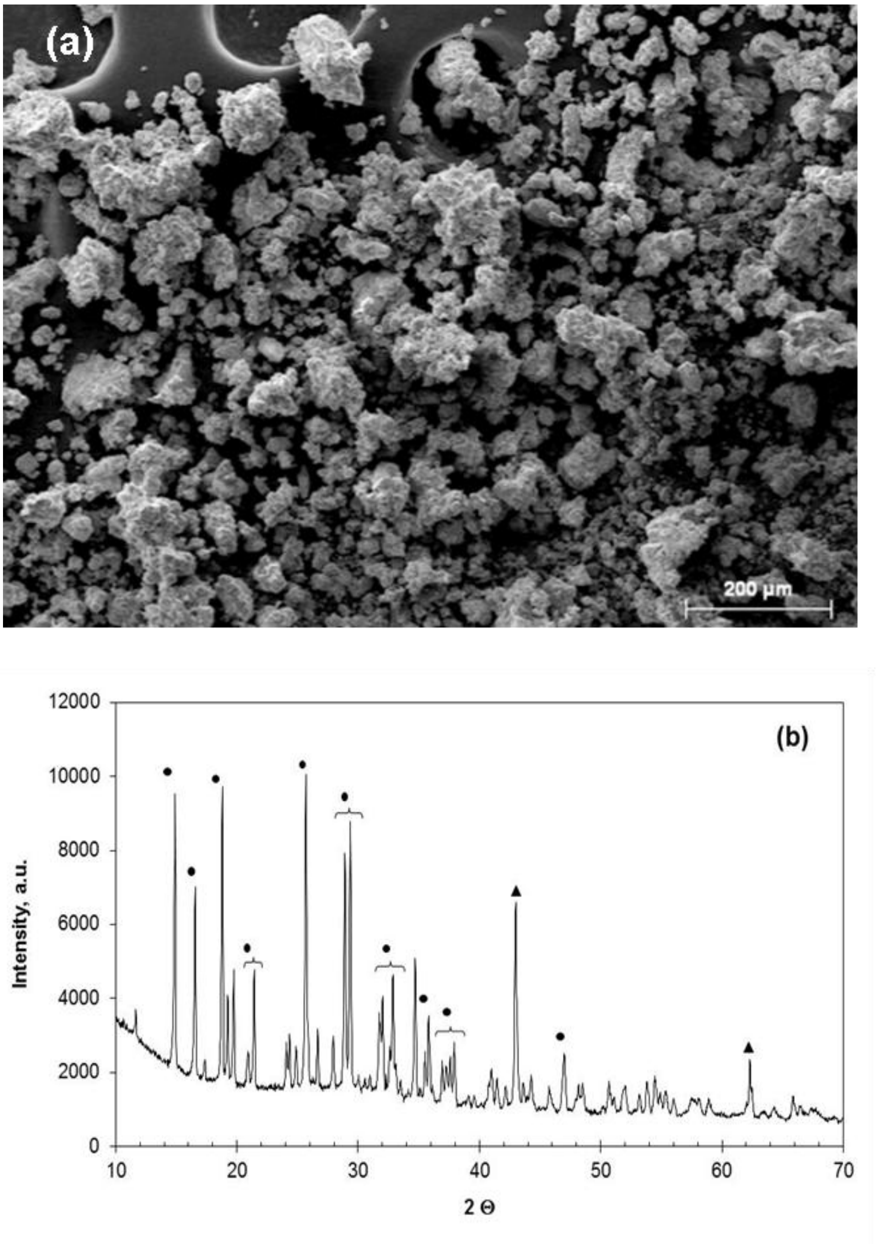

Fig. 1. (a) scanning electron micrograph and (b) X-ray diffractogram of the stabilizing agent. ● Newberyite; ▲ Periclase.

2.3. Struvite precipitation batch experiments

The struvite precipitation batch experiments, performed in a Jar-Test device (Flocculator 2000, Kemira), were carried out with 0.6 L of pig manure and several additions of SA at 37 ºC. The tested concentrations were 5, 10, 25, 30, 40, 50, 60, 75 and 100 kg m^{-3} of SA, which gives a N:P:Mg molar ratio between 1:0.17:0.28 and 1:3.3:5.7. However, in the present study, the molar ratio is not a good working parameter because of the lower reactivity of the LG-MgO and the nonreactive core of the SA particles [18]. The reactors were continuously stirred at 15 min^{-1} for a period of 24 h (86,400 s) to ensure the complete reaction of the SA. In order to analyze the interaction between the SA and the PM the treatment was evaluated by means of pH and total ammonia nitrogen (TAN) evolution, observed for each experimental trial at 0, 0.25, 2, 4, 8 and 24 hours.

2.4. Continuous reactor set-up

The study made use of three identical $2.5 \cdot 10^{-3}$ m^3 semi-continuous stirred tank reactors (S-CSTR) with a working volume of $2 \cdot 10^{-3}$ m^3. The gas system consisted of a water trap, an on-line biogas measuring device (Ritter MGC-1) and an acid trap. The operational temperature, which was ensured by circulating water from a heated water bath through a jacket surrounding the reactor, was fixed at 37 ºC. The reactor medium was continuously mechanically-stirred at 80 min^{-1}. The hydraulic retention time (HRT) of the three reactors was fixed at 20 days. The control reactor (R1) was fed only with pig manure, while the operational reactors (R2 and R3) were supplied with pig manure and stabilizing agent. The SA concentration in the feedstock was 5 kg m^{-3} for R2 and 30 kg m^{-3} for R3. The SA was mixed with the pig manure just before the feeding. The reactors were purged and then fed once a day. The influent and the effluent were collected through a pipe using a 0.1 L syringe. The biogas composition of the digesters headspace was analyzed three times per week by a Shimadzu GC-2010+ gas chromatograph. The biogas and methane productions are reported at standard temperature and pressure conditions (i.e. 0 ºC and 100 kPa).

2.5. Analytical procedure and methods

Analyses of the total fraction were performed directly on the raw samples. For analyses of the soluble fraction (i.e. volatile fatty acids (VFA), anions and cations), the samples were centrifuged at 1,252 x g (relative centrifugal force) for 10 minutes and then the supernatant was filtered through a 0.45 µm filter (Millipore HAWP02500). Total solids (TS) and volatile solids (VS) were determined in accordance with the guidelines given by the standard methods 2540G [27]. TAN (NH_3 plus NH_4^+) and total Kjeldahl nitrogen (TKN) were performed according to the standard methods procedure 4500-NH_3D and 2500-N_{org}B [27]. The free ammonia concentration was calculated by means of equation 1 [28]:

$$\mathrm{NH_3} = \frac{TAN \cdot 10^{pH}}{e^{\left(\frac{6344}{273.15+T}\right)} + 10^{pH}} \qquad \text{(eq. 1)}$$

Total (TA) and partial (PA) alkalinity were determined by a titration method at pH 4.3 and at 5.75, respectively, and the intermediate alkalinity (IA) by the difference between TA and PA [27]. Individual VFAs (acetate, propionate, butyrate and valerate) were analyzed by an HP-5890 Serie II chromatograph equipped with a capillary column (Nukol^{TM}) and flame ionization detector as described in Astals et al. [29]. Ions (Cl^-, PO_4^{3-}, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) were determined in an 863 Advanced Compact IC Metrohm ionic chromatographer using Metrosep columns (Metrohm). For cations the system was equipped with a Metrosep C4 – 150/4.0 mm column with an eluent (1.7 mol m^{-3} HNO_3 and 0.7 mol m^{-3} dipicolinic acid) flow of $1.5 \cdot 10^{-8}$ m^3 s^{-1}. For anions the system was equipped with a Metrosep A Supp 4 150/4.0 mm column with an eluent (1.7 mol m^{-3} $NaHCO_3$ and 1.8 mol m^{-3} Na_2CO_3) flow of $1.6 \cdot 10^{-8}$ m^3 s^{-1}. The biogas composition was analyzed by a Shimadzu GC-2010+ gas chromatograph equipped with a capillary column (Carboxen® - 1010 PLOT) and a thermal conductivity detector. The chromatograph oven temperature program was as follows: hold 360 s at 40 ºC; ramp to 230 ºC at 0.42 ºC s^{-1}, hold 120 s. Injector and detector temperature was set to 200 and 230 ºC, respectively. Helium with a fix linear velocity of 0.29 m s^{-1} was used as carrier gas.

With regard to the stabilizing agent and the precipitate physicochemical characterization the following analysis were performed. The chemical composition of the major and minor elements and the loss of ignition (LOI) was determined by X-ray Fluorescence Spectroscopy (XRF) using a Philips PW2400 X-ray sequential spectrophotometer. X-ray diffraction pattern was performed in a Bragg-Brentano Siemens D-500 powder diffractometer with CuK_α radiation to obtain information about the crystalline phases. To determine the particle structure and morphology a SEM Quanta 200 FEI analyzer equipped with an energy dispersive spectrometer analyzer (EDX) was used. Bulk density was measured with helium pycnometer [18,30].

3. Results and discussion

3.1. The potential of the stabilizing agent to precipitate struvite

3.1.1. Effect of the stabilizing agent on pH

Fig. 2a shows the evolution of the pH over time for all SA additions. The addition of SA to PM involved a rapid decrease in the pH values, followed by an increase until the equilibrium pH (pH_{eq}) was reached. Three different scenarios could be distinguished as a function of the SA addition: (i) low SA addition (5 and 10 kg m^{-3}) showed a slight decrease of about 0.7 pH points, followed by a comparatively fast increase in pH until the pH_{eq} was reached. The pH_{eq} was about one pH point higher than the initial pH. (ii) High SA addition (40, 50, 60, 75 and 100 kg m^{-3}) showed a reduction in pH from 7.7 to 6.4, followed by a slight increase to an pH_{eq} of between 7.1 and 7.3. (iii) Medium SA addition (25 and 30 kg m^{-3}) showed characteristics of both previously described scenarios. On the one hand, the initial pH reduction was similar to the reductions obtained in the high concentration assays, where the minimum pH value was 6.5. On the other hand, the pH recovery and the pH_{eq} were similar to those obtained in the low concentration assays, even though the pH_{eq} value was slightly lower.

The observed pH evolution can be explained through the acid-base pairs present in the pig manure and the modifications made by the introduction of the stabilizing agent. Initially, the pH of the PM was mostly fixed by the carbon dioxide/hydrogen carbonate and the ammonium/ammonia equilibrium (eq. 2 and 3). Then, the addition of the stabilizing agent reduced the pH, a fact that can be explained largely by the combination of two factors: (i) the H_3O^+ ions involved in the struvite precipitation equilibrium and (ii) the reduction of the TAN concentration in the system since it was precipitated as struvite [17]. Moreover, the presence of lime (CaO) in the LG-MgO could also contribute to diminishing the CO_3^{2-}/HCO_3^- concentration. However, it is difficult to establish the solubility equilibrium of calcium phosphates formed during the formulation of the stabilizing agent. It is important to highlight that the struvite precipitation could take place either with the magnesium phosphate particles present in the stabilizing agent (eq. 4), or with the magnesium and phosphates released from the LG-MgO, which reacted with the NH_4^+ present in the reactor medium (eq. 5). Finally, the pH increased until the pH_{eq} was achieved.

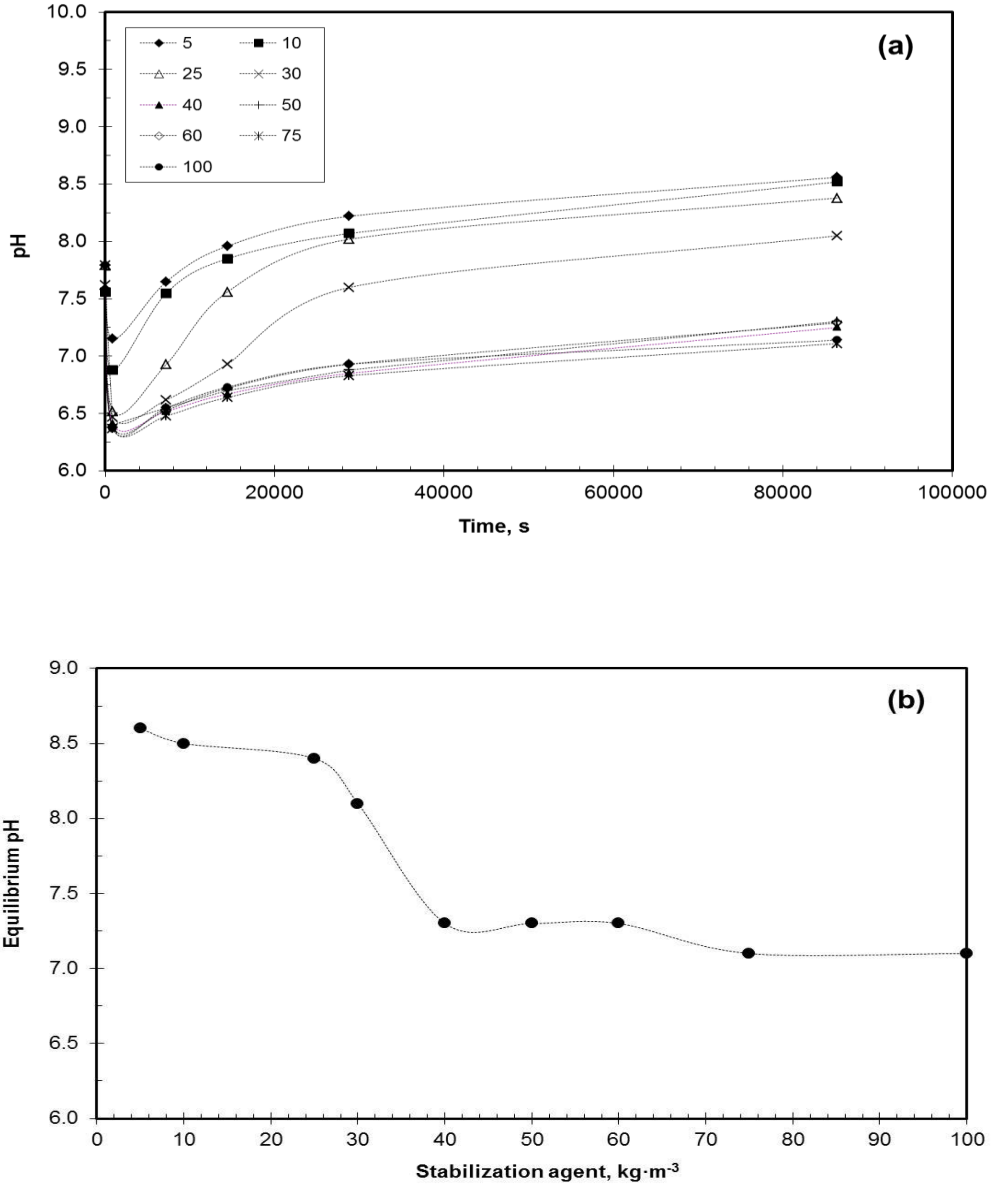

Fig. 2. (a) pH evolution in the course of time and (b) equilibrium pH for different stabilizing agent additions of the discontinuous experiments.

As can be seen in Fig. 2b, the pH_{eq} decreased as the amount of SA increased. The pH_{eq} of the assays with high SA addition was about 7.2. This value matches the logarithmic acid constant (pKa) of the second proton of the phosphoric acid. Therefore, in these conditions, the phosphates released from the SA cause the $H_2PO_4^-/HPO_4^{2-}$ acid-base balance to control the final pH value. By contrast, the pH_{eq} of the assays with low and medium SA addition, and therefore with a lower phosphate concentration, could be affected not only by the lower struvite formation and the lower TAN removal, but also by the CO_2 stripping that may have reduced the concentration of acid compounds in the reactor medium [31,32]. The later phenomena could also have taken place in the assays with high SA addition; however, it would have been masked by the high concentration of phosphate.

$$CO_{2\,(aq)} + 2H_2O \leftrightarrow HCO_3^- + H_3O^+ \qquad \text{(eq. 2)}$$

$$NH_4^+ + H_2O \leftrightarrow NH_{3\,(aq)} + H_3O^+ \qquad \text{(eq. 3)}$$

$$MgHPO_4 \cdot 3H_2O_{(s)} + NH_4^+ + 4H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O_{(s)} + H_3O^+ \qquad \text{(eq. 4)}$$

$$Mg^{2+} + HPO_4^{2-} + NH_4^+ + 4H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O_{(s)} + H_3O^+ \qquad \text{(eq. 5)}$$

3.1.2. Effect of the stabilizing agent on TAN removal efficiency

The evolution of the TAN for the tested SA additions is shown in Fig. 3a. The quick reduction in TAN concentration at the beginning of the assays was related to struvite precipitation, as was the quick initial pH reduction (Fig. 2a). It should be pointed out that even though the composition of the precipitate was not analyzed, all the necessary conditions were met for struvite precipitation. In the first quarter-hour low SA addition assays removed about 0.3 kg m^{-3} of TAN, while medium and high SA addition removed about 1 kg m^{-3} of TAN due to the higher ion concentration (Fig. 3a). Later on, the TAN concentration in low SA addition assays climbs and the pH rises. This phenomenon could be explained by struvite dissolution result of the pH reduction in the reactor medium [33,34]. However, no struvite dissolution, even at a lower pH value, was detected in the medium and high SA addition. This fact could be explained by the higher phosphate and magnesium concentration in the reactor medium and a higher pH in the interface layer covering the particles of SA. After struvite dissolution, the low SA addition assays reached a pH value near 8, which caused struvite precipitation and therefore TAN removal to restart [31]. In contrast, the medium and high SA addition assays continued to remove TAN throughout the entire experiment, but at a lower rate. The lesser reaction rate could be related to the formation of struvite on the SA particles surface and the pH of the reactor medium. On the one hand, Chimenos et al. [18], who precipitated ammonium and phosphates from cochineal waste wasters using the same magnesium by-product, corroborated that the LG-MgO particles surface was covered by struvite, while the inside of the LG-MgO particle had not reacted with the aqueous medium and remain unchanged. The present results confirmed that the struvite formation was controlled on the basis of the shrinking core model; hence the phosphate and ammonium diffusion was blocked by the struvite crystals [18, 30]. On the other hand, it is well known that struvite precipitation is feasible between pH values of 7 and 11 [32], with an optimum between 8 and 9. However, the lower pH in the digester medium not only reduced the struvite nucleation time [31-33], but also improved newberyite stability [35], which slowed down the dissolution of phosphate and ammonium.

Finally, Fig. 3b shows that the reduction in TAN concentration was not proportional to the SA addition. Specifically, in the low and medium SA addition assays the TAN removal efficiency improved as the SA addition increased. It is possible that under these

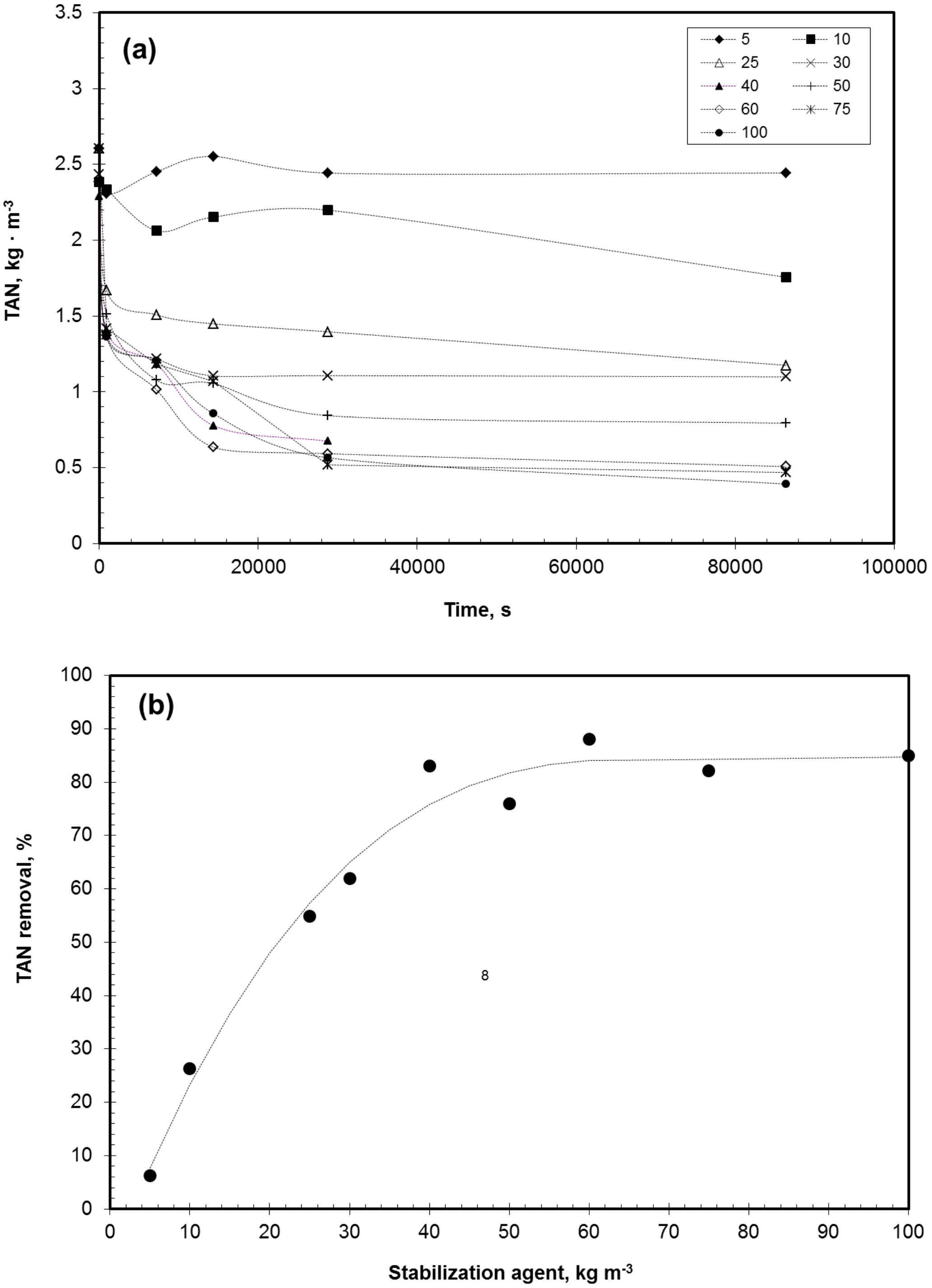

Fig. 3. (a) TAN evolution in the course of time and (b) the TAN removal efficiency for different stabilizing agent additions after 24 hours of the discontinuous experiments.

conditions the ion concentration was not high enough to remove all the available TAN. Nevertheless, the maximum TAN removal efficiencies, about 83%, were reached for all the high SA addition assays (40 to 100 kg m^{-3}), a scenario in which an increase in the stabilizing agent addition did not lead to a higher struvite precipitation.

3.2. Mesophilic anaerobic digestion coupled with struvite precipitation

The results obtained in the batch experiments showed the high capacity of the stabilizing agent to reduce the TAN concentration of the pig manure. However, a long term digester operation is necessary to evaluate the process feasibility and to guarantee that the stabilizing agent does not introduce any harmful compound for the anaerobic biomass. As aforementioned, 5 and 30 kg m^{-3} were chosen as a SA concentration in the feed supply. These concentrations enabled the behavior of the low and medium SA additions to be evaluated. It should be noted that, even presenting better TAN removal efficiencies, high SA additions were not considered due to high pH reduction as well as high costs associated to the SA price and transportation.

At the outset, the three reactors were inoculated with digestate from a centralized pig manure anaerobic digestion plant. This approach made it possible to obtain an adapted anaerobic consortium and, therefore, reduce the start-up period. After a lag time of 40 days similar steady-state conditions were achieved in all reactors as shown by the constant pH, alkalinity ratio, VFA concentration and biogas production rate. Afterwards and during 110 days the SA was added to the fed supply of R2 and R3, while R1, kept as a reference, was fed only with PM (Fig. 4). Two different strategies were followed in order to achieve the desired SA concentration in the reactor medium. In R2 the SA concentration increased gradually because it was always fed with the designed feed supply (5 kg m^{-3}), while the SA concentration in R3 increased dramatically because the reactor was fed with an influent of 200 kg m^{-3} during the first three days and then of the required SA addition (30 kg m^{-3}); no process inhibition was detected in either case. Once the new steady-state conditions were achieved for both reactors (after 30 days) a set of analyses was carried out during four HRT in order to characterize the PM, the biogas and the effluent of the three reactors (Table 2).

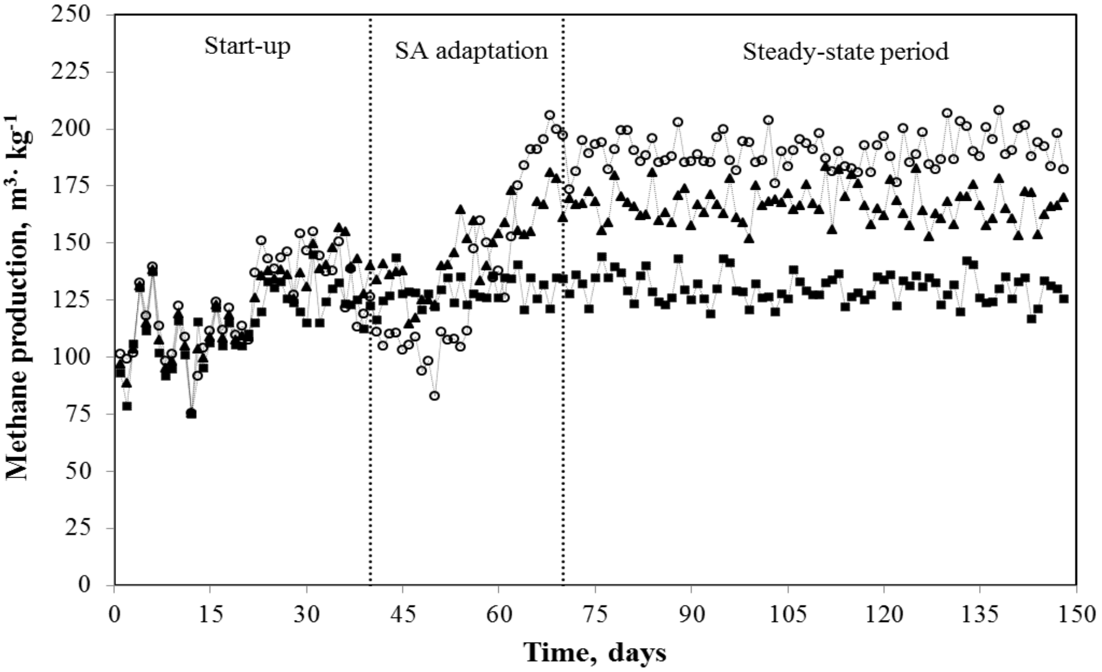

Fig. 4. Specific methane production in the R1 (■), R2 (▲) and R3 (○).

The evaluation of digestion stability was one of the most important factors to take into account since it enables to consider an AD process to occur without risk of acidification. It was especially important here because the stabilizing agent was formulated with low-grade magnesium oxide, a by-product of the combustion of natural magnesite, which could introduce contaminants to the reactor medium and therefore inhibit the activity of the microorganisms [6,36]. In the present work, the digestion stability was monitored by means of the intermediate-to-partial alkalinity (IA/PA) ratio and the total volatile fatty acids-to-total alkalinity (TVFA/TA) ratio, which should be below 0.4 to ensure stable digestion [29,37-39]. Other authors have evaluated reactor stability using the intermediate-to-total alkalinity (IA/TA) ratio; however, the IA/TA ratio is less sensitive than the IA/PA ratio, not been adequate for systems with high alkalinity like pig manure digesters [29]. The average IA/PA ratio was 0.20, 0.23 and 0.24, while the average TVFA/TA ratio was 0.007, 0.007 and 0.006 for R1, R2 and R3, respectively. As these values were far below the proposed limit values, it could be assured that the process was operating without risk of acidification and hence that the SA did not exert a negative effect on the consortium of microorganisms. It is important to note that the TA values decreased as the SA addition increased; however, the TA for all digesters was much higher than 2 kg m^{-3} of $CaCO_3$, which is considered to be the lower limit for AD safe operation [40,41]. The explanation for this phenomenon could lie in the reduction in the TAN concentration as well as in CO_2 stripping, which may have caused struvite precipitation and resulting hydronium liberation (eq. 4 and 5). This, in turn, would have reduced the concentration of acid and basic compounds in the liquid phase and increased the CO_2 percentage in the biogas (Table 2). Nonetheless, the differences in the TA values did not have an impact on the pH values for the digesters, since all three digesters presented pH values of around 8, a typical value for a manure digester [29 ,42].

All digesters were operated with the same HRT (20 days) and, as the SA did not provide biodegradable VS, with the same organic loading rate (1.1 kg m^{-3} day^{-1} of VS). The addition of the SA to the digester medium resulted in a 25% and a 40% increase in methane production for R2 and R3, respectively, when compared with the reference digester (R1). However, because of the different thermal stability of newberyite, periclase and struvite [43], the higher biogas production could not be correlated with a higher matter removal. In any case, the difference between the levels of methane produced could be related to the concentrations of TAN, magnesium and/or particles in the digester medium. Details are provided below.

As previously noted, TAN inhibition is especially distinct when digesting manures and a wide range of inhibiting TAN concentrations has been reported. As can be seen in Table 2 the TAN concentration in R2 was similar to that obtained in R1, with the concentration only reduced by 4%. In contrast, a large reduction in the TAN concentration, about 80%, was obtained for R3. However, the higher TAN removal efficiency of R3 in comparison with the one obtained in R2, which for both systems was related to struvite precipitation, did not make a substantial difference to the levels of methane production, which was only around 10%. These results highlighted that R1 and R2 were little inhibited by the TAN, indicating that the biomass was well adapted to the substrate and therefore to high TAN concentrations.

Another factor to take into account when explaining the difference between the levels of methane production was the magnesium concentration. Few studies had analyzed the effect of Mg^{2+} on anaerobic digestion and none of them, to our knowledge, address manure digestion. Nevertheless, it is clear that a surplus or deficit of Mg^{2+} can have a significant impact on the successful operation of an anaerobic digester [6]. As an example Kugelman and McCarty [44] found that Mg^{2+} concentrations between 0.075 and 0.150 kg m^{-3} were stimulatory for acetoclastic methanogens, while concentrations above 1 kg m^{-3} where reported to be inhibitory to differing degrees. In another study Schmidt et al. [45] reported optimal Mg^{2+} concentrations between 0.25 and 0.75 kg m^{-3} for methanosarcina thermophila in a UASB reactor. However, no methanosarcina is expected in the digesters under study due to the low VFA concentration. Although the optimal range of Mg^{2+} is not clear, what is quite clear is that a low concentration of Mg^{2+} can constrain the development of the anaerobic process. The Mg^{2+} concentration in the PM and R1 was below 0.2 kg m^{-3}, therefore a deficit of it in the digester medium was assumed. However, the digester supplied with SA had higher concentrations of Mg^{2+} in the digester medium, released from the LG-MgO (Table 2). Moreover, the

Table 2. Characterisation of the pig manure and the effluent of the three digesters

	Pig manure	**R1 Effluent (0 kg m^{-3})**	**R2 Effluent (5 kg m^{-3})**	**R3 Effluent (30 kg m^{-3})**
Influent and effluent composition				
TS (kg m^{-3})	35.0 ± 2.5	29.5 ± 1.6	35.7 ± 1.0	53.7 ± 2.9
VS (kg m^{-3})	21.7 ± 2.0	16.1 ± 1.2	20.7 ± 0.9	23.7 ± 1.4
pH	8.0 ± 0.2	8.1 ± 0.1	8.1 ± 0.1	8.0 ± 0.2
Partial Alk. (kg m^{-3})	6.5 ± 0.2	8.8 ± 0.2	8.0 ± 0.2	5.8 ± 0.4
Total Alk. (kg m^{-3})	8.5 ± 0.2	10.6 ± 0.2	9.8 ± 0.4	7.2 ± 0.5
VFA (kg m^{-3})	1.5 ± 0.2	0.07 ± 0.01	0.07 ± 0.01	0.04 ± 0.01
- Acetic acid (kg m^{-3})	1.2 ± 0.2	0.05 ± 0.01	0.06 ± 0.01	0.04 ± 0.01
- Propionic acid (kg m^{-3})	0.10 ± 0.01	n.d.	n.d.	n.d.
- Butyric acid (kg m^{-3})	0.09 ± 0.02	0.01 ± 0.01	0.01 ± 0.01	n.d.
- Valeric acid (kg m^{-3})	0.09 ± 0.01	0.01 ± 0.01	n.d.	n.d.
TAN (kg m^{-3})	2.2 ± 0.1	2.2 ± 0.1	2.1 ± 0.1	0.5 ± 0.1
TKN (kg m^{-3})	3.7 ± 0.07	3.8 ± 0.1	3.7 ± 0.13	3.7 ± 0.2
Chloride (kg m^{-3})	1.5 ± 0.1	1.5 ± 0.1	1.5 ± 0.1	1.5 ± 0.1
Phosphate (kg m^{-3})	0.3 ± 0.1	n.d.*	n.d.*	n.d.
Sodium (kg m^{-3})	0.8 ± 0.1	0.7 ± 0.1	0.8 ± 0.1	0.8 ± 0.1
Potassium (kg m^{-3})	2.0 ± 0.1	1.9 ± 0.1	2.0 ± 0.1	1.9 ± 0.1
Calcium (kg m^{-3})	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.3 ± 0.1
Magnesium (kg m^{-3})	n.d.	n.d.	0.05 ± 0.01	0.7 ± 0.1
Biogas characteristics				
Biogas production (m^{3} day^{-1})	-	380 ± 40	530 ± 100	600 ± 90
Methane content (%)	-	75 ± 3	70 ± 2	67 ± 3
Methane production (m^{3} day^{-1})	-	290 ± 30	370 ± 50	410 ± 40
SMP-V$_{R}$ (m^{3} m^{-3} day^{-1})	-	0.14 ± 0.02	0.18 ± 0.02	0.20 ± 0.02
SMP-VS$_{fed}$ (m^{3} kg^{-1})	-	0.13 ± 0.01	0.17 ± 0.02	0.19 ± 0.02

* n.d. no detected VFA (< 0.01 kg m^{-3}) and ions (< 20·10^{-3} kg m^{-3})
Where SMP-V$_{R}$ stands for specific methane production per volume of digester and SMP-V$_{fed}$ stands for specific methane production per kilogram of VS fed

phosphate concentration in R2 and R3 is almost negligible while R1 had about 0.3 kg m^{-3}, so it is clear that some Mg^{2+} present in R2 and R3 digester medium reacted with it to precipitate struvite (eq. 5).

Struvite precipitation was very important because it not only reduced the TAN concentration and supplied magnesium in the digester medium but also could have offered a high-capacity immobilization matrix for microorganisms. The immobilization of the anaerobic consortium is known to improve the anaerobic digestion process in manure, where natural zeolites, activated carbon and phosphorite ore, among others, have been reported to counteract various types of inhibition and to stabilize the anaerobic digestion process [10-12].

3.3. Stabilizing agent and the precipitate characterization

As can be seen in SEM micrographs, the particles of the stabilizing agent presented an amorphous morphology with a particle size below 200 μm (Fig. 1a). In contrast, most precipitate particles presented an orthorhombic structure typical of struvite crystals (Fig. 5a) [22,31,34] with a particle size between 200 and 500 μm. The analyzed particles were obtained from the continuous digesters. Three different types of particles can be found in the precipitate: (1) typical orthorhombic struvite crystals, (2) small orthorhombic struvite crystals grown above the stabilizing agent surface and (3) other minerals (Fig. 5a). Additionally, an X-ray analysis of the SA and the precipitate was used to identify the main mineralogical phases of the two compounds (Fig. 1b and 5b). The SA mainly consisted of newberyite ($MgHPO_4 \cdot 3H_2O$) and periclase (MgO), although other inert minerals could be detected in minor amounts, i.e. quartz (SiO_2), dolomite ($CaMg(CO_3)_2$) and gypsum ($CaSO_4 \cdot 2H_20$), whereas the X-ray diagram of the precipitate confirmed the presence of struvite. To be specific, struvite peaks were identified as the main phase, although newberyite and periclase were identified as minor phases. The presence of newberyite and periclase in the precipitate, non-reacted mineral, suggests that the struvite was formed on the particle surface while the nuclei of the SA particles remained unreacted. These results confirmed the coexistence of two mechanisms for struvite precipitation: (i) the formation and growth of the struvite on the SA particle surface (eq. 4), which was related to the small orthorhombic struvite crystals (Eq. 4) and (ii) the formation and growth of struvite from bulk solution (eq. 5), which was related to the typical orthorhombic struvite crystals.

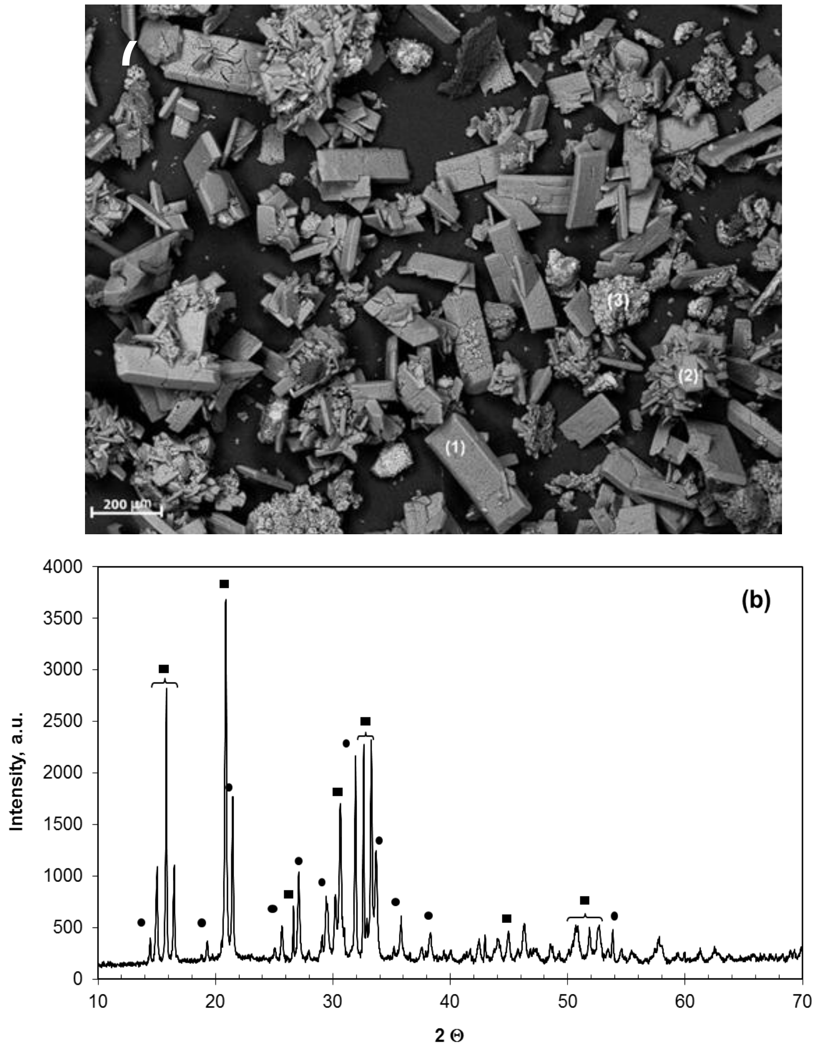

Fig. 5. (a) scanning electron micrograph ((1) are struvite particles growth in the digester medium, (2) are struvite particles growth on the surface of the stabilizing agent, (3) are other minerals) and (b) X-ray diffractogram of the precipitate obtained from the digesters effluent (● Newberyite; ▲ Periclase; ■ struvite).

Conclusions

The interaction between the pig manure and the stabilizing agent was evaluated in batch experiments for a wide range of additions. Three different scenarios were distinguished as function of the stabilizing agent concentration: low (5 and 10 kg m^{-3}), medium (25 and 30 kg m^{-3}) and high (40 to 100 kg m^{-3}). To be specific, ammonia removal efficiencies below 25% were obtained for low additions but, at the same time, lower pH fluctuations than high additions, which showed removal efficiencies up to 80%. Medium additions showed characteristics of both scenarios. The results obtained showed that the high capacity of the stabilizing agent to remove ammonia from pig manure.

The operation of three digesters during four hydraulic retention times showed that the addition of 5 and 30 kg m^{-3} of stabilizing agent into the digester fed resulted in a 25% and a 40% increase in methane production, respectively, when compared with the reference digester. These results were related to the reduction of the ammonia concentrations and the increase of magnesium and particles concentration in the digester medium. Moreover, as shown by biogas production, the alkalinity and volatile fatty acids values, the stabilizing agent did not exert a negative effect on the consortium of microorganisms. Therefore, the magnesium oxide by-product used to formulate the stabilizing agent did not introduce any harmful compound for the anaerobic biomass.

Finally, X-ray diffraction and scanning electronic microscopy confirmed struvite precipitation in addition to two precipitation mechanisms, reaction between ammonia and newberyite on the stabilizing agent particle surface and reaction between ammonia, phosphate and magnesium in the digester medium.

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GENERAL CONCLUSIONS

- A commercial high-grade MgO and three MgO-rich industrial by-products from the calcinations of natural magnesite have been examined for use in struvite precipitation. Four additional reagents (called stabilizing agents) were prepared by pre-treating the MgOs with phosphoric acid. This pre-treatment led to a stabilizing agent rich in newberyite or bobierrite depending on the reactivity of the precursor MgOs. The MgOs achieved total ammonia nitrogen removal extents ranging between 47 and 72%. The stabilizing agents with predominantly newberyite performed better (79-83% TAN removal) than their precursor MgOs. These results were significant because they suggested that it may be possible to use phosphoric acid pre-treatment to upgrade low-grade MgOs for struvite precipitation.
- Results showed the capacity of the stabilizing agent to promote struvite precipitation without causing a significant pH change and/or being inhibitory for anaerobic biomass. The stabilizing agent presented two main advantages over the other magnesium sources: (i) the avoidance of adding the phosphate source directly into the digester medium, and (ii) a low reactivity due to its high content in newberyite.
- The operation of three digesters during four hydraulic retention times showed that the addition of 5 and 30 kg m-3 of stabilizing agent into the digester fed resulted in a 25% and a 40% increase in methane production, respectively, when compared with the reference digester. These results were related to the reduction of the ammonia concentrations and the increase of magnesium and particles concentration in the digester medium. Moreover, as shown by biogas production, the alkalinity and volatile fatty acids values, the stabilizing agent did not exert a negative effect on the consortium of microorganisms. Therefore, the magnesium

oxide by-product used to formulate the stabilizing agent did not introduce any harmful compound for the anaerobic biomass.

RESUMEN

Capítulo 1. Recuperación de nutrientes

1.1 Introducción general

La digestión anaeróbica (DA) se presenta como una tecnología importante en la emergente economía de energías sostenibles [1]. La DA de residuos orgánicos produce energía renovable y una corriente residual llamada digestado, la cual es una mezcla de materia orgánica parcialmente degradada, microorganismos y materia inorgánica (incluidos nutrientes) [2]. Las ventajas de la DA sobre otras tecnologías son: i) tratamiento efectivo y económico de residuos orgánicos urbanos (aguas residuales y residuos sólidos) y ii) alternativa energética y económica para los sectores rurales a través del tratamiento de residuos agro-industriales y/o cultivos energéticos [3]. Hoy en día, la mayoría de las plantas de DA están enfocadas hacia el tratamiento de residuos con aprovechamiento energético, mientras que se ha prestado menor atención a la recuperación de nutrientes. Sin embargo, la continua demanda e incremento en los precios de los fertilizantes (P, N y K), obtenidos mayoritariamente de explotaciones mineras (recursos no renovables como el P y K) y síntesis con alto consumo energético (N – proceso Haber-Bosch), ha incrementado el interés en la recuperación de nutrientes a parir de corrientes residuales [4–6]. La manera más económica de recuperar nutrientes a partir de corrientes residuales es el uso de éstos como enmienda orgánica o fertilizantes orgánicos. Sin embargo. El uso de estos en la agricultura está restringido en función del contenido de Cu y Zn, salinidad, materia orgánica remanente, fitotoxicidad y características de higiene [7,8]. Lo cual hace necesario aplicar pre- o post-tratamientos con el fin de adecuar las corrientes residuales para uso agrícola [9]. Adicionalmente, la baja concentración de nutrientes en relación con el alto costo en trasporte hacia los campos puede conducir a una limitada e ineficiente recuperación de nutrientes.

Los recientes avances en recuperación de nutrientes de corrientes residuales proponen los siguientes tres pasos en continuo para lograr mejores resultados [10]: 1) acumulación; 2) liberación y 3) extracción de los nutrientes. La acumulación de los nutrientes puede realizarse a través de plantas, microorganismos o procesos físico-químicos (ej. Microalgas o organismos acumuladores de polifosfatos). La liberación de los nutrientes pude ser realizada con procesos bioquímicos (ej. Digestión anaeróbica) o tratamientos termoquímicos; y la extracción de los nutrientes puede ser realizada por procesos físico-químicos como la cristalización.

De los procesos de extracción de nutrientes por cristalización el procedimiento más utilizado es la precipitación de estruvita, el cual es atractivo debido a sus cualidades como fertilizante [11,12]. Desafortunadamente, la composición equimolar de la estruvita (magnesio, amonio y fosfato, $MgNH_4PO_4·6H_2O$) requiere adiciones de magnesio para la fijación de fosfato y de magnesio y fosfato para la fijación de amonio. Esto conlleva a que la viabilidad económica de la precipitación de estruvita este altamente influenciada por el costo de los reactivos de magnesio [13,14].

1.2 Eficiencia en el uso de reactivos para la eliminación de nitrógeno de purines a través de la precipitación de estruvita: estudio sobre el óxido de magnesio y subproductos relacionados

1.2.1 Introducción

Varios estudios han probado diferentes fuentes de magnesio de bajo costo para la precipitación de estruvita, ej. Salmuera [15], agua de mar [16], magnesita [17], productos de la pirolisis de magnesita [18], reciclado por pirolisis de estruvita [19] y subproductos del procesos de calcinación de magnesita [13,20]. Uno de los principales factores a estudiar respecto a las fuentes de magnesio, es la disolución del magnesio, ya que esta puede determinar la cinética del proceso de precipitación de estruvita [21]. Los estudios reportados hasta ahora sobre la precipitación de estruvita usando MgO están ampliamente enfocados en la fase acuosa, con poca atención en la disolución del MgO [22]. El presente estudio usa modelos químicos y experimentos para evaluar y entender la remoción de nitrógeno amoniacal del purín de cerdo usando diferentes fuentes de magnesio de bajo costo compuestos principalmente por MgO.

1.2.2 Materiales y métodos

Como fuentes de magnesio para este estudio se utilizaron MgO de alto grado (HGMgO) comercial y tres sub-productos industriales ricos en oxido de magnesio obtenidos de la calcinación de magnesita en hornos rotatorios a 1100ºC y 1800ºC para obtener magnesia caustica calcinada y magnesia calcinada a alta temperatura respectivamente. De acuerdo al contenido de MgO, los tres productos industriales fueron clasificados como MgO de bajo gado (LGMgO) y rotulados como PC8, PCC y Caustica P. Adicionalmente, los LGMgO y el HGMgO se pre-trataron con ácido fosfórico, los productos formados con este pre-tratamiento se llamaron agentes estabilizantes (SAs). Al igual que los LGMgO y el HGMgO, los SAs se caracterizaron por fluorescencia de rayos X (XRF) (Tabla 1).

Los experimentos de fijación de amonio se realizaron a 25ºC en un dispositivo de test de jarras. Los reactores se agitaron continuamente por 4 horas y se realizaron medidas de pH, nitrógeno amoniacal total (TAN) y PO_4^{3-} a las 0, 0.5, 1, 1.5, 2, 3 y 4 horas. Las relaciones de N:P:Mg utilizados (incluyendo la concentración inicial en el purín) fueron 1:1:1.6 para los reactivos de MgO (LGMgOs y el HGMgO); y 1:1:1.3, 1:1:1.6, 1:1:1.3 y 1:1:1.8 para los agentes estabilizantes SA-MgO, SA-PC8, SA-Caustica P y SA-PCC, respectivamente.

Tabla 1 - Caracterización semi-cuantitativa

Reactivos de MgO

	Units	HGMgO	PC8	Caustica P	PCC
MgO	%	89.8	68.6	79.4	61.1
P_2O_5	%	-[#]	-	-	-
CaO	%	1.5	9.0	9.9	9.8
SO_3	%	0.0	8.1	0.0	4.7
Fe_2O_3	%	0.0	2.7	2.9	2.3
SiO_2	%	0.0	2.5	3.8	2.3
LOI (1100 °C)	%	8.7	8.7	8.7	19.5
Reactivity*	s	90	445	2655	2725

Agentes estabilizantes

		SA-HGMgO	SA-PC8	SA-Caustica P	SA-PCC
MgO	%	27.4	25.3	25.8	25.9
P_2O_5	%	39.7	28.8	36.5	27.0
CaO	%	0.4	3.0	2.3	3.6
SO_3	%	0.0	0.0	0.0	0.0
Fe_2O_3	%	0.0	0.9	0.9	0.9
SiO_2	%	0.0	1.2	1.3	2.0
LOI (1100 °C)	%	32.4	40.0	33.0	40.2

* A partir del test del ácido cítrico

[#] "-" significa no medido/irrelevante

El modelo químico fue desarrollado mediante la utilización del software PheeqC (versión 3). Este software permite calcular las condiciones que satisfacen el equilibrio termodinámico en la fase acuosa y entre la fase acuosa y las fases del mineral añadido. En el modelo, el pH inicial y la composición de la fase acuosa del purín de cerdo se establece según los valores medidos experimentalmente antes de la adición de reactivos, posteriormente se utiliza el balance de carga de los iones para calcular el carbono inorgánico total (el único ion relevante no medido experimentalmente). Junto con las diferentes fuentes de reactivos de MgO se añadió una cantidad conocida de K_2HPO_4 al modelo como fase en equilibrio altamente soluble. Luego la periclasa (MgO) se adicionó en el modelo en cantidades progresivamente crecientes (siempre totalmente disuelta) hasta que la predicción del modelo coincidía con la medida experimental respecto a la eliminación de TAN y pH en el tiempo. Esta cantidad de periclasa se asume que refleja el grado de disolución de reactivo en el experimento. La medida de disolución (en el modelo) se convirtió en una cantidad equivalente de magnesio y se comparó con la cantidad de magnesio adicionada inicialmente. A partir de esta comparación se calcula la eficiencia de utilización de magnesio.

Para los SAs. se utiliza un enfoque de modelo similar Pero en vez de añadir periclasa, se añade bobierrite o newberyita (dependiendo de la forma dominante medida por XRD). Todos los minerales añadidos al modelo siempre estuvieron totalmente disueltos y nunca llegaron a limitaciones de solubilidad. Las cantidades relativas de periclasa vs. bobierrita o newberyita añadidas al modelo, dependen de que el pH y que la eliminación de TAN coincidieran con los resultados experimentales. La eficiencia de uso de magnesio y fosfato se calculan comparando las cantidades de magnesio y fosfato añadidas al modelo con los datos experimentales.

1.2.3 Resultados y discusión

La Fig.1a presenta los difractogramas obtenidos para los diferentes reactivos de MgO, en este se aprecia que en todas las muestras predomina la periclasa y que el PC8 y PCC también contiene magnesita y dolomita. Por otra parte, Fig. 1b muestra los difractogramas obtenidos para los SAs. Estos resultados indican que el pre-tratamiento con ácido fosfórico disuelve la periclasa y principalmente forma newberyita en el caso del SA-PCC y SA-Caustica P, y bobierrita en el casa del SA-HGMgO y SA-PC8. Estas diferencias en composición de los SAs están correlacionadas con las reactividades relativas de sus precursores. El HGMgO y el PC8 son los agentes con mayor reactividad, mientras que el PCC y la Caustica P fueron los precursores con menor reactividad.

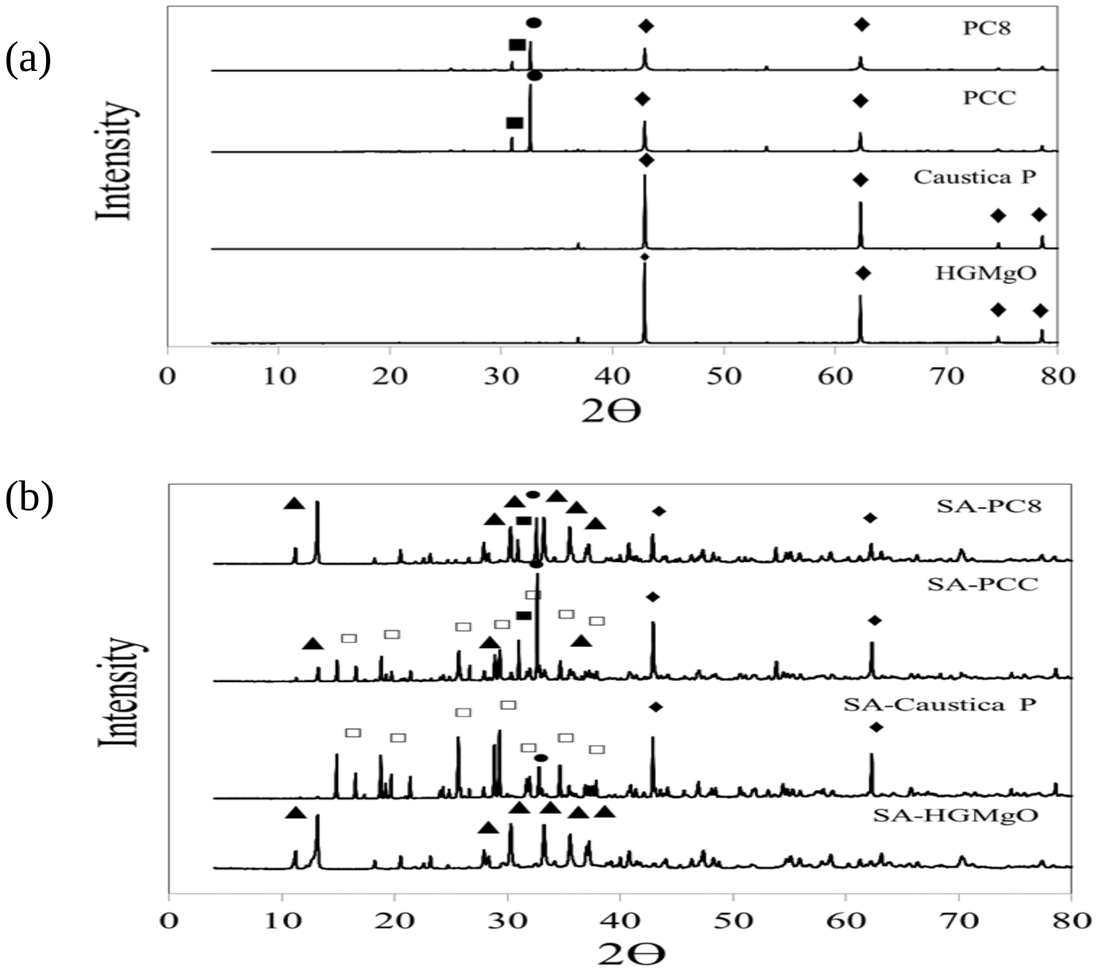

Fig. 1 – Resultados de XRD análisis para (a) HGMgO, LG-MgOs y (b) sus respectivos agentes estabilizantes (SAs), indicando las señales caracteristicas para periclasa (♦), magnesita (●), dolomita (■), bobierrita (▲) and newberyita (□).

En los experimentos de fijación de TAN, los reactivos de MgO se añadieron como fuentes de Mg^{2+} y K_2PO_4 como fuente PO_4^{3-}, respectivamente. En general, la capacidad de los reactivos de MgO para hidratarse y convertirse en $Mg(OH)_2$ está influenciada por la concentración MgO, mineral de origen y condiciones de calcinación [23,24]. Este hecho se ve reflejado en el incremento del pH (Fig. 2a) por disolución del MgO y liberación de hidroxilos. Adicionalmente, la eliminación de TAN (Fig. 2d) refleja la tendencias en el pH medido, lo que sugiere que la disolución del MgO libera Mg^{2+} para precipitar estruvita fijando el TAN. La fijación de TAN oscila desde 47 hasta 72%. El análisis del modelo y los resultados experimentales claramente muestran que la remoción de TAN está limitada por el suministro de Mg^{2+}. Adicionalmente, el modelo indica que todos los reactivos de MgO fueron pobremente disueltos, con solamente un 31-45% del magnesio adicionado disponible para la formación de estruvita (ver Tabla 2).

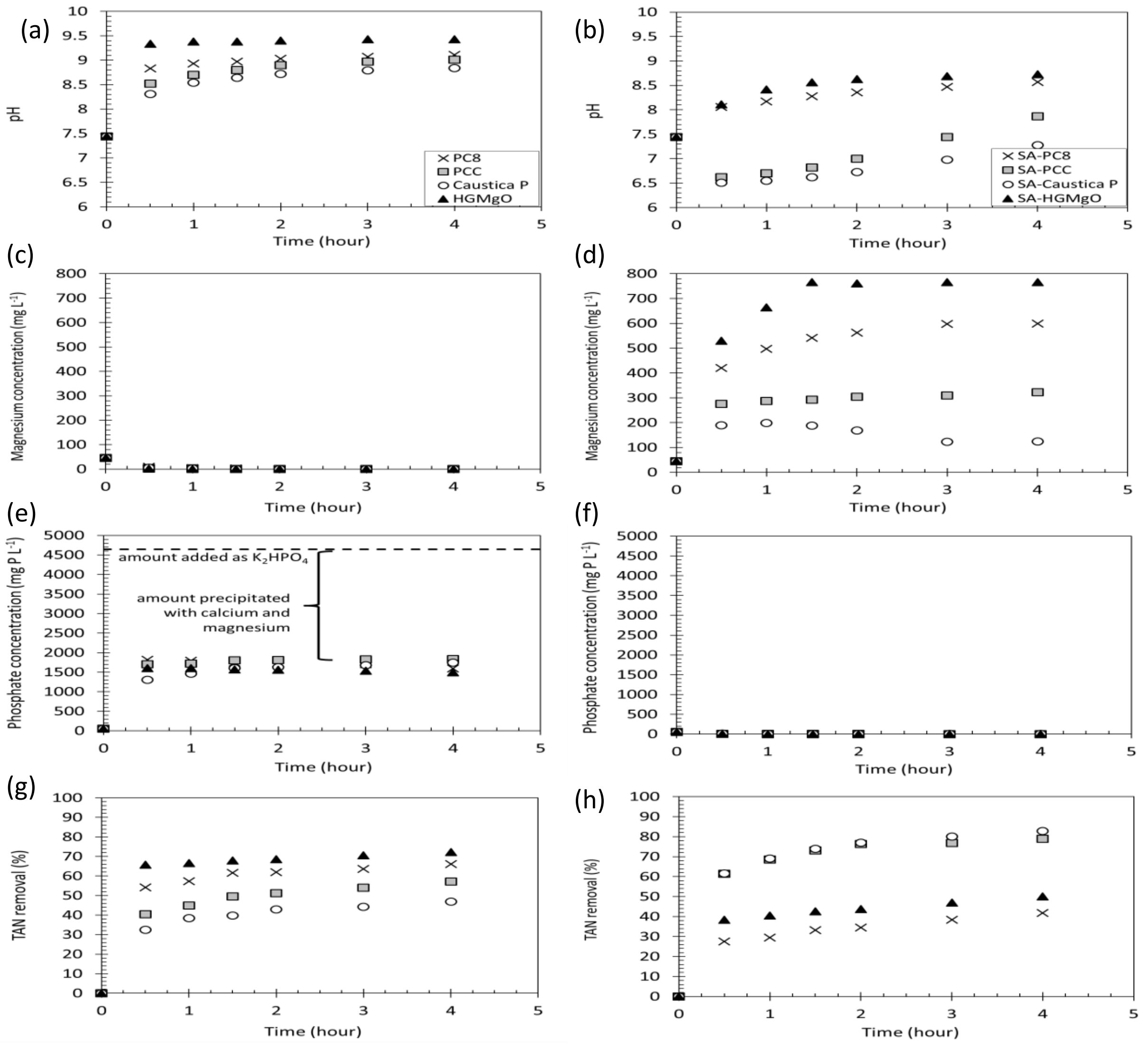

Fig. 2 – Resultados de la remoción de TAN mostrando las medidas de pH, concentraciones de Mg^{2+} y PO_4^{3-}; y el porcentaje de romoción de TAN usando los MgO (a, b, c, d) y los SAs (e, f, g, h) tests using the stabilizing agents (SAs).

Tabla 2 – Comparación de los resultados del modelo y los resultados experimentales a 4 horas de experimento usando MgO y K_2HPO_4

	HGMgO		PC8		Caustica P		PCC	
	Exp.[a]	Modelo[b]	Exp.[a]	Modelo[b]	Exp.[a]	Modelo[b]	Exp.[a]	Modelo[b]
pH	9.43	9.55	9.11	9.41	8.84	9.16	9.01	9.31
Mg (mg L^{-1})	0	0.23	0	0.18	0	0.13	0	0.16
Ca (mg L^{-1})	588	163	328	163	520	163	298	163
TAN (mg N L^{-1})	585	700 [c]	715	860	1,121	1,126	903	981
PO_4^{3-} (mg P L^{-1})	1,498	1,495	1,599	1,604	1,742	2,192	1,833	1,868
Pericalsa (MgO) añadida al modelo (mM) [e]	-[d]	100	-	88	-	69	-	80
Equivalente de magnesio añadido como periclasa (mM)	223	-	223	-	223	-	223	-
Eficiencia del Mg [e]	-	45%	-	39%	-	31%	-	36%
Valores de índice de saturación								
Periclasa (MgO)	-	-8.9	-	-9.2	-	-9.8	-	-9.5
Brucita ($Mg(OH)_2$)	-	-4.1	-	-4.5	-	-5.1	-	-4.7
Magnesita ($MgCO_3$)	-	-0.7	-	-0.9	-	-1.2	-	-1.0
Dolomita ($CaMg(CO_3)_2$)	-	2.3	-	2.1	-	1.7	-	1.9
Estruvita ($MgNH_4PO_4$)	-	0	-	0	-	0	-	0

[a] Valores medidos a 4 horas (asumiendo que se ha llegado al equilibrio)

[b] Resultados del modelo

[c] Valores de TAN calculados en el modelo pueden ser ligeramente mayor que los experimentales ya que no se tienen en cuanta las pérdidas de TAN por stripping

[d] "-" significa no relevante

[e] Porcentaje de magnesio añadido que es viable para la formación de estruvita,. Este es calculado comparando la cantidad de magnesio añadida a cada experimento con la cantidad de periclasa requerida por el modelo para satisfacer el balance de masa y la composición final de la fase acuosa.

Los experimentos utilizando SAs como fuente de Mg^{2+} y PO_4^{3-} muestran que existe una correlación entre la respuesta experimental y la composición de los SAs. Los resultados con SA-PCC y SA-Caustica P (mayormente newberyita) fueron similares, al igual que los resultados con SA-PC8 y SA-HGMgO (mayormente bobierrite) fueron similares. Con SA-PCC y SA-Caustica P el pH inicial decreció a 6.5, probablemente debido a la liberación de protones causada por la precipitación de estruvita. Después de 30 min, las medidas de pH incrementan gradualmente, probablemente a la disolución de periclasa residual. Aunque el PO_4^{3-} es apenas medible (Fig. 2g), el análisis del modelo muestran que el SA-Caustica P y el SA-PCC fueron muy eficientes suministrando PO_4^{3-} para la precipitación de estruvita. 78-82% del PO_4^{3-} añadido como SA-Caustica P y SA-

PCC estuvo disponible para la precipitación de estruvita (ver Tabla 3). Esta alta eficiencia de uso de PO_4^{3-} se traslada a la alta eficiencia de remoción de TAN que alcanza valores de 79-83%. Lo cual es significativo considerando que los LGMgO precursores (Caustica P y PCC) presentaron una pobre fijación de TAN (45-58%). Estos resultados indican que el pre-tratamiento con acido fosfórico podría potencialmente mejorar la eficiencia de fijación de TAN para los LGMgO. Por otra parte, los resultados utilizando SA-HGMgO y SA-PC8, muestran un incremento progresivo de pH (Fig. 2e), probablemente debido a la disolución de periclasa residual. A la vez que presentan un incremento en la liberación de magnesio en los primeros 30 min (Fig. 2f) que no es usado para la formación de estruvita. Resultando en una baja remoción de TAN. Esto está relacionado con la liberación de PO_4^{3-} por parte del SA-HGMgO y SA-PC8 que aparentemente limita la fijación de TAN, como lo indica el bajo índice de eficiencia de utilización de PO_4^{3-} (Tabla 3). Por otra parte, el SA-HGMgO y el SA-PC8 presentaron una inferior remoción de TAN comparado con sus precursores (HGMgO y PC8), lo cual indica que el pre-tratamiento en este caso con acido fosfórico no mejora su desempeño.

Implicaciones, eficiencia de uso de reactivos, estrategias

Un resultado interesante de los datos obtenidos, es la aparente habilidad del pre-tratamiento con ácido fosfórico para mejorar la eficiencia de remoción de TAN a través de la precipitación de estruvita de los LGMgO. Adicionalmente, los SAs obtenidos son seguros, fáciles de manejar, no invasivos y podrían presentar ventajas en comparación con la adición por separado de los MgOs y PO_4^{3-}. Sin embargo, el pre-tratamiento con ácido fosfórico no mejora la remoción de TAN en todos los casos. Lo cual sugiere la pregunta: *podría la baja eficiencia de utilización de magnesio ser explicada por las diferencias en composición y reactividad?*. Los óxidos de magnesio utilizados en este estudio presentan un rango diferente de reactividades y composición. Sin embargo, la eficiencia de uso de magnesio (Tabla 2) fue similar (31-45%) considerando que se esperaba resultados diferentes en función de las diferencias en la reactividad medida. De esta observación, se puede concluir que la eficiencia de uso de magnesio para precipitar estruvita solo está parcialmente influenciada por la reactividad. Adicionalmente, la eficiencia también parece estar ligeramente influenciada por la pureza del MgO. Ya que la remoción de TAN esta solo marginalmente mejorada por el HGMgO en comparación con los LGMgO (Fig. 2). De hecho, la mejora en el rendimiento mediante el pre-tratamiento con ácido fosfórico para la Caustica P y PCC, supero el rendimiento de la utilización de un MgO de mayor pureza (HGMgO). En general, estas observaciones sugieren que la eficiencia en uso de los MgO esta débilmente influenciada por la pureza del MgO y que la alta eliminación de TAN también se puede lograr con una pureza inferior de MgO añadido a una cantidad estequiométrica comparable.

Otro aspecto importante que afecta la eficiencia del proceso, es que en las condiciones experimentales, en la superficie de las partículas (LGMgO, HGMgO y SAs) se puede causar la nucleación de estruvita, restringiendo la difusión y disolución de los iones formadores de estruvita. En este sentido, elevados valores de pH (ej. por hidrólisis), una rápida liberación de Mg^{2+}/PO_4^{3-} y una elevada concentración iónica en el líquido podrían contribuir a una elevada supersaturación en la superficie de la partícula. Lo cual generaría una partícula con un núcleo compuesto por la fuente de magnesio (LGMgO, HGMgO y SAs) recubierta por una capa de estruvita.

Tabla 3 - Comparación de los resultados del modelo y los resultados experimentales a 4 horas de experimento usando SAs.

	SA-HGMgO		SA-PC8		SA-Caustica P		SA-PCC	
	Exp.	Modelo	Exp.	Modelo	Exp.	Modelo	Exp.	Modelo
pH [a]	8.73	8.73	8.57	8.57	7.28	7.28	7.87	7.85
Mg (mg L^{-1})	766	1,558	600	1,267	125	1,485	323	1,574
Ca (mg L^{-1})	74	164	91	164	211	163	214	163
TAN (mg N L^{-1})	1,054	1,059	1,228	1,227	361	363	446	456
PO_4^{3-} (mg P L^{-1})	0.1	0.21	0	0.26	1.6	14	0	2.8
Pericalsa (MgO) añadida al modelo (mM)	-	27	-	21	-	61	-	65
Newberyita añadida al modelo (mM)	-	-	-	-	-	124	-	117
Bobierrita añadida al modelo (mM)	-	37	-	31	-	-	-	-
Eficiencia de uso de Mg [a]	-	75%	-	49%	-	99%	-	72%
Eficiencia de uso de PO_4^{3-} [b]	-	49%	-	41%	-	82%	-	78%
Valores de índice de saturación								
Periclasa (MgO)	-	-6.2	-	-6.6	-	-9.0	-	-7.8
Bobierrita ($Mg_3(PO4)_2$)	-	-2.5	-	-2.8	-	-1.6	-	-1.8
Newberyita ($MgHPO_4.3H_2O$)	-	-2.4	-	-2.4	-	-0.6	-	-1.3
Brucita ($Mg(OH)_2$)	-	-1.4	-	-1.8	-	-4.2	-	-3.1
Magnesita ($MgCO_3$)	-	2.8	-	2.7	-	1.5	-	2.1
Dolomita (disordered, $CaMg(CO_3)_2$)	-	5.9	-	5.7	-	3.4	-	4.6
Estruvita ($MgNH_4PO_4$)	-	0	-	0	-	0	-	0

[a] Medido de igual manera que en la Tabla 2

[b] iguales principios de cálculo de eficiencia de uso de magnesio, pero considerando el fosfato añadido con los agentes estabilizantes

1.2.4 Conclusiones

Se han examinado cuatro óxidos de magnesio, uno de alto grado comercial y tres diferentes sub-productos industriales (ricos en MgO), para el uso en la precipitación de estruvita. Cuatro reactivos adicionales (llamados agentes estabilizantes) fueron preparados pre-tratando los óxidos de magnesio de partida con acido fosfórico. Este pre-tratamiento con lleva a la obtención de agentes estabilizantes ricos en newberyita y bobierrita dependiendo de la reactividad del precursor. Una remoción de nitrógeno amoniacal total de 47-72% fue presentada por los reactivos de MgO. Mientras que los agentes estabilizantes compuestos mayoritariamente por newberyita presentaron una remoción de 79-83%. Estos resultados son significativos ya que sugieren que es posible que el pre-tratamiento con ácido fosfórico incremente el rendimiento de los sub-productos industriales (ricos en MgO) en la precipitación de estruvita. Por otra parte, los agentes estabilizantes mayoritariamente compuestos por bobierrita presentaron un peor rendimiento de remoción de nitrógeno amoniacal total que sus respectivos precursores. El análisis del modelo mostró que la formación de estruvita estaba limitada por la disolución de magnesio y fosfato, la cual está fuertemente afectada por las limitaciones cinéticas. Se propuso un por el cual las condiciones cerca a la superficie de las partículas causan la no deseada nucleación de estruvita, inhibiendo la disolución y reduciendo notablemente la eficiencia del reactivo.

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Capitulo 2. Acoplamiento de la digestión anaeróbica y la precipitación de estruvita.

2.1 Introducción general

La DA es una tecnología ampliamente utilizada para el tratamiento de residuos orgánicos, cuya implementación ha ido incrementando en los últimos años [1,2]. El diseño de digestores, operación y desempeño, así como inconvenientes operacionales, están relacionadas con la naturaleza de los residuos orgánicos [3], los cuales pueden ser clasificados en cinco categorías diferentes [4,5]: (i) lodos de depuradora; (ii) estiércol animales; (iii) residuos de la industria alimenticia, incluidas residuos de mataderos; (iv) cultivos energéticos y residuos forestales, incluidos algas; y (v) fracción orgánica de residuos sólidos urbanos. Sin embargo, la configuración de los digestores es menos diversa y la mayoría de los reactores son reactores continuos de mezcla completa y reactores de flujo ascendente [6–8]. A pesar de estos factores, la necesidad de mejorar la viabilidad económica de las plantas de DA, directamente relacionada con la producción de biogás, ha hecho que la mayor atención se preste en buscar técnicas que mejoren el rendimiento del proceso. En este sentido, se han aplicado diferentes enfoques con el fin de incrementar la producción de biogás en los digestores, tales como: (i) uso de la co-digestión, que permite incrementar la velocidad de carga orgánica; (ii) realización de pre-tratamientos para incrementar la bio-disponibilidad de los residuos; (iii) mejorar de la configuración y condiciones operacionales de los reactores; y (iv) uso de aditivos para estimular la actividad microbiana y/o reducir la concentración de agentes inhibitorios. En los últimos años, han sido varias las revisiones bibliográficas enfocadas en estas mejoras técnicas [9–15]. Sin embargo, estos reportes están mayormente centralizados en hacer pre-tratamientos y co-digestión, mientras que una menor atención se ha puesto en la introducción de aditivos en los digestores. Por una parte, los aditivos inorgánicos comprende reactivos, minerales y fuentes residuales capaces de proveer micronutrientes, reducir el efecto de inhibidores o ser usados como soporte para inmovilizar biomasa. Por otra parte, los aditivos biológicos incluyen la bioaugmentación, típicamente la dosis de inoculo con mayor actividad metanogénica, y la adición de enzimas capaces de facilitar la solubilización de la materia orgánica.

2.2 Factibilidad de acoplar la digestión anaeróbica y la precipitación de estruvita en el mismo reactor: evaluación de diferentes fuentes de magnesio.

2.2.1 Introducción.

Diferentes esfuerzos han sido desarrollados para reducir la inhibición por nitrógeno amoniacal en la DA. Entre ellos, la adición de materiales con capacidad de intercambio catiónico (por ejemplo: bentonita, glauconita, fosforita y zeolitas) o materias con capacidad de adsorción (ej. arena, óxidos de magnesio, sepiolitas y zeolitas) han mostrado buenos resultados [16–20]. Igualmente, en años recientes la posibilidad de acoplar la DA y la precipitación de estruvita ($MgNH_4PO_4 \cdot 6H_2O$) en el mismo reactor han llamado la atención. La obtención de estruvita despierta gran interés, ya que ésta presenta como valor añadido la posibilidad de ser comercializada posteriormente como fertilizante de lenta liberación[21–24].

La precipitación de estruvita ocurre de manera natural cuando la concentración de Mg^{2+}, NH_4^+ y PO_4^{3-} excede el producto de solubilidad de la estruvita [25]. Con lo cual, la precipitación de estruvita en muchos sistemas de DA requiere la adición de compuestos químicos, ya que la concentración de Mg^{2+} y PO_4^{3-} es típicamente inferior a la del NH_4^+ [26]. Para este propósito, diferentes fuentes de magnesio ($MgSO_4$, $Mg(OH)_2$, $MgCl_2$, MgO) y fosfato (H_3PO_4, sales de fosfato) han sido estudiadas [27]. A modo de ejemplo, Uludag-Demirer y col. [28] investigaron el efecto de la adición de $MgCl_2$, $Mg(OH)_2$ y Na_2HPO_4 en la DA, observando que no se presentaba ningún incremento en la producción de metano a pesar de la reducción en la concentración de NH_4^+. Los autores observaron que los digestores suplementados con $Mg(OH)_2$ y Na_2HPO_4 sufrieron inhibición por cationes (Na^+ y Mg^{2+}) y pH (pH por encima de 8.5), mientras que los digestores suplementados con $MgCl_2$ y Na_2HPO_4 no presentaron problemas de pH y solo presentaron inhibición por cationes. Al contrario, Lee y col. [29] operaron satisfactoriamente digestores continuos suplementados con $MgCl_2$ a una relación Mg:P 1:1 y ajustando el pH entre 7.7 y 8.3. Los autores concluyeron que el incremento en la producción de metano del 50% es debido a la reducción en la concentración de nitrógeno amoniacal de 6 a 2 g N L^{-1}. Demirer y col. [30] demostraron que la adición de $MgCl_2$ (0.92 y 1.87 g Mg^{2+} L^{-1}) a un digestor anaeróbico de lodos de depuradora con una concentración inicial de 1.4 g NH_4-N L^{-1} y 0.06 g PO_4^{3-}P L^{-1} permite la recuperación del 50% de nutrientes (N y P) en forma de estruvita. Adicionalmente, los autores afirman que no hay un impacto significado en el rendimiento de metano y la población de microorganismos metanogénicos.

El objetivo de este estudio es comparar el desempeño de cinco diferentes fuentes de magnesio (ej. $MgCl_2$, $Mg(OH)_2$, HG-MgO, LG-MgO y SA) en reactores, simultaneando los procesos de la DA y la precipitación de estruvita dentro del mismo reactor. Este estudio también tiene la intención de identificar los factores limitantes de aplicabilidad al combinar los dos procesos en el mismo reactor.

2.2.2 Materiales y métodos

Se ha desarrollado el test de potencial de biometanización de acuerdo con Angelidaki y col. [31], conservando una relación de sólidos volátiles entre inoculo y sustrato de 2. La Tabla 1 muestra las cantidades de reactivos de magnesio suministrado en cada ensayo, los cuales se realizaron por triplicado. Las fuentes de magnesio utilizadas en este experimento corresponden a las previamente mencionadas en el apartado 1.2.

Tabla 1. Dosis de magnesio y fosfato adicionado en cada ensayo

	Mg^{2+} (g·L^{-1})	**TP (g·L^{-1})**	**N:P:Mg**
Control	-	-	-
$MgCl_2$	3.30	0.42	1:1:1
$Mg(OH)_2$	3.30	0.42	1:1:1
SA(1)	1.00	0.07	6:1:1.7
SA(2)	2.87	0.21	2:1:1.7
SA(3)	5.75	0.42	1:1:1.7
HG-MgO(1)	1.00	0.07	6:1:1.7
HG-MgO(2)	2.87	0.21	2:1:1.7
HG-MgO(3)	5.75	0.42	1:1:1.7
LG-MgO(1)	1.00	0.07	6:1:1.7
LG-MgO(2)	2.87	0.21	2:1:1.7
LG-MgO(3)	5.75	0.42	1:1:1.7

2.2.3 Resultados y discusión

La utilización de reactivos ($MgCl_2$ y $Mg(OH)_2$) como fuentes de magnesio precursores de la formación de la estruvita causaron una reducción significativa en el rendimiento de metano, comparado con el control. La adición de $MgCl_2$ redujo el rendimiento de producción de metano de 148 a 61 mL CH_4 gVS^{-1}, mientras que la adición de $Mg(OH)_2$ causo inhibición del proceso (Figura 1a). Para los ensayos con adición de $MgCl_2$, la baja concentración de ácidos grasos volátiles (VFA) al final de los ensayos (Tabla 2) indica que bajo estas condiciones hay un efecto inhibitorio en los microorganismos formadores de ácido en relación con la biomasa metanogénica. Esta afirmación cumple con los mecanismos de inhibición reportados para el potasio [32], el cual es el catión suministrado por la fuente de fosfato (K_2HPO_4). La concentración de potasio en estas condiciones fue de 14 g L^{-1} (Tabla 2), concentración que se encuentra en el umbral de inhibición (6 – 29 g L^{-1}) reportada por otros autores [32,33]. Por el contrario, la distribución al final de los ensayos con adición de $Mg(OH)_2$ (por ejemplo: alta concentración de propionato, butirato y valerato junto con la relativa baja concentración de acetato) podría sugerir que bajo estas condiciones los metanógenos utilizadores de hidrogeno fueron más inhibidos que los utilizadores de acetato y las bacterias formadoras de ácido. El impacto negativo del test de $Mg(OH)_2$ en la DA podría estar relacionada con dos diferentes factores: (i) las propiedades básicas del $Mg(OH)_2$ que incrementaron el pH a valores de 8.5 y (ii) la alta concentración de potasio en el digestor.

Tabla 2. Características al final del ensayo batch.

	Unid.	Control	$MgCl_2$	$Mg(OH)_2$	HG-MgO(1)	HG-MgO(2)	HG-MgO(3)	LG-MgO(1)	LG-MgO(2)	LG-MgO(3)	SA(1)	SA(2)	SA(3)
pH	-	7.31	6.72	8.46	7.57	8.51	9.21	7.73	9.05	10.38	7.29	7.18	7.00
TP	$mg \cdot L^{-1}$	551	510	1310	440	214	1319	346	1039	1815	498	493	1041
TAN	$mg \cdot L^{-1}$	2498	954	1699	2553	1968	1512	2472	1775	1171	2406	1529	567
Mg^{2+}	$mg \cdot L^{-1}$	41	1086	288	831	674	514	770	707	534	715	1198	1836
K^+	$mg \cdot L^{-1}$	2067	13917	15418	4273	7351	12526	4276	7413	11881	2382	2226	2032
VFA	$mg \cdot L^{-1}$	115	190	1984	117	4664	17574	130	13143	18847	199	166	159
Acetato	$mg \cdot L^{-1}$	99	115	327	93	317	14899	130	10715	15696	159	137	134
Propionato	$mg \cdot L^{-1}$	-	44	895	-	1587	1095	-	868	1333	12	-	-
Butirato	$mg \cdot L^{-1}$	17	32	280	24	290	770	-	701	841	28	29	25
Valerato	$mg \cdot L^{-1}$	-	-	459	-	2471	758	-	719	724	-	-	-

TP: Fosforo total
TAN: Nitrógeno amoniacal total
VFA: Ácidos grasos volátiles

El uso de los sub-productos industriales (HG-MgO y LG-MgO) como fuente de magnesio también llevo a una reducción en la producción de metano (Figura 1b,c). Al igual que los reactores suplementados con $MgCl_2$ y $Mg(OH)_2$, el pH y la concentración de K^+ se presentan como las principales fuentes de inhibición. Un Comportamiento totalmente diferente fue presentado por la adición de SA. Las dosis baja y media de SA (SA(1) y SA(2)) mostraron un potencial de biometanización igual al control, mientras que la dosis alta de SA (SA(3)) presento un pequeño detrimento en el potencial de biometanización (Figura 1d). Sin embargo, la capacidad de fijar amonio, sin presentar efectos negativos en el desarrollo de la digestión, muestran la idoneidad del SA como reactivo capaz de precipitar estruvita acoplado a la DA en un único reactor. La mayor ventaja de los SA sobre las otras fuentes de magnesio es la anulación de la adición directa de fuentes de fosfato al medio digestor. Nótese que la adición directa de ácido fosfórico podría causar formación de espumas y desplazamiento del equilibrio químico de los carbonatos y afectar el pH, mientras que la adición de sales de fosfato podría incrementar la concentración de cationes (Na^+ y K^+) que podrían llegar a causar inhibición [26]. Adicionalmente, el bajo impacto del SA en la DA podría también estar relacionada con el alto contenido de newberyita, ya que la newberyita es no-tóxico para los sistemas biológicos [34].

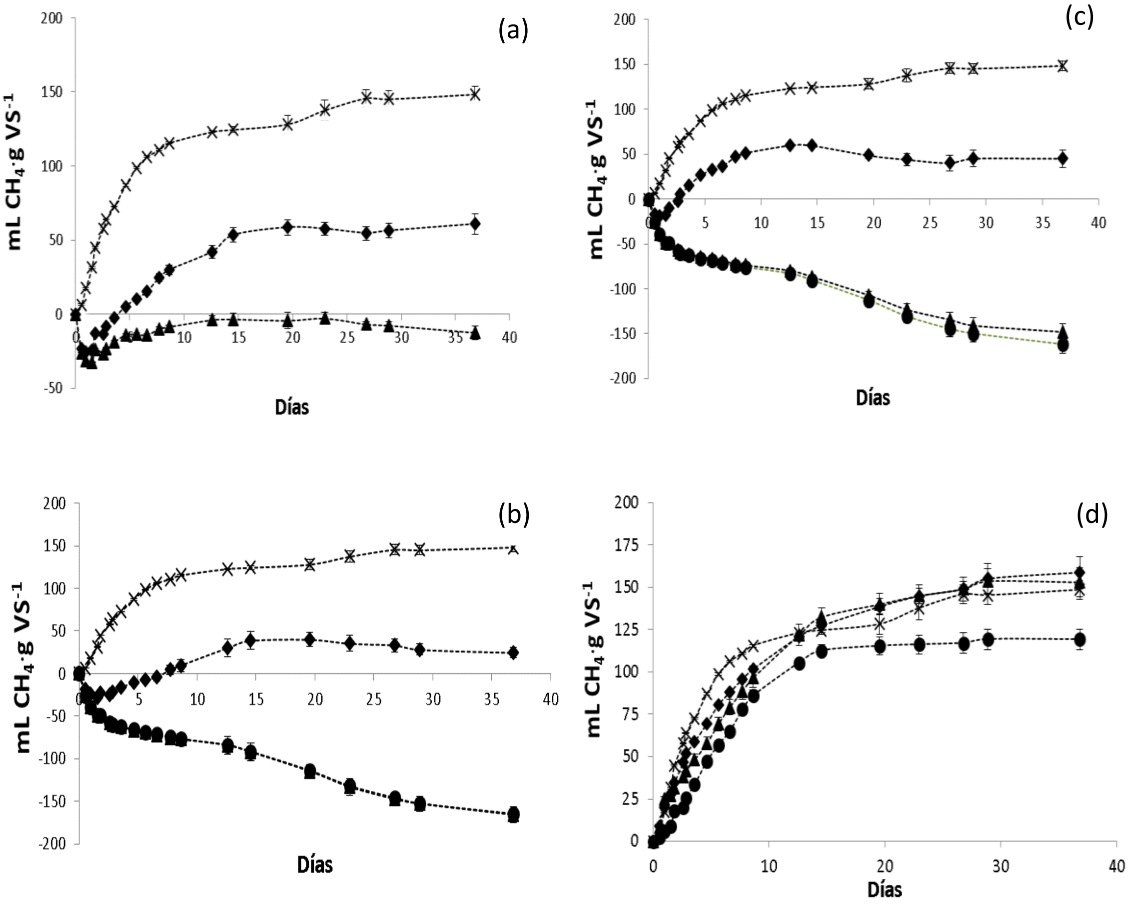

Figura. 1. Producción acumulativa de metano (×) y; (a) (♦) $MgCl_2$ y (▲) MgOH; (b) (♦) HG-MgO(1), (▲) HG-MgO(2) y (●) HG-MgO(3); (c) (♦) LG-MgO(1), (▲) LG-MgO(2) y (●) LG-MgO(3); (d) cada adición de SA (♦) 5 mg L^{-1}, (▲) 15 mg L^{-1} y (●) 30 mg L^{-1}

2.2.4 Conclusiones

El presente estudio evalúo la viabilidad de combinar la digestión anaeróbica y la precipitación de la estruivita en el mismo reactor a través de diferentes fuentes de magnesio. A partir de los resultados obtenidos puede concluirse que la adición de $Mg(OH)_2$, así como las altas dosis de sub-productos industriales ricos en MgO, presentaron inhibición del proceso de digestión, relacionado con el incremento del pH y la concentración de K^+. Así mismo, la utilización de $MgCl_2$ y bajas dosis de los sub-productos industriales ricos en MgO, también mostraron una reducción significativa en el rendimiento de metano comparada con el control.

En contraste, el agente estabilizante SA no presento inhibición. Los resultados en esta serie experimental muestran que el agente estabilizante para promover la precipitación de la estruvita no causa un cambio significativo de pH o inhibición en la biomasa anaeróbica.

2.3 Mejora de la digestión anaeróbica de purines de cerdo por la adición en el mismo reactor de agente estabilizante formulado con oxido de magnesio de bajo contenido.

2.3.1 Introducción

En la DA un amplio rango de concentraciones de inhibición por nitrógeno amoniacal total (TAN) han sido reportadas, variando de 1.5 a 14 kg m^{-3}. Estas diferencias tan grandes pueden ser atribuidas a las características del sustrato y el inoculo, condiciones (temperatura y pH) y los periodos de adaptación [32,35]. El TAN en reactores anaeróbicos presenta dos formas en equilibrio: amoniaco (NH_4^+) y amonio libre (NH_3). Ambas formas han sido reportadas como inhibidores de la actividad metanogénica siendo el NH_3 la forma más toxica. La concentración de NH_3 depende principalmente de tres parámetros, la concentración de TAN, temperatura y pH [36,37]. Como se ha mencionado en los anteriores apartados, diferentes esfuerzos se han realizado para mitigar la inhibición por TAN en la DA, y acoplar la precipitación de estruvita con la DA en el mismo reactor se presenta como una alternativa viable.

El objetivo del presente estudio es acoplar la precipitación de estruvita y la DA en el mismo reactor usando agente estabilizante (formulado con un sub-producto de óxido de magnesio) como agente impulsor de la precipitación de estruvita. Para lograr este objetivo se propone: i) determinar la eficiencia de eliminación de TAN con diferentes dosis de magnesio añadido, ii) comparar la operación y la eficiencia a largo plazo de un digestor anaeróbico sin y con adición de agente estabilizante; y iii) identificar los mecanismos de precipitación de la estruvita.

2.3.2 Materiales y métodos

Se realizaron experimentos de precipitación por lotes (batch), en reactores cerrados, utilizando 0.6 L de purín de cerdo y varias dosis de SA a 37ºC. Las concentraciones de SA utilizados fueron 5, 10, 25, 30, 40, 50, 60, 75 y 100 g SA L^{-1}, las cuales presentaron una relación molar de N:P:Mg entre 1:0.17:0.28 y 1:3.3:5.7. Los reactores fueron continuamente agitados a 15 min^{-1} por un periodo de 24h para asegurar la reacción completa del SA. Con el fin de analizar la interacción entre el SA y el purín de cerdo se avaluaron el pH y TAN en el tiempo a 0, 0.25, 2, 4, 8 y 24 horas.

Como continuación a los ensayos por lotes, se realizó también un estudio en medio continuo, utilizando tres reactores agitados de mezcla completa de 2.5 L y volumen de trabajo de 2 L. Los reactores fueron operados a 37ºC y tiempo de retención hidráulica de 20 días. El reactor control (R1) fue alimentado únicamente con purín de cerdo, mientras que los demás reactores (R2 y R3) fueron alimentados con purín de cerdo y suplementados con SA. Las concentraciones de SA en la alimentación fueron 5 g L^{-1} para R2 y 30 g L^{-1} para R3. El SA fue mezclado con el purín de cerdo justo antes de cada alimentación.

2.3.3. Resultados y discusión

Ensayos por lotes (batch)

La Figura 1a muestra la evolución del pH en el tiempo para todas las adiciones de SA. La adición de SA al purín involucra un rápido descenso en los valores de pH, seguido por un incremento hasta alcanzar el equilibrio. Este comportamiento puede ser explicado mediante los pares acido-base presentes en el purín de cerdo y las modificaciones hechas por la introducción de SA. Inicialmente, el pH del purín está mayoritariamente controlado por los equilibrios de dióxido de carbono/hidrogeno-carbonato y de amoniaco/amonio (Eq. 1 y 2).

Posteriormente a la adición del SA, se presenta una reducción del pH, efecto que puede ser explicado por la combinación de 2 factores (i) liberación de H_3O^+ envueltos en el proceso de precipitación y (ii) la reducción de la concentración de TAN en el sistema mediante la precipitación de estruvita [26]. Es importante señalar que la precipitación de la estruvita podría tener lugar en la superficie de las propias partículas de SA (eq. 3), o con el fosfato y magnesio disuelto en el seno de la solución (eq. 4).

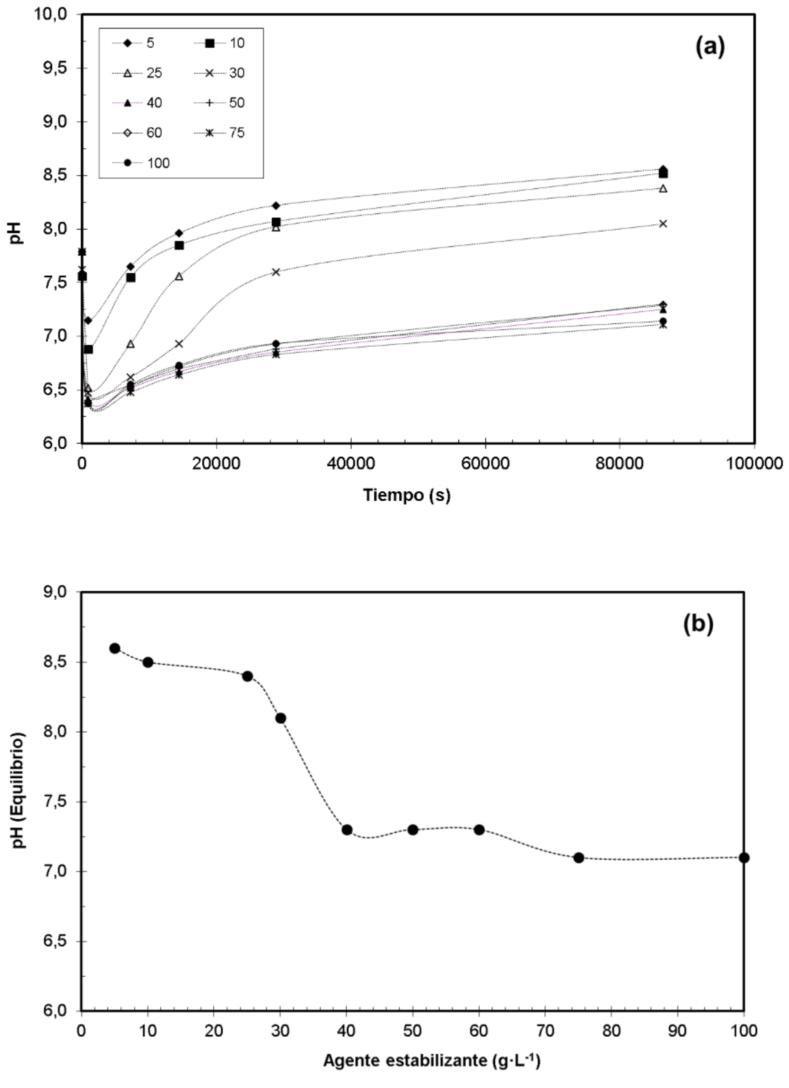

Figura 1. (a) Evolución del pH en el tiempo y (b) equilibrio de pH a diferentes dosis de agente estabilizante

Como se observa en la Fig. 1b, en adiciones de SA por encima de los 40 g L^{-1}, el pH_{eq} decrece a medida que la concentración de SA incrementa hasta alcanzar un valor estable de 7.2. Este valor coincide con el logaritmo de la constate ácida (pKa) del segundo protón del ácido fosfórico. Con lo cual, en estas condiciones, la solubilización de fosfatos del SA causa que el balance acido-base del $H_2PO_4^-/HPO_4^{2-}$ controle el valor de pH final.

$$\mathrm{CO_{2\,(aq)} + 2H_2O \;\leftrightarrow\; HCO_3^- + H_3O^+} \qquad \text{(eq. 1)}$$

$$\mathrm{NH_4^+ + H_2O \;\leftrightarrow\; NH_{3\,(aq)} + H_3O^+} \qquad \text{(eq. 2)}$$

$$\mathrm{MgHPO_4{\cdot}3H_2O_{(s)} + NH_4^+ + 4H_2O \;\leftrightarrow\; MgNH_4PO_4{\cdot}6H_2O_{(s)} + H_3O^+} \qquad \text{(eq. 3)}$$

$$\mathrm{Mg^{2+} + HPO_4^{2-} + NH_4^+ + 4H_2O \;\leftrightarrow\; MgNH_4PO_4{\cdot}6H_2O_{(s)} + H_3O^+} \qquad \text{(eq. 4)}$$

La evolución de la concentración de TAN para las adiciones de SA se muestran en la Figura 2a. En esta se observa que la reducción de TAN al comienzo de los ensayos están relacionadas con la precipitación de estruvita. Así como la reducción inicial de pH (Figura 1a). La Figura 2b muestra que la reducción final de la concentración TAN no es proporcional a la adición de SA. Específicamente, adiciones inferiores a 40 g L^{-1} presentan un incremento progresivo con la adición de SA. En estas condiciones es posible que la concentración de iones no sea suficiente para eliminar todo el TAN disponible. No obstante, las máximas eficiencias de eliminación de TAN, cerca del 83%, fueron alcanzadas para todos los ensayos con adiciones entre (40 y 100 g L^{-1}), condiciones en las cuales el incremento en la adición de SA no conduce a una mayor eliminación de estruvita.

Los resultados en los ensayos por lotes (batch) muestran la gran capacidad del SA de reducir la concentración de TAN en el purín de cerdo. Sin embargo, para la dosificación de SA a un digestor es necesario evaluar la operación y estabilidad a largo plazo con el fin de garantizar que las dosis de SA no introduce compuestos nocivos para la biomasa anaeróbica.

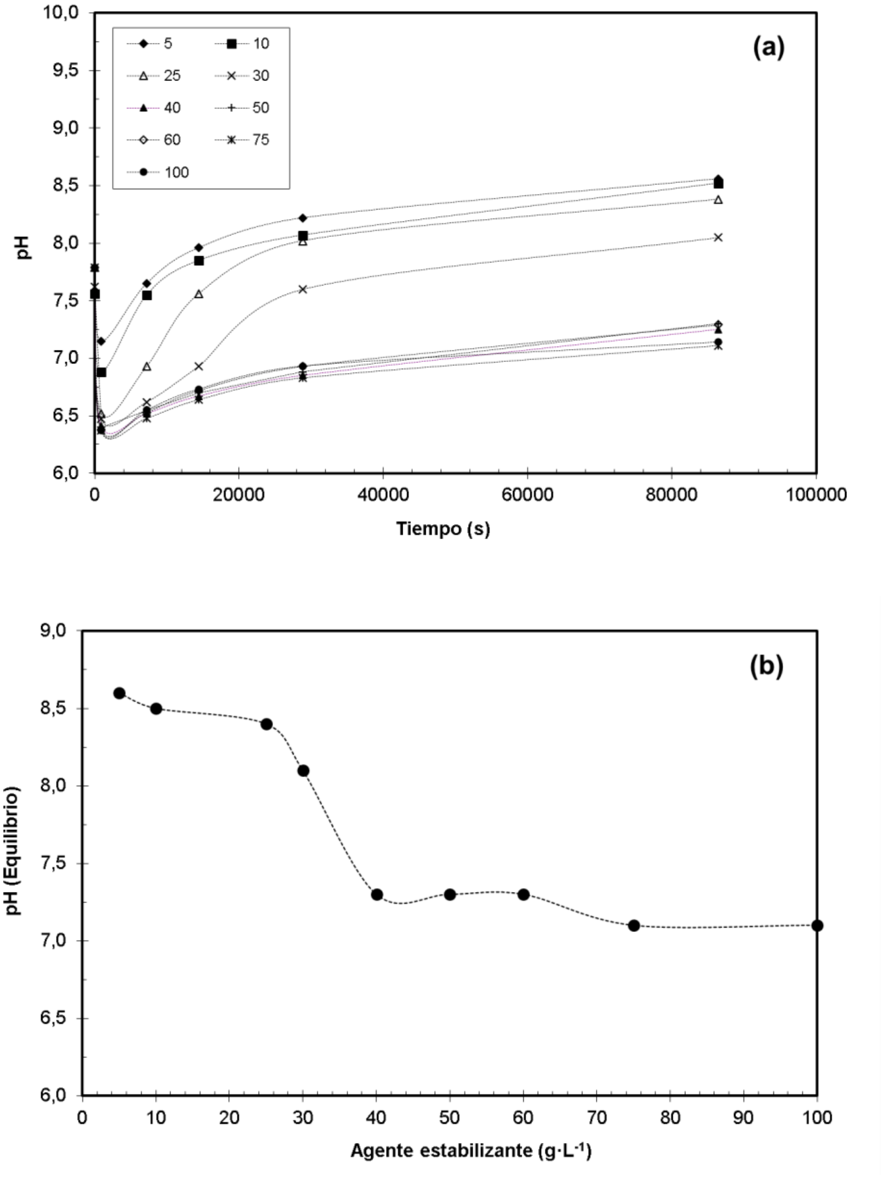

Figura 2. (a) Evolución de TAN en el tiempo y (b) Eficiencia de remoción de TAN a diferentes adiciones de TAN a 24 horas.

Reactores continuos

Al comienzo, los tres reactores fueron inoculados con digestado proveniente de una planta centralizada de purín de cerdo. Después de un periodo de adaptación de 40 días, los tres reactores presentaron condiciones constantes de pH, alcalinidad, ácidos grasos volátiles y producción de biogás. Posteriormente, y durante un período de 110 días, fueron adicionadas las dosis de SA a los reactores R2 y R3, mientras que R1 se mantuvo como reactor de referencia. Dos diferentes estrategias fueron utilizadas para alcanzar la concentración de SA en los digestores. En el R2 la concentración de SA fue adicionada gradualmente, mientras que la concentración en el R3 fue incrementada drásticamente y posteriormente suplementado en las alimentaciones diarias para mantener la concentración en el interior del digestor. Una vez las condiciones operacionales fueron alcanzadas se mantuvieron los reactores por cuatro tiempos de retención hidráulica con el fin de evaluar la adición de SA.

La evaluación de la estabilidad del digestor fue uno de los factores importantes a realizar, teniendo en cuenta que esto permite considerar si en el proceso de DA se desarrolla sin acidificación [38]. Esto es especialmente importante porque el agente estabilizante fue formulado con oxido de magnesio de bajo contenido, un sub-producto comercial obtenido durante la calcinación de magnesita natural, lo cual podría introducir contaminantes al reactor y, por lo tanto, inducir la inhibición de la actividad de los microorganismos [32,39]. En el presente trabajo, la estabilidad de la digestión fue monitoreada mediante la relación entre la alcalinidad intermedia y parcial (IA/PA) y la relación de ácidos grasos volátiles totales y alcalinidad (TVFA/TA), las cuales deberían estar por debajo de 0.4 para asegurar la estabilidad de la digestión [40]. El promedio de la relación IA/PA fue de 0.20, 0.23 y 0.24, mientras que el promedio de la relación de TVFA/TA fue de 0.007, 0.007 y 0.006 para R1, R2 y R3 respectivamente. Estos valores se encuentran muy por debajo de los valores límites propuestos, lo cual asegura que el proceso fue operado sin riesgo de acidificación y, por lo tanto, el SA no presenta un efecto negativo sobre los microorganismos. Es importante notar que los valores de alcalinidad total decrecen con el incremento de la adición de SA; sin embargo, la alcalinidad total para todos los digestores fue mucho mayor que 2 kg m^{-3} de $CaCO_3$, el cual es considerado el límite inferior para la operación segura de la DA [38]. Por otra parte, todos los digestores fueron operados con el mismo tiempo de retención hidráulica (20 días) y con la misma carga orgánica (1.1 kgVS m^{-3}d^{-1}). La adición de SA a los digestores resulto en un incremento de 25 y 40% en la producción de metano para R2 y R3, respectivamente, comparado con el digestor control (R1) (Tabla 1). Este incremento puede estar relacionado con la reducción en la concentración de TAN, presencia de magnesio y partículas de estruvita y newberyita en el medio de digestión.

Tabla 1. Caracterización del purín de cerdo alimentado y los efluentes

	Purín	**Efluente R1 (0 kg m^{-3})**	**Efluente R2 (5 kg m^{-3})**	**Efluente R3 (30 kg m^{-3})**
Composición del alimento y efluentes				
TS (kg m^{-3})	35.0 ± 2.5	29.5 ± 1.6	35.7 ± 1.0	53.7 ± 2.9
VS (kg m^{-3})	21.7 ± 2.0	16.1 ± 1.2	20.7 ± 0.9	23.7 ± 1.4
pH	8.0 ± 0.2	8.1 ± 0.1	8.1 ± 0.1	8.0 ± 0.2
Alk. Parcial (kg m^{-3})	6.5 ± 0.2	8.8 ± 0.2	8.0 ± 0.2	5.8 ± 0.4
Alk. Total (kg m^{-3})	8.5 ± 0.2	10.6 ± 0.2	9.8 ± 0.4	7.2 ± 0.5
VFA (kg m^{-3})	1.5 ± 0.2	0.07 ± 0.01	0.07 ± 0.01	0.04 ± 0.01
- **Ac. acético** (kg m^{-3})	1.2 ± 0.2	0.05 ± 0.01	0.06 ± 0.01	0.04 ± 0.01
- **Ac. propiónico** (kg m^{-3})	0.10 ± 0.01	n.d.	n.d.	n.d.
- **Ac. Butírico** (kg m^{-3})	0.09 ± 0.02	0.01 ± 0.01	0.01 ± 0.01	n.d.
- **Ac. Valérico** (kg m^{-3})	0.09 ± 0.01	0.01 ± 0.01	n.d.	n.d.
TAN (kg m^{-3})	2.2 ± 0.1	2.2 ± 0.1	2.1 ± 0.1	0.5 ± 0.1
TKN (kg m^{-3})	3.7 ± 0.07	3.8 ± 0.1	3.7 ± 0.13	3.7 ± 0.2
Cl^- (kg m^{-3})	1.5 ± 0.1	1.5 ± 0.1	1.5 ± 0.1	1.5 ± 0.1
PO_4^{3-} (kg m^{-3})	0.3 ± 0.1	n.d.*	n.d.*	n.d.
Na^+ (kg m^{-3})	0.8 ± 0.1	0.7 ± 0.1	0.8 ± 0.1	0.8 ± 0.1
K^+ (kg m^{-3})	2.0 ± 0.1	1.9 ± 0.1	2.0 ± 0.1	1.9 ± 0.1
Ca^{2+} (kg m^{-3})	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.3 ± 0.1
Mg^{2+} (kg m^{-3})	n.d.	n.d.	0.05 ± 0.01	0.7 ± 0.1
Biogás				
Producción de biogás (m^3 day^{-1})	-	380 ± 40	530 ± 100	600 ± 90
Metano (%)	-	75 ± 3	70 ± 2	67 ± 3
Producción de Metano (m^3 day^{-1})	-	290 ± 30	370 ± 50	410 ± 40
SMP-V_R (m^3 m^{-3} day^{-1})	-	0.14 ± 0.02	0.18 ± 0.02	0.20 ± 0.02
SMP-VS_{fed} (m^3 kg^{-1})	-	0.13 ± 0.01	0.17 ± 0.02	0.19 ± 0.02

* n.d. no detectado para VFA (< 0.01 kg m^{-3}) y iones (< 20·10^{-3} kg m^{-3})

Donde SPM-V_R es la producción especifica de metano por volumen de digestor y SPM-VS_{fed} es la producción específica de metano por kilogramo de VS alimentado.

Como se puede observar en la Tabla 1, la concentración de TAN en el R2 es similar que la obtenida en R1, con una reducción de solo el 4%. Al contrario, una reducción en la concentración de TAN del 80% se observa en el R3. Sin embargo, la alta eficiencia en la eliminación de TAN en R3 en comparación con la obtenida en R2, la cual está relacionada con la precipitación de estruvita, no hace una diferencia substancial en la producción de metano, que fue de solo el 10%.

Otro factor a tener en cuenta cuando se explica la diferencia entre los niveles de producción de metano es la concentración de magnesio en solución. Pocos estudios han analizado el efecto de Mg^{2+} en la DA. No obstante, no es claro que la presencia o déficit de Mg^{2+} pueda tener un impacto significativo en la correcta operación de la DA [32]. Y aunque no es claro el rango óptimo de concentración de Mg^{2+}, lo que es ligeramente claro es que las bajas concentraciones de Mg^{2+} puede limitar el desarrollo del proceso de digestión anaeróbica. La concentración de Mg^{2+} en el purín de cerdo y R1 está por debajo de 0.2 kg m^{-3}, con lo cual el déficit en el digestor es asumido. Sin embargo, los digestores suplementados con SA tienen una concentración mayor de Mg^{2+}, 0.05 y 0.7 kg m^{-3} para R2 y R3 respectivamente. Por otra parte, la precipitación de estruvita no sólo es importante en la reducción de la concentración de TAN y suplir magnesio al digestor, sino también ofrece una alta capacidad de brindar una matriz de inmovilización de los microorganismos. La inmovilización de los microorganismos anaeróbicos es conocida por mejorar el proceso de digestión anaeróbica. Como ejemplo, la utilización de zeolitas, carbón activado y fosforita, entre otros, has sido reportados como agentes capaces de contrarrestar varios tipos de inhibición y estabilizar procesos de digestión.

La Figura 3a muestra las imágenes de micrografía de barrido electrónico de partículas obtenidas de los digestores continuos. En estas se puede observar tres tipos de partículas precipitadas: (1) típicos cristales ortorrómbicos de estruvita, (2) pequeños cristales de estruvita crecidos sobre la superficie de los agentes estabilizantes y (3) otros minerales. Adicionalmente, los análisis de difracción de rayos-X (Figura 3b) muestran a la estruvita como la fase predominante, mientras que la newberyita y la periclasa fueron identificadas como fases minoritarias. La presencia de newberyita y periclasa en el precipitado, siguiere que la estruvita se ha formado en la superficie de las partículas del agente estabilizante, mientras el núcleo de estas queda sin reaccionar, siguiendo un modelo de núcleo no reaccionante. Estos resultados confirman la existencia de dos mecanismos de precipitación: (i) la formación y crecimiento de la estruvita en la superficie de las partículas de SA y (ii) la formación y crecimiento de la estruvita en el seno del digestor.

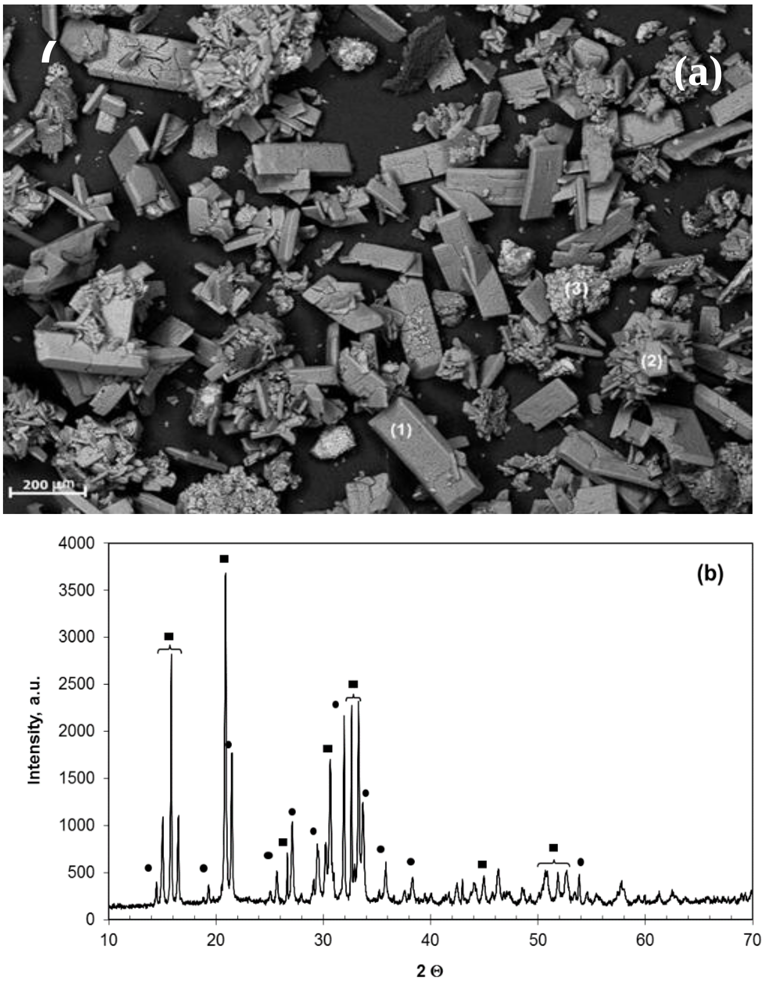

Figura 3. (a) micrografías de barrido electrónico ((1) partículas de estruvita crecidas en el seno del medio de digestión, (2) partículas de estruvita crecidas en la superficie de las partículas de agente estabilizante, (3) otros minerales) y (b) difractograma del precipitado obtenido en el efluente de digestión (● Newberyita; ▲ Periclasa; ■ Estruvita).

2.3.4 Conclusiones

La adición de agente estabilizante al purín de cerdo presento una máxima eficiencia de remoción de nitrógeno amoniacal total del 80%. La operación de los digestores mostró que la adición de agente estabilizante de 5 y 30 g L^{-1} al digestor resulta en un incremento del 25 y 40% en la producción de metano, respectivamente, comparado con el reactor de referencia. Este resultado puede estar relacionado con la reducción de la concentración de amonio y el incremento de la concentración de magnesio y concentración de partículas en el medio de digestión. Adicionalmente, los resultados de alcalinidad y ácidos grasos volátiles muestran que la adición de agente estabilizante no presenta un efecto negativo en los microorganismos anaeróbicos.

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ANNEXES

Annex 1.

***Abbreviations*:**

ACS:	Acetyl-CoA synthesis
AD:	Anaerobic digestion
BA:	Bottom ash
BMP:	Biomethane potential test
CODH:	Carbon monoxide dehydrogenase
CM:	Caw manure
COD:	Chemical oxygen demand
CSTR:	Continuous stirred tank reactor
EBPR:	Enhanced biological phosphorus removal
FISH:	Fluorescence in situ hybridization
FA:	Fly ash
FDH:	Formate dehydrogenase
FVW:	Fruit and vegetable waste
HG-MgO:	High grade magnesium oxide
HRT:	Hydraulic retention times
GT:	Grease trap
JPC:	Jatropha press cake
LAS:	Linear alkylbenzene sulfonates
LMC:	Lignocellulytic microbial consortium
LG-MgO:	Low grade magnesium oxide
MNBA:	Micro and nano BA
MNFA:	Micro and nano FA
MSW:	Municipal solid waste
MSWI:	Municipal solid waste incinerator
NP:	Nanoparticles
NS:	Nutrient supplement
OFMSW:	Organic fraction of municipal solid waste
OLR:	Organic loading rate
ORP:	Oxidative-reductive potential
PBRs:	Permeable reactive barriers
PM:	Pig manure
SA:	Stabilization agent
SEM:	Scanning electron micrographic
SS:	Sewage sludge
SMP:	Specific methane production
SRB:	Sulfate reducing bacteria
SODM:	Superoxide dismutase
SAO:	Syntrophic acetate oxidation
TOCef:	Total Organic Carbon Effluent
TS:	Total Solids

UASB:	Upflow anaerobic sludge blanked
VS:	Volatile solids
VSS:	Volatile suspended solids
VFA:	Volatile fatty acids
XRF:	X-ray fluorescence
ZVI:	Zero valent iron

Annex 2.

List of Publications:

Romero-Güiza M.S., Astals S., Chimenos J.M., Martínez M., Mata-Alvarez J. (2014). Improving Anaerobic Digestion of Pig Manure by Adding in the Same Reactor a Stabilizing Agent Formulated with Low-Grade Magnesium Oxide. Biomass and Bioenergy 67, 243-251

Romero-Güiza M.S., Astals S., Mata-Alvarez J., Chimenos JM. (2015) Feasibility of coupling anaerobic digestion and struvite precipitation in the same reactor: Evaluation of different magnesium sources. Chemical Engineering Journal 270, 542-548

Romero-Güiza M.S., Mata-Alvarez J., Chimenos JM. Astals S. (2015) Nutrient recovery technologies for anaerobic digestion systems: An overview. Submitted on *revista ION*

Romero-Güiza M.S., Tait S., Astals S., del Valle-Zarmeño R., Martínez M., Mata-Alvarez J., Chimenos JM. (2015) Reagent use efficiency with removal of nitrogen from pig slurry via struvite: A study on magnesium oxide and related by-products. Submitted on Water Research

Romero-Güiza M.S., Vila J., Mata-Alvarez J., Chimenos JM. Astals S. (2015) The role of additives on anaerobic digestion: a review. Submitted on Renewable & Sustainable Energy Review

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Romero-Güiza M.S., Peces M. Astals S., Benavent J., Valls J., Mata-Alvarez J. (2014). Implementation of a prototypal optical sorter as core of the new pre-treatment configuration of a mechanical-biological treatment plant treating OFMSW through anaerobic digestion. Applied Energy 135, 63-70

Astals S**.**, Romero-Güiza M., Mata-Alvarez J. (2013). Municipal Solid Waste: Energy recovery from the organic fraction base on anaerobic digestion. In: German A., Ferreira F. (eds.) Alternative Energy. Springer. London – UK. DOI 10.1007/978-3-642-40680-5

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Annex 3.

Published papers:

Romero-Güiza M.S., Astals S., Chimenos J.M., Martínez M., Mata-Alvarez J. (2014). Improving Anaerobic Digestion of Pig Manure by Adding in the Same Reactor a Stabilizing Agent Formulated with Low-Grade Magnesium Oxide. Biomass and Bioenergy 67, 243-251

Romero-Güiza M.S., Astals S., Mata-Alvarez J., Chimenos JM. (2015) Feasibility of coupling anaerobic digestion and struvite precipitation in the same reactor: Evaluation of different magnesium sources. Chemical Engineering Journal 270, 542-548

Romero-Güiza M.S., Peces M. Astals S., Benavent J., Valls J., Mata-Alvarez J. (2014). Implementation of a prototypal optical sorter as core of the new pre-treatment configuration of a mechanical-biological treatment plant treating OFMSW through anaerobic digestion. Applied Energy 135, 63-70

BIOMASS AND BIOENERGY 67 (2014) 243–251

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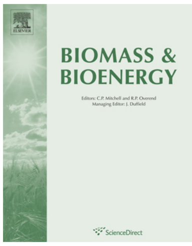

Improving anaerobic digestion of pig manure by adding in the same reactor a stabilizing agent formulated with low-grade magnesium oxide

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ARTICLE INFO

Article history:
Received 27 June 2012
Received in revised form
12 April 2014
Accepted 25 April 2014
Available online 2 June 2014

Keywords:
Anaerobic digestion
Swine manure
Chemical precipitation
Struvite
Ammonia inhibition
Scanning electronic microscopy

ABSTRACT

Struvite precipitation and pig manure anaerobic digestion were coupled in the same reactor in order to mitigate the inhibitory effect of free ammonia and avoid precipitator costs. The stabilizing agent used to facilitate struvite precipitation was formulated with low-grade magnesium oxide by-product; an approach that would notably reduce struvite processing costs. The interaction between pig manure and stabilizing agent was analyzed in batch experiments, on a wide range of stabilizing agent additions from 5 to 100 kg m^{-3}. The monitoring of the pH and ammonia removal during 24 h showed the high capacity of the stabilizing agent to remove ammonia; removal efficiencies above 80% were obtained from 40 kg m^{-3}. However, a long-term anaerobic digester operation was required to assess the feasibility of the process and to ensure that the stabilizing agent does not introduce any harmful compound for the anaerobic biomass. In this vein, the addition of 5 and 30 kg m^{-3} of the stabilizing agent in a pig manure continuous digester resulted in a 25% (0.17 m^3 kg^{-1}) and a 40% (0.19 m^3 kg^{-1}) increase in methane production per mass of volatile solid, respectively, when compared with the reference digester (0.13 m^3 kg^{-1}). Moreover, the stability of the process during four hydraulic retention times guarantees that the stabilizing agent did not exert a negative effect on the consortium of microorganisms. Finally, scanning electron microscopy and X-ray diffraction analysis confirmed the presence of struvite as well as two precipitation mechanisms, struvite precipitation on the stabilizing agent surface and in the bulk solution.

1. Introduction

Today, in most countries, intensive pig farming is concentrated in certain regions. There, the high production of pig manure linked to the insufficient amount of available land makes pig manure management and treatment important to minimize its contaminant potential [1,2]. Amongst all the treatment options, anaerobic digestion (AD) is a technology that is widely used since it: (i) avoids volatile organic compound emissions, (ii) stabilizes organic matter and (iii) recovers energy through methane production [3]. However, pig

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http://dx.doi.org/10.1016/j.biombioe.2014.04.034
0961-9534/

manure AD regularly presents low efficiencies due to the high concentration of ammonia and its low hydrolysis rate [3,4].

In AD, a wide range of inhibiting total ammonia nitrogen (TAN) concentrations have been reported, varying from 1.5 to 14 kg of nitrogen per cubic meter, where differences can be attributed to the characteristics of the substrates and the inoculum, the environmental conditions (mainly temperature and pH) and the adaptation periods [5,6]. TAN in anaerobic reactors has two forms: unionized or free ammonia (NH_3) and ionized ammonia or ammonium (NH_4^+). Although both forms have been reported as inhibitors of methanogenic activity NH_3 is the most toxic form. NH_3 concentration depends basically on three parameters, i.e. TAN concentration, temperature and pH [7,8]. In order to mitigate the inhibitory effects of NH_3 many successful research efforts have been carried out before AD like air stripping, zeolite addition, clay addition and struvite precipitation [9–14]. However, these technologies would involve the construction and operation of another unit, which would be, in most cases, unfeasible for small and medium biogas plants.

High TAN removal efficiencies have been obtained for several waste streams by adding magnesium (Mg^{2+}) and phosphate (PO_4^{3-}) to precipitate struvite ($MgNH_4PO_4 \cdot 6H_2O$), which is a valuable slow-release fertilizer [15–17]. The addition of magnesium and phosphate is necessary to ensure the formation of struvite, since usually the amount of them in waste streams, like in pig manure, is not high enough to remove all NH_4^+ [12,17,18]. Nevertheless, the high price of raw materials and the large quantities of phosphate and magnesium required to achieve high ammonia removal efficiencies might cause a significant increase in processing costs, making struvite precipitation unfeasible [19,20]. To solve this problem, some researchers have used magnesium by-products as raw materials [18–21]. Another option to reduce the struvite processing cost is to couple anaerobic digestion and struvite precipitation in the same reactor. This approach has only been studied by Lee et al. [22] in a continuous food waste digester with $MgCl_2$ addition and by Uludag-Demirer et al. [23] in batch manure digesters with $MgCl_2$ and $Mg(OH)_2$ addition. However, to our knowledge, no references have been found evaluating the utilization of magnesium by-products within the reactor to precipitate struvite during anaerobic digestion. The introduction of inhibitory and/or toxic compounds for the anaerobic biomass is the main drawback when an industrial by-product wants to be introduced in an anaerobic digester [1]. Therefore, in addition to the ammonium removal potential of the by-product, a long-term digester operation is required to assess the viability of the process.

The main objective of the present study is to couple anaerobic digestion and struvite precipitation in the same reactor where a stabilizing agent, formulated with a magnesium oxide by-product, is used to facilitate struvite precipitation. To achieve this goal the research sought to: (i) determine the ammonium removal efficiency when different doses of stabilizing agent are added to pig manure; (ii) compare the long-term operation performance of a pig manure anaerobic digester with and without the addition of a stabilizing agent; and (iii) identify the struvite precipitation mechanisms.

2. Materials and methods

2.1. *Source of the low-grade magnesium oxide and pig manure*

Low-grade magnesium oxide (LG-MgO) powder was supplied by Magnesitas Navarras, S.A. (Navarra, Spain). LG-MgO was generated during the calcination of natural magnesite in a rotary kiln at 1100 °C to obtain caustic calcined magnesia and then was collected in the fabric filters of the air pollution control system. Table 1 sets out the chemical composition of the major elements shown by X-ray fluorescence (XRF) to be the most stable corresponding oxides as well as the other physicochemical parameters.

Pig manure (PM, see Table 2 for its characterization) and digested pig manure, used as inoculum, were collected from a centralized anaerobic digestion plant. The facility digests at mesophilic conditions around 100,000 metric tons of pig manure per year utilizing the VALPUREN® process [2]. After collection, the pig manure was stored at 4 °C until it was used.

2.2. *Formulation of the stabilizing agent*

The stabilizing agent (SA) was formulated according to the procedure described in the patent [24]. Briefly, phosphoric acid was added slowly to an aqueous slurry of LG-MgO with a high solid-to-liquid ratio. The exothermic acid-base reaction generated a mixture with a high content of newberyite ($MgHPO_4 \cdot 3H_2O$) and other magnesium phosphate compounds, such as magnesium phosphate tribasic ($Mg_3(PO_4)_2$) and magnesium phosphate dibasic ($MgHPO_4$), which coated the particles of LG-MgO that did not react on the basis of the shrinking core model [25,26]. Then, the compound was dried and crushed to a particle size of about 500 μm.

As a result, instead of adding LG-MgO and phosphoric acid directly into the reactor, the stabilizing agent was formulated in advance obtaining a solid product in powder form, non-toxic or aggressive and easy to handle [24]. Table 1 presents the chemical composition of the major elements shown by

Table 1 – X-ray fluorescence characterization of the LG-MgO and the stabilizing agent.

	LG-MgO	SA
Oxides composition		
MgO (%)	63.7	31.8
CaO (%)	9.9	4.7
SO_3 (%)	4.1	1.1
Fe_2O_3 (%)	2.4	1.2
SiO_2 (%)	2.0	0.9
K_2O (%)	0.3	<0.1
Al_2O_3 (%)	0.2	<0.1
V_2O_5 (%)	0.1	0.26
MnO (%)	0.1	0.1
P_2O_5 (%)	<0.1	32.8
Physicochemical parameters		
Loss of ignition (1100 °C) (%)	16.7	27.4
Density ($kg\ m^{-3}$)	3200	
Specific surface ($m^2\ kg^{-1}$)	10,400	

Table 2 – Characterisation of the pig manure and the effluent of the three digesters.

	Pig manure	R1 effluent (0 kg m^{-3})	R2 effluent (5 kg m^{-3})	R3 effluent (30 kg m^{-3})
Influent and effluent composition				
TS (kg m^{-3})	35.0 ± 2.5	29.5 ± 1.6	35.7 ± 1.0	53.7 ± 2.9
VS (kg m^{-3})	21.7 ± 2.0	16.1 ± 1.2	20.7 ± 0.9	23.7 ± 1.4
pH	8.0 ± 0.2	8.1 ± 0.1	8.1 ± 0.1	8.0 ± 0.2
Partial alk. (kg m^{-3})	6.5 ± 0.2	8.8 ± 0.2	8.0 ± 0.2	5.8 ± 0.4
Total alk. (kg m^{-3})	8.5 ± 0.2	10.6 ± 0.2	9.8 ± 0.4	7.2 ± 0.5
VFA (kg m^{-3})	1.5 ± 0.2	0.07 ± 0.01	0.07 ± 0.01	0.04 ± 0.01
Acetic acid (kg m^{-3})	1.2 ± 0.2	0.05 ± 0.01	0.06 ± 0.01	0.04 ± 0.01
Propionic acid (kg m^{-3})	0.10 ± 0.01	n.d.	n.d.	n.d.
Butyric acid (kg m^{-3})	0.09 ± 0.02	0.01 ± 0.01	0.01 ± 0.01	n.d.
Valeric acid (kg m^{-3})	0.09 ± 0.01	0.01 ± 0.01	n.d.	n.d.
TAN (kg m^{-3})	2.2 ± 0.1	2.2 ± 0.1	2.1 ± 0.1	0.5 ± 0.1
TKN (kg m^{-3})	3.7 ± 0.07	3.8 ± 0.1	3.7 ± 0.13	3.7 ± 0.2
Chloride (kg m^{-3})	1.5 ± 0.1	1.5 ± 0.1	1.5 ± 0.1	1.5 ± 0.1
Phosphate (kg m^{-3})	0.3 ± 0.1	n.d.*	n.d.*	n.d.
Sodium (kg m^{-3})	0.8 ± 0.1	0.7 ± 0.1	0.8 ± 0.1	0.8 ± 0.1
Potassium (kg m^{-3})	2.0 ± 0.1	1.9 ± 0.1	2.0 ± 0.1	1.9 ± 0.1
Calcium (kg m^{-3})	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.3 ± 0.1
Magnesium (kg m^{-3})	n.d.	n.d.	0.05 ± 0.01	0.7 ± 0.1
Biogas characteristics				
Biogas production (m^3 day^{-1})	–	380 ± 40	530 ± 100	600 ± 90
Methane content (%)	–	75 ± 3	70 ± 2	67 ± 3
Methane production (m^3 day^{-1})	–	290 ± 30	370 ± 50	410 ± 40
SMP-V$_R$ (m^3 m^{-3} day^{-1})	–	0.14 ± 0.02	0.18 ± 0.02	0.20 ± 0.02
SMP-VS$_{fed}$ (m^3 kg^{-1})	–	0.13 ± 0.01	0.17 ± 0.02	0.19 ± 0.02

* n.d., no detected VFA (<0.01 kg m^{-3}) and ions (<20·10^{-3} kg m^{-3}). SMP-V$_R$ stands for specific methane production per volume of digester and SMP-V$_{fed}$ stands for specific methane production per kilogram of VS fed.

XRF to be the most stable corresponding oxides as well as the other physicochemical parameters.

Moreover, the scanning electronic microscopy (SEM) shows that the stabilizing agent has an amorphous morphology with a particle size below 200 μm (Fig. 1a).

2.3. *Struvite precipitation batch experiments*

The struvite precipitation batch experiments, performed in a Jar-Test device (Flocculator 2000, Kemira), were carried out with 0.6 L of pig manure and several additions of SA at 37 °C. The tested concentrations were 5, 10, 25, 30, 40, 50, 60, 75 and 100 kg m^{-3} of SA, which gives an N:P:Mg molar ratio between 1:0.17:0.28 and 1:3.3:5.7. However, in the present study, the molar ratio is not a good working parameter because of the lower reactivity of the LG-MgO and the nonreactive core of the SA particles [18]. The reactors were continuously stirred at 15 min^{-1} for a period of 24 h (86,400 s) to ensure the complete reaction of the SA. In order to analyze the interaction between the SA and the PM the treatment was evaluated by means of pH and total ammonia nitrogen (TAN) evolution, observed for each experimental trial at 0, 0.25, 2, 4, 8 and 24 h.

2.4. *Continuous reactor set-up*

The study made use of three identical 2.5·10^{-3} m^3 semi-continuous stirred tank reactors (S-CSTR) with a working volume of 2·10^{-3} m^3. The gas system consisted of a water trap, an on-line biogas measuring device (Ritter MGC-1) and an acid trap. The operational temperature, which was ensured by circulating water from a heated water bath through a jacket surrounding the reactor, was fixed at 37 °C. The reactor medium was continuously mechanically stirred at 80 min^{-1}. The hydraulic retention time (HRT) of the three reactors was fixed at 20 days. The control reactor (R1) was fed only with pig manure, while the operational reactors (R2 and R3) were supplied with pig manure and stabilizing agent. The SA concentration in the feedstock was 5 kg m^{-3} for R2 and 30 kg m^{-3} for R3. The SA was mixed with the pig manure just before the feeding. The reactors were purged and then fed once a day. The influent and the effluent were collected through a pipe using a 0.1 L syringe. The biogas composition of the digesters headspace was analyzed three times per week by a Shimadzu GC-2010 + gas chromatograph. The biogas and methane productions are reported at standard temperature and pressure conditions (i.e. 0 °C and 100 kPa).

2.5. *Analytical procedure and methods*

Analyses of the total fraction were performed directly on the raw samples. For analyses of the soluble fraction (i.e. volatile fatty acids (VFA), anions and cations), the samples were centrifuged at 1252 × *g* (relative centrifugal force) for 10 min and then the supernatant was filtered through a 0.45 μm filter (Millipore HAWP02500). Total solids (TS) and volatile solids (VS) were determined in accordance with the guidelines given

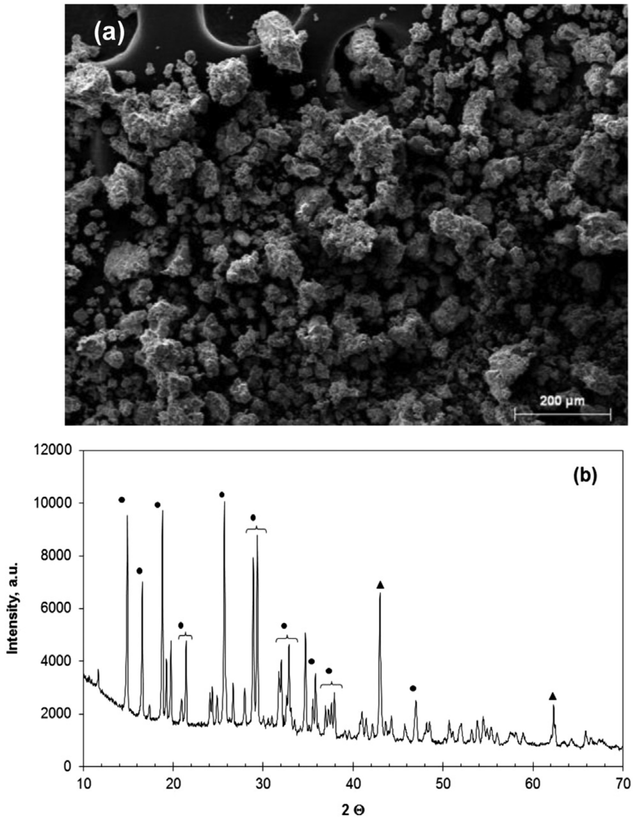

Fig. 1 – (a) Scanning electron micrograph and (b) X-ray diffractogram of the stabilizing agent. ●, Newberyite; ▲, periclase.

by the standard methods 2540G [27]. TAN (NH_3 plus NH_4^+) and total Kjeldahl nitrogen (TKN) were performed according to the standard methods procedure 4500-NH_3D and 2500-N_{org}B [27]. The free ammonia concentration was calculated by means of Eq. (1) [28]:

$$NH_3 = \frac{TAN \cdot 10^{pH}}{e^{\left(\frac{6344}{273.15 + T}\right)} + 10^{pH}} \tag{1}$$

Total (TA) and partial alkalinity (PA) were determined by a titration method at pH 4.3 and at 5.75, respectively, and the intermediate alkalinity (IA) by the difference between TA and PA [27]. Individual VFAs (acetate, propionate, butyrate and valerate) were analyzed by an HP-5890 Serie II chromatograph equipped with a capillary column (Nukol™) and flame ionization detector as described in Astals et al. [29]. Ions (Cl^-, PO_4^{3-}, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) were determined in an 863 Advanced Compact IC Metrohm ionic chromatographer using Metrosep columns (Metrohm). For cations the system was equipped with a Metrosep C4 – 150/4.0 mm column with an eluent (1.7 mol m^{-3} HNO_3 and 0.7 mol m^{-3} dipicolinic acid) flow of $1.5 \cdot 10^{-8}$ m^3 s^{-1}. For anions, the system was equipped with a Metrosep A Supp 4150/4.0 mm column with an eluent (1.7 mol m^{-3} $NaHCO_3$ and 1.8 mol m^{-3} Na_2CO_3) flow of $1.6 \cdot 10^{-8}$ m^3 s^{-1}. The biogas composition was analyzed by a Shimadzu GC-2010 + gas chromatograph equipped with a capillary column (Carboxen® – 1010 PLOT) and a thermal conductivity detector. The chromatograph oven temperature program was as follows: hold 360 s at 40 °C; ramp to 230 °C at 0.42 °C s^{-1}, hold 120 s. Injector and detector temperature was set to 200 and 230 °C, respectively. Helium with a fix linear velocity of 0.29 m s^{-1} was used as carrier gas.

With regard to the stabilizing agent and the precipitate physicochemical characterization the following analysis were performed. The chemical composition of the major and minor elements and the loss of ignition (LOI) was determined by X-ray Fluorescence Spectroscopy (XRF) using a Philips PW2400 X-ray sequential spectrophotometer. X-ray diffraction pattern was performed in a Bragg-Brentano Siemens D-500 powder diffractometer with CuK$_\alpha$ radiation to obtain information about the crystalline phases. To determine the particle structure and morphology an SEM Quanta 200 FEI analyzer equipped with an energy dispersive spectrometer analyzer (EDX) was used. Bulk density was measured with helium pycnometer [18,30].

3. Results and discussion

3.1. *The potential of the stabilizing agent to precipitate struvite*

3.1.1. *Effect of the stabilizing agent on pH*

Fig. 2a shows the evolution of the pH over time for all SA additions. The addition of SA to PM involved a rapid decrease in

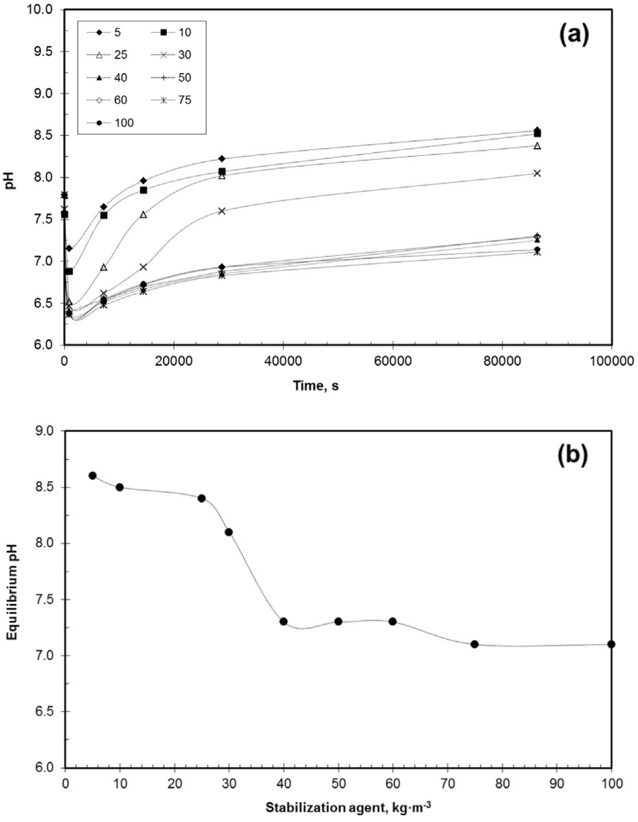

Fig. 2 – (a) pH evolution in the course of time and (b) equilibrium pH for different stabilizing agent additions of the discontinuous experiments.

the pH values, followed by an increase until the equilibrium pH (pH_{eq}) was reached. Three different scenarios could be distinguished as a function of the SA addition: (i) low SA addition (5 and 10 kg m^{-3}) showed a slight decrease of about 0.7 pH points, followed by a comparatively fast increase in pH until the pH_{eq} was reached. The pH_{eq} was about one pH point higher than the initial pH. (ii) High SA addition (40, 50, 60, 75 and 100 kg m^{-3}) showed a reduction in pH from 7.7 to 6.4, followed by a slight increase to a pH_{eq} of between 7.1 and 7.3. (iii) Medium SA addition (25 and 30 kg m^{-3}) showed characteristics of both previously described scenarios. On the one hand, the initial pH reduction was similar to the reductions obtained in the high concentration assays, where the minimum pH value was 6.5. On the other hand, the pH recovery and the pH_{eq} were similar to those obtained in the low concentration assays, even though the pH_{eq} value was slightly lower.

The observed pH evolution can be explained through the acid-base pairs present in the pig manure and the modifications made by the introduction of the stabilizing agent. Initially, the pH of the PM was mostly fixed by the carbon dioxide/hydrogen carbonate and the ammonium/ammonia equilibrium (Eqs. (2) and (3)). Then, the addition of the stabilizing agent reduced the pH, a fact that can be explained largely by the combination of two factors: (i) the H_3O^+ ions involved in the struvite precipitation equilibrium and (ii) the reduction of the TAN concentration in the system since it was precipitated as struvite [17]. Moreover, the presence of lime (CaO) in the LG-MgO could also contribute to diminishing the CO_3^{2-}/HCO_3^- concentration. However, it is difficult to establish the solubility equilibrium of calcium phosphates formed during the formulation of the stabilizing agent. It is important to highlight that the struvite precipitation could take place either with the magnesium phosphate particles present in the stabilizing agent (Eq. (4)), or with the magnesium and phosphates released from the LG-MgO, which reacted with the NH_4^+ present in the reactor medium (Eq. (5)). Finally, the pH increased until the pH_{eq} was achieved.

As can be seen in Fig. 2b, the pH_{eq} decreased as the amount of SA increased. The pH_{eq} of the assays with high SA addition was about 7.2. This value matches the logarithmic acid constant (pK_a) of the second proton of the phosphoric acid. Therefore, in these conditions, the phosphates released from the SA cause the $H_2PO_4^-/HPO_4^{2-}$ acid–base balance to control the final pH value. By contrast, the pH_{eq} of the assays with low and medium SA addition, and therefore with a lower phosphate concentration, could be affected not only by the lower struvite formation and the lower TAN removal, but also by the CO_2 stripping that may have reduced the concentration of acid compounds in the reactor medium [31,32]. The later phenomena could also have taken place in the assays with high SA addition; however, it would have been masked by the high concentration of phosphate.

$$CO_{2(aq)} + 2H_2O \leftrightarrow HCO_3^- + H_3O^+ \quad (2)$$

$$NH_4^+ + H_2O \leftrightarrow NH_{3(aq)} + H_3O^+ \quad (3)$$

$$MgHPO_4 \cdot 3H_2O_{(s)} + NH_4^+ + 4H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O_{(s)} + H_3O^+ \quad (4)$$

$$Mg^{2+} + HPO_4^{2-} + NH_4^+ + 4H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O_{(s)} + H_3O^+ \quad (5)$$

3.1.2. *Effect of the stabilizing agent on TAN removal efficiency*

The evolution of the TAN for the tested SA additions is shown in Fig. 3a. The quick reduction in TAN concentration at the beginning of the assays was related to struvite precipitation, as was the quick initial pH reduction (Fig. 2a). It should be pointed out that even though the composition of the precipitate was not analyzed, all the necessary conditions were met for struvite precipitation. In the first quarter-hour low SA addition assays removed about 0.3 kg m^{-3} of TAN, while medium and high SA addition removed about 1 kg m^{-3} of TAN due to the higher ion concentration (Fig. 3a). Later on, the TAN concentration in low SA addition assays climbs and the pH rises. This phenomenon could be explained by struvite dissolution result of the pH reduction in the reactor medium [33,34]. However, no struvite dissolution, even at a lower pH value, was detected in the medium and high SA addition. This fact could be explained by the higher phosphate and magnesium concentration in the reactor medium and a higher pH in the interface layer covering the particles of SA. After struvite dissolution, the low SA addition assays reached a pH value

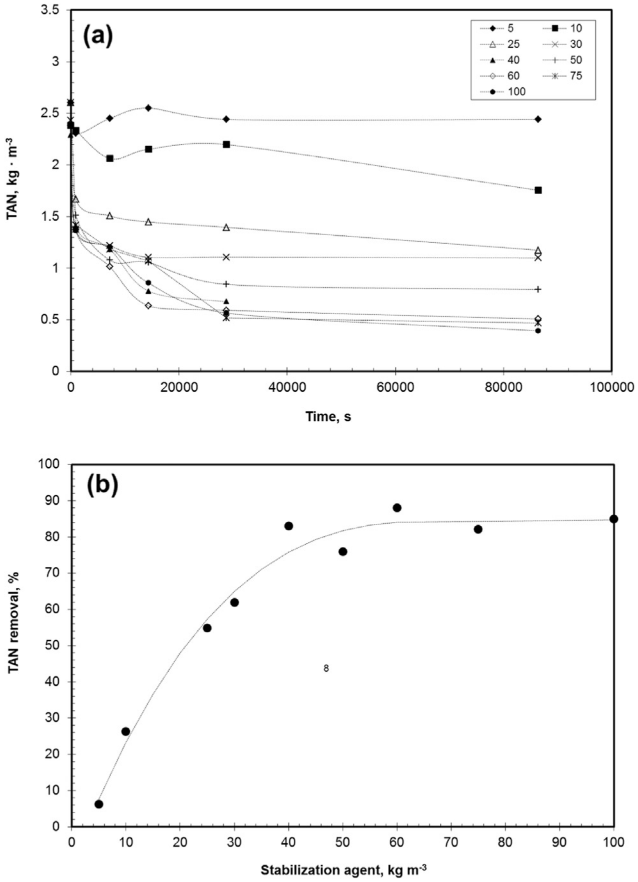

Fig. 3 – (a) TAN evolution in the course of time and (b) the TAN removal efficiency for different stabilizing agent additions after 24 h of the discontinuous experiments.

near 8, which caused struvite precipitation and therefore TAN removal to restart [31]. In contrast, the medium and high SA addition assays continued to remove TAN throughout the entire experiment, but at a lower rate. The lesser reaction rate could be related to the formation of struvite on the SA particles surface and the pH of the reactor medium. On the one hand, Chimenos et al. [18], who precipitated ammonium and phosphates from cochineal waste wasters using the same magnesium by-product, corroborated that the LG-MgO particles surface was covered by struvite, while the inside of the LG-MgO particle had not reacted with the aqueous medium and remain unchanged. The present results confirmed that the struvite formation was controlled on the basis of the shrinking core model; hence the phosphate and ammonium diffusion was blocked by the struvite crystals [18,30]. On the other hand, it is well known that struvite precipitation is feasible between pH values of 7 and 11 [32], with an optimum between 8 and 9. However, the lower pH in the digester medium not only reduced the struvite nucleation time [31–33], but also improved newberyite stability [35], which slowed down the dissolution of phosphate and ammonium.

Finally, Fig. 3b shows that the reduction in TAN concentration was not proportional to the SA addition. Specifically, in the low and medium SA addition assays the TAN removal efficiency improved as the SA addition increased. It is possible that under these conditions the ion concentration was not high enough to remove all the available TAN. Nevertheless, the maximum TAN removal efficiencies, about 83%, were reached for all the high SA addition assays (40–100 kg m^{-3}), a scenario in which an increase in the stabilizing agent addition did not lead to a higher struvite precipitation.

3.2. *Mesophilic anaerobic digestion coupled with struvite precipitation*

The results obtained in the batch experiments showed the high capacity of the stabilizing agent to reduce the TAN concentration of the pig manure. However, a long-term digester operation is necessary to evaluate the process feasibility and to guarantee that the stabilizing agent does not introduce any harmful compound for the anaerobic biomass. As aforementioned, 5 and 30 kg m^{-3} were chosen as SA concentration in the feed supply. These concentrations enabled the behavior of the low and medium SA additions to be evaluated. It should be noted that, even presenting better TAN removal efficiencies, high SA additions were not considered due to high pH reduction as well as high costs associated to the SA price and transportation.

At the outset, the three reactors were inoculated with digestate from a centralized pig manure anaerobic digestion plant. This approach made it possible to obtain an adapted anaerobic consortium and, therefore, reduce the start-up period. After a lag time of 40 days similar steady-state conditions were achieved in all reactors as shown by the constant pH, alkalinity ratio, VFA concentration and biogas production rate. Afterwards and during 110 days the SA was added to the fed supply of R2 and R3, while R1, kept as a reference, was fed only with PM (Fig. 4). Two different strategies were followed in order to achieve the desired SA concentration in the reactor medium. In R2 the SA concentration increased gradually because it was always fed with the designed feed supply (5 kg m^{-3}), while the SA concentration in R3 increased dramatically because the reactor was fed with an influent of 200 kg m^{-3} during the first three days and then of the required SA addition (30 kg m^{-3}); no process inhibition was detected in either case. Once the new steady-state conditions were achieved for both reactors (after 30 days) a set of analyses was carried out during four HRT in order to characterize the PM, the biogas and the effluent of the three reactors (Table 2).

The evaluation of digestion stability was one of the most important factors to take into account since it enables to consider an AD process to occur without risk of acidification. It was especially important here because the stabilizing agent was formulated with low-grade magnesium oxide, a by-product of the combustion of natural magnesite, which could introduce contaminants to the reactor medium and therefore inhibit the activity of the microorganisms [6,36]. In the present work, the digestion stability was monitored by means of the intermediate-to-partial alkalinity (IA/PA) ratio and the total volatile fatty acids-to-total alkalinity (TVFA/TA) ratio, which should be below 0.4 to ensure stable digestion [29,37–39]. Other authors have evaluated reactor stability using the intermediate-to-total alkalinity (IA/TA) ratio; however, the IA/TA ratio is less sensitive than the IA/PA ratio, not been adequate for systems with high alkalinity like pig manure digesters [29]. The average IA/PA ratio was 0.20, 0.23 and 0.24, while the average TVFA/TA ratio was 0.007, 0.007 and 0.006 for R1, R2 and R3, respectively. As these values were far below the proposed limit values, it could be assured that the process was operating without risk of acidification and hence that the SA did not exert a negative effect on the consortium of microorganisms. It is important to note that the TA values decreased as the SA addition increased; however, the TA for all digesters was much higher than 2 kg m^{-3} of $CaCO_3$, which is considered to be the lower limit for AD safe operation [40,41]. The explanation for this phenomenon could lie in the reduction in the TAN concentration as well as in CO_2 stripping, which may have caused struvite precipitation and resulting hydronium liberation (Eqs. (4) and (5)). This, in turn, would have reduced the concentration of acid and basic compounds in the liquid phase and increased the CO_2

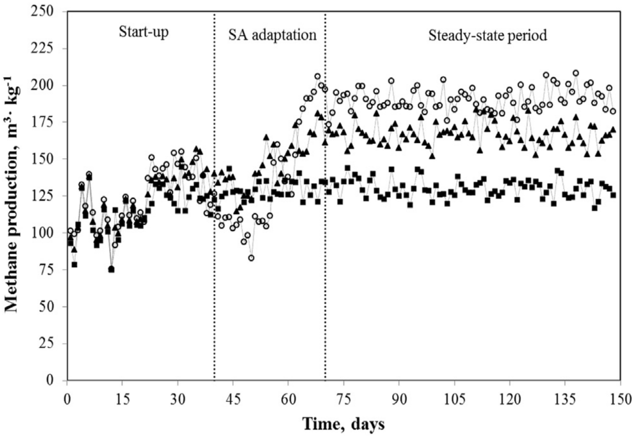

Fig. 4 – Specific methane production in the R1 (■), R2 (▲) and R3 (○).

percentage in the biogas (Table 2). Nonetheless, the differences in the TA values did not have an impact on the pH values for the digesters, since all three digesters presented pH values of around 8, a typical value for a manure digester [29,42].

All digesters were operated with the same HRT (20 days) and, as the SA did not provide biodegradable VS, with the same organic loading rate (1.1 kg m^{-3} day^{-1} of VS). The addition of the SA to the digester medium resulted in a 25% and a 40% increase in methane production for R2 and R3, respectively, when compared with the reference digester (R1). However, because of the different thermal stability of newberyite, periclase and struvite [43], the higher biogas production could not be correlated with a higher matter removal. In any case, the difference between the levels of methane produced could be related to the concentrations of TAN, magnesium and/or particles in the digester medium. Details are provided below.

As previously noted, TAN inhibition is especially distinct when digesting manures and a wide range of inhibiting TAN concentrations has been reported. As can be seen in Table 2 the TAN concentration in R2 was similar to that obtained in R1, with the concentration only reduced by 4%. In contrast, a large reduction in the TAN concentration, about 80%, was obtained for R3. However, the higher TAN removal efficiency of R3 in comparison with the one obtained in R2, which for both systems was related to struvite precipitation, did not make a substantial difference to the levels of methane production, which was only around 10%. These results highlighted that R1 and R2 were little inhibited by the TAN, indicating that the biomass was well adapted to the substrate and therefore to high TAN concentrations.

Another factor to take into account when explaining the difference between the levels of methane production was the magnesium concentration. Few studies had analyzed the effect of Mg^{2+} on anaerobic digestion and none of them, to our knowledge, address manure digestion. Nevertheless, it is clear that a surplus or deficit of Mg^{2+} can have a significant impact on the successful operation of an anaerobic digester [6]. As an example, Kugelman and McCarty [44] found that Mg^{2+} concentrations between 0.075 and 0.150 kg m^{-3} were stimulatory for acetoclastic methanogens, while concentrations above 1 kg m^{-3} where reported to be inhibitory to differing degrees. In another study Schmidt et al. [45] reported optimal Mg^{2+} concentrations between 0.25 and 0.75 kg m^{-3} for methanosarcina thermophila in a UASB reactor. However, no methanosarcina is expected in the digesters under study due to the low VFA concentration. Although the optimal range of Mg^{2+} is not clear, what is quite clear is that a low concentration of Mg^{2+} can constrain the development of the anaerobic process. The Mg^{2+} concentration in the PM and R1 was below 0.2 kg m^{-3}, therefore a deficit of it in the digester medium was assumed. However, the digester supplied with SA had higher concentrations of Mg^{2+} in the digester medium, released from the LG-MgO (Table 2). Moreover, the phosphate concentration in R2 and R3 is almost negligible while R1 had about 0.3 kg m^{-3}, so it is clear that some Mg^{2+} present in R2 and R3 digester medium reacted with it to precipitate struvite (Eq. (5)).

Struvite precipitation was very important because it not only reduced the TAN concentration and supplied magnesium in the digester medium but also could have offered a high-capacity immobilization matrix for microorganisms. The immobilization of the anaerobic consortium is known to improve the anaerobic digestion process in manure, where natural zeolites, activated carbon and phosphorite ore, among others, have been reported to counteract various types of inhibition and to stabilize the anaerobic digestion process [10–12].

3.3. *Stabilizing agent and the precipitate characterization*

As can be seen in SEM micrographs, the particles of the stabilizing agent presented an amorphous morphology with a particle size below 200 μm (Fig. 1a). In contrast, most precipitate particles presented an orthorhombic structure typical of struvite crystals (Fig. 5a) [22,31,34] with a particle size between 200 and 500 μm. The analyzed particles were obtained from the continuous digesters. Three different types of particles can be found in the precipitate: (1) typical orthorhombic struvite crystals, (2) small orthorhombic struvite crystals grown above the stabilizing agent surface and (3) other minerals (Fig. 5a). Additionally, an X-ray analysis of the SA and the precipitate was used to identify the main mineralogical

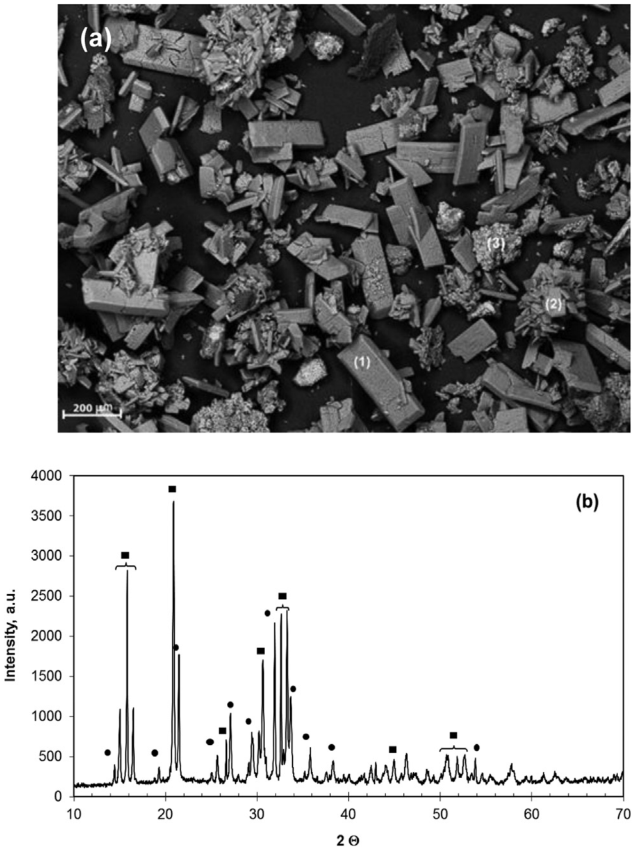

Fig. 5 – (a) Scanning electron micrograph ((1) are struvite particles growth in the digester medium, (2) are struvite particles growth on the surface of the stabilizing agent, (3) are other minerals) and (b) X-ray diffractogram of the precipitate obtained from the digesters effluent (●, Newberyite; ▲, periclase; ■, struvite).

phases of the two compounds (Figs. 1b and 5b). The SA mainly consisted of newberyite ($MgHPO_4 \cdot 3H_2O$) and periclase (MgO), although other inert minerals could be detected in minor amounts, i.e. quartz (SiO_2), dolomite ($CaMg(CO_3)_2$) and gypsum ($CaSO_4 \cdot 2H_2O$), whereas the X-ray diagram of the precipitate confirmed the presence of struvite. To be specific, struvite peaks were identified as the main phase, although newberyite and periclase were identified as minor phases. The presence of newberyite and periclase in the precipitate, non-reacted mineral, suggests that the struvite was formed on the particle surface while the nuclei of the SA particles remained unreacted. These results confirmed the coexistence of two mechanisms for struvite precipitation: (i) the formation and growth of the struvite on the SA particle surface (Eq. (4)), which was related to the small orthorhombic struvite crystals (Eq. (4)) and (ii) the formation and growth of struvite from bulk solution (Eq. (5)), which was related to the typical orthorhombic struvite crystals.

4. Conclusions

The interaction between the pig manure and the stabilizing agent was evaluated in batch experiments for a wide range of additions. Three different scenarios were distinguished as function of the stabilizing agent concentration: low (5 and 10 kg m^{-3}), medium (25 and 30 kg m^{-3}) and high (40–100 kg m^{-3}). To be specific, ammonia removal efficiencies below 25% were obtained for low additions but, at the same time, lower pH fluctuations than high additions, which showed removal efficiencies up to 80%. Medium additions showed characteristics of both the scenarios. The results obtained showed that the high capacity of the stabilizing agent to remove ammonia from pig manure.

The operation of three digesters during four hydraulic retention times showed that the addition of 5 and 30 kg m^{-3} of stabilizing agent into the digester fed resulted in a 25% and a 40% increase in methane production, respectively, when compared with the reference digester. These results were related to the reduction of the ammonia concentrations and the increase of magnesium and particles concentration in the digester medium. Moreover, as shown by biogas production, the alkalinity and volatile fatty acids values, the stabilizing agent did not exert a negative effect on the consortium of microorganisms. Therefore, the magnesium oxide by-product used to formulate the stabilizing agent did not introduce any harmful compound for the anaerobic biomass.

Finally, X-ray diffraction and scanning electronic microscopy confirmed struvite precipitation in addition to two precipitation mechanisms, reaction between ammonia and newberyite on the stabilizing agent particle surface and reaction between ammonia, phosphate and magnesium in the digester medium.

Acknowledgments

The authors would like to thank ACC1Ó and FEDER (VALTEC09-1-0016), as part of the framework “Programa Operatiu de Catalunya”, the Spanish Ministerio de Economía y Competividad (CTM2011-24897) and Magnesitas Navarras S.A. for their support and funding of this research project. The authors are grateful to VAG, S.L. (Valoritzacions Agroramaderes de les Garrigues) for providing samples and sampling facilities. Sergi Astals Garcia is also grateful to the Spanish Ministerio de Ciencia e Innovación for his doctoral grant (CTM2008-05986).

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Feasibility of coupling anaerobic digestion and struvite precipitation in the same reactor: Evaluation of different magnesium sources

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HIGHLIGHTS

- Different magnesium sources were evaluated to reduce ammonia inhibition.
- A magnesium based stabilizing agent was used to facilitate struvite precipitation.
- The stabilizing agent was the unique non-harmful magnesium source.
- Anaerobic digestion and struvite precipitation were coupled in the same reactor.

ARTICLE INFO

Article history:
Received 31 October 2014
Received in revised form 13 February 2015
Accepted 14 February 2015
Available online 20 February 2015

Keywords:
Anaerobic digestion
Ammonium inhibition
Chemical precipitation
Struvite
Magnesium
Pig manure

ABSTRACT

The feasibility of coupling anaerobic digestion and struvite precipitation in the same reactor was evaluated to enhance manure anaerobic digestion methane yields through ammonia inhibition mitigation. Five different magnesium sources were tested as a struvite (ammonia sequestration agent) precursor, i.e. $MgCl_2$, $Mg(OH)_2$, two industrial by-products rich in MgO but with different reactivity, and a stabilizing agent. The latter was formulated in advance with the low reactivity industrial by-product and phosphoric acid. The effect of each magnesium source on anaerobic digestion as well as its struvite precipitation capacity was evaluated through biomethane potential tests. Results indicated that all magnesium sources were able to reduce ammonia concentration to different extents. However, the stabilizing agent was the unique magnesium source that did not inhibit the anaerobic digestion process. The avoidance of adding a phosphate source directly into the digester medium and the high newberyite content were the advantages of the stabilizing agent over the other magnesium sources. Finally, a series of experiments indicated that if anaerobic digestion and struvite precipitation are combined in a single reactor, stabilizing agent addition should be carried out through several small additions rather than few large additions.

1. Introduction

The capacity to mineralise organic matter, reduce greenhouse gases emissions, produce an effluent with good fertilising qualities and, overall, energy recovery through methane production have made anaerobic digestion (AD) a widely used technology to treat animal manure [1,2]. However, a wide variety of factors have been reported as inhibitors of the AD process and, therefore, to reduce its methane yield [3]. Among all inhibitors, ammonia nitrogen is especially distinct when digesting animal manure [4,5]. Ammonia nitrogen is produced by the biological degradation of nitrogenous organic matter in the acidogenesis step and it remains in the digester medium in two forms, NH_4^+ and NH_3, which are in equilibrium depending mainly on temperature and pH [6,7]. Although both forms have been reported as inhibitors of methanogenic activity, the capacity to diffuse into the cell, causing proton imbalance and/or potassium deficiency makes NH_3 the most harmful form [8–10].

Many research efforts have been made to mitigate ammonia nitrogen inhibition in AD. Among them, the addition of material with ion exchange capacity (e.g. bentonite, glauconite, phosphorite and zeolites) or inorganic absorbent materials (e.g. clay, manganese oxides and zeolites) have shown good results [9,11–15]. Likewise, struvite ($MgNH_4PO_4{\cdot}6H_2O$) precipitation prior or after AD has taken great interest since it is very valuable as slow-releasing

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http://dx.doi.org/10.1016/j.cej.2015.02.057
1385-8947/

fertiliser [16]. Struvite precipitation naturally occurs when the combined concentration of Mg^{2+}, NH_4^+ and PO_4^{3-} exceed the struvite solubility product [17,18]. Therefore, the precipitation of struvite in manures requires the addition of chemical compounds since the concentration of Mg^{2+} and PO_4^{3-} are very low in relation to NH_4^+ concentration [19]. Several magnesium ($MgSO_4$, $Mg(OH)_2$, $MgCl_2$, MgO) and phosphate (H_3PO_4, phosphates salts) sources have been successfully applied to facilitate struvite precipitation [20–22]; nonetheless, the high cost of the pure or high-grade magnesium compounds has limited its full-scale implementation [23]. In this vein, the use of industrial magnesium by-products seems to be a cost-effective alternative to overcome this problem [2,24,25]. Another option to minimise struvite precipitation cost is to combine struvite precipitation and AD in the same reactor; however, this approach has been had limited study. Uludag-Demirer et al. [26] who investigated the effect of $MgCl_2$, $Mg(OH)_2$ and Na_2HPO_4 in batch manure digesters, did not observe any improvement on the methane yield. The authors concluded that the digesters supplied with $Mg(OH)_2$ and Na_2HPO_4 suffered cation (Na^+ and Mg^{2+}) and pH inhibition, while the digesters supplied with $MgCl_2$ and Na_2HPO_4 had only cation inhibition. Contrariwise, Lee et al. [27] satisfactorily operated a continuous biowaste digester combined with struvite precipitation, where $MgCl_2$ was added to reach a Mg:P molar ratio of 1:1 and pH was adjusted between 7.7 and 8.3. The authors concluded that the 50% methane production improvement was due to the reduction of ammonia nitrogen concentration from 6.0 to 2.0 g N L^{-1}. Similarly, Romero-Güiza et al. [2] recorded a 25% and 40% methane production improvement when dosing 5 and 30 g L^{-1} of a stabilizing agent formulated with low-grade magnesium oxide, respectively, in a continuous pig manure digester. The authors related the methane yield improvement to the reduction of the ammonia concentrations, the increase of magnesium concentration, and the presence of particles in the digester medium. Even though the literature is scarce, the disparity between studies suggest that there are aspects from the magnesium sources that have not been considered (e.g. cation availability, reagent solubility and reactivity) but which might have a significant role on the feasibility of this promising approach.

The main goal of this study was to compare the performance of five different magnesium sources (i.e. $MgCl_2$, $Mg(OH)_2$, high-grade MgO, low-grade MgO and a stabilizing agent) in reactors coupling anaerobic digestion and struvite precipitation. The study also aims to identify the factors that may limit the applicability of combining both processes in a single reactor.

2. Materials and methods

2.1. Analytical methods

The major and minor components of the magnesium sources and the loss of ignition (LOI) were determined by X-ray fluorescence (XRF) using a Philips PW2400 X-ray sequential spectrophotometer. X-ray diffraction patterns were performed in a Bragg-Brentano Siemens D-500 powder diffractometer with CuKα radiation to obtain information about the crystalline phases. Scanning electronic micrographs were obtained with a SEM Quanta 200 FEI analyser equipped with an energy dispersive spectrometer analyser. The reactivity of the MgO samples was determined by the citric acid method, which measures the time needed by 2.0 g of powdered MgO in 100 mL of 0.4 N citric acid solution to reach pH 8.2. Citric acid results indicate the hydration and dissolution capability of the MgO particles [28]. The specific surface area of the MgO samples was determined using the BET single point method with a Micromeritics Tristar 3000 porosimeter.

Total solids (TS) and volatile solids (VS) were determined following the guidelines given by the standard methods 2540G [29] with minor modifications [30]. Inorganic carbon (IC) were measured by means of a Shimadzu 5055 TOC-VCSN TOC analyser. Individual volatile fatty acids (VFAs; acetate, propionate, butyrate and valerate) were analysed by a HP 5890-Serie II chromatograph as for Astals et al. [31]. Anions (Cl^- and PO_4^{3-}) and cations (NH_4^+, K^+, Ca^{2+} and Mg^{2+}) were determined in an 863 Advanced Compact IC Metrohm ionic chromatographer using Metrosep columns [32]. Total ammonia nitrogen (TAN) comprises both forms NH_4^+ and NH_3, while total phosphate (TP) is the sum of $H_2PO_4^-$ and HPO_4^{2-} (main phosphate species under assay pH conditions). Biogas composition was analysed by a Shimadzu GC-2010+ gas chromatograph equipped with a capillary column (Carboxen® – 1010 PLOT) and a thermal conductivity detector [2].

2.2. Pig manure, inoculum and chemical reagents origin

Pig manure and digested pig manure, used as inoculum, were collected from a centralized mesophilic anaerobic digestion plant, which treats around 100,000 tons of pig manure per year. After collection, both samples were stored at 4 °C. Prior to commencement of the biomethane potential (BMP) tests inoculum was degassed at 37 °C for one week. Pig manure and the inoculum characterisation is given in Table 1.

Analytical grade $MgCl_2$, $Mg(OH)_2$, and K_2HPO_4 were purchased from Panreac Quimica, S.A. (Barcelona, Spain). The two industrial by-products, named as high-grade magnesium oxide (HG-MgO) and low-grade magnesium oxide (LG-MgO) according to their MgO content, were provided by Magnesitas Navarras, S.A. (Navarra, Spain). HG-MgO and LG-MgO were obtained from the calcination of natural magnesite in rotary kiln at 1100 °C to obtain caustic calcined magnesia. HG-MgO is the finest fraction (<1 mm) of the calcined magnesia collected at the bottom of the furnace, while LG-MgO is a by-product collected as cyclone dust in the fabric filters from the air pollution control system. The stabilizing agent (SA) was formulated with LG-MgO and phosphoric acid following Romero-Güiza et al. [2]. Briefly, phosphoric acid was slowly added to an aqueous slurry of LG-MgO with a high solid-to-liquid ratio. The exothermic acid–base reaction generated a solid with a high content of newberyite ($MgHPO_4{\cdot}3H_2O$) and other magnesium phosphate compounds, which inner core did not react on the basis of the shrinking core model and remained as LG-MgO. Then, the

Table 1
Pig manure and inoculum characterization.

	Units	Pig manure	Inoculum
TS	g L^{-1}	32.1	47.2
VS	g L^{-1}	21.0	29.9
pH	–	7.5	8.0
TAN	mg N L^{-1}	1785	2490
TP	mg P L^{-1}	36	33
Mg^{2+}	mg L^{-1}	37	36

Table 2
Semi-quantitative characterisation of HG-MgO, LG-MgO and SA.

	Units	HG-MgO	LG-MgO	SA
MgO	%	89.8	63.4	31.8
P_2O_5	%	–	–	32.8
CaO	%	1.5	8.7	4.7
SO_3	%	–	3.8	1.1
Fe_2O_3	%	–	2.4	1.2
SiO_2	%	–	3.2	0.9
V_2O_5	%	–	0.3	0.3
MnO	%	–	0.1	0.1
LOI (1100 °C)	%	3.3	8.9	24.7
Reactivity	s	90	2280	>3000
BET surface area	m^2 g^{-1}	8.83	10.87	11.94

Table 3
Magnesium and phosphate addition for each assay.

	Mg^{2+} ($g L^{-1}$)	TP ($g L^{-1}$)	N:P:Mg
Control	–	–	–
$MgCl_2$	3.30	0.42	1:1:1
$Mg(OH)_2$	3.30	0.42	1:1:1
SA(1)	1.00	0.07	6:1:1.7
SA(2)	2.87	0.21	2:1:1.7
SA(3)	5.75	0.42	1:1:1.7
HG-MgO(1)	1.00	0.07	6:1:1.7
HG-MgO(2)	2.87	0.21	2:1:1.7
HG-MgO(3)	5.75	0.42	1:1:1.7
LG-MgO(1)	1.00	0.07	6:1:1.7
LG-MgO(2)	2.87	0.21	2:1:1.7
LG-MgO(3)	5.75	0.42	1:1:1.7

compound was dried and crushed to a particle size of about 500 μm. The chemical composition of HG-MgO, LG-MgO and SA is shown in Table 2.

2.3. Biomethane potential test

BMP tests were carried out following the stages defined by Angelidaki et al. [33] in 115 mL serum bottles at mesophilic conditions. The bottles were filled with: (i) 40 mL of inoculum; (ii) the amount of pig manure that met an inoculum to substrate ratio of 2 (VS-basis) (30 mL); (iii) deionised water, used to adjust the same effective volume for all tests (80 mL); and (iv) varying amounts of $MgCl_2$, $Mg(OH)_2$, HG-MgO, LG-MgO, SA and K_2HPO_4. The amount of reagent/s added in each assay is provided in Table 3. A control assay containing inoculum and pig manure was used to determine pig manure specific methane potential. A blank assay containing inoculum and no substrate was used to correct for background methane potential in the inoculum. Bottles headspace were flushed with N_2 for one minute ($3 L min^{-1}$), sealed with a PTFE/Butyl septum retained with an aluminium crimp cap and placed in a water bath set at 37 °C. Tests were mixed by swirling once a day. All tests were carried out in triplicate, and all error bars indicate 95% confidence in the average of the triplicate. Biogas production during the running test was measured with a vacumeter (Ebro – VAM 320). Biogas composition was analysed with a GC analyser after each sample event. Accumulated volumetric methane production in time was calculated considering the biogas produced, once converted at standard temperature and pressure conditions (i.e. 0 °C and 1 bar), and the methane composition in the biogas.

Eleven different Mg doses were tested, i.e. $MgCl_2$, $Mg(OH)_2$, three HG-MgO doses, three LG-MgO doses, and three SA doses. Note that SA supplied both Mg and P, while K_2HPO_4 was added for the rest of Mg sources as P source (Table 3). $MgCl_2$ and $Mg(OH)_2$ were tested individually, reagents dosage was adjusted to obtain a N:P:Mg molar ratio of 1:1:1 according to pig manure TAN concentration. The three SA additions were selected considering the results obtained in a previous study by the author Romero-Güiza et al. [2]. The tested SA additions were 5, 15 and 30 $g SA L^{-1}$ which gave a N:P:Mg molar ratio of 6:1:1.7, 2:1:1.7 and 1:1:1.7, respectively (tests were named as SA(1), SA(2) and SA(3) respectively). HG-MgO and LG-MgO along with K_2HPO_4 doses were performed considering the Mg and P additions in the SA assays. Both MgO by-products experiments were labelled as MgO(1), MgO(2) and MgO(3) as solid dose increased (Table 3).

2.4. Struvite precipitation with SA in batch experiments

Struvite precipitation batch experiments were performed in a Jar-Test device (Flocculator 2000, Kemira) at 37 °C. All reactors had 0.6 L of pig manure, and four SA doses were tested (i.e. 5, 10, 15 and 30 $g SA L^{-1}$). Reactors were continuously stirred at 15 min^{-1} to ensure particles were maintained in suspension in the slurry, providing the reaction. The process was monitored by means of pH, IC, TAN, Mg^{2+} and TP, measured for each experimental trial at 0, 0.25, 0.5, 1, 2 and 4 h.

3. Results and discussion

3.1. Effect of the magnesium source on anaerobic digestion

The utilisation of analytical grade Mg sources, $MgCl_2$ and $Mg(OH)_2$, as struvite precursors caused a significant reduction of pig manure methane yield when compared to control ($p = 0.0001$, $p < 0.0001$), which is in agreement with those results published by Uludag-Demirer et al. [26]. $MgCl_2$ addition reduced pig manure methane yield from 148 to 61 $mL CH_4 g^{-1}$ VS, whereas $Mg(OH)_2$ addition led to a complete breakdown of the AD process (Fig. 1a). Regarding the $MgCl_2$ assay, the low VFA concentration at the end of the BMP indicates that the inhibitory agent had a toxic effect on acid-forming microorganisms rather than on methanogenic biomass. This statement is fulfilled by the mechanisms reported for potassium inhibition [3], which is the cation supplied by the phosphate source (K_2HPO_4). Potassium concentration in the $MgCl_2$ digester was 14 $g L^{-1}$ (Table 4), which is within the potassium threshold concentration (6–29 $g L^{-1}$) found by other authors [3,34]. Hence, it is most likely that potassium was the compound partially inhibiting the AD process. Additionally, the minor accumulation of acetate at the end of the BMP dismisses magnesium as source of inhibition, since it has been reported as inhibitor of the acetate-consuming methanogens [3,35,36]. Contrariwise, the VFA distribution at the end of the $Mg(OH)_2$ BMP (i.e. high concentration of propionate, butyrate and valerate together with the relatively low concentration of acetate) may suggest that hydrogen-utilising methanogens were more inhibited than acetate-utilising methanogens and acid-forming bacteria by $Mg(OH)_2$ test conditions. Actually, $Mg(OH)_2$ assay produced less methane than the blank assay, thus giving negative accumulated methane values throughout the test. The detrimental impact of $Mg(OH)_2$ test conditions on AD performance might be linked to two different factors: (i) $Mg(OH)_2$ basic property, which made digester pH rise to 8.5, and (ii) the high concentration of potassium in the digester medium.

The use of industrial by-products (HG-MgO and LG-MgO) as magnesium sources also led to a lower manure methane yield (Fig. 1b and c). However, the extent of it varied with the by-product concentration. Low magnesium doses (HG-MgO(1) and LG-MgO(1)) presented similar behaviours than that observed for $MgCl_2$, i.e. partial reduction of the methane yield, neutral pH and no accumulation of VFA at the end of the BMP (Table 4). Although K^+ concentration was lower than observed in $MgCl_2$ test, K^+ can still be identified as the inhibitory agent of both tests. The HG-MgO medium dose (HG-MgO(2)) test, which AD process was completely breakdown, presented a similar pH and VFA distribution at the end of the BMP than the recorded for $Mg(OH)_2$. Accordingly, pH increase and K^+ concentration were the two potential inhibitory phenomena. However, the higher VFA concentration at the end of the HG-MgO(2) assay in a half K^+ concentration, when compare with $Mg(OH)_2$, indicates that pH increase was more detrimental to methanogens than K^+ concentration. The high HG-MgO dose (HG-MgO(3)) as well as the medium and high LG-MgO doses (LG-MgO(2) and LG-MgO(3)) also resulted in a complete breakdown of the AD process (Fig. 1b and c). Nevertheless, the high pH values (>9) and the fact that acetate was the main VFA at the end of the assays suggest that both hydrogenotrophic and acetoclastic methanogens were inhibited under this pH condition.

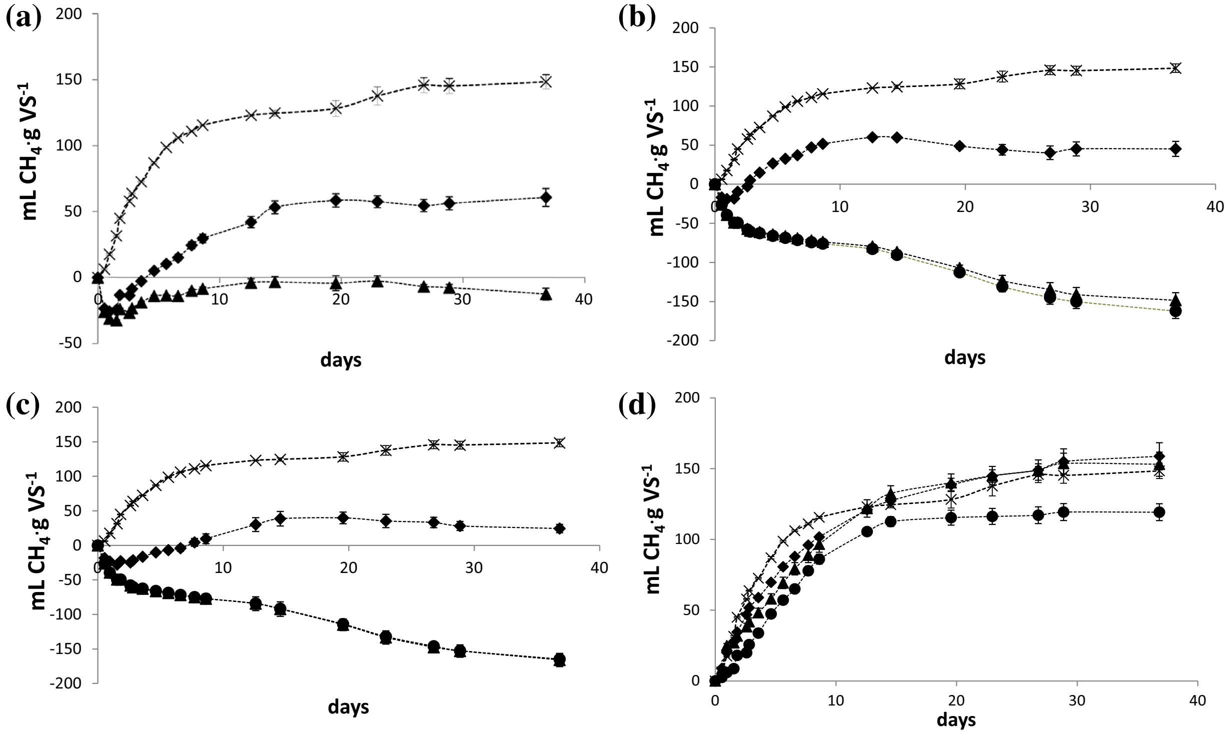

Fig. 1. Cumulative methane production curve of pig manure (×) and; (a) (♦) $MgCl_2$ and (▲) MgOH; (b) (♦) HG-MgO(1), (▲) HG-MgO(2) and (●) HG-MgO(3); (c) (♦) LG-MgO(1), (▲) LG-MgO(2) and (●) LG-MgO(3); (d) each SA addition (♦) SA(1), (▲) SA(2) and (●) SA(3).

Table 4
Characterisation of the BMP tests at the end of the assay.

	Units	Control	$MgCl_2$	$Mg(OH)_2$	HG-MgO(1)	HG-MgO(2)	HG-MgO(3)	LG-MgO(1)	LG-MgO(2)	LG-MgO(3)	SA(1)	SA(2)	SA(3)
pH	–	7.31	6.72	8.46	7.57	8.51	9.21	7.73	9.05	10.38	7.29	7.18	7.00
TP	mg L^{-1}	551	510	1310	440	214	1319	346	1039	1815	498	493	1041
TAN	mg L^{-1}	2498	954	1699	2553	1968	1512	2472	1775	1171	2406	1529	567
Mg^{2+}	mg L^{-1}	41	1086	288	831	674	514	770	707	534	715	1198	1836
K^+	mg L^{-1}	2067	13,917	15,418	4273	7351	12,526	4276	7413	11,881	2382	2226	2032
VFA	mg L^{-1}	115	190	1984	117	4664	17,574	130	13,143	18,847	199	166	159
Acetate	mg L^{-1}	99	115	327	93	317	14,899	130	10,715	15,696	159	137	134
Propionate	mg L^{-1}	–	44	895	–	1587	1095	–	868	1333	12	–	–
Butyrate	mg L^{-1}	17	32	280	24	290	770	–	701	841	28	29	25
Valerate	mg L^{-1}	–	–	459	–	2471	758	–	719	724	–	–	–

The SA additions presented a completely different trend than the other magnesium sources since no severe inhibition phenomena were recorded. Low and medium SA doses (SA(1) and SA(2)) showed the same methane potential as control, while the high SA dose (SA(3)) presented a slight reduction of manure methane potential (from 148 to 127 mL CH4 g^{-1} VS) (Fig. 1d). The capability of fixing TAN, different extents, without a negative effect on AD performance shows the suitability of SA as a reagent able to couple anaerobic digestion and struvite precipitation in a single reactor. The main advantage of the SA over the other magnesium sources is the avoidance of adding the phosphate source directly into the digester medium. Note that phosphoric acid direct addition may cause a lot of foam (effervescences) due to the displacement of the IC equilibrium as well as pH problems, while the required concentration of cation (Na^+ or K^+) supplied by the phosphate salt has been identified as inhibitor of the AD process in the present study and by Uludag-Demirer et al. [26]. Moreover, the low impact of SA on AD performance might also be related to its high newberyite content, since newberyite has a low reactivity (Table 2) and is non-toxic for biological systems [37]. Finally, it should be noted that the equal and the reduced methane yield for SA(1) and SA(3), respectively, when compared to control are in disagreement with the methane production increase (25% and 40%, respectively) reported in our previous study when dosing the same amount of SA into a continuous pig manure digester [2]. This phenomenon may be related to the stirring and feeding difference between batch and continuous systems. In the continuous experiment SA concentration was added gradually and diluted (1/20) once introduced in the digester, while in BMP SA was added in a single dose. Therefore, BMP reactors had a higher ion concentration (e.g. Mg^{2+} and PO_4^{3-}) and less adaptation time for the anaerobic biomass. Whereby, these results suggest better results could have been obtained if the same amount of SA was dosed through small additions.

3.2. Struvite precipitation with stabilizing agent in batch experiments

To better comprehend the effect of SA addition on pig manure, the evolution of pH, TAN, IC, TP and Mg^{2+} were followed when four different SA doses (5, 10, 15 and 30 g L^{-1}) were added to pig manure.

As shown in Fig. 2a, all SA additions caused a reduction of pH during the first 30 min and then pH increased progressively, which is similar to the behaviour observed in our previous publication [2].

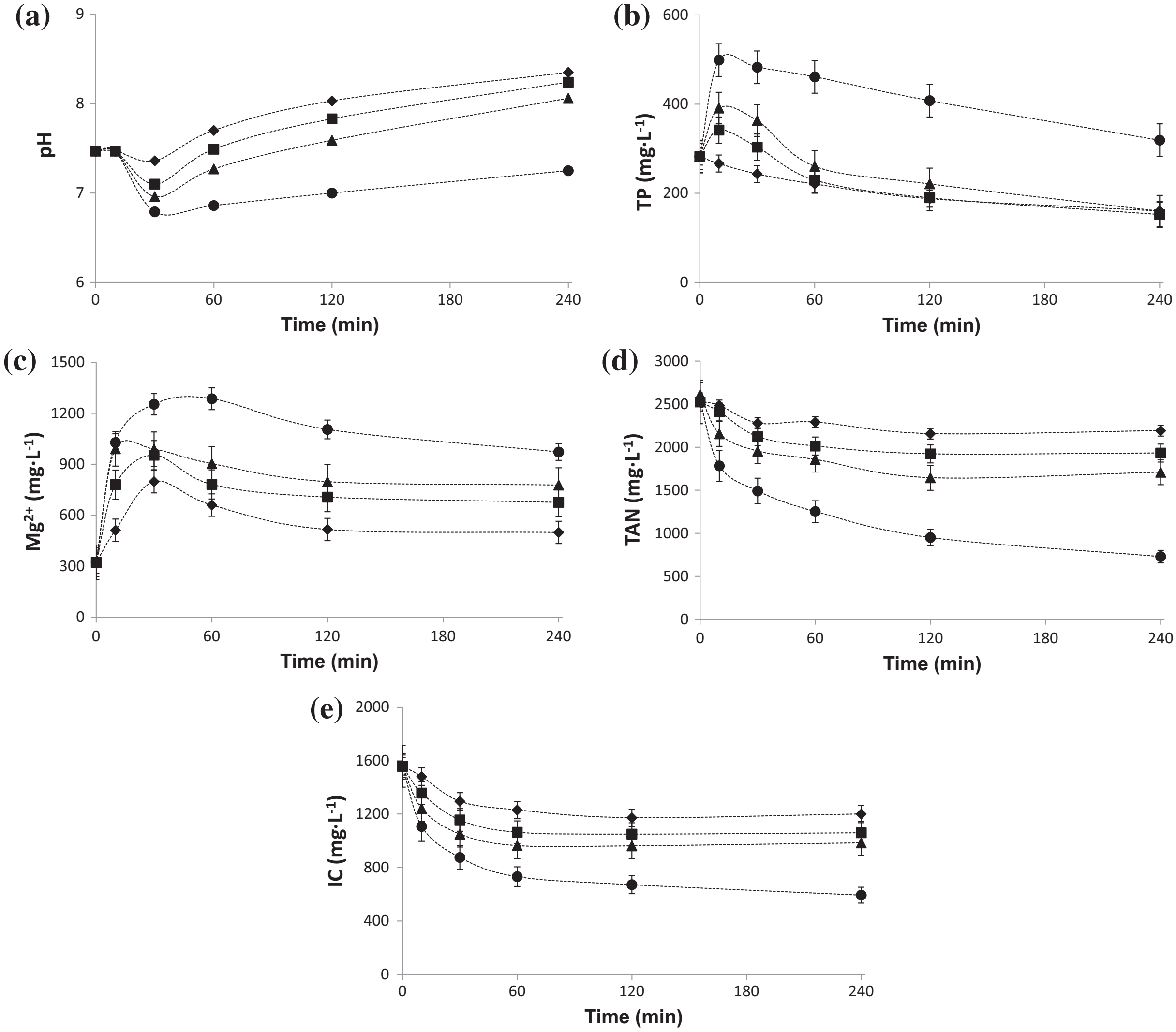

Fig. 2. (a) pH, (b) P-PO$_4^{3-}$, (c) Mg^{2+}, (d) TAN, and (e) IC evolution in the course of time for the different SA additions, i.e. (♦) 5 g L^{-1}, (■) 10 g L^{-1}, (▲) 15 g L^{-1} and (●) 30 g L^{-1}.

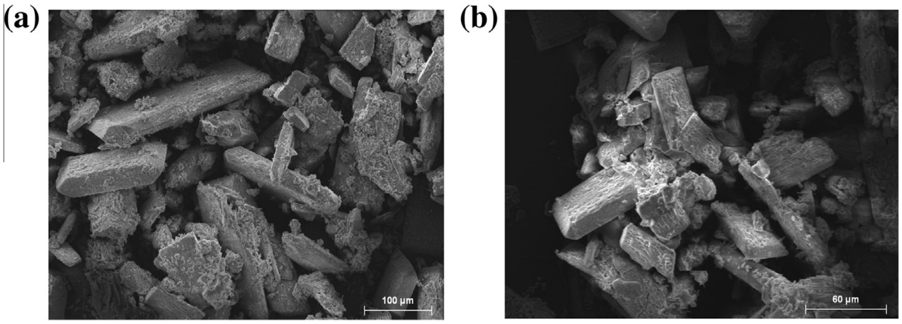

Fig. 3. Scanning electron micrograph of (a) struvite particles growth in the digester medium, and (b) struvite particles growth in the surface of the stabilizing agent.

Accordingly, pH reduction can be related to the reaction mechanisms involved during the struvite precipitation: (i) the proton released by the displacement of the P equilibrium and (ii) TAN fixation (Fig. 2b and d). With the exception of 30 g SA L^{-1}, struvite precipitation (directly related to TAN removal (Fig. 2d)) took place during the first 60 min of the assays, since from then on TAN concentration remained constant over time. The lower pH drop at low SA doses together with the short reaction time suggest that, when combining AD and struvite precipitation, SA addition should be carried out through several small additions rather than few large doses. This strategy would also allow to reach higher SA doses without affecting the AD process, since struvite precipitation extent increased as SA dose increased; where 5, 10, 15 and 30 g SA L^{-1} additions led to TAN removals of 35%, 41%, 52% and 76%, respectively. Likewise, the IC (CO_2/HCO_3^-) abatement during the first stages of the process (Fig. 2e) was due to the precipitation of calcium carbonates, promoted by the lime content in SA (Table 2), and the liberation of protons during the struvite precipitation, which together with system operational conditions (constant agitation and open to the atmosphere) facilitated CO_2 stripping. For a second time, small SA doses will help to avoid pH changes in the digestion medium and diminish CO_2 stripping. In this matter, the pH evolution of 5, 10 and 15 g SA L^{-1} pH evolution was mostly a result of the concentration of IC and TAN (NH_4^+/NH_3) in the digester medium, while for 30 g SA L^{-1} the TP ($H_2PO_4^-/HPO_4^{2-}$) concentration also had an important role.

The increase of TP and Mg^{2+} concentration at the beginning of the assay indicated the total and/or partial solubilisation of some SA particles, where TP came mainly from newberyite solubilisation while Mg^{2+} came from both newberyite solubilisation and magnesium oxide hydrolysis (Fig. 2b and c). Furthermore, the profile of the TP and Mg^{2+} concentration confirmed the coexistence of the two struvite precipitation mechanisms suggested by Romero-Güiza et al. [2]: (i) the reaction of the TAN with the newberyite present in the SA particle (Eq. (1)) and (ii) the reaction of the TAN with the TP and Mg^{2+}, released by the newberyite and/or magnesium oxide, in the liquid phase (Eq. (2)) (Fig. 3):

$$MgHPO_4 \cdot 3H_2O_{(S)} + NH^+_{4\,(aq)} + 4H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O_{(S)} + H_3O^+_{(aq)} \qquad (1)$$

$$Mg^{2+}_{(aq)} + HPO_4^{2-}{}_{(aq)} + NH^+_{4\,(aq)} + 7H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O_{(S)} + H_3O^+_{(aq)} \qquad (2)$$

4. Conclusions

The present study evaluated the feasibility of combining anaerobic digestion and struvite precipitation in the same reactor through five different magnesium sources. The addition of $Mg(OH)_2$ as well as the higher dose of the two industrial by-products rich in MgO resulted in a complete breakdown of the anaerobic digestion process; likely due to the increased pH and K^+ concentration, supplied by phosphate source (K_2HPO_4), in the digester medium. $MgCl_2$ and the lower dose of both industrial by-products showed a significant reduction of the methane yield when compared to pig manure (control), but pH remained within neutral values. The latter assays were possibly only inhibited by the increased K^+ concentration. In contrast, no relevant inhibition phenomenon was recorded when the stabilizing agent assays was used as struvite precursor. Results showed the capacity of the stabilizing agent to promote struvite precipitation without causing a significant pH change and/or being inhibitory for anaerobic biomass. The stabilizing agent presented two main advantages over the other magnesium sources: (i) the avoidance of adding the phosphate source directly into the digester medium, and (ii) a low reactivity due to its high content in newberyite. A final series of experiments suggested that when AD and struvite precipitation are combined in a single reactor, stabilizing agent addition should be carried out through several small additions rather than few large doses.

Acknowledgements

The authors would like to thank ACC1Ó and FEDER (VALTEC09-1-0016), as part of the framework “Programa Operatiu de Catalunya”, the Spanish Ministerio de Economía y Competividad (CTM2011-24897) and Magnesitas Navarras S.A. for their support and funding of this research project. The authors are grateful to VAG, S.L. (Valoritzacions Agroramaderes de les Garrigues) for providing samples and sampling facilities.

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Applied Energy 135 (2014) 63–70

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Implementation of a prototypal optical sorter as core of the new pre-treatment configuration of a mechanical–biological treatment plant treating OFMSW through anaerobic digestion

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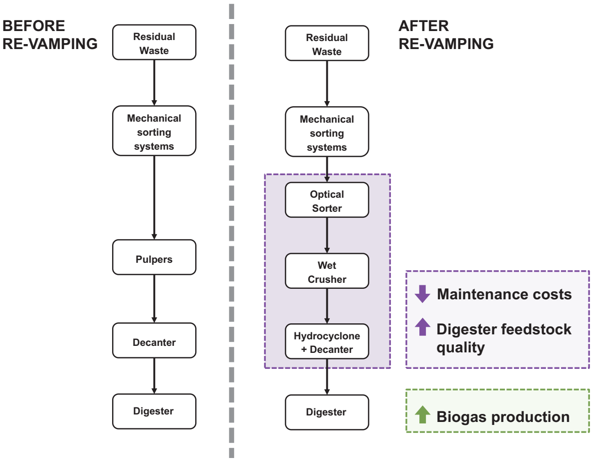
HIGHLIGHTS

- Mechanical–biological treatment plant flowsheet and mass balance are provided.
- A prototypal optical sorter is the core of the new pre-treatment line.
- High level of propionate and H_2S were sorted out during digester star-up.
- The new configuration showed an energy index of 2.2 kW $h_{produced}$/kW $h_{consumed}$.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 May 2014
Received in revised form 7 August 2014
Accepted 18 August 2014

Keywords:
Anaerobic digestion
MSW
Biowaste
Revamping
Pretreatment
Start-up

ABSTRACT

The pre-treatment of the organic fraction of municipal solid waste is one of the main challenges in mechanical–biological treatment plants equipped with anaerobic digesters. The present study shows the successful revamping of the Sant Adrià del Besós plant pre-treatment line, where a prototypal optical sorter, a wet-crusher, and a hydrocyclone–decanter substituted the previous pulper and decanter system. The prototypal optical sorter, which uses near-infrared spectroscopy, was able to enhance the organic matter content from 40% to 60% in a more efficient and less energy demanding way than conventional systems. The new configuration not only improved digester feedstock and performance but also led to a significant reduction of the treatment and maintenance costs. The high methane yield of the digester, between 480 and 580 $CH_4\ m^3\ t^{-1}$ VS, together with an energy efficiency index of 2.2 kW $h_{produced}$/kW $h_{consumed}$, demonstrated the viability of this novel configuration with respect to conventional ones. Thus, optical sorting arises as a new alternative for mechanical–biological treatment plants that needs to be constructed or revamped.

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http://dx.doi.org/10.1016/j.apenergy.2014.08.077
0306-2619/

1. Introduction

Anaerobic digestion (AD) is a globally recognized technology for the treatment of the organic matter present in the municipal solid waste (MSW) [1,2]. Today, this technology can be found in most developed and developing countries. However, it is Europe, with more than 210 plants, where MSW-AD is more developed and implemented [3]. MSW treatment starts with the sorting and collection of MSW, which is designed by local or regional authorities. The organic fraction of MSW (OFMSW) can be collected as [4]: (i) biowaste, which comes from source sorted collection, (ii) mixed waste, which comes from non-source sorted collection, and (iii) residual waste, which is the organic matter remaining after biowaste collection.

The AD of the OFMSW is associated to mechanical–biological treatment (MBT) plants [5]. MTB plants consist of a serie~~s~~ of mechanical pre-processing stages, followed by a biological stage that stabilizes the biodegradable matter under controlled anaerobic and/or aerobic conditions [6]. Even though the design and performance of MBT plants is conditioned by the quality of the received waste, MBT plants are typically divided in the following steps: reception, selection, conditioning of the organic matter, biological stabilization, and products treatment [7]. The current commercial technologies mainly differ on the organic matter conditioning and the anaerobic digestion design, since standard equipment is found in the other steps [8]. Independently of the OFMSW quality, all MBT plants require prior to AD a mechanical pre-treatment to remove undesired compounds from the digester feedstock and enhance digester performance [9,10]. Obviously, the pre-treatment step is more intense in some cases than in others depending on the waste origin and digester design.

The preparation of the organic matter prior AD is one of the main concerns about OFMSW anaerobic digestion at MBT plants. In conventional MBT plants, the sorting of the organic matter is done through a series of physical pre-treatments such as bag openers, trommels, sieves, screw presses, shredders, magnetic sorters, mills and/or pulpers [11]. However, some studies have shown that high amounts of the biodegradable material is rejected during these pre-treatments [12–14]. In some cases, the mechanical selection is not enough to reduce the undesired materials in the digester feedstock and they finish inside the digester not without problematic issues. These problems are especially noticeable in MBT plants treating mixed or residual waste. High levels of undesired materials (i.e. glass, dirt, debris, metals and plastics among others) can led to plant malfunction or even failure due to pipe/equipment wearing and dossing and/or material accumulation in the digester.

To improve the organic matter mechanical selection some equipment and strategies have been developed. For instance, the company Waste Solution Technology has developed a water-based separation process where the incoming waste is processed by soaking, separating, melting and precipitating in order to achieve high separation rates [15]. Another example is the process SORDISEP (sorting, digestion and wet separation), developed by the company Organic Waste Systems. The SORDISEP process applies conventional dry sorting techniques prior waste AD, while the digestate is processed through a wet separation system which aims to recover recyclable products [16]. For biowaste, the company VMpress technologies has developed a pre-treatment called pressure extruder. The system separates the organic matter from the other compounds by pressure exertion, i.e. pushing the waste in a transversal piston over a holey steel plate [17]. As can be observed, a lot of effort is being put into the development of pre-treatments for OFMSW with higher organic matter recovery and reduced maintenance and operation costs. In this vein, near-infrared (NIR) spectroscopy has been proved to be one of the most efficient and advanced tools for continuous monitoring and controlling of process and product quality in food processing industry [18]. However, it has not been until this study that the use of NIR spectroscopy has been applied to OFMSW selection and treatment.

This publication presents the successful implementation of a novel pre-treatment configuration for the revamping of the MBT plant of Sant Adrià del Besós (Barcelona metropolitan area, Spain). The core of the pre-treatment line is a prototypal NIR optical sorter calibrated to separate biodegradable compounds (organic matter, paper and cardboard) from undesired waste compounds. In addition to the pre-treatment line revamping, the paper reports the anaerobic digester start-up and steady-state operation; becoming the unique publication describing the revamping, start-up and steady operation of full-scale AD-MBT plant. Finally, an electricity balance was carried out to analyze the efficiency of the novel configuration.

2. Materials and methods

2.1. Plant configuration

The MBT plant of Sant Adrià del Besós known as ‘‘Mediterranean Ecoparc’’ (Barcelona metropolitan area, Spain), treats about 190,000 tons per year (wet basis) of residual waste from Barcelona and three nearby municipalities [19]. The MBT plant, which is located close to city neighborhoods, was built in 2004 in a reduced area (9000 m^2). These factors influenced the plant configuration and operation, as well as its revamping. The current mechanical pre-treatment line consists of reception storage, hand-sorting cabins, dual trommel, vibrating screen, magnetic sorting, and optical sorting. The optical sorter Mistral vision by PELLENC ST utilizes NIR spectroscopy to separate biodegradable compounds from the undesired compounds regardless of its color and shape [20–22]. The sorter was configured to perform an upward air ejection (i.e. ejecting the desired compounds), which is the preferred configuration when contamination wants to be avoided (e.g. rolling and not properly ejected materials). NIR spectroscopy is based on the absorption of electromagnetic radiation at wavelengths between 780 and 2500 nm. Specifically, organic matter NIR spectra comprise broad bands arising from overlapping absorptions corresponding mainly to overtones and combinations of vibrational modes involving C–H, O–H, and N–H chemical bonds [18]. The organic rich stream from the optical sorter is derived to the biological treatment, where some other pre-treatments (i.e. wet-crusher, hydrocyclone–decanter system and feeding tank) are carried out to refine the AD feedstock. The wet AD is carried out in a 5200 m^3 continuous stirred tank reactor (CSTR). The digester medium is mixed by both high pressure biogas injection, which is distributed at the bottom of the digester through a series of stainless steel injectors, and pump recirculation. The biogas generated is stored in a gasometer and burned in three combined heat and power (CHP) units (1.3 MW h per unit). The digester effluent is separated into a solid fraction (cake), which is sent to a composting plant, and a liquid fraction (centrate), which is recirculated to the wet-crusher in order to dilute the digester feedstock.

2.2. Analytical methods

Total solids (TS), volatile solids (VS) were determined following the standard methods procedure 2540G [23] with minor modifications [24]. pH was determined using a Crison 5014T pH probe. Volatile fatty acids (VFAs) (acetate, propionate, butyrate and valerate) were analyzed by a HP 5890-Serie II chromatograph equipped with a capillary column (Nukol™) and flame ionization detector [25]. The biogas composition was analyzed by a Shimadzu GC-2010+

gas chromatograph equipped with a capillary column (Carboxen®-1010 PLOT) and a thermal conductivity detector [26].

The waste characterization analyses (classification of the different waste compounds) of the different MBT plant streams were done from a representative subsample (1–1.5 kg) of the bulk sample (5–7 kg). The subsample was a mixture of different aliquots obtained after properly mixing and dividing the bulk sample using the coning and quartering method.

2.3. Biomethane potential test

Biomethane potential (BMP) tests were carried out at 37 °C following the stages defined by Angelidaki et al. [27]. The tests were performed in 250 mL serum bottles, closed hermetically with PTFE/Butyl septa and plastic screw caps. The bottles were filled with: (i) 150 mL of inoculum from a mesophilic sewage sludge digester; (ii) the amount of substrate that met an inoculum to substrate ratio of 2 (VS-basis); and (iii) deionized water, used to adjust the same effective volume for all tests (200 mL). Blank controls, filled only with inoculum and water, were performed to determine the background effect of the inoculum. The biogas production was calculated from the pressure in the headspace volume by using a vacuometer (Ebro – VAM 320). Biogas production is reported at standard conditions (0 °C, 1 bar) and error bars indicate 95% confidence in the average of the quadruplicate.

3. Results and discussion

3.1. Revamping strategy

The Mediterranean Ecoparc was designed with a maximum operational capacity of 260,000 t y^{-1} (wet basis) of residual waste; nonetheless, it normally treats 190,000 t y^{-1} (wet basis). The residual waste that receives the plant is composed, as an average, of: 30% organic matter (food, kitchen and yard waste), 35% recyclable material (some plastics, ferrous and non-ferrous metals and glass), and 35% refusal material (bulky goods, dirt, some plastics, clothing, wood, building waste, household hazardous waste and other miscellaneous wastes). The initial plant configuration consisted of a mechanical sorting system (i.e. reception storage, hand-sorting cabins, dual trommel, magnetic sorting and vibrating screen) to recover recyclable materials and to obtain a rich organic stream for AD. The organic stream was further processed through pulper systems and a decanters before the single-stage AD, which was carried out at wet conditions (2–3% TS). With this configuration, the plant showed low biogas yields and several operational problems linked to the undesired materials in the organic matter stream. The major problems were the accumulation of compounds into the pulpers walls and in the anaerobic digester bottom, which provoked pump and pipes blockages and continuous damages into the equipment. After some months of operation, the accumulation of compounds (mainly inorganic) at the bottom of the digester caused continuous damages to the equipment which increased the treatment costs until unfeasible. Consequently, the biological step was stopped and re-designed.

The pulper systems have demonstrated good performance at MBT plants treating biowaste [28]. However, at MBT plants handling residual waste, where the income waste contains larger amounts of undesired compounds along with lower contents of organic matter than biowaste, the pulper systems have shown poorer performances. Bernstad et al. [12], who compared different mechanical pre-treatments to separate organic household waste in full-scale facilities, reported that pulpers problems were related to the poor organic stream quality and high maintenance costs. Consequently, it was necessary to seek for a new sorting solution able to provide a better quality organic stream. Several alternatives (e.g. rotary drum reactors and new pulper design) were proposed. However, the R&D department proposed the replacement of the pulper system by a new sorting system composed of an optical sorter, a wet-crusher and a hydrocyclone–decanter device, which was able to enhance the quality of the organic stream, comply with the space limitations of the plant, and adjust to the investment capacity of the company.

Fig. 1 shows the current MBT plant configuration (the box indicates the new equipment). The core of the new configuration is the prototypal optical sorter, which classifies the stream from the vibrating stream into biodegradable (organic matter and paper) and non-biodegradable materials. The biodegradable stream is then transferred into a wet-crusher, which aims to reduce the organic matter particle size and adjust the feedstock concentration. The water used to dilute the feedstock is supernatant from centrifugation of digester effluent. The wet-crusher also generates a refusal stream, mainly formed of textile fibers and other light materials. Finally, the organic matter stream passes through the hydrocyclone–decanter system, which is able to remove heavy compounds (e.g. metals, glass and dirt) reducing the equipment and piping damage. As a general trend, the objective for the optical

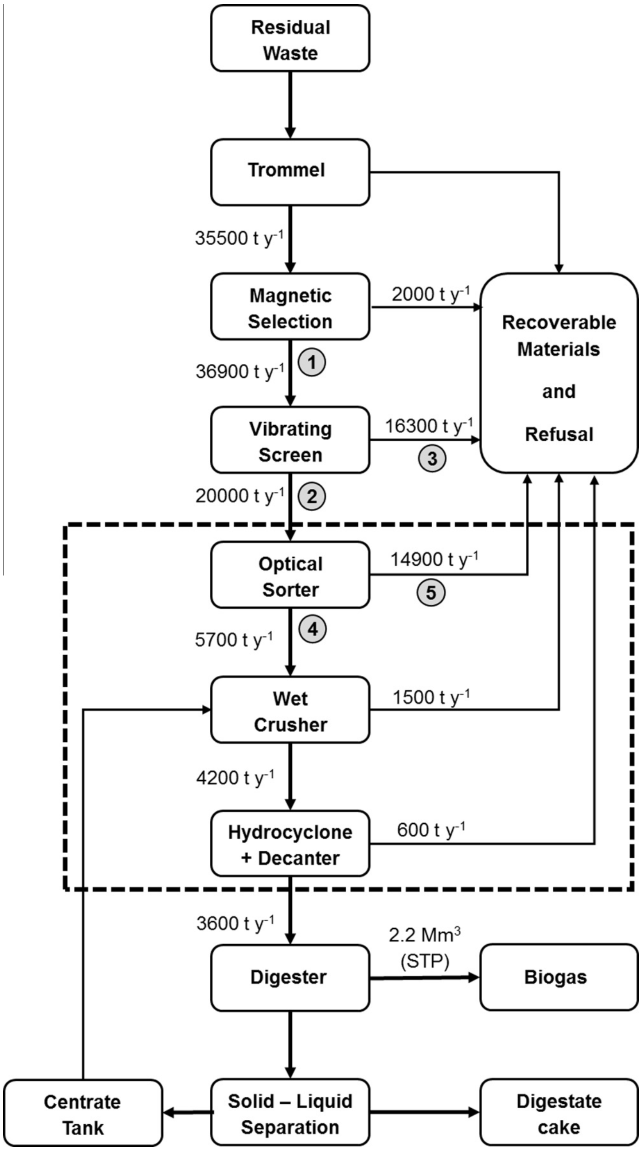

Fig. 1. Flowsheet of the Mediterranian Ecoparc (flows in dry basis).

sorter and the hydrocyclone–decanter is to reduce the amount of undesired material in the digester feedstock, while the wet-crusher main goal is to improve its mechanical and physical properties (e.g. rheology, homogeneity and heat transfer).

Table 1 shows the composition of the relevant streams of the MBT plant pointed out in Fig. 1. As can be observed, the trommel system, the hand-sorting and the magnetic selection are able to procure a stream (flow 1) with a high content of biodegradable matter (39% organic matter and 26% paper and cardboard). Flow 1 is driven to the vibrating screen, which represent the first physical selection fully devoted to improve the digester feedstock. The vibrating screen (30 mm mesh, square holes) shows high efficiencies (~70%) in removing undesired compounds (dirt, glass, debris, textile and metals); nonetheless, high quantities of biodegradable matter are also lost in this step. It should be noted that the configuration of the vibrating screen is a compromise between undesired compounds removal efficiency and organic matter losses. The refusal of the vibrating screen (flow 3) is sent to energy recovery, while the organic stream (flow 2) is moved to the optical sorter. The optical sorter consists of a NIR detection system able to separate biodegradable organic matter from undesired compounds. The optical sorted configuration was optimized to include some kind of paper (tissue and recycled) and remove other kind, especially cardboard, from the digester feedstock. With the selected configuration, the refusal of the optical sorter (flow 5) is mainly composed of cardboard, other papers, glass and textile. The main advantage of the optical sorter is its ability to generate a rich biodegradable stream (flow 4) along with low organic matter losses (~30%). The organic stream coming out the optical sorter is driven to a wet-crusher and afterwards to a hydrocyclone–decanter device. Finally, the digester feedstock is shortly stored in the feeding tank before being pumped into the AD.

The overall mass balance of the MBT plant shows that about 13,000 t y^{-1} (wet basis) of the biodegradable matter entering the plant is treated through AD. This values is in agreement with most MBT plants [29], where most of the organic matter ends in the reject fraction together with undesired compounds [13]. In this particular case, the residual waste contains a low percentage of biodegradable matter, which is frequently attached to undesired compounds. Despite the organic losses, the new pre-treatment line has clearly shown a better performance than the previous one.

3.2. Biomethane potential test results

The biodegradable matter entering the digester is composed by organic matter (70%) and paper and cardboard (30%). Fig. 2A shows the profile of the biogas production of both organic matter and paper and cardboard hand-separated from the organic stream derived from the optical sorter and prior its crushing. The organic matter presented a higher specific biogas production (870 m^3 biogas t^{-1} VS$_{fed}$) than paper and cardboard (600 m^3 biogas t^{-1} VS$_{fed}$). Although the paper and cardboard presented a lower biodegradability, the obtained values highlight their feasibility as anaerobic substrates. Fig. 2B shows the specific biogas production of four different feedstock samples (crushed samples). The samples, due to its heterogeneity, presented a specific biogas production between 660 and 780 m^3 biogas t^{-1} VS$_{fed}$. As expected, the feedstock specific biogas potential was between the organic matter and the paper and cardboard one. Nevertheless, the values were somehow lower than the expected considering the proportion between organic matter and paper and cardboard. This may be related to the heterogeneity of the sample as well as the contribution of non-biodegradable compounds to the VS quantification (especially plastics).

The effect of the particle size reduction in the process kinetics can be assessed by comparing the slope of the biogas production in Fig. 2A (without crushing) and B (wet-crushed). However, by adjusting the profile to a first-order kinetics model, it is possible to determine the disintegration constant of each sample. Paper and cardboard as well as organic matter without crushing presented a disintegration constant of 0.06 ± 0.01 d^{-1}, while the crushed samples presented a disintegration constant of 0.16 ± 0.02 d^{-1}. These values clearly show that particle size reduction led to higher biodegradation kinetics. Actually, 65% of the particles from the wet-crusher had a particle size lower than 2 mm. It is well known

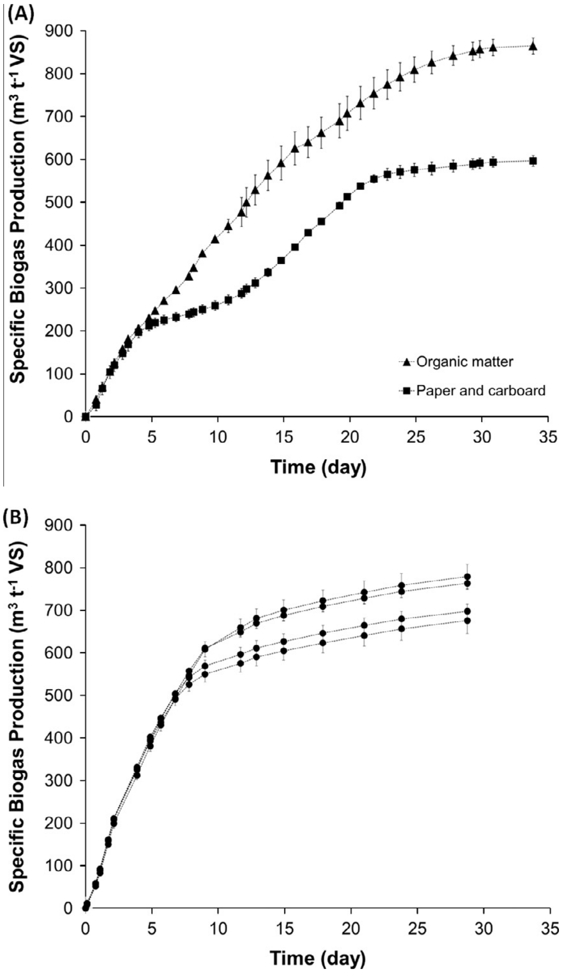

Fig. 2. Specific biogas production for (A) organic matter and paper and cardboard and (B) four digester feedstock crushed samples.

Table 1
Average characterization of the different streams shown in Fig. 1 (% wet basis).

Flow	1	2	3	4	5
Organic matter	38.9	39.0	37.7	60.0	23.4
Paper and cardboard	26.2	38.7	11.3	25.6	48.7
Dirt[a]	13.6	4.8	23.2	4.9	4.7
Glass	8.6	8.2	8.8	1.6	13.2
Debris	4.8	2.2	7.6	2.5	2.0
Plastic packages	1.3	2.6	0.2	1.0	3.8
Textile	1.4	0.6	2.3	1.0	0.3
Ferrous metals	1.5	–	3.2	–	–
Non-ferrous metals	0.4	1.4	0.8	0.1	2.4
Plastic wrap & bags	0.6	0.1	1.1	0.2	–
Wood	0.2	0.8	0.5	1.2	0.5
Others	2.5	1.6	3.4	1.9	1.4
Flow t y^{-1} (wet basis)	78,000	40,400	37,600	14,900	25,500
Flow t y^{-1} (dry basis)	36,900	20,000	16,300	5700	14,900
TS g L^{-1}	47.3	49.6	43.3	38.1	58.5
VS g L^{-1}	25.0	30.1	18.5	24.8	34.2

[a] Dirt include clay, sand, silt and ceramics among others.

that particle size reduction increases the surface area available to the microorganisms and therefore, it makes organic matter more bioaccessible, which results in a higher degradation kinetics and, sometimes, biogas yield [5,11,30].

3.3. Digester start-up

As soon as the new pre-treatment units were optimized, the digester operation was started. The digester, operated at 37 °C, was inoculated with 600 m^3 of digested sewage sludge from a wastewater treatment plant of the Barcelona metropolitan area. The digester feeding during the first 90 days was realized according to Fig. 3A. As a general trend, the feeding was progressively increased from 50 up to 200 m^3 per day until the volume inside the digester reached 4500 m^3 (85% of the full capacity). During the first 15 days, the feeding ranged between 50 and 80 m^3 day^{-1}, which represented an organic load between 0.5 and 4.0 t VS d^{-1} (Fig. 3B). At day 15, when the digester volume reached 1000 m^3, the methane concentration in the biogas was 50% (Fig. 3C); nonetheless, the gas pressure was not enough to fill the gasometer. At the same time, the digester presented complications related to high H_2S concentration in the biogas (up to 1900 ppm) and high VFA concentration in the digester medium (Fig. 3D and E).

The H_2S in the biogas was result of the dissolved sulfides present in the digester medium, which came from sulfate reduction by sulfate reducing bacteria. H_2S is toxic, can damage most equipment and smells bad [31]. Moreover, H_2S is inhibitory for anaerobic biomass. It is known that inhibition by sulfide can happen in two stages: the primary inhibition comes from the competition for common organic and inorganic substrates between sulfate reducing bacteria and methanogenic archaea, which decreases the methane production; and, the secondary inhibition results from the toxicity of sulfide to various microbial groups [32]. The inhibitory sulfide levels reported in the literature range between 100 and 800 ppm for ionized hydrogen sulfide and between 50 and 400 ppm for the unionized form [33,34]. The strategy used to remove H_2S from the gas and the liquid phase was to dose a solution of $FeCl_3$ (40% by mass) to precipitate FeS [35]. Thereafter, an average of 6.5 kg of $FeCl_3$ solution per ton of organic matter fed (wet basis) were dosed into the digester medium. After $FeCl_3$ dosing, the H_2S concentration dropped from 1900 to 50 ppm in 5 days (15th–20th day), which was accompanied by a subsequent drop of the propionic acid concentration from 2800 to 100 mg L^{-1} (Fig. 3D and E). Despite these facts, no remarkable change on pH values was recorded. Between day 30 and 50, the digester presented another increase of the H_2S concentration likely due to the higher feeding volume; however, no accumulation of VFA was observed. It is worth to highlight that accumulation of VFA in the digester medium, especially propionic, can lead the digester failure. Actually, propionic acid evolution has been suggested as a key parameter

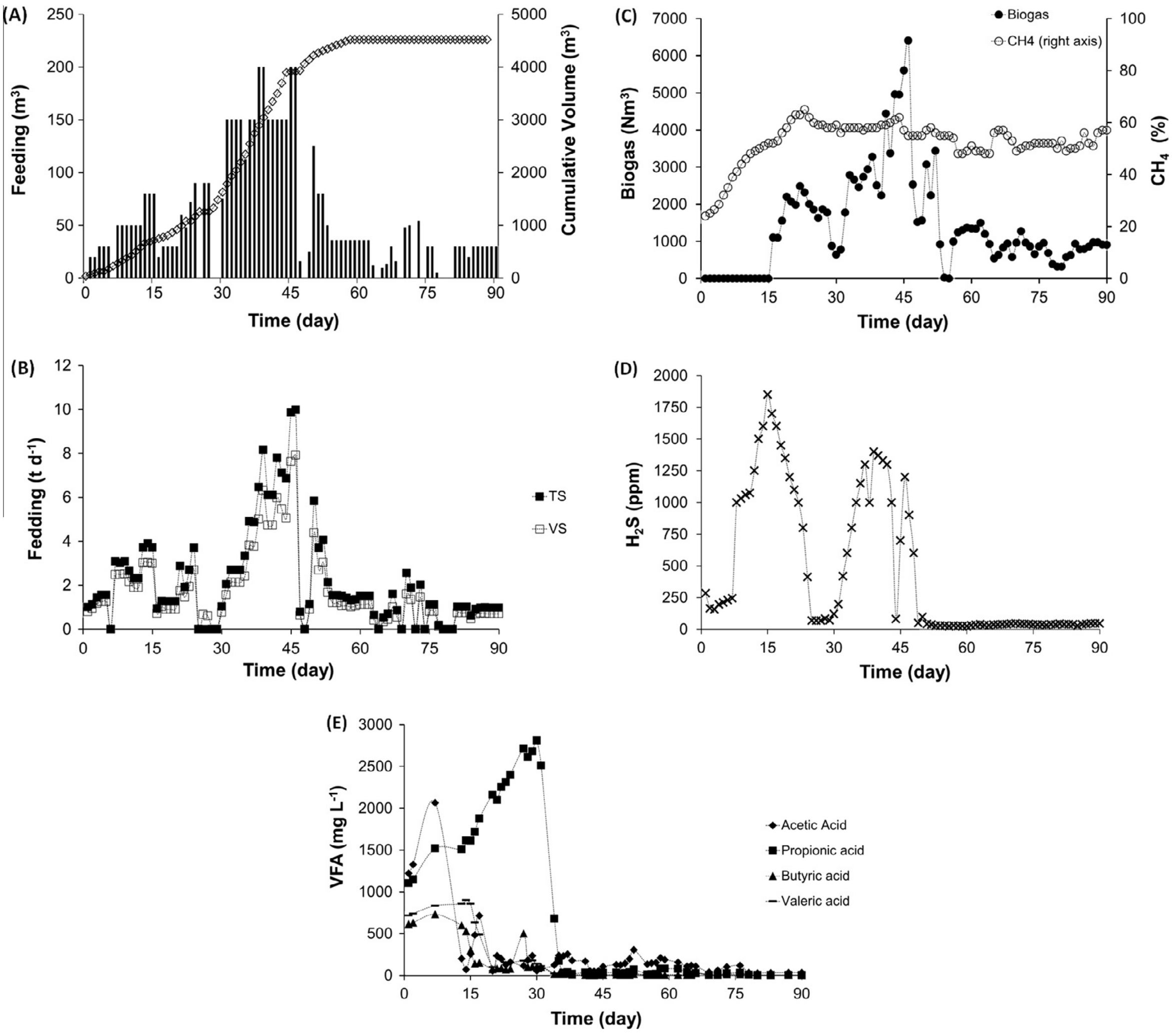

Fig. 3. Start-up monitoring. (A) Feeding (bars, left axis) and cumulative volume (◇, right axis); (B) feeding TS and VS; (C) biogas production and its methane content; (D) H_2S in the biogas and (E) VFA concentration.

to be followed when recovering or restarting anaerobic digesters [36].

At the 60th day, the digester was completely filled (4500 m^3) (Fig. 3A). With the full working capacity completed, the digester was fed with about 40 t d^{-1}, which was 20% less than the planned working load. The lower loading rate was decided with the aim of reducing overloading risk and procuring favorable conditions for biomass adaptation [37]. It should be noted that the start-up and stabilization of OFMSW digesters require long time periods because the inoculum employed is no fully adapted to the waste and the digester operation conditions [38]. During the next 30 days (60th–90th), the digester biogas production averaged 800 Nm^3 per day (methane concentration 50–58%), while no remarkable accumulation of VFAs or H_2S were observed. H_2S levels in the biogas were controlled by adding $FeCl_3$ into the digester medium. Whereby, the star-up period was considered to be concluded and the steady-state operation begun.

3.4. Digester steady-state operation

In the first year of operation at steady-state conditions, the digester was operated with a HRT of 20–40 days and an OLR of 0.2–2.6 kg VS m^{-3} d^{-1}, respectively (Fig. 4A). The variability of the digester OLR is linked to the social and cultural dynamic of its location, which causes periods of maximum and minimum waste treatment. These dynamics can affect the correct performance of the digester and sometimes led to digester failure, specifically by OLR excess [39]. In this first operation year, the maximum OLR was 2.6 kg VS m^{-3} d^{-1} (December–January), which never exceeded the maximum design value (4.0 kg VS m^{-3} d^{-1}) (Fig. 4A). Regarding the digester performance, it can be observed that the digester reached the maximum specific methane production (SMP) at the end of the start-up period (Fig. 4). The high SMP was consequence of the depletion of the biodegradable matter accumulated in the digester during the filling period, as well as the lower OLR of this period, which allowed a larger degradation of the waste. After the start-up period, the digester was operated without any significant disturbances during six months (90th–270th day), which allowed to monitor digester steady-state operation. During this period of time, the OLR and the HRT varied between 0.8 and 1.7 kg VS m^{-3} d^{-1}, and between 20 and 40 days, respectively, while the digester SMP ranged from 480 to 580 m^3 CH_4 t^{-1} VS. During this period of time, the good digester performance was also reflected by the stable digester pH (7.3–7.9) and VFA concentration (40–200 mg L^{-1}). Later on, a failure of the feeding pump caused a temporary reduction of the digester OLR from 1.5 to 0.2 kg VS m^{-3} d^{-1}. Afterwards, the digester ORL was increased from 0.2 to 2.6 kg VS $m^{-3}d^{-1}$ with no significant effect over digester performance. Although the SMP (410–510 m^3 CH_4 t^{-1} VS) of this latter period was slightly lower than the previous ones, difference may be related to the slightly lower HRT, which may had caused a reduction of the substrate biodegradation capacity and biogas production.

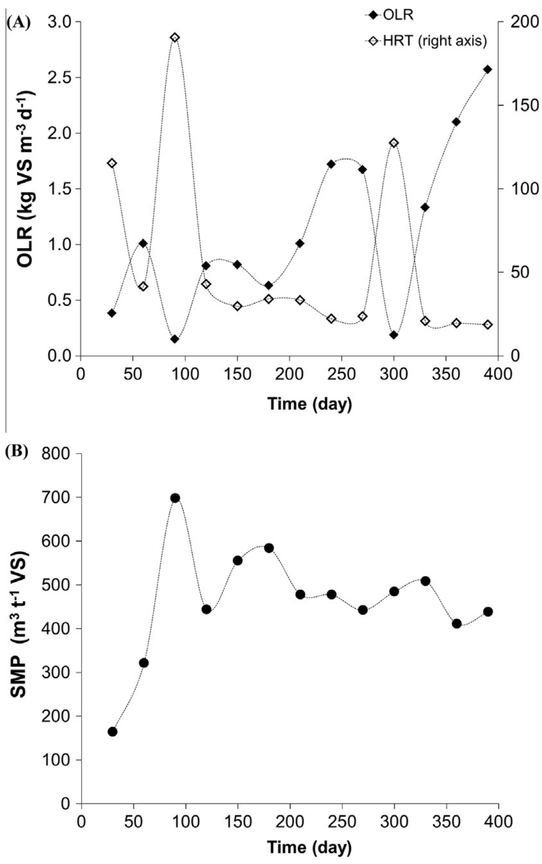

Fig. 4. Digester performance during the first operation year. (A) OLR and HRT and (B) Specific methane production.

The comparison of the digester performance with other reported full-scale MBT plants (Table 2) shows that the HRT of the Mediterranian Ecoparc is within the average operational conditions, whereas the OLR is in the low range. Regarding the methane yield, the values recorded in this MBT plant (480 and 580 m^3 CH_4 t^{-1} VS) were higher than previously reported plants, which SMP ranges between 140 and 400 m^3 CH_4 t^{-1} VS. The higher methane yield of the studied plant may be related to the higher quality of the digester feedstock achieved through the optical sorter, the relatively low OLR, and the faster degradation kinetics provided by the wet-crusher particle size reduction.

3.5. Economic and energetic considerations

To assess the economic feasibility of the new pre-treatment line an electricity balance was carried out since other expenses were negligible (e.g. water and fuel). The calculation of the electricity balance comprises the major forms of energy produced and consumed. The electricity consumption considered all pre-treatments units as well as digester pumping and stirring, while the only source of electricity is the one produced by the combustion of the biogas in a CHP unit. The CHP units have an efficiency index of 0.4 for electricity generation. Considering the nominal potential and the time consumed for each pre-treatment stage and digester equipment, the energy consumption of the renovated pre-treatment line during the first year of operation was estimated as 3650 MW h. On the other hand, the energy recovered through biogas combustion was 8150 MW h (value obtained by the power converter), which led to an energy efficiency index of 2.2 kW $h_{produced}$/kW $h_{consumed}$. Compared to Bassano MBT plant [40], the energy efficiency of the Mediterranian Ecoparc is lower than the line processing biowaste (4.3 k W $h_{produced}$/kW $h_{consumed}$) but higher than the line treating mixed waste (1.4 kW $h_{produced}$/kW $h_{consumed}$). Although the literature data is scarce, the comparison between the energetic efficiency index of the Mediterranian Ecoparc and the Bassano's mixed waste treatment line indicates the energetic advantage of the prototypal pre-treatment configuration in comparison with the traditional one. Moreover, the chosen revamping design (optical sorter and wet-crusher) was the most economically feasible option, since the economical investment was 70% lower than the other considered alternatives (e.g. new pulpers and pressure extruder). Even more, when compared to the previous pre-treatment configuration, the new implementation has shown a 27% and 50% reduction of the treatment and

Table 2
Specific methane production reported in some full-scale MTB plants.

Plant	Residual	Digestion	Temperature (°C)	OLR (kg VS m^{-3} d^{-1})	HRT (day)	SMP (m^3 CH_4 t^{-1} VS)	Reference
Amiens	Biowaste	Dry	37	–	–	205	[41]
Barcelona	Residual Waste	Wet	37	0.8–1.7	20–40	440–580	This study
Bassano	Biowaste	Dry	39	4–6	40–60	400	[40]
Bassano	Mixed Waste	Dry	37	3–8	50–70	140	[40]
Engelkriche	Biowaste	Dry	37	–	–	280	[41]
Perth	Mixed Waste	Dry	55	–	12	440[a]	[42]
South Shropshire	Biowaste	Wet	42	2.5	80	402	[43]
Tilburg	Biowaste	Dry	37	–	–	225	[41]
Toronto	Biowaste	Wet	37	5	17	377	[44]
Verona	Mixed waste	Semi-dry	55	1.2		160	[45]

[a] Expressed in m^3 biogas t^{-1} VS.

maintenance cost, respectively, which together with the increase of the biogas production have significantly increased the plant economic viability.

4. Conclusions

The accumulation of undesired materials from the organic fraction of municipal solid waste caused low biogas yields and operational problems to the mechanical–biological treatment plant of Sant Adrià del Besós. Accordingly, a new pre-treatment line was implemented to improve the quality of the anaerobic digestion feedstock. The novel pre-treatment line is equipped with a: (i) prototypal optical sorter, which classifies the stream from the vibrating stream into biodegradable and non-biodegradable materials, (ii) a wet-crusher, which improves the feedstock mechanical and physical properties, and (iii) a hydrocyclone–decanter, which removes heavy compounds. During anaerobic digester start-up, which lasted 90 days, the system presented difficulties related to the accumulation of H_2S in the biogas and propionic acid in the digester medium. The former was diminished by the addition of a $FeCl_3$ solution; while the latter was reduce by the digester microbial activity. During steady-state operation, the digester showed high methane yields (from 480 to 580 m^3 CH_4 t^{-1} VS) and no remarkable operational problems. Finally, an energy efficiency index of 2.2 kW $h_{produced}$/kW $h_{consumed}$ proved the viability of this novel configuration with respect to conventional ones.

Acknowledgments

The authors are grateful to CESPA, S.A. and the Ecoparc del Mediterrani, S.A. for the support and funding of this project. The authors are also thankful to Cristian Velasco Granero for helping in sample collection and process monitoring.

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