Universitat de Girona

SBR TECNOLOGY FOR WASTEWATER TREATMENT: SUITABLE OPERATIONAL CONDITIONS FOR A NUTRIENT REMOVAL

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ISBN: 84-689-0880-0
Dipòsit legal: GI-121-2005

Universitat de Girona

UdG lequia
Laboratori d'Enginyeria Química i Ambiental

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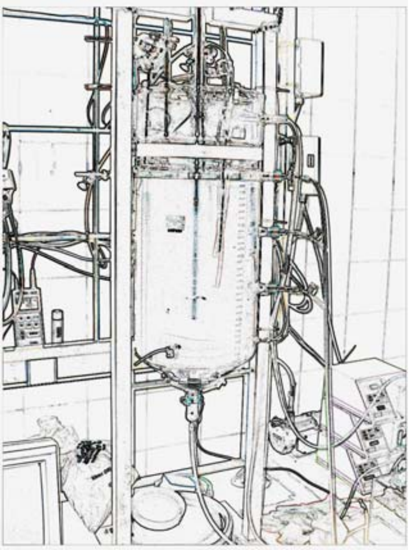
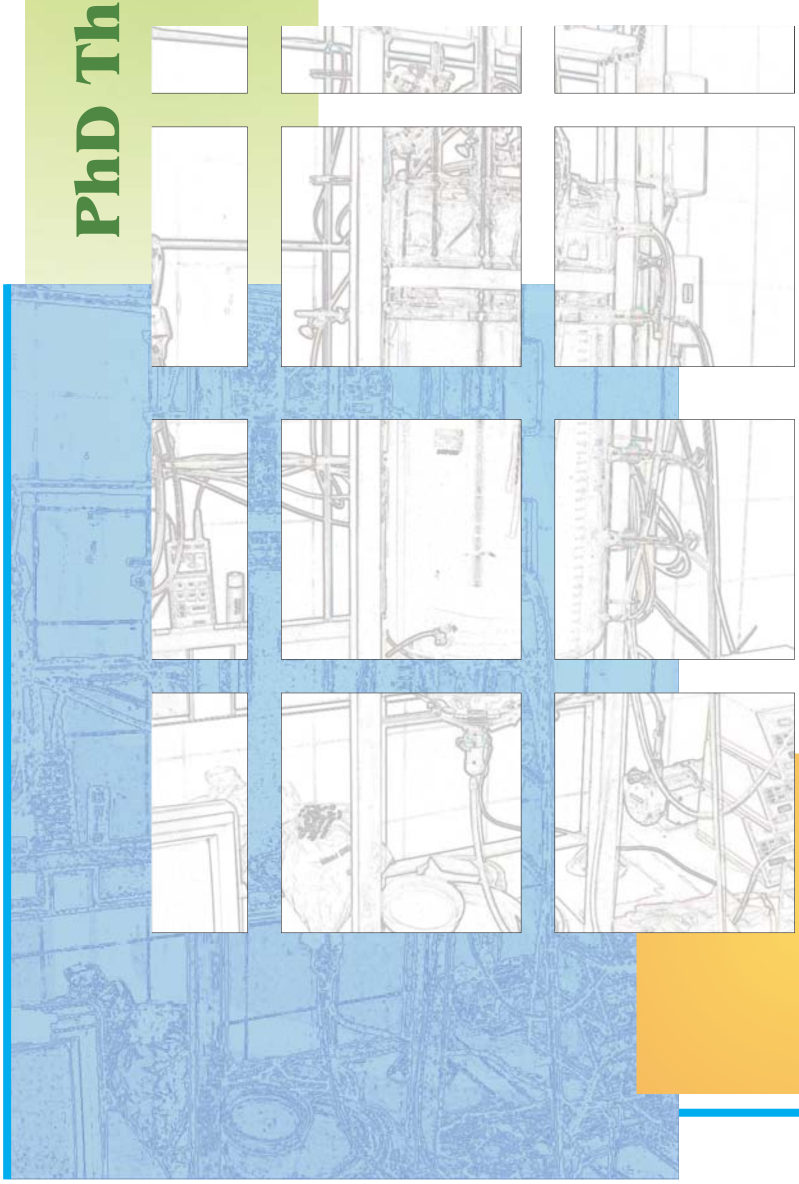
suitable operational conditions for nutrient removal

PhD Thesis - 2004





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DEPARTAMENT D'ENGINYERIA QUÍMICA, AGRÀRIA I

TECNOLOGIA AGROALIMENTÀRIA

LABORATORI D'ENGINYERIA QUÍMICA I AMBIENTAL

TESI DOCTORAL

SBR TECHNOLOGY FOR WASTEWATER TREATMENT:

SUITABLE OPERATIONAL CONDITIONS FOR A NUTRIENT REMOVAL

Memòria presentada per Mª Teresa Vives Fàbregas

per optar al títol de Doctor Medi Ambient per la Universitat de Girona.

Girona, setembre de 2004

Mª DOLORS BALAGUER CONDOM I JESÚS COLPRIM GALCERAN, Professors d'Enginyeria Química del Departament d'Enginyeria Química, Agrària i Tecnologia Agroalimentària (EQATA) de la Universitat de Girona,

CERTIFIQUEN:

Que la llicenciada Mª Teresa Vives Fàbregas ha dut a terme, sota la seva direcció, el treball que, amb el títol *"SBR technology for wastewater treatment: suitable operational conditions for a nutrient removal"*, presenta en aquesta memòria, la qual constitueix la seva Tesi per optar al Grau de Doctor Medi Ambient.

I perquè en prengueu coneixement i tingui els efectes que correspongui, presentem davant la Facultat de Ciències de la Universitat de Girona l'esmentada Tesi i signem aquest certificat.

Girona, setembre del 2004.

Mª Dolors Balaguer Condom　　　　　　Jesús Colprim Galceran

FINANCIAL SUPPORT

This thesis has been financed through the companies CIDA HIDROQUÍMICA SA from 1999 to 2001, CESPA GR from 2001 to 2002 and INIMA Servicios de Medio Ambiente (Grupo OHL) from 2002 to 2004, and the *Spanish Government* (MCYT-DPI-2002-04579-C02-02).

The author would like to thank the different kind of financial support during this thesis.

RESUM

Actualment, la legislació ambiental ha esdevingut més restrictiva pel que fa a la descàrrega d'aigües residuals amb nutrients, especialment en les anomenades àrees sensibles o zones vulnerables. Arran d'aquest fet, s'ha estimulat el coneixement, desenvolupament i millora dels processos d'eliminació de nutrients.

El Reactor Discontinu Seqüencial (RDS) o Sequencing Batch Reactor (SBR) en anglès, és un sistema de tractament de fangs actius que opera mitjançant un procediment d'omplerta-buidat. En aquest tipus de reactors, l'aigua residual és addicionada en un sol reactor que treballa per càrregues repetint un cicle (seqüència) al llarg del temps. Una de les característiques dels SBR és que totes les diferents operacions (omplerta, reacció, sedimentació i buidat) es donen en un mateix reactor.

La tecnologia SBR no és nova d'ara. El fet, és que va aparèixer abans que els sistema de tractament continu de fangs actius. El precursor dels SBR va ser un sistema d'omplerta-buidat que operava en discontinu. Entre els anys 1914 i 1920, varen sorgir certes dificultats moltes d'elles a nivell d'operació (vàlvules, canvis el cabal d'un reactor a un altre, elevat temps d'atenció per l'operari...) per aquests reactors. Però no va ser fins a finals de la dècada dels '50 principis del '60, amb el desenvolupament de nous equipaments i noves tecnologies, quan va tornar a ressorgir l'interès pels SBRs. Importants millores en el camp del subministrament d'aire (vàlvules motoritzades o d'acció pneumàtica) i en el de control (sondes de nivell, mesuradors de cabal, temporitzadors automàtics, microprocessadors) han permès que avui en dia els SBRs competeixin amb els sistemes convencional de fangs actius.

L'objectiu de la present tesi és la identificació de les condicions d'operació adequades per un cicle segons el tipus d'aigua residual a l'entrada, les necessitats del tractament i la qualitat desitjada de la sortida utilitzant la tecnologia SBR. Aquestes tres característiques, l'aigua a tractar, les necessitats del tractament i la qualitat final desitjada determinen en gran mesura el tractament a realitzar. Així doncs, per tal d'adequar el tractament a cada tipus d'aigua residual i les seves necessitats, han estat estudiats diferents estratègies d'alimentació.

El seguiment del procés es realitza mitjançant mesures on-line de pH, OD i RedOx, els canvis de les quals donen informació sobre l'estat del procés. Alhora un altre paràmetre que es pot calcular a partir de l'oxigen dissolt és la OUR que és una dada complementària als paràmetres esmentats.

S'han avaluat les condicions d'operació per eliminar nitrogen d'una aigua residual sintètica utilitzant una estratègia d'alimentació esglaonada, a través de l'estudi de l'efecte del nombre d'alimentacions, la

definició de la llargada i el número de fases per cicle, i la identificació dels punts crítics seguint les sondes de pH, OD i RedOx.

S'ha aplicat l'estratègia d'alimentació esglaonada a dues aigües residuals diferents: una procedent d'una indústria tèxtil i l'altra, dels lixiviats d'un abocador. En ambdues aigües residuals es va estudiar l'eficiència del procés a partir de les condicions d'operació i de la velocitat del consum d'oxigen. Mentre que en l'aigua residual tèxtil el principal objectiu era eliminar matèria orgànica, en l'aigua procedent dels lixiviats d'abocador era eliminar matèria orgànica i nitrogen.

S'han avaluat les condicions d'operació per eliminar nitrogen i fòsfor d'una aigua residual urbana utilitzant una estratègia d'alimentació esglaonada, a través de la definició del número i la llargada de les fases per cicle, i la identificació dels punts crítics seguint les sondes de pH, OD i RedOx.

S'ha analitzat la influència del pH i la font de carboni per tal d'eliminar fòsfor d'una aigua sintètica a partir de l'estudi de l'increment de pH a dos reactors amb diferents fonts de carboni i l'estudi de l'efecte de canviar la font de carboni.

Tal i com es pot veure al llarg de la tesi, on s'han tractat diferents aigües residuals per a diferents necessitats, un dels avantatges més importants d'un SBR és la seva flexibilitat.

RESUMEN

Actualmente, la legislación ambiental se ha convertido más restrictiva por lo que concierne al vertido de aguas residuales con nutrientes, especialmente en las llamadas áreas sensibles o zonas vulnerables. A partir de este hecho, se ha estimulado el conocimiento, desarrollo y mejora de los procesos de eliminación de nutrientes.

El Reactor Discontinuo Secuencial (RDS) o Sequencing Batch Reactor (SBR) en inglés, es un sistema de tratamiento de fangos activados que opera mediante un procedimiento de llenado-vaciado. En este tipo de reactores, el agua residual es adicionada en un solo reactor que trabaja por cargas repitiendo un ciclo (secuencia) a lo largo del tiempo. Una de les características de los SBR es que todas las diferentes operaciones (llenado, reacción, sedimentación y vaciado) se dan en el mismo reactor.

La tecnología SBR no es nueva. De hecho, apareció antes que el sistema de tratamiento continuo de fangos activados. El precursor de los SBR fue un sistema de llenado-vaciado que operaba en discontinuo. Entre los años 1914 y 1920, surgieron ciertas dificultades muchas de ellas a nivel de operación (válvulas, cambios de caudal de un reactor a otro, elevado tiempo de atención por parte del operario...) para estos reactores. Pero no fue hasta finales de la década de los ‘50 principios de los ’60, con el desarrollo de los nuevos equipamientos y las nuevas tecnologías, cuando volvió a resurgir el interés en los SBRs. Importantes mejoras en el campo de los suministro de aire (válvulas motorizadas o de acción neumática) y en el de control (sondas de nivel, medidores de caudal, temporizadores automáticos, microprocesadores) han permitido que hoy en día los SBRs compitan con los sistemas convencionales de fangos activados.

El objetivo de la presente tesis es la identificación de las condiciones de operación adecuadas para un ciclo según el tipo de agua residual en la entrada, las necesidades del tratamiento y la calidad deseada de la salida utilizando la tecnología SBR. Estas tres características, el agua a tratar, las necesidades del tratamiento y la calidad final deseada determinan en gran medida el tratamiento a realizar. Así pues, para poder adecuar el tratamiento a cada tipo de agua residual y a sus necesidades, han sido estudiados diferentes estrategias de alimentación.

El seguimiento de los cambios de las medidas en línea de pH, OD y RedOx proporciona información sobre el proceso. A su vez, otro parámetro que se puede calcular a partir del OD es la OUR que también da información del proceso.

Se han evaluado las condiciones de operación para eliminar nitrógeno de una agua residual sintética utilizando una estrategia de alimentación escalonada, a partir del estudio del efecto del número de alimentaciones, la definición de la longitud y el número de fases por ciclo, y la identificación de los puntos críticos siguiendo las sondas de pH, OD y RedOx.

Se ha aplicado la estrategia de alimentación escalonada a dos aguas residuales diferentes: una procedente de una industria textil y la otra, de los lixiviados de un vertedero. En las dos aguas residuales se estudió la eficiencia del proceso a partir de las condiciones de operación y de la velocidad de consumo de oxigeno. Mientras que en el agua residual textil el principal objetivo era eliminar materia orgánica, en el agua procedente de los lixiviados del vertedero era eliminar materia orgánica y nitrógeno.

Se han evaluado las condiciones de operación para eliminar nitrógeno y fósforo de una agua residual urbana utilizando una estrategia de alimentación escalonada, a partir del estudio de la definición de la longitud y el número de fases por ciclo, y la identificación de los puntos críticos siguiendo las sondas de pH, OD y RedOx.

Se han analizado la influencia del pH y la fuente de carbono para eliminar fósforo de un agua sintética a partir del estudio del incremento de pH en dos reactores con diferentes fuentes de carbono y el estudio del efecto de cambiar la fuente de carbono.

Como se puede apreciar a lo largo de la tesis, donde se han tratado diferentes aguas residuales para a diferentes necesidades, una de las ventajas más importantes de los SBR es su flexibilidad.

ABSTRACT

Nowadays, environmental legislation has become more restricted in the nutrient wastewater discharge, especially in the sensitive areas and vulnerable zones. So, many studies have been stimulated on the understanding, developing and improving the biological nutrient removal processes.

The Sequencing Batch Reactor (SBR) is a fill-and-draw activated sludge system for wastewater treatment. In this system, wastewater is added to a single reactor which operates in a batch treatment mode repeating a cycle (sequence) continuously. All the operations (fill, react, settle and draw) are achieved in a single batch reactor.

SBR technology is not new. In fact, it precedes the use of continuous flow activated sludge technology. The precursor to this was a fill-and-draw system operated on batch, similar to the SBR. Between 1914 and 1920, many difficulties were associated with operating these fill-and-draw systems, most resulting from the process valving required to switch flow from one reactor to another, operator attention required… Interest in SBRs was revived in the late 1950s and early 1960s, with the development of new equipment and technology. Improvements in aeration devices (i.e. motorized valves, pneumatically actuated valves) and controls (level sensors, flowmeters, automatic timers, microprocessors) have allowed SBRs to successfully compete with conventional activated sludge systems.

The aim of this thesis consists in the identification of suitable operation conditions for a cycle according to kind of influent wastewater, treatment requirements and effluent quality using a SBR technology. The influent wastewater, treatment requirements and effluent quality desire determinate in great measure the treatment to realize. So, different studies have been carried out in order to obtain a suitable treatment for each wastewater and requirement using a step-feed strategy.

By means of on-line pH, DO and ORP measurements are possible follow the status of the process. At the same time another parameter, that complements all these, is the OUR calculated through DO dada.

Evaluation the operation conditions for nitrogen removal using a step-feed strategy for a synthetic wastewater through the study of the effect of number of filling events, the definition of the length and number of phases for a cycle, and the identification of the critical points following the pH, DO and ORP sensors.

Application of the step-feed strategy in two different industrial wastewaters: textile wastewater and landfill leachate wastewater. In both wastewaters, the efficiency has been studied through the operational conditions and oxygen uptake rate. While in the textile wastewater the main objective was only organic matter removal, in the landfill leachate wastewater was carbon and nitrogen removal.

Evaluation of the operation conditions for nitrogen and phosphorus removal using a step-feed strategy for an urban wastewater through, the definition of the number and length of phases for a cycle, and the identification of the critical points following the pH, DO and ORP sensors.

Influence of pH and carbon source in phosphorus removal using synthetic wastewater through the study of pH increase in two different carbon sources and the effect of change of carbon source.

As it can be observed in this thesis, where it is treated different wastewaters for different requirements, one of the main advantages of the SBR is its flexibility.

PREFACE

The increasingly stricter nitrogen and phosphorus limits on wastewater discharges have stimulated studies on the understanding, developing and improving the single sludge biological nutrient removal process. The Sequencing Batch Reactor (SBR) has proven to be viable alternative to the continuous-flow systems in carbon and nutrient removal from domestic and industrial wastewaters.

By means of the identification of suitable operation conditions for a cycle according to kind of influent wastewater, treatment requirements and effluent quality using a SBR technology, so, different studies have been carried out in order to obtain a suitable treatment for each wastewater and requirement.

This thesis project memory has been organized in the purpose to firstly introduce to the reader to the biological nutrient removal and the SBR technology, with a brief overview of SBR operation, on-line monitoring data and the state of the art (Chapter 1). Secondly, the objectives (Chapter 2) proposed to give a general idea of the work planned and later the specific for each study included in the thesis. Chapter 3 presents the characteristics of the two sequencing batch reactors used during whole experimental studies and described all the analytical methods.

The results have been divided in chapters which explain different treatments (carbon, nitrogen and phosphorus removal) for different sources. Table 0 summarizes each treatment studied in the SBR depending on the kind of wastewater used (synthetic or real) and the treatment requirements (carbon, nitrogen or phosphorus removal). A total of five treatments from Chapter 4 to 8 have been reported in this thesis, with a common characteristic, the use of a step-feed strategy in a sequencing batch reactor.

In the Chapter 4 has been studied the operation conditions for nitrogen removal using a step-feed strategy for a synthetic wastewater. In the Chapter 5 and 6, two industrial applications of a textile wastewater and a landfill leachate wastewater have been applied for organic matter, and carbon and nitrogen removal, respectively. In both cases, the efficiency of the process has been demonstrated through the operational conditions and oxygen uptake rate (OUR). Chapter 7 relates the study of the operation conditions evaluation for nitrogen and phosphorus removal using a step-feed strategy for an urban wastewater. And the last part of results, Chapter 8, the influence of pH and carbon source in phosphorus removal using synthetic wastewater have been analysed through the study of pH increase in two different carbon sources and the effect of change of carbon source.

Finally, the conclusions and a global evaluation of all results are given in Chapter 9 and the references list (Chapter 10). An annex section (Chapter 11) is also presented where are listed the publications which have been carry out with this thesis project as well as the contributions to international conferences.

Table 0: Summary of treatments for the different wastewaters to treat.

Treatment	Wastewater			
	Synthetic	Real		
		Urban	Industrial	
C	Chapter 4	Chapter 7	Chapter 5	Chapter 6
N				
P	Chapter 8			

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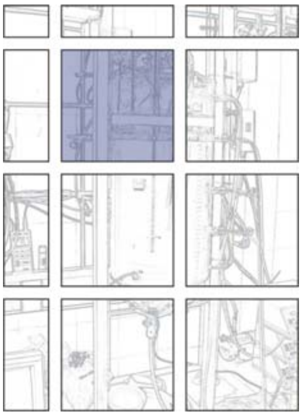

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INTRODUCTION

1.1 Nutrient problems

There are several reasons for, or benefits in, utilizing biological nutrient removal (BNR) processes for the treatment of wastewaters. They may be classified as environmental benefits, economical benefits and operational benefits. The most important of these is the control of eutrophication in the effluent receiving media, which is an environmental benefit. Historically, treatment requirements were determined by the need to protect the oxygen resources of the receiving water, and this was accomplished primarily through the removal of putrescible solids and dissolved organics from the wastewater before discharge. In more recent years, considerable emphasis has been placed on also reducing the quantities of nutrient discharged (i.e., nitrogen and phosphorus) because they stimulate the growth of algae and other photosynthetic aquatic life, which lead to accelerated eutrophication, excessive loss of oxygen resources, and undesirable changes in aquatic population (Randall *et al.*, 1992).

It is for this reason European Legislation became more restrictive in the nutrient wastewaters discharge, through the European Directive 91/217/CEE. This directive is responsible for the procedures in the designating of sensitive areas and vulnerable zones, and the application of treatment selection criteria established in Spain. In general, all the sensitive areas are watercourses and all the vulnerable zones are groundwaters. Many of the watercourses declared as Sensitive Areas run through one of the Vulnerable Zones.

In Table 1-1 and Table 1-2 the European legislation regarding urban wastewater discharges according to the European Directive 91/271/EEC is presented. While Table 1-1 shows the fixed requirements of discharge from all urban wastewater treatments, Table 1-2 is more restricted, focusing on the nutrient discharge in the sensitive areas depending on local situation.

However, directives for the treatment for less than 2000 p.e. are not imposed by the European Directive as it only explains than urban wastewaters need to be treated. Therefore, the Autonomous Government of Catalonia included these treatments in its own Clean-up Program of Urban Wastewaters (Programa de Sanejament d'Aigües Residuals Urbanes (PSARU, 2002). This program, PSARU, has as a main objective, the definition of all the actuations to achieve the contamination reduction of urban wastewater in populations than less than 2000 p.e.

Table 1-1: Requirements for discharge from urban wastewater treatment plants according to Directive 91/271/EEC.

Parameters	Concentrations		Minimum % of reduction (1)		Reference method of measurement
	p.e.>10000	2000<p.e.<10000	p.e.>10000	2000<p.e.<10000	
Biological Oxygen Demand at 20ºC without nitrification (2)	25 mg/L O_2		70-90		Homogenized, unfiltered, undecanted sample. Determination of dissolved oxygen before and after five-day incubation at 20ºC ± 1ºC, in complete darkness. Addition of nitrification inhibitor.
			40 under (*)		
Chemical Oxygen Demand	125 mg/L O_2		75		Homogenized, unfiltered, undecanted sample Potassium dichromate
Total suspended Solids	35 mg/L (3)		90 (3)		- Filtering of a representative sample through a 0.45µm filter membrane. Drying at 105ºC and weighing. - Centrifuging of a representative sample (for a least five mins with mean acceleration of 2800 to 3200 g), drying at 105ºC and weighing.
	35 under (*)	60 under (*)	90 under (*)	70 under (*)	

(1) Reduction in relation to the load of the influent.

(2) The parameter can be replaced by another parameter: total organic carbon (TOC) or total oxygen demand (TOD) if a relationship can be established between BOD5 and the substitute parameter.

(3) This requirement is optional.

(*) Urban wastewater discharges to waters situated in high mountain regions (over 1500m above sea level).

Table 1-2: Requirements for discharge from urban wastewater treatment plants to sensitive areas which are subject to eutrophication according to Directive 91/271/EEC. One or both parameters may be applied depending on local situation.

Parameters	Concentrations		Minimum % of reduction (1)	Reference method of measurement
	p.e >100000	10000<p.e.<100000		
Total Phosphorus	1 mg/L P	2 mg/L P	80	Molecular absorption spectrophotometry.
Total Nitrogen (2)	10 mg/L N.	15 mg/L N (3)	70-80	Molecular absorption spectrophotometry.

(1) Reduction in relation to the load of the influent.

(2) Total nitrogen means: the sum of total Kjeldahl-nitrogen (N-organic + NH3), nitrate nitrogen (N-NO3-) and nitrite nitrogen (N-NO2-).

(3) Alternatively, the daily average must not exceed 20 mg/L N. This requirement refers to a water temperature of 12ºC or more during the operation of the biological reactor of the wastewater treatment plant. As a substitute for the condition concerning the temperature, it is possible to apply a limited time of operation, which takes into account the regional climatic conditions.

Where p.e is population equivalent and corresponds to 60 mg/L BOD_5. ((PSARU, 2002))

1.2 Biological Nutrient Removal

1.2.1 BIOLOGICAL NITROGEN REMOVAL

Biological nitrogen removal is used in wastewater treatment when there are concerns regarding eutrophication, when either groundwater must be protected against elevated nitrate ($N\text{-}NO_3^-$) concentrations or when wastewater treatment plant effluent is used for groundwater recharge or other claimed water applications. Biological nitrogen removal can be accomplished in a two stages treatment: aerobic nitrification and anoxic denitrification(EPA (1993)).

I Nitrification

Nitrification is the term used to describe the two-step biological process in which ammonia ($N\text{-}NH_4^+$) is oxidized to nitrite ($N\text{-}NO_2^-$) and nitrite is oxidized to nitrate ($N\text{-}NO_3^-$), under aerobic conditions and using oxygen as the electron acceptor. The need for nitrification in wastewater treatment arises from water quality concerns over the effect of ammonia on receiving water with respect to DO concentration and fish toxicity, from the need to provide nitrogen removal to control the eutrophication, and in the control for water-reuse applications including groundwater recharge (Metcalf and Eddy (2003)).

Aerobic autotrophic bacteria are responsible for nitrification in activated sludge and biofilm processes. Nitrification, as noted above, is a two-step process involving two groups of bacteria. In the first stage, ammonia is oxidized to nitrite (equation 1.1) by one group of autotrophic bacteria called Nitroso-bacteria or Ammonia Oxidizing Bacteria (AOB). In the second stage, nitrite is oxidized to nitrate (equation 1.2) by another group of autotrophic bacteria called Nitro-bacteria or Nitrite Oxidizer Bacteria (NOB). It should be noted that the two groups of autotrophic bacteria are distinctly different.

$$NH_4^+ + \frac{3}{2}O_2 \longrightarrow NO_2^- + H_2O + 2H^+ \qquad \text{(eq. 1.1)}$$

$$NO_2^- + \frac{1}{2}O_2 \longrightarrow NO_3^- \qquad \text{(eq. 1.2)}$$

Therefore, total oxidation reaction is described as equation 1.3:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \qquad \text{(eq. 1.3)}$$

These autotrophic microorganisms derive energy for growth from the oxidation of inorganic nitrogen compounds, using inorganic carbon as their source of cellular carbon. In addition, the amount of alkalinity required to carry out the reaction (equation 1.3) can be estimated as equation 1.4:

$$NH_4^+ + 2HCO_3^- + 2O_2 \rightarrow NO_3^- + 2CO_2 + 3H_2O \qquad \text{(eq. 1.4)}$$

In the above equation, for each g of ammonia (as N) converted, 7.14 g of alkalinity as $CaCO_3$ will be required [calculated as 2*(50 g $CaCO_3$/eq)/14]. (Metcalf and Eddy (2003))

II Denitrification

The biological reduction of nitrate to nitric oxide, nitrous oxide, and nitrogen gas is termed denitrification or dissimilating nitrate reduction. Biological denitrification is coupled to the respiratory electron transport chain, and nitrate and nitrite are used as electron acceptor for the oxidation of a variety of organic or inorganic electron donors.

A wide range of bacteria has been shown as capable of denitrification, but similar microbial capability has also been found in algae or fungi. Bacteria capable of denitrification are both heterotrophic and autotrophic. Most of these heterotrophic bacteria are facultative aerobic organisms with the ability to use oxygen as well as nitrate or nitrite, and some can also carry out fermentation in the absence of nitrate or oxygen (Metcalf and Eddy (2003)).

Biological denitrification involves the biological oxidation of many organic substrates in wastewater treatment using nitrate or nitrite as the electron acceptor instead of oxygen. In the absence of DO or under limited DO concentrations, the nitrate reductase enzyme in the electron transport respiratory chain is induced, and helps to transfer hydrogen and electrons to the nitrate as the terminal electron acceptor. The nitrate reduction reactions involve the different reduction steps from nitrate to nitrite, to nitric oxide, to nitrous oxide, and to nitrogen gas.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

The electron donor as an organic substrate is obtained through: the easily biodegradable

COD in the influent wastewater (equation 1.5) or produced during endogenous decay, or an exogenous source such methanol (equation 1.6) or acetate (equation 1.7). Different electron donors give different reaction stoichiometries as observed below.

$$10NO_3^- + C_{10}H_{19}O_3N \longrightarrow 5N_2 + 10CO_2 + 3H_2O + 10OH^- + NH_3 \quad \text{(eq. 1.5)}$$

$$6NO_3^- + 5CH_3OH \longrightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH^- \quad \text{(eq. 1.6)}$$

$$8NO_3^- + 5CH_3COOH \longrightarrow 4N_2 + 10CO_2 + 6H_2O + 8OH^- \quad \text{(eq. 1.7)}$$

The term $C_{10}H_{19}O_3N$ is often used to represent the biodegradable organic matter in wastewaters.

In all the above heterotrophic denitrification reactions, one equivalent of alkalinity is produced per equivalent of N-NO_3^- reduced, which equates to 3.57 g of alkalinity (as $CaCO_3$) production per g of nitrate nitrogen reduced. So, one-half of the amount destroyed by nitrification can be recovered (Metcalf and Eddy (2003)).

1.2.2 BIOLOGICAL PHOSPHORUS REMOVAL

The removal of phosphorus by a biological process is known as Enhanced Biological Phosphorus Removal (EBPR). Phosphorus removal is generally done to control eutrophication because phosphorus is a limiting nutrient in most freshwater systems. The principal advantages of biological phosphorus removal are the reduction of chemical costs and lower sludge production than in chemical precipitation (Metcalf and Eddy (2003)).

The enhanced biological phosphorus removal consists of incorporating the phosphorus present in the influent into cell biomass, which subsequently is removed from the process as a result of sludge wasting. The organisms responsible for this task are the phosphorus accumulating organisms (PAOs). To incorporate the phosphorus into the cell biomass it is necessary to apply two different conditions, anaerobic and aerobic, in order to encourage the biomass to grow and consume phosphorus.

EBPR has three main characteristics: anaerobic organic matter uptake and storage, anaerobic phosphate release and aerobic phosphate uptake far in excess of cell growth requirements. At the same time, three are storage compounds which play an important role in the metabolism of EBPR process. These are polyphosphate, glycogen and poly-hydroxy-alcanoates (PHA). PHA can be found as poly-hydroxybutyrate (PHB) or poly-hydroxyvalerate

(PHV).

Under anaerobic conditions, PAOs can accumulate Volatile Fatty Acids (VFAs) mainly acetate, produced by COD fermentation. Then, the VFA is stored inside the cell as poly-hydroxyalkanoates (PHAs), basically poly-hydroxybutyrate (PHB). The energy (in the form of Adenosine Tri-Phosphate, ATP) for this process is obtained from the degradation of stored polyphosphate (polyP) and glycolysis of the glycogen utilisation giving reducing power ($NADH_2$). The poly-phosphate degradation results in the release of orthophosphate in the liquid media (Figure 1.1).

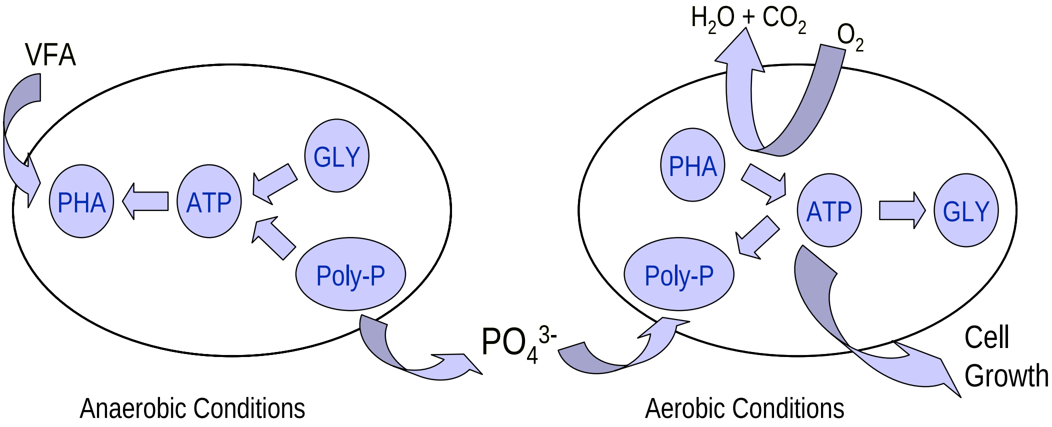

Figure 1.1: Schematic diagram of the metabolism of polyphosphate-accumulating organisms under anaerobic and aerobic conditions

Whereas under aerobic or anoxic conditions, the PHA is metabolised providing energy ($NADH_2$) and carbon source, to produce more cells and replenish the glycogen pool. Thus, the energy, $NADH_2$ is converted into ATP. The energy from ATP is used by PAOs to grow, take up the excess soluble orthophosphate in order to recover and increase the polyphosphate (polyP) pool in the cell, and to form glycogen (Figure 1.1), in turn leading to a net phosphate removal from the wastewater.

The main difference between aerobic and anoxic phosphate uptake is that for the formation of ATP under anoxic conditions, nitrate is used. The rest of the metabolism of PAOs under aerobic and anoxic conditions remains identical.

Under anoxic conditions, however, approximately 40% less ATP is formed per amount of $NADH_2$ than under aerobic conditions. This low ATP/$NADH_2$ ratio means an end result of lower biomass production under anoxic conditions.

The metabolism of PAOs can be characterised as a cyclic storage and consumption process of glycogen and polyphosphate (Figure 1.2). As well as the energy needed for growth, extra energy is also necessary to execute and maintain this cycle. Because of this the metabolism of PAOs requires more energy than that of other heterotrophic microorganisms (non-PAOs). In an aerobic activated sludge process, PAOs would not be able to survive like the other heterotrophic micro-organisms. An anaerobic phase and a rapid uptake of substrate in the anaerobic phase constitute the key factors in maintaining PAOs in a biological phosphorus removal process. Conditions for this rapid uptake are glycogen and polyphosphate cycles. In the aerobic/anoxic phase the recovery of glycogen and polyphosphate for PAOs may be more important than bacterial growth (Janssen (2002)).

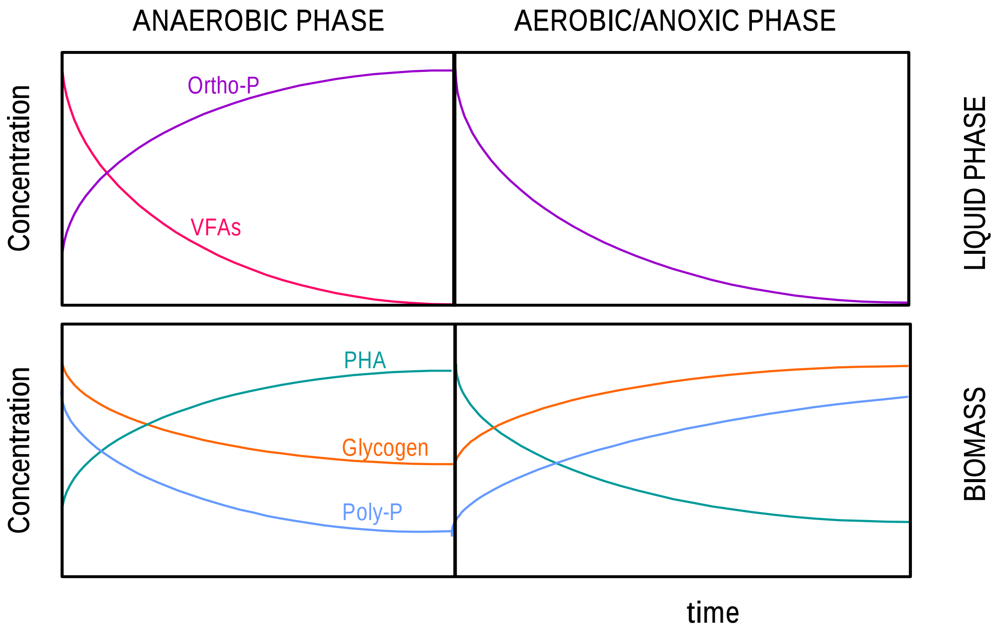

Figure 1.2: Metabolism of the biological phosphorus removal process including glycogen and PHA cycles.

The reactions of biological phosphorus removal process are complicated. A simplified set of reactions is shown in the equations 1.8, 1.9 and 1.10, taking into account the COD which is mainly acetate with the propionate expressed as HAc-COD, and P transformations only (Henze (2002)).

Anaerobic process:

$$0.4\,\text{g}\,\text{PP-P} + 1\,\text{g}\,\text{HAc-COD} \longrightarrow 0.4\,\text{g}\,\text{P-PO}_4^{3-} + 1\,\text{g}\,\text{PHA-COD} + 0.04\,\text{g}\,\text{H}^+ \quad \text{(eq. 1.8)}$$

Aerobic storage:

$$0.2\,\mathrm{g\,PHA\text{-}COD} + 1\,\mathrm{g\,P\text{-}PO_4^{3-}} \longrightarrow 1\,\mathrm{g\,PP\text{-}P} + 0.1\,\mathrm{g\,OH^-} \qquad \text{(eq.1.9)}$$

Aerobic growth (with maximum yield, Y_{PAO}=0.63):

$$1.6\,\mathrm{g\,PHA\text{-}COD} + (-0.6\,\mathrm{g\,O_2\text{-}COD}) \longrightarrow 1\,\mathrm{g\,PAO\text{-}COD} \qquad \text{(eq. 1.10)}$$

Total process, expressed in the equation 1.11, corresponds to anaerobic plus aerobic reactions (growth and storage with, $Y_{PAO,obs}$=0.3 g COD/g COD):

$$20\,\mathrm{g\,HAc\text{-}COD} + 1\,\mathrm{g\,P\text{-}PO_4^{3-}} \longrightarrow 6\,\mathrm{g\,PAO\text{-}COD} + 1\,\mathrm{g\,PP\text{-}P} + 0.1\,\mathrm{g\,OH^-} \qquad \text{(eq. 1.11)}$$

The performance of EBPR can become unstable, especially when it is applied in combination with the biological nitrogen removal process. This instability could be explained by competition with Glycogen Accumulating Organisms (GAOs) or the introduction of nitrate into the anaerobic phase (Saito *et al.*, 2004).

1.3 Sequencing Batch Reactor (SBR)

The Sequencing Batch Reactor (SBR) is the name given to a wastewater treatment system based on activated sludge and operated in a fill-and-draw cycle. The most important difference between SBR and the conventional activated sludge systems is that reaction and settle take place in the same reactor. Basically, all SBR have five phases in common (Figure 1.3), which are carried out in sequence as follows:

1. Fill: Raw wastewater flows into the reactor and mixes with the biomass held in the tank.

2. React: The biomass consumes the substrate under controlled conditions: anaerobic, anoxic or aerobic reaction depending on the kind of treatment applied.

3. Settle: Mixing and aeration are stopped and the biomass is allowed to separate

from the liquid, resulting in a clarified supernatant.

4. Draw: Supernatant or treated effluent is removed.
5. Idle: This is the time between cycles. Idle is used in a multitank system to adjust cycle times between SBR reactors. Because Idle is not a necessary phase, it is sometimes omitted. In addition, sludge wasting can occur during this phase.

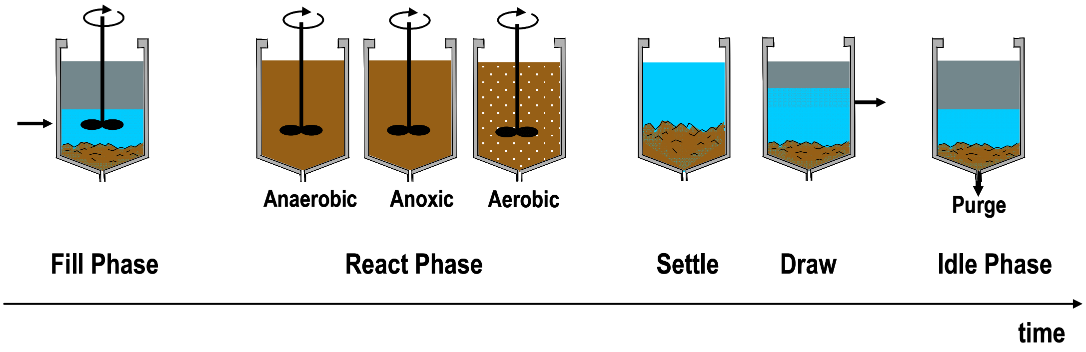

Figure 1.3: Typical sequence operation in an SBR process.

The conditions applied during the fill and react phases must be adjusted according to the treatment objectives (organic matter, nitrogen or phosphorus removal).

As before mentioned, during the **fill phase** the wastewater enters the reactor. The main effect of the fill phase, however, is to determine the hydraulic characteristics of the bioreactor. The kind of fill strategy applied depends upon a variety of factors, including the nature of the facility and the treatment objectives.

When focusing on the length of the fill phase both short and long fill phases are found. If the fill is short, the process will be characterized by a high instantaneous process loading factor, thereby making it analogous to a continuous system with a tanks-in-series configuration. In that case, the biomass will be exposed initially to a high concentration of organic matter and other wastewater constituents, but the concentration will drop over time. Conversely, if the fill phase is long, the instantaneous process loading factor will be small and the system will be similar to a completely mixed continuous flow system in its performance. This means that the biomass will experience only low and relatively constant concentrations of the wastewater constituents. The long fill can be applied during the whole operational time becoming a continuous fill phase. (Grady (1999)).

Others strategies of filling can be applied such as a focus on the number of filling events.

The classical operation of SBR is executing a sole filling event during a cycle, but more than one filling event (two, three …) mainly in nutrient removal and getting, in some cases, a continuous filling.

At the same time, three variations of the fill phase can also be applied depending on the strategy: static fill, mixed fill and aerated fill. If the fill phase is static, influent wastewater is added to the biomass already present in the reactor. Static fill is characterized by no mixing or aeration, meaning that there will be a high substrate (food) concentration when mixing begins. A high food to microorganisms (F/M) ratio creates an environment favourable to floc forming organisms versus filamentous organisms ((EPA, 1999)), which provides good settling characteristics for the sludge. Additionally, static fill conditions favour organisms that produce internal storage products during high substrate conditions, a requirement for biological phosphorus removal. Static fill may be compared to using “selector” compartments in a conventional activated sludge system to control the F/M ratio. If the fill phase is mixed, the influent is mixed with the biomass, which then initiates biological reactions. During mixed fill, bacteria biologically degrade the organics and use residual oxygen or alternative electron acceptors, such as nitrate. In this environment, denitrification can occur under these anoxic conditions. In the conventional biological nutrient removal (BNR) activated sludge system, mixed fill is comparable to the anoxic zone which is used in denitrification. Anaerobic conditions can also be achieved during the mixed fill phase. After the microorganisms use the nitrate, sulphate becomes the electron acceptor. Anaerobic conditions are characterized by the lack of oxygen and sulphate as the electron acceptor ((EPA, 1999)).

During the **react phase**, the biomass is allowed to act upon the wastewater constituents. The biological reactions (the biomass growth and substrate utilization), initiated in the fill phase, are completed in the react phase, in which anaerobic, anoxic or aerobic mix phases are available. So the fill phase should be thought of as a “fill plus react” phase with react continuing after the fill has ended. As a certain total react period will be required to achieve the process objectives, if the fill period is short, the separate react period will be long, whereas if the fill period is long the separate react period will be short to nonexistent. The two periods are usually specified separately because of the impact that each one has on the performance of the system.

During aerobic reaction phase, the aerobic reactions initialized during the aerobic fill are completed and nitrification can be achieved. If the anoxic reaction is applied, denitrification can be attained. And in the anaerobic reaction phase, phosphorus removal can be achieved (EPA, 1999).

All these facts reflect one of the main advantages of the batch reactors, namely flexibility. SBRs are especially preferred when nutrient removal is important, because enrichment in nitrifiers and denitrifiers and phosphorus removal bacteria may take place in the same vessel by simply changing the mixing and aeration conditions and time schedules. Nevertheless, SBRs also present many advantages for processes envisaging mainly carbonaceous load removal (Irvine *et al.*, 1997; Wilderer *et al.*, 2001).

- The easily modifiable operation is adequate for **sludge bulking control**. The cyclic change of substrate concentration is known to be a selection factor against certain strains of filamentous bacteria. The operational flexibility of an SBR allows the control of filamentous bacteria through feast/famine cycles. A high substrate concentration may be imposed by a static fill operation and the react phase may be followed by an extended phase of starvation which, in turn, promotes the enrichment of flock-forming bacteria and the accumulation of exopolymers,

- The operation conditions (alternating high/low substrate concentrations) induce the selection of **robust bacteria**. The sludge adaptation to variations in the oxygen and substrate concentrations, in the course of a cycle and on a long-term basis, renders it capable of maintaining good performance under **shock loads**,

- The SBR system provides the flexibility needed to treat a **variable wastewater** (load and composition) by simply adjusting the cycle time (e.g. using the time set aside for the idle phase), the duration of each phase or the mixing/aeration pattern during each cycle,

- The ability to hold contaminants until they have been completely degraded makes the system excellent for the treatment of **hazardous compounds**,

- The concentration of biomass in the stream leaving the system can be kept low by **minimising turbulence** during the settle phase,

- The settle phase can be extended to increase **sludge thickening** thus decreasing water content in the wasted sludge,

- The capacity to adjust the energy input and the fraction of volume used according to the influent loading can result in a **reduction in operational costs**. In addition, less space is required as all operations occur in one basin.

A controlled unsteady-state system such as the SBR is adequate for the treatment of severely variable or even seasonal wastewaters. In reality, most wastewaters have an unsteady behaviour, although the treatment facilities are often designed to be operated in a steady-state (Irvine *et al.*, 1997). The SBR process has been reported as a viable alternative in wastewater treatment of different industries, including textile dyeing and finishing effluents (Artan *et al.*, 1996; Beckert and Burkert, 2000; Torrijos and Moletta, 1997).

But, the SBR also has some disadvantages. The main drawbacks of the SBR process are outlined below (EPA, 1999):

- A higher level of sophistication, (compared to conventional systems), especially for larger systems, of timing units and controls is required.

-Higher level of maintenance (compared to conventional systems) associated with more sophisticated controls, automated switches and automated valves.

- Potential of discharging floating or settled sludge during the draw or decant phases with some SBR configurations.

- Potential plugging of aeration devices during selected operating cycles, depending on the aeration system used by the manufacturer.

- Potential requirement for equalization after SBR, depending on the downstream processes.

1.3.1 OPERATING CHARACTERISTICS IN SBR PROCESS

The SBRs operate in repeated **cycles** sequentially. A **cycle** is a group of operations or phases comprising between the beginning (fill) and the end (draw or idle) of a wastewater treatment. These cycles are defined by five phases: fill, react, settle, draw and idle. The **total cycle time** (t_C) is the sum of all these phases as presented in equation 1.12. Sometimes idle phase is not necessary and it is omitted.

$$t_C = t_F + t_R + t_S + t_D + t_I \qquad \text{(eq. 1.12)}$$

Where:
t_C: total cycle time, h
t_F: fill time, h
t_R: react time, h
t_S: settle time, h
t_D: draw time, h
t_I: idle time, h

Furthermore, the conditions applied during the react phase can be different depending on the performance desired (organic matter, nitrogen or phosphorus removal). So, aerobic, anoxic or anaerobic reaction time can be found in the react time (equation 1.13). Hence:

$$t_R = t_{AE} + t_{AX} + t_{AN} \qquad \text{(eq. 1.13)}$$

Where: t_{AN}: anaerobic react time, h t_{AX}: anoxic react time, h
t_{AE}: aerobic react time, h

Also, it is important to note that a cycle has a different **effective time** to different than total cycle time. This fact is a consequence of the inoperative phases or physic operation such as settle (solid-liquid separation) and draw (decant), where no biological conversion is assumed to occur. The **effective time** (t_E) can be defined as equation 1.14:

$$t_E = t_C - (t_S + t_D + t_I) \qquad \text{(eq. 1.14)}$$

Where: t_c: total cycle time, h t_S: settle time, h
t_D: draw time, h t_I: idle time, h

The **number of cycles** (N_C) per day is determined through the total cycle time (t_C), as is shown in equation 1.15:

$$N_C = \frac{24}{t_C} \qquad \text{(eq. 1.15)}$$

Where: N_C: number of cycles per day t_c: total cycle time, h

Throughout the cycle, an SBR can operate with different volumes due to the filling and draw phases. Then, **total reactor volume** (V_T) can be defined as the maximum working volume and the **filling volume** (V_F) as the volume of wastewater filled and discharged every cycle. The difference between filling volume and total reactor volume is the **minimum volume** (V_{MIN}, equation 1.16), i.e. volume that always remains inside the reactor.

$$V_{MIN} = V_T - V_F \qquad \text{(eq. 1.16)}$$

Where: V_T: total reactor volume or working volume, L
V_{MIN}: minimum volume, L V_F: filling volume, L

Comparable to the **sludge recycle ratio** in the continuous flow system is the ratio between minimum volume and filling volume (V_{MIN}/V_F) (Artan *et al.*, 2001).

Another parameter related to volume is the **exchange ratio** per cycle (V_F/V_T), ratio between fill volume and total reactor volume, which is found in the SBR design.

The definition of **hydraulic retention time** (HRT) for an SBR is based on the equation 1.17 of the continuous systems.

$$HRT = \frac{V_T}{Q} \qquad \text{(eq. 1.17)}$$

Where: HRT: hydraulic retention time, d Q: daily wastewater flow rate, L/d

The flow (Q) in an SBR is defined by the product of filling volume (V_F) and number of cycles per day (N_C), equation 1.18:

$$Q = V_F \cdot N_C \qquad \text{(eq. 1.18)}$$

Where: V_F: filling volume, L N_C: number of cycles per day

By combining equation 1.17 and 1.18, the HRT can be expressed as equation 1.19:

$$HRT = \frac{t_C}{V_F / V_T} \cdot \frac{1}{24} \qquad \text{(eq. 1.19)}$$

Where: t_C: total cycle time, h V_F/V_T: exchange ratio

Assuming that all reactions happen during the effective time (t_E), a correction factor can be introduced into the **effective factor** (f_E) corresponding to the ratio between effective time and total cycle time, i.e. equation 1.20:

$$f_E = \frac{t_E}{t_C} \qquad \text{(eq. 1.20)}$$

Where: f_E: effective factor t_E: effective time, h
t_C: total cycle time, h

Thus, an **effective hydraulic retention time** (HRT_E)can be calculated as equation 1.21:

$$HRT_E = HRT \cdot f_E \qquad \text{(eq. 1.21)}$$

Where: HTR_E: effective hydraulic retention time, d f_E: effective factor

The **solid retention time** (SRT) determines the amount of biomass in the SBR, thereby determining its overall average performance. Thus, solid retention time (SRT) is expressed as equation 1.22, assuming that biomass concentration inside the reactor (X) is practically constant during whole cycle.

$$SRT = \frac{V_T \cdot X}{Q_W \cdot X_W} \qquad \text{(eq. 1.22)}$$

Where: STR: solid retention time, d Q_W: waste flow rate, L/d
X_W: waste biomass concentration, mg/L V_T: total reactor volume, L
X: biomass concentration inside the reactor with full filling, mg/L

It is also necessary to define an **effective solid retention time** (SRT_E, equation 1.23), as HRT, and then:

$$SRT_E = SRT \cdot f_E \qquad \text{(eq. 1.23)}$$

Where: STR_E: effective solid retention time, d f_E: effective factor

1.4 On-line Monitoring for nutrient removal

Microbiological activity in the organic matter and nutrient removal involve physical and chemical changes which can be detected through on-line monitoring pH, Dissolved Oxygen (DO) and Oxidation-Reduction Potential (ORP) measurements during a cycle. These changes can give further interesting information for control or process state evaluation. Different critical points[1] can be detected by means of these relatively simple sensors (pH, ORP and DO) under aerobic or anoxic conditions.

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[1] The critical points are the result of either biological reactions or the change of the operational conditions.

1.4.1 PH

The change in pH value during a cycle of a biological system responds to microbial reactions, and, hence, the pH variation often provides a good indication of ongoing biological reactions, e.g. increases in pH for ammonification and denitrification and decreases in pH owing to nitrification. Different critical points can be detected in the pH curve (Figure 1.4), as described below.

If only organic matter is achieved under aerobic conditions, the pH is affected by the stripping of CO_2 and as a consequence an increase of pH occurs (Figure 1.4, left side).

In systems where carbon and nitrogen removal are required, the pH can present two critical points; Ammonia Valley and Nitrate Apex. These points can appear in the pH curve when nitrification and denitrification occur. Under aerobic conditions, CO_2 is expelled from the solution by air-stripping initially raised pH, the reduction of alkalinity by prevailing nitrification decreases the pH until it reached a minimum (Figure 1.4, right side). This minimum in the pH profile is called Ammonia Valley and corresponds to the end of nitrification. After the ammonia valley, the pH increases due to the stripping of CO_2. The increases in the pH should be more noticeable in a system lacking strong buffer capacity. The pH variation range depends on the wastewater alkalinity.

Under anoxic conditions and if organic matter is available, ongoing denitrification increases the pH of the system. Thereafter the pH reaches to an inflection point before decreasing slightly (Figure 1.4, right side). This local peak is named Nitrate Apex and corresponds to complete denitrification (Chang and Hao, 1996).

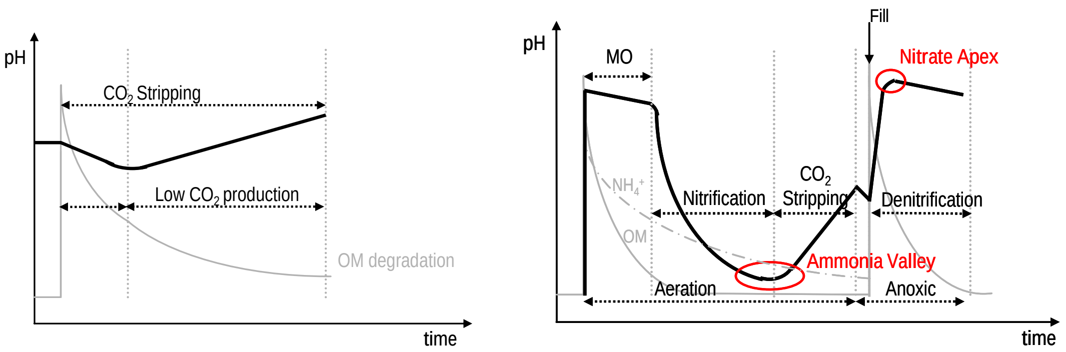


Figure 1.4: Dynamic evolution of pH showing the critical point in the different phases.

1.4.2 OXIDATION-REDUCTION POTENTIAL (ORP)

Oxidation reduction Potential (ORP) is a measure of the oxidative state in an aqueous system and can be a useful tool for indicating the biological state of a system. The ORP curve can present two critical points: α and Nitrate Knee as is presented in Figure 1.5 (left side).

ORP evolution is closely related to the dissolved oxygen profile, under aerobic conditions. The ORP curve rises with the aeration until an inflection point. This critical point is called α (α_{ORP}, Figure 1.5 left side) and means that nitrification is completed.

Under anoxic conditions, the ORP profile decreases until the inflection point (Figure 1.5 left side). This point is called Nitrate Knee and corresponds to the elimination of accumulated nitrate and nitrite (NO_x^-) (Paul *et al.*, 1998).

1.4.3 DISSOLVED OXYGEN (DO)

The change in the Dissolved Oxygen (DO) curve responds to microbial reactions, microorganisms utilize oxygen as an electron acceptor under aerobic conditions. Under a constant oxygen supply, a α critical point can be detected with the DO probes, as presented in Figure 1.5 (right side).

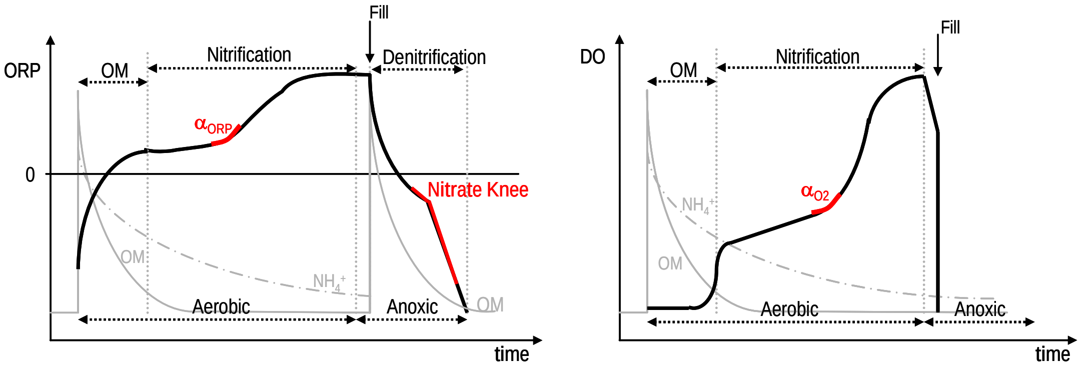


Figure 1.5: Dynamic evolution of ORP (left) and DO (right) showing the critical point in different phases.

Under aerobic filling phases the organic carbon oxidation is very high and requires a large quantity of oxygen which causes a DO decline to a low level in the reactor. When organic matter is close to being completely removed, a sudden DO increase is observed. Afterwards, the main reaction is the oxidation of ammonia (nitrification) and here the DO rises progressively. When ammonium in the reactor is almost exhausted, the DO concentration is quickly increased and appears an inflection point, the α_{O2} critical point (Figure 1.5 right). The critical point α_{O2} can also appear generally on the ORP curve (α_{ORP}) (Paul *et al.*, 1998).

1.5 State of the art: Bibliography summaries of SBR

Many authors have studied different operational strategies for removing organic matter, nitrogen and phosphorus in an SBR. Table 1-4 presents a summary of several works focusing on the operational strategy using the SBR process.

Table 1-4 has been classified firstly by the treatment, carbon and nitrogen removal or carbon, nitrogen and phosphorus removal; then, by the number of reactors used to accomplish the requirements, and later by the number of filling events (M), 1, 2,... and ∞ for continuous flow.

Table 1-3 : Nomenclature used in the Table 1-4.

Kinds of Wastewater	WW	(SW,UW, IW)
	SW	Synthetic Wastewater
	UW	Urban Wastewater
	IW	Industrial Wastewater
	UIW	Urban and Industrial Wastewater
External Carbon Source	ECS	(Yes or not)
Number of reactor for the same process	Nº R	(1 or 2)
Number of filling events	M	(1, 2, 3...∞)
Total cycle time	t_C	
Efficiency time	t_E	
Exchange ratio	V_F/V_T	
Hydraulic Retention Time	HRT	
Solid Retention Time	SRT	
Food to Microorganisms	F/M	
Total Suspended Solids	MLSS	
Biological Chemical Demand (BOD_5)	*	
Total nitrogen expressed as		
	a	Ammonium as total nitrogen
	b	Total Kjeldahl Nitrogen as total nitrogen
	c	Nitrates as total nitrogen
	d	Organic nitrogen as total nitrogen

Other parameters that are collected in the Table 1-4 are the kind of wastewater (WW), if an external carbon source (ECS) is used, influent characteristics, operation conditions and the efficiencies.

Table 1-3 presents a summary of all the nomenclature of the gathered parameters and subscripts, relating the available form of the Total Nitrogen (TN), used in the Table 1-4.

Observing Table 1-4, most of the authors operate with one reactor and a sole filling event to remove carbon, nitrogen or phosphorus. Some of them use external carbon sources to achieve a good removal. Meanwhile, only few authors work with different filling events and without external carbon source obtaining higher efficiencies than in a one filling event without an external carbon source.

Table 1-4: Summaries of different SBR treatments.

References					Influent			Operation							Efficiency		
	WW	ECS	NºR	M	COD	TN	P	t_c	t_R	V_F/V_T	HRT	SRT	F/M	MLSS	C	N	P
				-	mg/L	mg/L	mg/L	h	h		d	d		mg/L	%	%	%
Carbon and Nitrogen Removal																	
Andreottola *et al.*, 2001	IW	No	1	1	1400	252	8.5	12	11	0.5	1		0.17		91	95.2^b	
Coelho *et al.*, 2000	SW	No	1	∞	513	50^d		8	4.5					4500	97.7	99.6	
	SW	No	1	∞	513	50^d		2.4	1.6					4500	99.3	99.2	
	SW	No	1	∞	513	50^d		1.5	1.1					4500	98.1	90.8	
	SW	No	1	∞	513	50^d		2.1	1.2					4500	98.1	100	
	SW	No	1	∞	513	50^d		2.3	1.4					4500	99.2	99.4	
	SW	No	1	1	513	50^d		1.9	1.0					4500	98.1	97.6	
Dangcong *et al.*, 2001	SW	No	1	1	600	65.4	52.2	6	4.5	0.33	0.5	30					
	SW	No	1	1	600	65.4	52.2	6	4.5	0.33	0.5	20					
	SW	No	1	1	600	65.4	52.2	4	2.5	0.5	0.33	20					
	SW	No	1	1	600	65.4	52.2	4	2.5	0.6675	0.25	20					

References					Influent			Operation							Efficiency		
	WW	ECS	NºR	M	COD	TN	P	t_c	t_R	V_F/V_T	HRT	SRT	F/M	MLSS	C	N	P
				-	mg/L	mg/L	mg/L	h	h		d	d		mg/L	%	%	%
Carbon and Nitrogen Removal																	
Dangcong *et al.*, 2001	SW	No	1	1	600	65.4	52.2	4	2.5	0.5	0.33	20					
	SW	No	1	1	600	65.4	52.2	4	2.5	0.5	0.33	20					
	SW	No	1	1	600	65.4	52.2	4	2.5	0.6675	0.25	20					
	SW	No	1	1	600	65.4	52.2	4	2.5	0.5	0.33	20					
Diamadopoulos *et al.*, 1997	UIW	No	1	1	1090	133^b	4.9	24	23	0.5	2		0.156	3500	85.5	48.8	
	UIW	No	1	1	1090	133^b	4.9	24	23	0.5	2		0.156	3500	81.9	47.7	
	UIW	No	1	1	1090	133^b	4.9	24	23	0.5	2		0.156	3500	79.3	35.0	
	UIW	No	1	1	1090	133^b	4.9	24	23	0.5	2		0.156	3500	67.7	63.2	
Doyle *et al.*, 2001	IW	No	2	1	1100	8801		6	5.5		0.24	10		3000-13000			
Garrido *et al.*, 2001	IW	No	1	2	1000-4000	150-500		24	23	0.23	4.4			3000-9000	98	60-99	
Puig *et al.*, accepted	UW	No	1	6	532	53,6		8	6.5	33	1.11	23	0.26	3040	92	95	
Shin *et al.*, 1998	UW	No	1	1	79	91		12	10					3579	75	94*/-F	

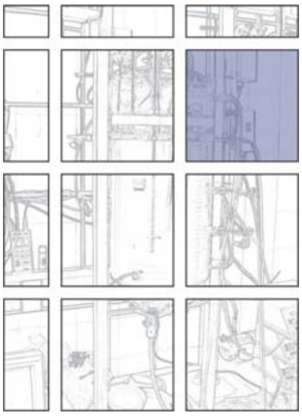
References				Influent			Operation							Efficiency		
	WW	ECS	NºR	M	COD	TN	P	t_C	t_E	V_F/V_T	HRT	SRT	F/M	MLSS	C	N	P
				-	mg/L	mg/L	mg/L	h	h		d	d		mg/L	%	%	%
Carbon and Nitrogen Removal																	
Tam *et al.*, 1994	SW	Yes	1	1	300	42	6	12	8.75	0.8	0.625			2000		97	
Villaverde *et al.*, 2000	SW	No	1	1	1500	630^b					0.83	20		9000	83	23	
	SW	No	1	1	1500	630^b					0.83	20		9000	95	36	
	SW	No	1	1	1500	630^b					0.83	20		9000	84	33	
	SW	No	1	1	1500	630^b					0.83	20		9000	84	29	
	IW	Yes	1	1	1500	630^b					1.67	20		9000	70	23	
	IW	No	1	1	1500	630^b					1.67	20		9000	68	27	
	IW	No	1	1	1500	630^b					2.5	20		9000	77	58	
	IW	No	1	1	1500	630^b					2.5	17		9000	89	69	
	IW	No	1	1	1500	630^b					1.67	17		9000	90	79	
Yu *et al.*, 2000;Paul *et al.*, 1998	SW	No	1	∞	300	41		6				10-15	0.1-0.3	1500-3000	86-91	80-84	

References					Influent			Operation							Efficiency		
	WW	ECS	NºR	M	COD	TN	P	t_c	t_E	V_F/V_T	HRT	SRT	F/M	MLSS	C	N	P
				-	mg/L	mg/L	mg/L	h	h		d	d		mg/L	%	%	%
Carbon, Nitrogen and Phosphorus Removal																	
Akin and Ugurlu, 2004	SW	No	1	1	400	53^a	21	12	10.5	0.25		25			97	37	80
	SW	No	1	1	400	53^a	21	12	10	0.25		25			97	78	67
Bernades and Klapwijk, 1996	UW	Yes	2	1	443	71^b	7	4.4	3.7	0.3	3.3	20		3030			
	UW	Yes	2	1	443	71^b	7	1.6	1.4	0.83	1.2			5240			
Chang and Hao, 1996	UW	Yes	1	1	296	30.1	6.9	8	6	0.5	0.67	15	0.16-0.23	3050	95	61	78
	UW	Yes	1	1	313	28.8	4.8	6	3.5	0.5	0.5	10	0.19-0.26	2670	91	78.5	97.9
Choi *et al.*, 1997	IW	No	1	1	46180	4455^a	702	24	23.9		44		0.025		97	93.4	88.5
	IW	No	1	1	42525	4966^a	652	24	23.9		33		0.025		97	99.9	78.1
Choi *et al.*, 2001	UW	No	2	2	200	25	5				0.3	25		4000		52	88
	UW	No	2	1							0.6	25		5000			
Escaler and Mujeriego, 2001	UW	No	1	1	270	30.2	6.8	6	5.25	0.5		12			83	53	30
Hamamoto *et al.*, 1997	SW	No	1	1	169*	35.8	41.5	6	3	0.25	1		0.096			12	0
	SW	No	1	1	169*	35.8	41.5	6	3	0.25	1		0.090			50	8
	SW	No	1	1	169*	35.8	41.5	6	3	0.25	1		0.085			64	18

References					Influent			Operation							Efficiency		
	WW	ECS	NºR	M	COD	TN	P	t_C	t_E	V_F/V_T	HRT	SRT	F/M	MLSS	C	N	P
				-	mg/L	mg/L	mg/L	h	h		d	d		mg/L	%	%	%
Carbon, Nitrogen and Phosphorus Removal																	
Hamamoto *et al.*, 1997	SW	No	1	1	169*	35.8	41.5	6	3	0.25	1		0.083			84	58
	SW	No	1	1	169*	35.8	41.5	6	3	0.25	1		0.083			86	96
	UW	No	1	1	170-290	30-45	4-5	6	3	0.33	1		0.059			86	82
	UW	No	1	1	200	43	7	6	3	0.24						74	71
	UW	No	1	1	200	43	7	6	3	0.24						90	83
	UW	No	1	1	200	43	7	6	3	0.24						96	93
Johansen *et al.*, 1997	UW	No	1	1	349	28.7	7.8	6	4.26	0.29		28	0.1	4000	86	80	63
Kabacinski *et al.*, 1998	IW	No	1	1	740	55	7.5	6	4			26			97	74	89
Kargi and Uygur, 2003	SW	No	1	1	1200	60	18		10.5			10			93	83	62
	SW	No	1	1	1200	60	18		10.5			10			98	89	64
	SW	No	1	1	1200	60	18		10.5			10			96	96	90
Keller *et al.*, 1997	IW	No	1	1	1400-2400	170-200^b	35-55	6	5.5		0.75	20			94	97	75
	IW	No	1	1	2300-3000	180-200^b	35-55	6	5.5		1	20			96	97	85

References					Influent			Operation							Efficiency		
	WW	ECS	NºR	M	COD	TN	P	t_C	t_E	V_F/V_T	HRT	SRT	F/M	MLSS	C	N	P
				-	mg/L	mg/L	mg/L	h	h		d	d		mg/L	%	%	%
Carbon, Nitrogen and Phosphorus Removal																	
Keller *et al.*, 2001	UW	No	1	1	563	54.5	9.7	4	3.3		1.95	23			95	96	84
Kuba *et al.*, 1996	SW	No	2	1	400	119^a	15	6							100	88	99
Lee *et al.*, 2001	SW	No	1		600	40	15	8		0.5		12			92	88	100
	SW	No	1		400	40	10	8		0.5		14			92	88	100
	SW	No	1		400	30	10	8		0.5		18			92	88	100
	SW	No	1		300	30	10	8		0.5		18			92	88	100
Obaja *et al.*, 2003	IW	Yes	1	1	2255	909	88.7	8			1	11		2160	64.1	99	97.8
	IW	Yes	1	1	2962	1194	117.3	8			1	11		3390	70.3	98	97.5
	IW	Yes	1	1	3744	1509	144	8			1	11		2420	70.2	99	97.3
	IW	Yes	1	1	3970	1650	150	8			1	11		3650	69.1	98	94.8
Rim *et al.*, 1997	UW	No	1	1	139*	45.0	3.9	6	4.67	0.55	0.34				95.2	62.8	86.7
	UW	No	1	1	139*	45.0	3.9	8	6.83	0.55	0.34				94.2	65.1	88.5
	UW	No	1	1	139*	45.0	3.9	12	10	0.55	0.34				93.3	55.7	75.8

References					Influent			Operation							Efficiency		
	WW	ECS	NºR	M	COD	TN	P	t_C	t_E	V_F/V_T	HRT	SRT	F/M	MLSS	C	N	P
				-	mg/L	mg/L	mg/L	h	h		d	d		mg/L	%	%	%
Carbon, Nitrogen and Phosphorus Removal																	
Tasli *et al.*, 1999	DW	No	1	1	420	72	11	6	4.5	0.31				2560		71	62
	DW	No	1	1	300	40	9	6	5	0.37				2930		32.5	35.6
	DW	No	1	1	320	37	8.2	6	7	0.44				2550		44.6	41
	DW	No	1	1	325	35	9	6	7	0.44				2175		39	61
	DW	Yes	1	1	350	50	8	6	5	0.37				1980		76	42.5
	DW	Yes	1	1	490	46	7.5	6	5	0.37				2240		56	46.7
	DW	Yes	1	1	530	65	8	6	5	0.37				2400		81	98
	DW	Yes	1	1	360	49	9.6	6	5	0.37				2040		75	89.6
Tilche *et al.*, 1999	IW	No	1	5	28760	2153[b]	450	24	20	0.1	10	15			98.8	98.6	98.0
Yu *et al.*, 1997	SW	No	1	∞	300	41	5.5	8	6.5			10-15	0.1-0.3	1500-3000	86	60	21
	SW	No	1	∞	300	41	5.5	5.15	3.65			10-15	0.1-0.3	1500-3000	88	74	20
	SW	No	1	∞	300	41	5.5	7.95	6.95			10-15	0.1-0.3	1500-3000	91	81	61



2

OBJECTIVES

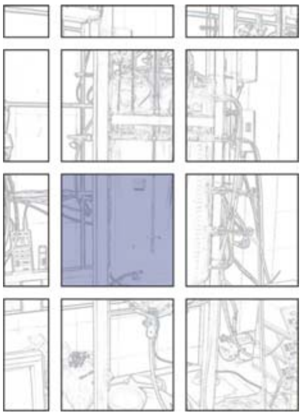
The increasingly stricter nitrogen and phosphorus limits on wastewater discharges have stimulated studies on the understanding, developing and improving the single sludge biological nutrient removal process. The Sequencing Batch Reactor (SBR) has proven to be viable alternative to the continuous-flow systems in carbon and nutrient removal from domestic and industrial wastewaters.

The aim of this thesis consists in the identification of suitable operation conditions for a cycle according to kind of influent wastewater, treatment requirements and effluent quality using a SBR technology. The influent wastewater, treatment requirements and effluent quality desire determinate in great measure the treatment to realize. So, different studies have been carried out in order to obtain a suitable treatment for each wastewater and requirement.

The proposed objectives of this thesis are described below:

- Evaluate different step-feed strategies for nitrogen removal using synthetic wastewater throughout the study of the effect of a different number of filling events, the definition of the number and the length of the phases for a cycle. And also, the study of the critical points by following the on-line pH, DO and ORP data to evaluate the status of the SBR.

- Applicate the step-feed strategy in a textile wastewater for organic matter removal through the determination of operational conditions in order to accomplish the organic matter requirement and the maximum discharge peak flow. It also looks at the application of the OUR advantages as a tool to study the biodegradability efficiency of the process
- Applicate of the step-feed strategy in a landfill leachate wastewater to achieve organic matter and nitrogen removal through the determination of the operational conditions and the application of the OUR advantages as a tool to study the biodegradability efficiency of the process.
- Evaluate different step-feed strategies for removing nitrogen and phosphorus from an urban wastewater through the definition of the number and the length of the phases for a cycle, the number and the duration of filling events. And also, the identification of the critical points following the on-line pH, DO and ORP data.
- Evaluate the influence of pH and carbon source to remove phosphorus for a synthetic wastewater through the study of the effect of increasing the pH in two different carbon sources and studying the effect of carbon source change.



3

MATERIALS AND METHODS

3.1 Experiment set-up

The experimental study of this research thesi was carried out in two parts. Thus, the results presented in chapters 4, 5, 6 and 7 were conducted at the Universitat de Girona (UdG, Girona, Spain) in the LEQUIA's laboratory, while the results presented in chapter 8 were in the laboratory of the Advanced Wastewater Management Centre (AWMC, Brisbane, Australia) during a pre-doctoral stage.

3.1.1 LEQUIA's SBR

The experiment set-up was located in the laboratory of the Department EQATA in Girona (Girona, Spain). The lab-scale SBR (Figure 3.1) was composed of a cylindrical glass reactor working with a maximum volume of 30 litres and which was able to be adjusted to operate at a minimum volume of 14 litres (which is the residual volume at the end of each SBR cycle).

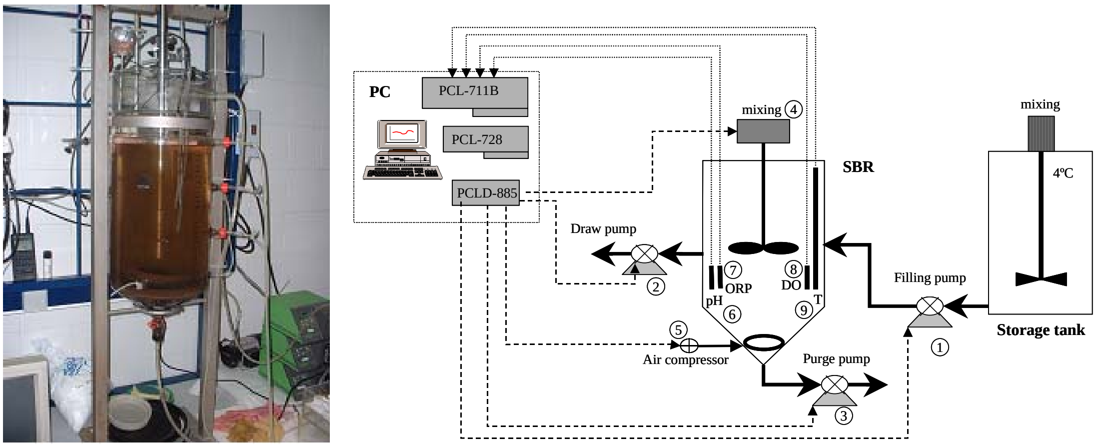


Figure 3.1: Schematic overview of SBR. The data acquisition and control software was responsible for the operation of peristaltic pumps (1,2,3), reactor mixing (4) and air supply control (5); as well as on-line monitoring of reactor pH (6), ORP (7), DO (8) and Temperature (9).

The SBR was operated in a fill-react-settle-&-draw mode following a predefined cycle and repeated continuously. During all filling and reaction phases, a mixing device (a marine helix turning at 400 rpm or less) kept the reactor contents under homogenous conditions at all times. Aerobic conditions were achieved by either compressed air or air injection. Filling, purging and extraction events were conducted by three different peristaltic pumps (Watson Marlow). At the end of the reaction time and before the settling phase of each cycle, excess biomass was removed from the reactor under aerobic conditions and while being mixed, to maintain the desired Sludge Retention Time (SRT). During extraction periods, treated wastewater was discharged from the reactor until a predefined minimum reactor water level (from 14 litres) was reached. The operational temperature was kept around 20ºC by the room temperature control system available. The reactor was equipped with a floating-probes system for on-line monitoring of pH (EPH-M10), Oxidation-Reduction Potential (ORP-M10), Temperature (PT-100) and Dissolved Oxygen (WTW OXI 340).

The wastewater was initially kept in a storage tank without refrigeration but later was slowly mixed at 4ºC and stored refrigerated in a 150 litres tank. This tank had a function to minimise microbiological activity by keeping the temperature at 4ºC.

The SBR was operated by means of an in-house developed data acquisition and control software program developed by LabView (Figure 3.2). The software was able to repeat over time a previously defined cycle operation by controlling the switching on/off of filling, the purge and draw peristaltic pumps, the mixing device, and the air supply. The monitoring module was able to acquire on-line pH (EPH-M10), oxidation-reduction potential (ORP-M10), temperature (PT-100), and dissolved oxygen concentration (WTW OXI 340) presenting them in a graphical interface. The data acquisition and control system was composed of different interface cards (PCL-711B, PCL-728 and, PCLD-885 from Advantech), probes and transmitters. Signals were sampled and the mean values stored in a simple text file for further processing.

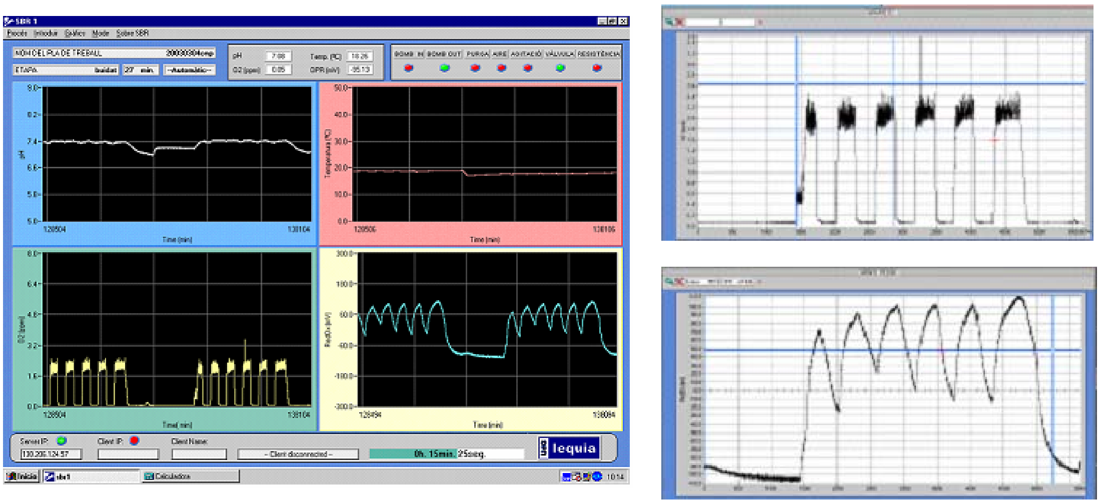


Figure 3.2: Screen of the program developed by Lab-View.

3.1.2 AWMC's SBR

The experimental set-up was located in the laboratory of the AWMC in Brisbane (Queensland, Australia). Three cylindrical sequencing batch reactors (Figure 3.3) with a working volume of 8L and minimum volume of 6 L. The reactor worked with a hydraulic retention time (HRT) of 24h. At the end of the aerobic period 250 mL of sludge was removed from the reactor keeping the sludge retention time (SRT) of 8 days. Filling and purging events were conducted by two different pumps, while the extraction of the effluent was realized by gravity through a control valve. The reactor was constantly mixed with a propeller except during settling and withdrawn phases. Nitrogen gas was bubbled into the reactor during the anaerobic period to maintain strict anaerobic conditions. Aerobic conditions were achieved by compressed air supply.

The reactor was equipped with on-line monitoring of Dissolved Oxygen (YSI model 5739, Yellow Springs, USA) and pH (Ionode IJ44, TPS, Brisbane, Australia). The dissolved oxygen

(DO) concentration was controlled at 3 ± 0.2 mg/L using an on/off control valve. The pH was controlled during the anaerobic and aerobic phases at 7 ± 0.1 using a one-way controller that dosed 0.5M HCl when the pH was above the set-point. The whole system was controlled automatically by a PLC system (Opto 22, Temecula, USA).

Figure 3.3: Pictures of the experimental set-up in the AWMC laboratory.

3.2 Chemicals

All the chemicals used in all the studies, except the reagents used in the AWMC lab, Australia, were grade reagents of PANREAC with analytical purity (PA), special reagent (RE) used for analysis and only pure (PRS) for the synthetic feed. In the AWMC lab, the chemicals used were analytical grade reagents and supplied by either Asia Pacific Specialty Chemical Ltd. (Australia) or BDH Chemicals, Australia.

3.3 Analytical Methods

The analytical methods used during the whole experimental part are described below: Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Total Solids (TS), Volatile Solids (VS), Chemical Oxygen Demand (COD), Volatile Fatty Acids (VFA), Ammonium ($N\text{-}NH_4^+$), Total

Kjeldahl Nitrogen (TKN), Nitrites ($N\text{-}NO_2^-$), Nitrates ($N\text{-}NO_3^-$) and Phosphate ($P\text{-}PO_4^{3-}$).

3.3.1 MIXED LIQUOR SUSPENDED SOLIDS (MLSS) AND MIXED LIQUOR VOLATILE SUSPENDED SOLIDS (MLVSS)

Mixed Liquor Suspended Solids (MLSS) and Mixed Liquor Volatile Suspended Solids (MLVSS) were analysed according to the analytical methods 2540D and 2450E of Standard Methods (APHA (1998)).

For MLSS determination, a well-mixed sample was filtered through a weight standard glass-fibre filter (GF/C 47 mm) and the residue retained on the filter was dried overnight to a constant weight at 103-105ºC. The weight of the filter and the dried residue was determined and used to calculate the MLSS in mg/L.

MLVSS was determined by the combustion of the MLSS filter in a furnace at a temperature of 550ºC for one hour. Then, partially cooled in air until most of the heat had been dissipated and transferred to a desiccator. After cooling in a desiccator, the filter was weighed. The difference between the weight with the dried residue and the combustion residue were used to calculate the MLVSS in mg/L.

3.3.2 TOTAL SOLIDS (TS) AND VOLATILE SOLIDS (VS)

Total Solids (TS) and Volatile Solids (VS) were analysed according to the analytical methods 2540B and 2450C of Standard Methods (APHA (1998)).

For TS determination, an amount of well-mixed sample was put in a weight capsule and dried overnight to a constant weight at 103-105ºC. The weight of the capsule and the capsule with the dried residue was determined and used to calculate the TS in mg/L.

VS was determined by the combustion of the TS capsule in a furnace at a temperature of 550ºC over one hour. Then, partially cooled in air until most of the heat had been dissipated and transferred to a desiccator. After cooling in a desiccator, the capsule was weighed. The difference between the weight with the dried residue and the combustion residue were used to calculate the VS in mg/L.

3.3.3 CHEMICAL OXYGEN DEMAND (COD)

Total and Soluble Chemical Oxygen Demand was analysed by adapting the analytical method 5220B of Standard Methods (APHA (1998)).

The COD was determined by an oxidation of a boiling mixture of chromic and sulphuric acids. The sample was refluxed in a strong acid solution with an excess of potassium dichromate ($K_2Cr_2O_7$). After two hours of digestion, the remaining unreduced $K_2Cr_2O_7$ was titrated with ferrous ammonium sulphate to determine the amount of $K_2Cr_2O_7$ consumed and the oxidizable matter was calculated in terms of oxygen equivalent.

3.3.4 VOLATILE FATTY ACIDS (VFA)

Volatile Fatty Acids (VFA) were measured using high performance liquid chromatography (HPLC) with a HPX-87H 300mm x 7.8mm, BioRad Aminex ion exclusion HPLC column operated at 65ºC. VFA samples were obtained through filtering mixed liquor from the SBR using 0.22 µm Millex GP syringe driven filters.

This analysis was performed at the Advanced Wastewater Management Centre (AWMC) laboratories in Brisbane (Queensland, Australia).

3.3.5 TOTAL NITROGEN (TN)

Total nitrogen (TN) was determined as the sum of ammonium nitrogen ($N\text{-}NH_4^+$), organic nitrogen ($N\text{-}N_{org}$), nitrites ($N\text{-}NO_2^-$) and nitrates ($N\text{-}NO_3^-$) concentrations as mg/L N-TN. Every compound was analysed independently as described below.

3.3.6 AMMONIUM ($N\text{-}NH_4^+$)

Ammonium ($N\text{-}NH_4^+$) was analysed by adapting the analytical method 4500-NH_3.B-C of Standard Methods (APHA (1998)).

For ammonium determination, a sample of water or wastewater was distilled into a solution of boric acid. The ammonia in the distillate could be determined either titrimetrically with a standard H_2SO_4 and a pHmeter. The result was expressed in mg/L $N\text{-}NH_4^+$.

Distiller: BÜCHI B-324

Automatic titration: Titrino 719S Metrohm

Register: Citizen IDP 460 RF

3.3.7 TOTAL KJELDAHL NITROGEN (TKN)

Total Kjeldahl Nitrogen method determines nitrogen in the trinegative state or the sum of organic nitrogen ($N\text{-}N_{org}$) and ammonia nitrogen ($N\text{-}NH_4^+$). Having the ammonia nitrogen concentration, organic nitrogen can be determined. Total Kjeldahl Nitrogen (TKN) was analysed by adapting the analytical method 4500-N_{org}.B of Standard Methods (APHA (1998)).

TKN determination existed in the presence of H_2SO_4 and a catalyst agent (i.e. Selenium), ammonio nitrogen of many organic materials was converted to ammonium. Free ammonia also was converted to ammonium. After the digestion, this ammonium was analysed by distillation (3.3.6).

3.3.8 ORGANIC NITROGEN (N_{ORG})

Organic nitrogen can be calculated as the difference between Total Kjeldahl Nitrogen (TKN) and ammonium nitrogen (N-NH4+). The result is presented as mg/L $N\text{-}N_{org}$.

3.3.9 NITRITES ($N\text{-}NO_2^-$) AND NITRATES ($N\text{-}NO_3^-$)

Nitrites ($N\text{-}NO_2^-$) and Nitrates ($N\text{-}NO_3^-$) can be analysed in different ways, during the experimental part of the research two methods were used: High Pressure Liquid Chromatography (HPLC) and Ion Chromatography (IC).

I High Pressure Liquid Chromatography (HPLC)

High Pressure Liquid Chromatography (HPLC) is a method for the determination of nitrite and nitrate. This method was adapted from Standard Methods (APHA (1998)).

Principle:

A water sample was injected into a stream of H_3PO_4/KH_2PO_4 buffer mobile phase maintained under high pressure. The anions of interest were separated on the basis of their relative affinities for a low capacity when they were passed through the column. The separated anions and their acids forms were measured by a spectrophotometer. They are identified on the basis of retention time as compared to standards. Quantitation is by measurement of peak area or peak height.

The High Performance Liquid Chromatography instrumental is described below:

Pump: Shimadzu LC-9 A

Manual injector: Rheodyne

Detector: UV-Vis Shimadzu SPD-6 AV

Registrator: Chromatopac C-R6 A Shimadzu

Column: Spherisorb SAX 5 μm 20 × 0.46 × 5 of Tracer Analítica S.L.

The method used for nitrites and nitrates determination was a constant isocratic flow system with a H_3PO_4/KH_2PO_4 buffer (0.05M en $H_2PO_4^-$ with pH adjusted at 3 with H_3PO_4) as eluent. The flow was 1 mL/min. The samples were filtered at 0.2 μm and injected manually through a loop of 20 μL. The anions were detected in a wavelength of 220nm with a Deuterium lamp. In these conditions nitrite retention time was around 9 minutes and nitrate 12 minutes. The total time for every sample was around 15 minutes.

II Ion Chromatography (IC)

Ion chromatography with chemical suppression of eluent conductivity is a method for the determination of common anions such as bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate. Nitrates, nitrites and phosphates were analysed by adapting method 4110B from Standard Methods (APHA (1998)).

Principle:

A water sample was injected into a stream of carbonate-bicarbonate eluent and passed through a series of ion exchangers. The anions of interest were separated on the basis of their relative affinities for a low capacity, strongly basic anion exchanger (guard and separator columns). The separated anions were directed through a hollow fiber cation exchanger membrane (fibre suppressor) or micromembrane suppressor bathed in continuously flowing strongly acid solution (regenerant solution). In the suppressor the separated anions are converted to their highly conductive acid forms and the carbonate-bicarbonate eluent was converted to weakly conductive carbonic acid. The separated anions and their acids forms are measured by conductivity. They are identified on the basis of retention time as compared to standards (Figure 3.4). Quantitation is by measurement of peak area or peak height.

The Ion Chromatography instrumental is described below:

Ion chromatography: Metrohm 761-Compact IC and 831 Compact autosampler

Column: Anion separator column Metrosep A Supp 5 – 250

Guard column: A Supp5 Guard

Detector: Conductivity (max. 50 µS/cm)

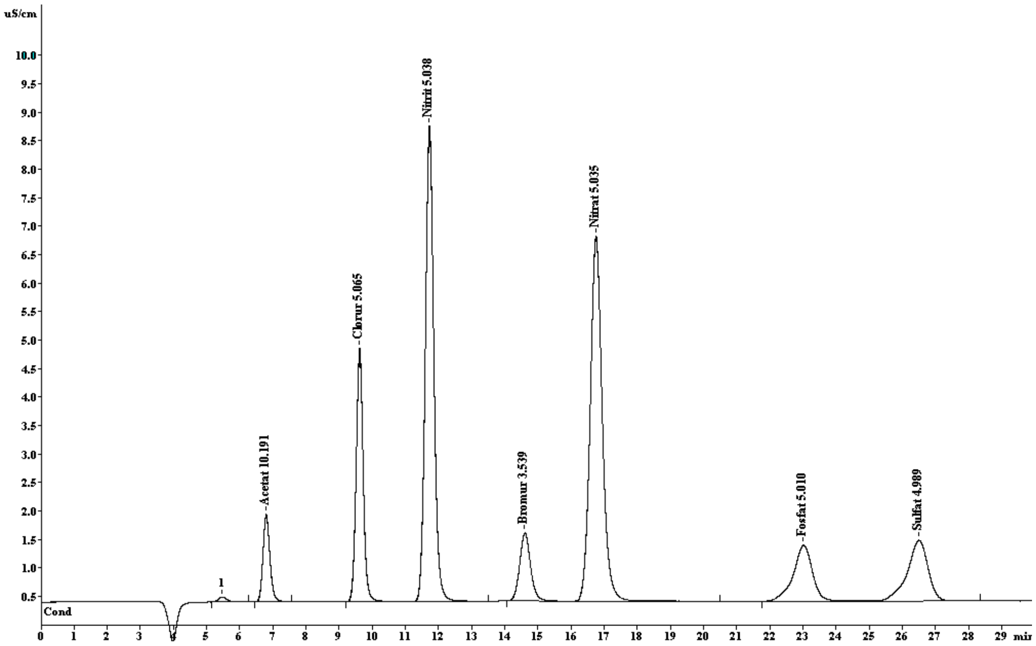


Figure 3.4: Typical chromatogram for a standard sample in an Ion Chromatography.

The method used for the determination of anions was a constant isocratic flow system with a carbonate-bicarbonate buffer (H_2CO_3/HCO_3^- 1mM / 3.2mM.) as eluent. The column flow was 0.7 mL/min and the pressure was around 10-12 MPa. Two regenerant solutions were used H_2SO_4 20 mM and distilled water. The samples were injected automatically through an 831 Compact autosampler and using a loop of 20 µL. In these conditions nitrite retention time was around 12 minutes, nitrate 17 minutes and phosphate 23 minutes. The total time for every sample was around 30 minutes.

All the samples were filtered at 0.2 µm before their introduction in the autosampler.

3.3.10 PHOSPHATE ($P\text{-}PO_4^{3-}$) DETERMINATION

Phosphorus analysis embodies two general procedural steps: conversion of the phosphorus form of interest to dissolved orthophosphate and determination of dissolved orthophosphate. Dissolved orthophosphate was analysed during the experimental part in three different ways.

I Vanadomolybdophosphoric acid colorimetric

Phosphate was analysed by the Vanadomolybdophosphoric acid colorimetric method 4500-P.C from Standard Methods (APHA (1998)).

In a dilute orthophosphate solution, ammonium molybdate reacted under acid conditions to form a heteropoly acid and a molybdophosphoric acid. In the presence of vanadium, yellow vanadomolybdophosphoric acid was formed. The intensity of the yellow colour was proportional to phosphate concentration.

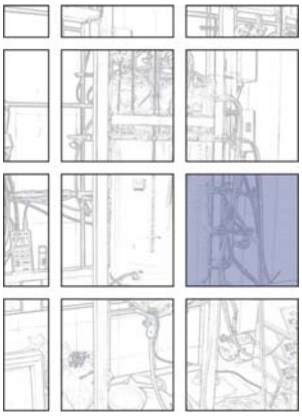
II Ion Chromatography (IC)

Phosphate was analysed by adapting method 4110B of Standard Methods (APHA (1998)) described in nitrates and nitrites determination (3.3.9II).

III Flow Injection Analyser (FIA)

Orthophosphate ($P\text{-}PO_4^{3-}$) was analysed using a Lachat QuikChem8000 Flow Injection Analyser (FIA). FIA samples were obtained through filtering mixed liquor from the SBR using 0.22 µm Millex GP syringe driven filters.

This analysis was performed at the Advanced Wastewater Management Centre (AWMC) laboratories in Brisbane (Queensland, Australia).



4

OPERATIONAL CONDITIONS FOR NITROGEN REMOVAL USING STEP-FEED STRATEGY

4.1 Summary

A step-feed strategy was applied in a Sequencing Batch Reactor (SBR) for nitrogen removal when treating synthetic wastewater in order to avoid the use of an external carbon source. Two and six filling events were applied to test the efficiency of the step-feed strategy. The study of the evolution of the different nitrogenous compounds throughout the cycle allowed information about the performance process to be obtained. At the same time, this information is available through relatively simple sensors that are able to measure on-line concepts such as pH, ORP and DO. By means of the analysis of the pH, ORP and DO profiles the critical points for the nitrification and denitrification can be identified. The complete ammonia removal corresponded exactly to the "Ammonia Valley" in the pH curves and the complete nitrate

removal corresponded to the "Nitrate Knee" in ORP curves.

4.2 Introduction

Two processes are necessary to achieve nitrogen removal: nitrification under aerobic conditions (Equation 1.3) and denitrification under anoxic conditions with carbon source presence (Equation 1.5), as described before in the Introduction (1.2.1). The key to the problem of nitrogen removal in an SBR is how to combine both processes in just one reactor. Different strategies for nitrogen removal have been applied to SBRs. The most commonly adopted strategy is a single filling event which consists of a reaction phase composed firstly by an anoxic phase, followed by an aerobic phase and finally, by a settling and discharging phase of treated wastewater (Keller *et al.*, 1997, Johansen *et al.*, 1997, Yu *et al.*, 1997 among others).

Nevertheless, a wide range of strategies can be applied to improve process efficiency: the addition of an external carbon source (Bernades and Klapwijk, 1996, Cheng J. and Liu B., 2001), sludge addition from A/O[2] reactors during anoxic periods (Ra *et al.*, 2000) or optimisation of filling phases during anoxic phases (Andreottola *et al.*, 2001 and Vives M.T. *et al.*, 2001). In the case of this last strategy, the authors use a step-feed strategy characterised by the alternation of aerobic and anoxic phases in a cyclic sequence.

The Sequencing Batch Reactor (SBR) allows the switching between different conditions in a temporal sequence throughout a cycle (i.e. aerobic, anoxic conditions). A combination of these conditions can lead to the accomplishment nitrogen removal. Then, a cycle could be as is complicate as required by the main objective. For this reason, it is necessary to know what happens inside the reactor at every moment. By means of simple parameters measured on-line such as pH, ORP and DO the evolution of the process is known in real-time. By analysing these parameter values it is possible to identify the end of nitrification (the ammonia valley: pH minimum, α_{O2}: the inflection point in the DO profile and α_{ORP}: the inflection point in the ORP profile) and denitrification (nitrate knee: inflection point in the ORP and nitrate apex: pH maximum) for the nitrogen removal (Paul *et al.*, 1998, Chang and Hao, 1996, Plisson-Saune *et al.*, 1996, Puig *et al.*, accepted).

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[2] A/O: Anoxic-Oxic continuous flow reactors

4.3 The SBR cycle definition

As previously stated, when an SBR is designed for nitrogen removal purpose, the process becomes more complex. Nitrification (the aerobic phase) and denitrification (the anoxic phase) must be accomplished. Denitrification could be one of the limiting steps of the process with regards to organic matter requirements. If the easily biodegradable substrate is not focused on the denitrification process, a partial denitrification could occur and, thus, high effluent nitrate concentrations may be found. This would be caused by a partial denitrification. A step-feed strategy is an option to reduce such phenomena and to improve the denitrification process without the external carbon source addition. This strategy takes care with the number of the filling events allocated in the anoxic phases in order to obtain better denitrification efficiency.

Different operational conditions may be defined to achieve a good performance for nitrogen removal using a step-feed strategy in the SBR: the order of the reaction phases (anoxic-aerobic or aerobic-anoxic pairs) and the number of fill-react pairs.

4.3.1 SELECTING THE PAIRS FOR THE REACTION PHASES

At the beginning of the cycle there is a filling phase which needs to be defined. Such definition depends on the treatment objectives. If the objective is nitrogen removal without an external carbon source addition, all the organic matter available for the filling phase would be used for denitrification purposes. Then, the best fill strategy is to feed under anoxic conditions. In this way, the organic matter present in the wastewater is used to denitrify the residual nitrates of the previous phases or cycle.

Another important factor to consider is the order of the reaction conditions: aerobic-anoxic or anoxic-aerobic. When both conditions are combined sequentially, at the end of the process some ammonia or nitrate could still be found in the effluent, depending on the order of the conditions. Figure 4.1 presents the ammonia and nitrate profiles during both reaction pairs: aerobic-anoxic pair (left) and anoxic-aerobic pair (right), always considering the filling process under anoxic conditions. When using an aerobic-anoxic pair sequence an effluent with residual ammonium can be found at the end of the cycle. On the other hand, when changed to an anoxic-aerobic pair sequence, the residual nitrogen in the effluent will be in nitrate form.

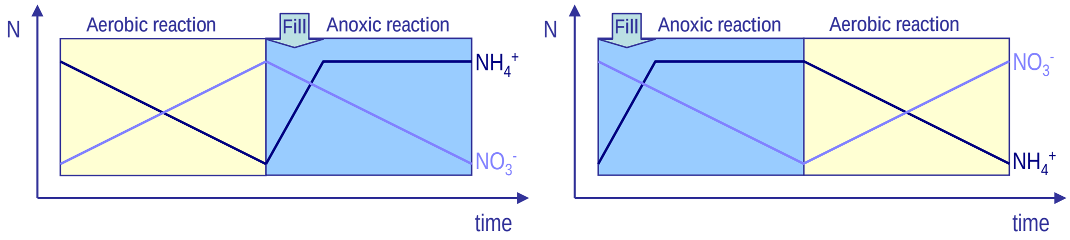


Figure 4.1: Ammonium and nitrate profiles during two different operations in the reaction phase: aerobic-anoxic conditions, on the left, and anoxic-aerobic conditions, on the right.

In the case of choosin an aerobic-anoxic conditions pair (Figure 4.1, left), when aerobic conditions are considered, the ammonium is nitrified to nitrate, meanwhile when there are anoxic conditions nitrate is denitrified and ammonia concentration increases due to addition of feed. So, at the end of an aerobic-anoxic pair, reactor contents present a high ammonium concentration. One of the consequences of ammonia discharge in treated wastewater is that the nitrification could be conducted into the receiving media, concluding with a significant consumption of dissolved oxygen that then would not be available for other living organisms (animals, plants etc.).

Nevertheless, if anoxic-aerobic conditions are selected (Figure 4.1, right), the anoxic phase starts with a high nitrate level, obtained from the previous aerobic phase, that is then denitrified because of the presence of organic matter. Meanwhile, the ammonium concentration increases because of the ammonia contents of the raw wastewater. Afterwards, under aerobic conditions, the ammonium is nitrified and nitrate is found in the final phase. When discharging nitrates into the receiving media, no dissolved oxygen consumption is produced, but a rising problem is able to be observed because of the nitrate denitrification during the settle phase prior to discharge. Both strategies have some problems with the effects on the receiving media or operation process problems. As it is easier to avoid operation process problems than receiving media effects, it is preferable to discharge oxidised nitrogen (i.e. nitrate) into the receiving media than to discharge ammonia. So, an anoxic-aerobic pair sequence (always filling during the anoxic conditions) is preferable to an aerobic-anoxic pair sequence for nitrogen removal.

In summary, the sequence to apply in a step-feed strategy would be a filling under anoxic conditions followed by an anoxic phase and ending with an aerobic phase to complete a full anoxic-aerobic pair sequence. In this way, under anoxic conditions it is possible to denitrify the nitrate obtained during the previous cycle. Meanwhile, under aerobic conditions the nitrification of accumulated ammonia during the previous anoxic phase is able to be achieved.

4.3.2 NUMBER OF FILLING-REACTION EVENTS DURING ONE CYCLE.

Once an anoxic-aerobic reaction pair has been selected, another important element to consider is the number of filling-reaction events (i.e. the number of anoxic-aerobic pairs to conduct per cycle). A step-feed strategy consists in a repeated sequence of fill-react which occurs more than once for a cycle; in other words, to perform more than one filling event followed by a reaction phase for a cycle. In this way, it is possible to reduce the amount of nitrogen concentration in the effluent depending on the number of filling-reaction events (M, henceforth refers to as filling events). Based on a simple nitrogen mass balance (during the last filling event) and, considering a complete nitrification/denitrification (under aerobic or anoxic conditions, respectively), final effluent nitrogen concentration could be calculated as Equation 4.1:

$$N_{EF} = N_{IN} \cdot \frac{V_F}{V_T} \cdot \frac{1}{M} \qquad \text{(eq. 4.1)}$$

Where:
N_{EF}: Total Nitrogen concentration in the effluent, mg/L
N_{IN}: Total Nitrogen concentration in the influent, mg/L
V_F/V_T: Exchange ratio
M: Number of filling events applied during a cycle.

Therefore, it is possible to estimate the nitrogen concentration at the end of the process (N_{EF}) by a previous definition of how many filling events (M) are needed for a specific influent nitrogen concentration (N_{IN}) operating under a pre-defined V_F/V_T fill fraction.

The number of filling events and V_F/V_T have a strong influence on the quality of the effluent as is demonstrated in Table 4-1 which presents the total effluent nitrogen concentration (N_{EF}) and the nitrogen removal percentage (%), as a function of the number of filling events (M) operating under a pre-defined exchange ratio (V_F/V_T) calculated by Equation 4.1.

Values have been obtained assuming an influent nitrogen concentration of 70 mg/L N, a global SBR cycle time of 8 hours and an effective fraction ($f_E=t_E/t_C$) of 0,8125 (6.5 hours of filling and reaction over an 8 hours cycle). Hydraulic retention time (HRT) and effective hydraulic retention time (HRT_E) are also calculated according to the section 1.3.1.

In order to distinguish between conditions with a nitrogen discharge lower or higher than 5 mg/L N or conditions with more than or less than a 90% nitrogen removal rate, Table 4-1 presents a red line that notes such different effluent nitrogen levels. If in the effluent more than 5 mg/L $N\text{-}NO_3^-$ remains some rising events can be observed in the settling phase, while values of over 90% of nitrogen removal must be indicative of good nitrogen removal efficiency.

Table 4-1: Relation between the ratio V_F/V_T and the number of filling events (M) where N_{EF} is nitrogen effluent concentration and % is percentage of nitrogen removal.

V_F/V_T	TRH (d)	TRH_E (d)	M											
			1		2		3		4		5		6	
			N_{EF}	%	N_{EF}	%	N_{EF}	%	N_{EF}	%	N_{EF}	%	N_{EF}	%
0.05	6.67	5.42	3.50	95.0	1.75	97.5	1.17	98.3	0.88	98.8	0.70	99.0	0.58	99.2
0.10	3.33	2.71	7.00	90.0	3.50	95.0	2.33	96.7	1.75	97.5	1.40	98.0	1.17	98.3
0.15	2.22	1.81	10.50	85.0	5.25	92.5	3.50	95.0	2.63	96.3	2.10	97.0	1.75	97.5
0.20	1.67	1.35	14.00	80.0	7.00	90.0	4.67	93.3	3.50	95.0	2.80	96.0	2.33	96.7
0.25	1.33	1.08	17.50	75.0	8.75	87.5	5.83	91.7	4.38	93.8	3.50	95.0	2.92	95.8
0.33	1.01	0.82	23.10	67.0	11.55	83.5	7.70	89.0	5.78	91.8	4.62	93.4	3.85	94.5
0.35	0.95	0.77	24.50	65.0	12.25	82.5	8.17	88.3	6.13	91.3	4.90	93.0	4.08	94.2
0.42	0.79	0.64	29.40	58.0	14.70	79.0	9.80	86.0	7.35	89.5	5.88	91.6	4.90	93.0
0.45	0.74	0.60	31.50	55.0	15.75	77.5	10.50	85.0	7.88	88.8	6.30	91.0	5.25	92.5
0.50	0.67	0.54	35.00	50.0	17.50	75.0	11.67	83.3	8.75	87.5	7.00	90.0	5.83	91.7

From Table 4-1, when increasing the exchange ratio (V_F/V_T) a lower hydraulic retention time (HRT) and effective hydraulic retention time (HRT_E) is obtained. Also, for a fixed number of filling events M (i.e., M=1) the higher the exchange ratio (V_F/V_T from 0.05 to 0.50) is, the higher the nitrogen concentration in the effluent (from 3.5 to 35.0) will be and the lower the nitrogen removal percentage (from 95% to 50%) will be. On the other hand, for a fixed exchange ratio (V_F/V_T), the higher the number of filling events M are, the lower the nitrogen concentration in the effluent will be and the higher the N removal (from 67% to 94.5) will be.

This chapter presents the nitrogen removal study using a step-feed strategy in an SBR when treating synthetic wastewater. Two and six filling events are applied to characterize the cycle and identify the main characteristic points of carbon and nitrogen removal (nitrification and denitrification) that are able to be observed with the on-line measurements (pH, Dissolved Oxygen and Oxidation-Reduction potential).

4.4 Objectives

The main objective of this chapter is to evaluate different step-feed strategies for nitrogen removal using synthetic wastewater throughout the study of the effect of a different number of filling events, the definition of the number and the length of the phases for a cycle. And also, the study of the critical points by following the on-line pH, DO and ORP data. These objectives are specified in:

- Define the length and number of phases for a cycle, it meants the number of pairs anoxic-aerobic.
- Study the effect of two and six filling events in the nitrogen removal.
- Identification of the critical points following the on-line pH, DO and ORP measurements to evaluate the status of the SBR.

4.5 Materials and Methods

4.5.1 ANALYTICAL METHODS

Throughout the whole operational study, synthetic and treated wastewaters were analysed for: Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Total and Soluble Chemical Oxygen Demand (COD), ammonium ($N\text{-}NH_4^+$), Total Kjeldahl Nitrogen (TKN), nitrites ($N\text{-}NO_2^-$, 3.3.9l) and nitrates ($N\text{-}NO_3^-$, 3.3.9l) according to the methodologies presented in the section 3.3.

4.5.2 SYNTHETIC WASTEWATER

The synthetic wastewater was prepared twice a week to reach a concentration of 600 mg/L COD, 80 mg/L N-TKN and 70 mg/L $N\text{-}NH_4^+$. The wastewater was basically composed of a mixed carbon source, an ammonium solution and, moreover, a phosphate buffer, an alkalinity control (350 mg/L $NaHCO_3$) and a microelements solution (adapted to Dangcong *et al.*, 2000). Solution compositions are described in Table 4-2.

Table 4-2: Synthetic Wastewater composition.

Name	Formula	Concentration	Solution
Sodium acetate	CH_3COONa	5 mg/L	Carbon source
Sodium propionate	CH_3CH_2COONa	5 mg/L	
Starch	$(C_6H_{10}O_5)_n$	5 mg/L	
Tryptone	-	5 mg/L	
Ethanol	CH_3CH_2OH	0.375 mL/L	
Dehydrated meat extract	-	105 mg/L	
Ammonium chloride	NH_4Cl	272.6 mg/L	Ammonium source
Manganese (II)chloride tetrahydrate	$MnCl_2.4H_2O$	275.525 mg/L	Microelements solution
Zinc chloride dihydrate	$ZnCl_2.2H_2O$	2.675 mg/L	
Copper (II) chloride dihydrate	$CuCl_2.2H_2O$	29.96 mg/L	
Magnesium sulphate heptahydrate	$MgSO_4.7H_2O$	8121 mg/L	
Iron (III) chloride hexahydrate	$FeCl_3.6H_2O$	1284 mg/L	
Calcium chloride dihydrate	$CaCl_2.2H_2O$	1963.45 mg/L	
Potassium dihydrogen phosphate	KH_2PO_4	25.5 mg/L	Phosphate buffer
Dipotassium hydrogen phosphate	K_2HPO_4	65.25 mg/L	
Disodium hydrogen phosphate heptahydrate	$Na_2HPO_4.7H_2O$	100.2 mg/L	

4.5.3 EXPERIMENT SET-UP

The SBR was composed of a cylindrical reactor with a maximum working volume of 30 L and a minimum working volume of 14L. The reactor was seeded with a nitrifying activated sludge from the wastewater treatment plant of Sils (Girona, Spain). A full description of the SBR is presented in the section 3.1.1. An 8 hours cycle was conducted in the SBR, treating 10 L of wastewater per cycle.

The SBR was operated by means of an in-house developed data acquisition and control software program developed by Lab-View. The software was able to repeat, over time, a previously defined operational cycle which controlled the on/off switch of all electrical devices (i.e. peristaltic pumps, electro-valves and mixing units). On-line mean values of pH, ORP, DO and Temperature were stored every 15 seconds in a simple text file for further processing.

4.5.4 OPERATIONAL CONDITIONS

The study was conducted over two different operational periods: Period 1 with two filling events and Period 2 with six filling events. An 8 hour cycle time was divided into reaction (395 minutes), settling (60 minutes) and discharge (25 minutes) phases and was used for whole the study. Nevertheless, distribution of anoxic filling, anoxic and aerobic phases for each period were different as presented in Figure 4.2. Constant oxygen supply flow was maintained throughout the whole study.

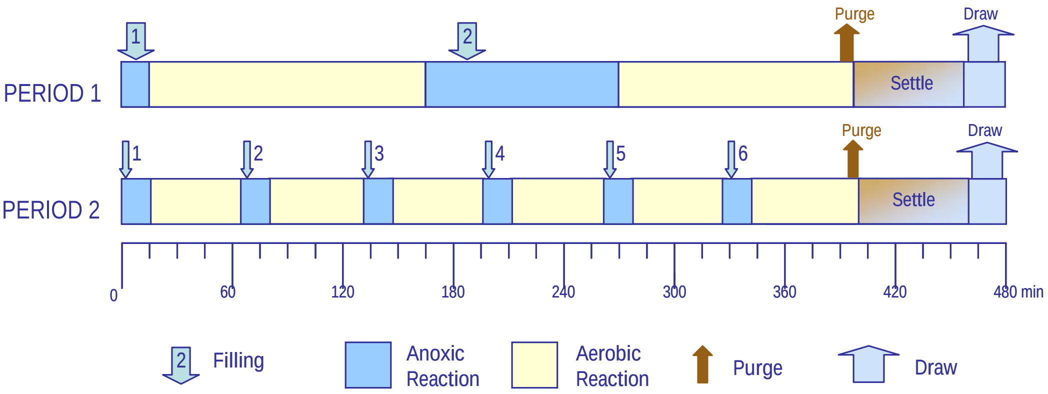


Figure 4.2: SBR cycle definition during periods 1 (two filling events) and 2 (six filling events) indicating anoxic, aerobic and filling phases.

Table 4-3 summarises the main operational parameters used during the experimental periods (1 and 2).

Table 4-3: Operational conditions applied during Period 1and 2. (* % Aerobic and Anoxic reaction time are calculated over the reaction time)

Description	Symbol	Units	Period 1	Period 2
Flow	Q	L/d	30	
Total cycle time	tc	h	8	
Effective fraction	f_E	-	0.82	
Exchange ratio	V_F/V_T	-	0.42	0.33
Minimum Volume	V_{MIN}	L	14	20
Effective time	$t_E= t_F+t_R$	h	6.58	6.55
Anoxic reaction time	%ANOXIC *	%	30.4	22.9
Aerobic reaction time	%AEROBIC *	%	69.6	77.1
Hydraulic retention time	HRT	d	0.8	1
Effective hydraulic retention time	HRT_E	d	0.66	0.82
Sludge retention time	SRT	d	26.7	33.3
Period length	-	days	70	30

During both periods 1 and 2, the SBR was treating 10 litres of wastewater per cycle. However, different hydraulic and sludge retention times for Period 1 and 2 were applied. In Period 1 the SBR worked with a minimum/maximum volume of 14/24, while in Period 2, minimum reaction volume was increased from 14 to 20 litres (minimum/maximum SBR volume of 20/30) giving an operational exchange ratio of 0.33.

During Period 1 a high aerobic time percentage was used in order to promote nitrifying biomass evolution (69.6% aerobic *vs.* 30.4% anoxic), while during Period 2 anoxic reaction time was reduced from 30.4 to 22.9% to an optimise nitrification/denitrification efficiency.

4.5.5 METHODOLOGY

The reactor performance was monitored throughout the experimental at least twice a week though the determination of the COD, solids and nitrogen (TKN, N-NO_3^-, N-NO_2^- and N-NH_4^+) in the influent and the effluent. The samples were obtained from the storage tank and at the end of the cycle from the withdrawn wastewater. Once per period, a cycle analysis was performed, to obtain a nitrogen profile, by taking samples every few minutes over 8 hours. Mixed-liquor suspended solids (MLSS) and mixed-liquor volatile suspended solids (MLVSS) were analysed at the end of the aerobic phase at least once every two weeks.

General reactor maintenance was routinely performed, involving tasks such as checking and testing the probes, checking the pump flow rates, replacing tube connections and cleaning the reactor.

4.6 Results and Discussion

4.6.1 PERIOD 1: TWO FILLING-REACTION EVENTS.

In the first study, Period 1, two filling events were adopted following the step-feed strategy for nitrogen removal. The feeding of the SBR was split into two equal parts (5L per feed, 10L per cycle) corresponding to both the filling events.

After 70 days of operation (Vives M.T., 2001), stable reactor behaviour was observed. The process efficiency is presented in Table 4-4, as averaged results during the whole operational period.

From the results gathered in Table 4-4, it is remarkable to note that whilst more than 90 % of organic matter and ammonium was removed, (92.7% and 93.7%, respectively), during the whole Period 1 the total nitrogen removal was around 82% due to the fact that denitrification was not completed (86.5%). In order to compare this with bibliographic values, the aerobic nitrification rate was calculated during the aerobic phases of the cycles for one day. A value between the range of 0.032-0.173 mg $N \cdot mg^{-1}$ SSV d^{-1} (Randall *et al.*, 1992) was obtained, which is acceptable from the point of view of an SBR process.

Table 4-4: Summarized results obtained in Period 1 (Vives M.T., 2001). *The aerobic nitrification rate is calculated with respect to the aerobic time.

Description	Symbol	Units	Period I
Percentage of organic matter removal	%MO	%	92.7
Nitrification Percentage	% Nit	%	93.7
Denitrification Percentage	% DN	%	86.5
Percentage of Nitrogen removal	% N	%	82.5
Aerobic Nitrification Rate*	V_{NitAE}	mg N $mg^{-1}SSVd^{-1}$	0.089
Food and Microorganism	F/M	mg COD $mg^{-1}SSVd^{-1}$	0.514
Mixed Liquor Suspended Solid	MLSS	mg L^{-1}	1890
Mixed Liquor Volatile Suspended Solid	MLVSS	$mg \cdot L^{-1}$	1688

To understand the behaviour of all nitrogen compounds inside the reactor, after process stabilization, a typical operational cycle was analysed and is presented in Figure 4.3. The figure shows both the nitrogen compounds (ammonium, nitrate and nitrite) evolution (top, Figure 4.3a) and the dynamic pH, DO and ORP evolution (bottom, Figure 4.3b).

In Figure 4.3a, the nitrogen compound evolution was clearly identified when distinguishing between wastewater additions, nitrification and denitrification processes. Thus, while anoxic feeding of the SBR was carried out (0-15 min. and 180-195 min., Figure 4.3), a sudden increase of nitrogen as an ammonia form until 16 mg/L $N\text{-}NH_4^+$ was detected. At the same time, a reduction of nitrate and nitrite to nitrogen gas was achieved in less than 15 minutes, because of the easy wastewater composition (see Table 4-2). This means a specific denitrification rate of 0.214 mg $N\text{-}NO_3^-$ $mg^{-1}VSS \cdot d^{-1}$, being higher than the bibliographic which considers a range from 0.03 to 0.35 mg $N\text{-}NO_3^-$ $mg^{-1}VSS \cdot d^{-1}$ (Metcalf and Eddy (2003)).Finally, with respect to the rest of the anoxic phase no reaction occurred and this means that optimization of this cycle was achieved.

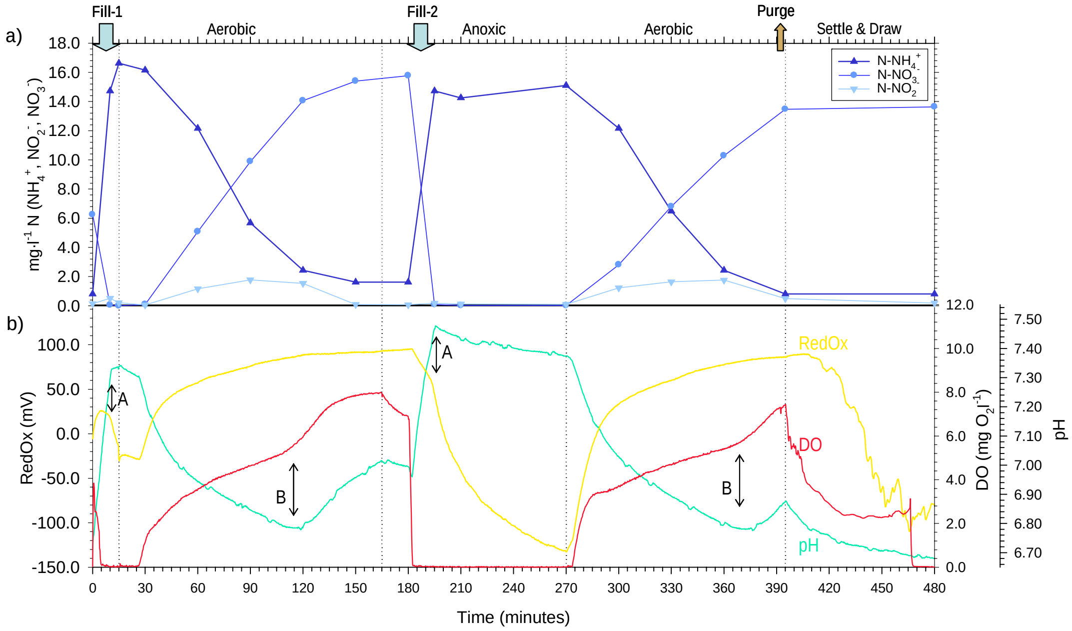


Figure 4.3: Typical cycle profile during Period 1. Nitrogen compound evolution: ammonia, nitrites and nitrates evolution are presented at the top (a) while at the bottom (b) the evolution of pH, DO and ORP after process stabilisation is shown.

Under aerobic conditions, 16.5 and 14.5 mg/L N-NH_4^+ respectively for the first and the second aerobic phases, were nitrified to nitrite and nitrate. Less than 1 mg/L N-NH_4^+ was detected at the end of each aerobic phase, with the specific nitrification rate being 0.107 mg N·mg^{-1} SSV d^{-1} higher than the average result of Period 1.

At the end of the cycle organic matter removal, nitrification and denitrification percentages were 91.9%, 98.7 and 82.2% respectively, while nitrogen removal was 81.1%, with final nitrogen effluent being at around 15 mg/L N (13.6 mg/L N-NO_3^-, 0.2mg/L N-NO_2^- and 0.8 mg/L N-NH_4^+). This nitrogen concentration, mainly in the form of nitrate, was a consequence of the nitrification of the ammonia contents of the last wastewater filling.

Table 4-5 presents a comparison between experimental and theoretical results for this profile. Theoretical results were obtained by applying Equation 4.1. Theoretically, nitrogen concentration in the effluent was expected to be over 16.4 mg/L N and experimentally it was found at a very close value: 14.6 mg/L N.

In Figure 4.3b, on-line monitoring of pH, DO and ORP probes clearly showed the critical points. Following these on-line parameters throughout the cycle it is possible to see the state of the reactor at every moment and to detect the end of the nitrification and the denitrification processes (the critical points).

Table 4-5: Comparison between experimental and theoretical concentrations during Period 1. *Theoretical results were calculated by applying Equation 4.1.

		Units	TKN	Ammonium	Nitrite	Nitrate	Total N
Influent		mg N/L	78.63	76.20	0.15	0.00	78.78
Effluent	Exp.	mg N/L	-	0.81	0.19	13.63	14.63
	Theor.*	mg N/L	-	0	16.38		16.38

In the first 15 minutes under the anoxic filling phases there was a constant increase of pH due to influent addition coupled with the denitrification process. Meanwhile, ORP decreased. When complete denitrification was achieved the pH and ORP evolution changed, showing the final denitrification critical point. Nitrate Apex in the pH and Nitrate Knee in the ORP (point A, Figure 4.3b) can be observed during both anoxic filling phases (minutes 10 and 195).

During the aerobic phases a constant decrease of pH was observed due to nitrification process. After a complete nitrification a slight pH increase was noted. This minimum (point B, Figure 4.3b) corresponds to the Ammonia Valley. At the same time the end of nitrification is also noted by a sudden increase of dissolved oxygen. This point is labelled as α_{O2} (point B in the DO profile). Figure 4.3b also shows how, during both aerobic phases the Ammonia Valley in the pH and α_{O2} in the DO curve evolution can be observed in minutes 125 and 375.

4.6.2 PERIOD 2: SIX FILLING-REACTION EVENTS.

In the second part, Period 2, six filling events were adopted to treat the synthetic wastewater in order to reduce the final nitrogen concentration. The filling volume of 10 litres was split into six equal parts (1.67 L), which means, a volume of 1.67 litres of influent wastewater was pumped into the reactor during the first 5 minutes at the beginning of each anoxic stage. The main difference between Period 1 and Period 2 was the increase in the number of filling events, the reduction of anoxic time to increase the aerobic time and the diminution of the exchange ratio from 0.42 to 0.33. General conditions are detailed in Table 4-3.

After 30 days of operation (Vives M.T., 2001), stable reactor behaviour was observed. The process efficiency is summarized in Table 4-6 through average values for Period 2.

Comparison between results obtained for both periods shows how a higher organic matter and nitrogen removal was achieved in the case of Period 2 (Table 4-6) with respect to Period 1 (Table 4-4). Organic matter and nitrogen percentage removal were 94.4 % and 89.8% respectively, while 92.7% and 82.5% of organic matter and nitrogen removal were found during

Period 1. At the same time, lower aerobic nitrification rate was found when compared with Period 1 when a rate of 0.052 mg N·mg^{-1} SSV d^{-1} aerobic nitrification was obtained. This value is included in the range of the bibliographic values from 0.032 to 0.173 mg N·mg^{-1} SSV d^{-1} (Randall *et al.*, 1992), but it is lower than Period 1. This could be as a consequence of the substrate concentration inside the reactor being lower due to a six filling event. Also, a decrease of the food and microorganisms ratio was achieved due to the reduction of filling ratio.

Table 4-6: Summarized of results obtained in Period 2 (Vives M.T., 2001). *The aerobic nitrification rate was calculated with respect to the aerobic time.

Description	Symbol	Units	Period 2
Percentage of organic matter removal	%MO	%	94.4
Nitrification Percentage	% Nit	%	95.1
Denitrification percentage	% DN	%	94.3
Percentage of Nitrogen removal	% N	%	89.8
Aerobic Nitrification Rate*	V_{NitAE}	mg N mg^{-1}SSVd^{-1}	0.052
Food and Microorganism	F/M	mg COD mg^{-1}SSVd^{-1}	0.308
Mixed Liquor Suspended Solid	MLSS	mg L^{-1}	2352
Mixed Liquor Volatile Suspended Solid	MLVSS	mg·L^{-1}	2263

After process stabilization a new operational cycle was analysed in order to understand the behaviour of all nitrogen compounds inside the reactor. The evolutions along the cycle are presented in Figure 4.4. The figure shows both the nitrogen compounds (ammonium, nitrate and nitrite) evolution (top, Figure 4.4a) and the dynamic pH, DO and ORP evolution (bottom, Figure 4.4b).

Figure 4.4a presents the performance of the nitrogen compounds evolution with the nitrification and the denitrification processes. Similar profiles of Figure 4.3 were obtained. An increase in ammonia concentration during anoxic filling events was clearly detected. Nevertheless, due to the reduction of filling volume (1.67 L in each filling) coupled with the increase of minimum volume (from 14 L in Period 1 and 20 L in Period 2), a reduction of maximum ammonia value in the reactor from 16 (Figure 4.3a) to 8 mg/L N-NH_4^+ (Figure 4.4a) was found.

At the beginning of the aerobic phases, the ammonia concentration was reduced rapidly to values less than 1 mg/L N-NH_4^+ obtaining a proportional increase of nitrate concentration. However, in this case the nitrate concentrations obtained at the end of the aerobic phases (complete nitrification) were over 5 mg/L N-NO_3^-. Meanwhile, during the anoxic periods, the denitrification was executed in 15 minutes. This was a consequence of the synthetic wastewater composition (mainly composed of easily biodegradable organic matter) that contributed to a rapid degradation. The specific denitrification rate for this cycle was 0.045 mg N-NO$_3^-$ mg^{-1}TSS·d^{-1}, this being the value in the bibliographic of between 0.03 and 0.35 mg N-NO$_3^-$ mg^{-1}VSS·d^{-1} (Metcalf and Eddy (2003)). In this case, it was lower than in Period 1 possibly due to the lower concentration of nitrate in the reactor.

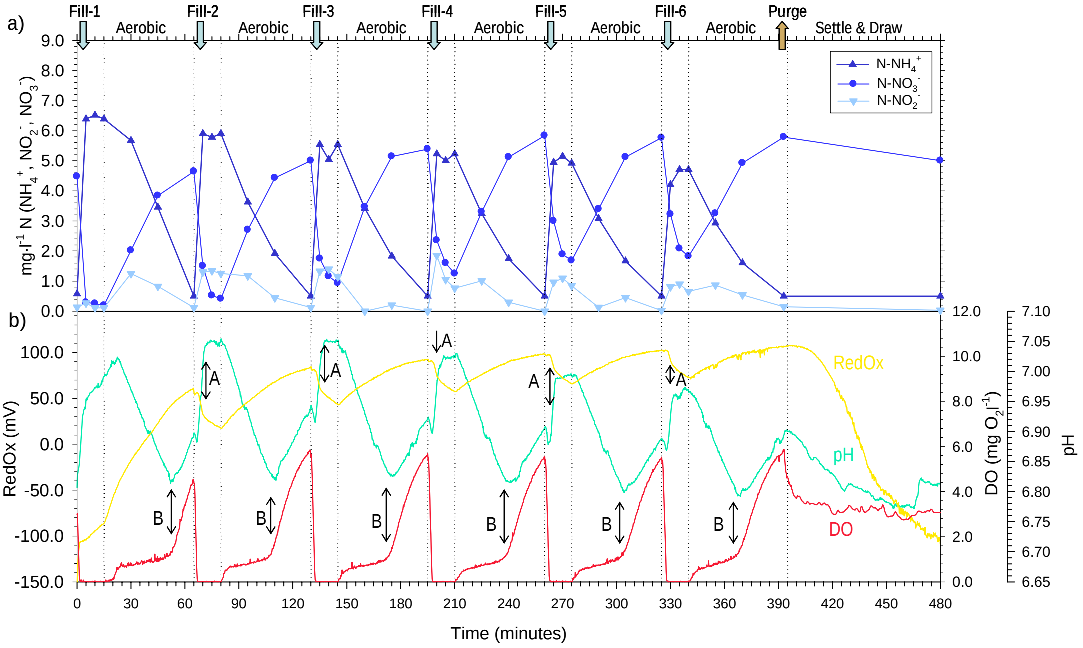


Figure 4.4: Typical cycle profile during Period 2. Nitrogen compound evolution: ammonia, nitrites and nitrates evolution is presented at the top (a) while at the bottom (b) shows the evolution of pH, DO and ORP after process stabilisation.

At the end of the cycle organic matter, nitrification and denitrification percentages were 91.9%, 94.5%, and 92.5% respectively, while nitrogen removal was 87.4%, making a final nitrogen concentration in the effluent of 5.8 mg/L N, mainly as a nitrate form (5.3 mg/L N-NO$_3^-$, 0.03 mg/L N-NO$_2^-$ and 0.5 mg/L N-NH$_4^+$).

As shown in Figure 4.4a, final nitrogen concentration of treated wastewater consisted mainly out of nitrate and showed values of over 6 mg N/L. Table 4-7 presents a comparison between experimental and theoretical results for this cycle in Period 2. Theoretical value was obtained by applying Equation 4.1 for the TKN value in the Table 4-7. Theoretically, nitrogen concentration in the effluent was expected to be over 4.2 mg/L N, while experimentally the result of 5.9 mg/L N was found.

On-line monitored pH, DO and ORP of the cycle (Figure 4.4b) clearly showed the critical points as was shown in the Figure 4.3b. As in Period 1, rapid nitrate depletion under anoxic conditions combined with influent additions avoided a clear detection of a Nitrate Knee (inflection point of ORP profile) and Nitrate Apex (maximum in pH profile). While Nitrate Apex (point A) was detected in almost all filling events (minutes 75, 140, 200, 265 and 335), Nitrate Knee only was detected in a few anoxic phases. On the other hand, under aerobic conditions a sudden increase of the DO profile (α_{O2}, point C) and an abrupt slope change (minimum) for the pH trend (Ammonia Valley, point B) were detected at 50, 110, 175, 235, 305 and 370 minutes.

Table 4-7: Comparison between experimental and theoretical concentrations during Period 2. *Theoretical result was calculated by applying Equation 4.1.

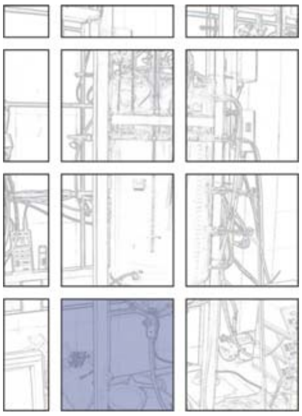
		Units	TKN	Ammonium	Nitrite	Nitrate	Total N
Influent		mg N/L	75.63	68.38	0.38	0.58	76.59
Effluent	Exp.	mg N/L	-	0.50	0.03	5.35	5.88
	Theor.*	mg N/L	-	0	4.20		4.20

4.7 Conclusions

The conclusions obtained in this chapter are related below:

- The step-feed methodology applied in this study has proved useful for nitrogen removal. The number of filling events (M) and the exchange ratio (V_F/V_T) has demonstrated themselves to be useful parameters to identify the nitrogen concentration in the effluent.
- The operation in a SBR using a number of filling events (M) of 2 and exchange ratio (V_F/V_T) of 0.33 in a 8 hour cycle, and treating a synthetic wastewater with a mean values of 600 mg/L COD and 70 mg/L N-NH_4^+ has concluded with an effluent of 55 mg/L COD and 14.6 mg/L N mainly as nitrate (13.6 mg/L N-NO_3^-).
- A step-feed strategy based on six filling events (M=6), V_F/V_T of 0.33 in a 8 hours cycle and promoting use of organic matter for denitrification purposes, has concluded with an effluent of 55 mg/L COD and 5.8 mg/L N mainly as nitrate (5.3 mg/L N-NO_3^-). During this period most of the time, the effluent concentrations have been lower than 5 mg N/L avoiding the rising problems.
- By on-line monitored pH, ORP and DO values, the process status and performance

can be followed in real time by the detection of critical points. Ammonia Valley coupled with α_{O2} can be the critical points which determine the end of the nitrification. Meanwhile Nitrate Knee coupled with Nitrate Apex show the end of the nitrification. All these critical points could be used for further work to optimise the process.



5

APPLICATION OF STEP-FEED STRATEGY FOR ORGANIC MATTER REMOVAL. A CASE STUDY WITH TEXTILE DYEING WASTEWATER

5.1 Summary

This study was undertaken to examine the feasibility of treating biologically textile wastewater for organic carbon removal using an SBR technology application. A lab scale SBR was conducted to remove organic matter (COD) following a step-feed strategy and by adjusting the operational SBR cycle according to the maximum discharge peak flow and carbon removal efficiency required. On the other hand, a simple characterisation of influent wastewater based on physical and chemical analysis was carried out and studied in terms of variability. By means of on-line Oxygen, Oxygen Uptake Rate (OUR) was calculated and used to study the biodegradability of the influent wastewater.

5.2 Introduction

Textile industries have a variable nature in terms of raw materials used, techniques employed, chemicals applied, batch units operations (screening, bleaching, dyeing etc.) and processes involved. In the specific case of textile dyeing industries, large water volumes and chemical consumption are required for the different processes. All this variability causes sudden changes in wastewater flow and composition frequently with these variations being frequently observed on wastewater characterization and treatment (Germirli Babuna *et al.*, 1999).

Textile dyeing wastewater is generally characterised by its intense colouring, caused by large amounts of unfixed remaining dyes; a large amount of refractory COD caused by high-molecular synthetic textile auxiliaries and dyes; (Rott and Minke, 1999). The differences in the composition and treatability of textile wastewaters from different sources and the performance of the industries mean that each industry needs to be considered as a separate case (Germirli Babuna *et al.*, 1999).

Many author have reported the use of biological treatment, specifically, sequencing batch reactor (SBR) in textile wastewaters as an efficient way for the removal of organic matter (Lourenço *et al.*, 2000, Lourenço *et al.*, 2001, Quezada *et al.*, 2000). The SBR system can tolerate shock loads and peak flows because of the equalising effect during the filling phase.

Due to the high variability of textile wastewaters it is important to analyse each wastewater throughout its biological treatment. The respirometric measurements based on Oxygen Uptake Rate (OUR) analyses can provide information about biomass activity inside the reactor or specifically about organic matter removal and nitrification processes under aerobic conditions. The Oxygen Uptake Rate (OUR) is the consumption of dissolved oxygen that is able to be related to the activity of existing biomass (heterotrophic and/or autotrophic) when transforming organic matter and ammonia to CO_2 and nitrite/nitrate, respectively.

By using OUR, it is possible to get more information on the biological wastewater treatment processes and the wastewater (Henze, 1992). The direct registration of the oxygen consumption rate in biological process allows a first insight into the metabolism of the microorganisms (Dircks *et al.*, 1999). Therefore, OUR is a powerful tool for assessing the condition of an activated sludge system and has already proven its usefulness in different research approaches to activated sludge monitoring and control. Respirometric techniques have been widely applied for wastewater characterisation (Spérandio and Paul, 2000; Torrijos *et al.*, 1994, Orupold *et al.*, 1999, Rozzi *et al.*, 1999), to perform treatability or inhibition tests (Torrijos *et al.*, 1994; Vanrolleghem *et al.*, 1994; Volskay and Grady, 1990) or for model calibration (Larrea *et al.*, 1992).

This chapter focuses on wastewater treatment for organic matter removal by treating textile wastewater using a step-feed strategy in an SBR. On the other hand, a simple characterisation of influent wastewater based on physical and chemical analysis was carried out and studied in terms of variability. At the same time, a simple reactor performance monitoring system was applied by following on-line reactor Oxygen Uptake Rate (OUR); taking advantage of on-line dissolved oxygen (DO) probe coupled with a simple ON-OFF control.

5.3 Objectives

The main objective of this chapter is to study the application of the step-feed strategy for the treatment of a textile wastewater for organic matter removal through the determination of operational conditions in order to accomplish the organic matter requirement and the maximum discharge peak flow. It also looks at the application of the OUR advantages as a tool to study the biodegradability efficiency of the process. These objectives are specified in:

- Study the operation conditions using different number of filling events (4, 3 and 2) and different length (6 and 8 hours) to accomplish with the organic matter requirement and according with the maximum discharge peak flow.
- Application of oxygen uptake rate (OUR) advantages to study the biodegradability efficiency of the process.

5.4 Materials and Methods

5.4.1 ANALYTICAL METHODS

Throughout the operational study, raw and treated wastewaters were analysed for: Total Solids (TS), Volatile Solids (VS), Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Chemical Oxygen Demand (COD), ammonium ($N\text{-}NH_4^+$) and Total Kjeldahl Nitrogen (TKN) according to the section 3.3

5.4.2 RAW WASTEWATER CHARACTERISTICS

Twice a week between 25 and 100 L of wastewater from the textile industry was received by the laboratory and stored in a 150 L tank at 4ºC to reduce biomass activity prior to SBR treatment. The following parameters: pH, conductivity, total and volatile solids contents, Chemical Oxygen Demand (COD), ammonium and TKN values were analysed for each drum of textile wastewater received. Note that depending on the volume to be treated more than one barrel may have been received. The textile wastewater composition is described below in the results section (5.5.1).

From the initial analyses, phosphate adjustment was carried out due to low phosphorus content by adding a phosphate buffer consisting of 25.5 mg/L KH_2PO_4, 65.25 mg/L K_2HPO_4 and 100.2 mg/L Na_2HPO_4. At the same time, the buffer maintained the influent wastewater pH between 7 and 8 units.

5.4.3 EXPERIMENT SET-UP

A cylindrical vessel with a maximum working volume of 25 litres was used as the SBR pilot plant. A full description of the SBR is presented in section 3.1.1.The reactor was seeded with a nitrifying activated sludge from the wastewater treatment plant of Sils (Girona, Spain). An 8 hours cycle was conducted in the SBR, treating from 5 to 2.5 L of wastewater per cycle. The dissolved oxygen supplied was controlled at 1.0 mg/L O_2 through set point OD.

The SBR was operated by means of an in-house developed data acquisition and control software program developed by Lab-View. The software was able to repeat, over time, a previously defined operational cycle which controlled the on/off switch of all electrical devices (i.e. peristaltic pumps, electro-valves and mixing units). On-line mean values of pH, ORP, DO and Temperature signals were sampled every 10 milliseconds and every 15 seconds mean values were stored in a simple text file for further processing.

5.4.4 OPERATIONAL CONDITIONS

The experimental study was conducted over three different operational periods as presented in Figure 5.1. Its operational conditions are summarized in Table 5-1. As a common characteristic in all operational periods, the filling phases of each cycle were always conducted under aerobic conditions, keeping the SBR under controlled aeration of 1.0 mg/L O_2 during all the filling and reaction times of each cycle.

During Period 1, the SBR was operated to adapt the activated sludge to textile wastewater. So, the influent was composed of a mixture of urban and textile wastewater at a ratio 1:1 (vol.:vol.) (Table 5-1). An 8 hour cycle with 4 filling events distributed throughout the time was performed which included reserving 1 hour for settling purposes and was followed by 30 minutes for drawing (Figure 5.1). In every cycle 5 litres of wastewater was treated maintaining the exchange ratio in 0.20.

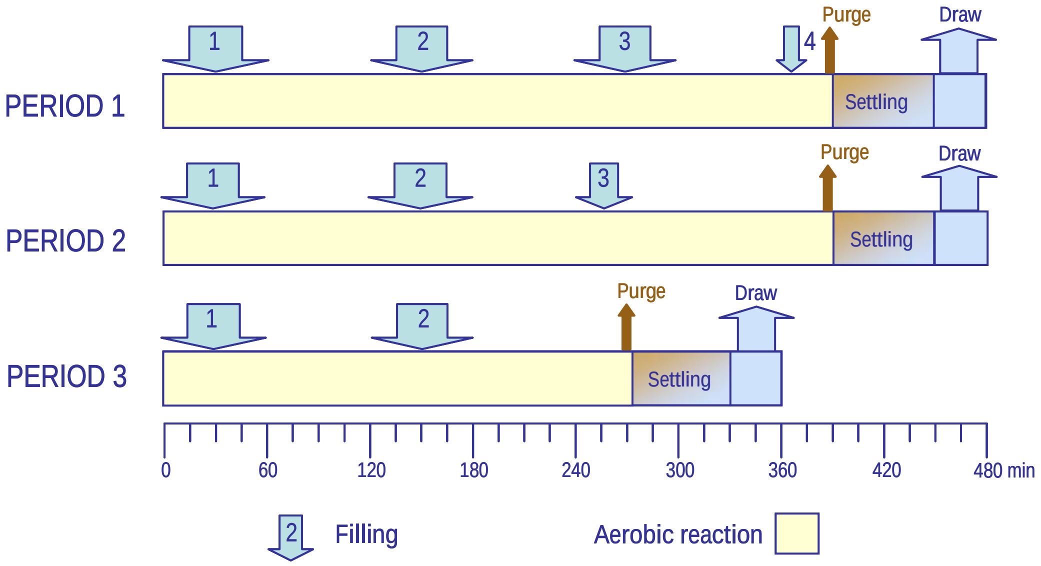


Figure 5.1: Operational periods during SBR operation showing SBR cycle duration and filling strategy.

In Period 2, the SBR was only fed with textile wastewater. The cycle was kept at the same conditions as in Period 1 except for a decrease in the filling events from 4 to 3. Modification of the number of filling events was mainly focused on reducing the high applied carbon load of Period 1. Such a reduction of applied carbon load also induced a reduction in the exchange ratios from 0.20 to 0.17 and in the filling volume from 5 to 4 L. Thus, a reduction of the exchanges ratios was translated as an increase in the hydraulic retention time and in the biodegradability.

At the end of the study, during Period 3, filling and reaction times were reduced to achieve a 6 hour cycle time by increasing the number of cycles per day from 3 (Periods 1 and 2) to 4 (Period 3). The reduction of cycle time was selected in order to accomplish regulations affecting the maximum peak flow discharges of treated wastewaters to the municipal sewer. At the same time, a diminution of the total aerobic time was achieved due to one more settling and withdrawing phases were realized in a day. The flow was equal to that in Period 2 but in every cycle 3 L of wastewater was introduced to the SBR instead of 4 L as in Period 2.

Table 5-1: Operational conditions applied durin whole the study.

Description	Symbol	Units	Period 1	Period 2	Period 3
Minimum Volume	V_{MIN}	L	20		
Total cycle time	tc	h	8		6
Effective fraction	f_E	-	0.83		0.79
Effective time	$t_E= t_F+t_R$	h	6.625		4.6
Wastewater ratio (Urban:Textile)	-	-	1:1-3	0:1	
Flow	Q	L/d	15	12	
Exchange ratio	V_F/V_T	-	0.20	0.17	0.13
Hydraulic retention time	HRT	d	1.67	2	1.92
Effective hydraulic retention time	HRT_E	d	1.38	1.66	1.47
Mean Carbon Load	L_{COD}	g COD·L^{-1}d^{-1}	0.31	0.24	0.28
Number of filling events	M	-	4	3	2
Period length	-	days	21	8	22

5.4.5 METHODOLOGY

The reactor performance was monitored throughout the experiment at least twice per week though the determination of the COD and solids in the influent and the effluent. The samples were obtained from the storage tank and at the end of the cycle from the withdrawn wastewater. Mixed-liquor suspended solids (MLSS) and mixed-liquor volatile suspended solids (MLVSS) were analysed at the end of aerobic phase twice a week.

General reactor maintenance was routinely performed, involving tasks such as checking and testing the probes, checking the pump flowrates, replacing tube connections and cleaning the reactor.

5.4.6 ON-LINE OUR DETERMINATION

The Oxygen Uptake Rate (OUR) is able to be calculated by several direct or indirect methods (Spanjers and Klapwijk, 1990, Ubay Çokgor *et al.*, 1998, Gutierrez, 2003). In a system such as this, where no air is transferred to the reactor, the OUR is easily able to be calculated as the slope of dissolved oxygen depletion according to the equation 5.1:

$$\mathrm{OUR} = -\frac{d[O_2]}{dt} = \mathrm{OUR}_{end} + \mathrm{OUR}_{ex} \qquad \text{(eq. 5.1)}$$

As stated before, the control scheme applied to keep DO level at 1.0 mg/L O_2 was based on a simple ON/OFF air injection strategy than resulted in an increase of DO during air ON periods and in a reduction of DO during air OFF periods. Because on-line DO levels were stored in a simple text file for each cycle operation, a further file processing was able to calculate OUR evolution cycle time by the DO depletion during air OFF periods. Nevertheless, only OUR values calculated with a minimum of 5 DO values and with a correlation coefficient (r^2) over 0.95 were considered.

5.5 Results and Discussion

5.5.1 WASTEWATER CHARACTERIZATION

Received wastewaters from the textile industry presented high composition variations mainly due to textile industry production planning, and as a consequence of the high number of different operating units. Table 5-2 and Figure 5.2 summarises such variation indicating the number of samples analysed for each parameter, the mean value, the standard deviation (σ) as well as the minimum and maximum values obtained.

Table 5-2: Raw textile wastewater composition variability prior to be added to the storage tank.

	Samples	Units	Mean Value ± σ	Min	Max.
pH	52	-	9.56 ± 1.49	6.92	12.47
Conductivity	52	μS	2120 ± 1561	64	7320
TS	49	mg/L	2251 ± 1442	512	8584
VS	48	mg/L	1228 ± 629	140	3150
Total COD	45	mg O_2/L	1905 ± 1087	720	7098
Ammonia	21	mg N-NH_4^+/L	52 ± 48	6	220
TKN	24	mg N/L	131 ± 114	12	407

As presented in Table 5-2, pH values were around 9.56±1.49 units clearly showing a basic characteristic of the wastewater to be treated. In Figure 5.2a such a characteristic is remarked upon by showing that only 5 samples presented values near to neutrality, but that there were never values under neutrality. In order to reduce the pH inhibition effect of the biological treatment, as stated above, a phosphate buffer was added to the wastewater.

With respect to conductivity values, all of them are located around 1800 μS (Figure 5.2b) in spite of some punctual analysis which reached values of over 6000 μS. Nevertheless, the homogenisation effect of the storage tank could easily deal with such variations resulting in a low conductivity variation for the SBR feeding.

Total and volatile solids (Figure 5.2c-d) also presented a high variability between 500 - 3500 mg/L for TS and 400-1700 mg/l for VS, always keeping a VS:TS ratio of around 0.5.

The textile wastewater also presented a significant variation of ammonia in the influent (Figure 5.2f) which ranged from 6 to 220 mg/L N, and with the mean value being around 52 mg/L N.

In analysing total COD values (Figure 5.2e) a variation ranging from 800 to 3000 mg/L could clearly be observed, resulting in a mean total COD value of 1900 mg/L with a high standard deviation of 1087 mg/L.

5.5.2 SBR PERFORMANCE: COD REMOVAL

Throughout two months the SBR was operated to achieve organic matter removal. The SBR was not obliged to perform nitrogen removal. COD levels under 1000 mg/L were required due to a forecast of 600 mg/L COD in the future. In this case the treated wastewater would be discharged into a local sewer going to an urban wastewater treatment plant.

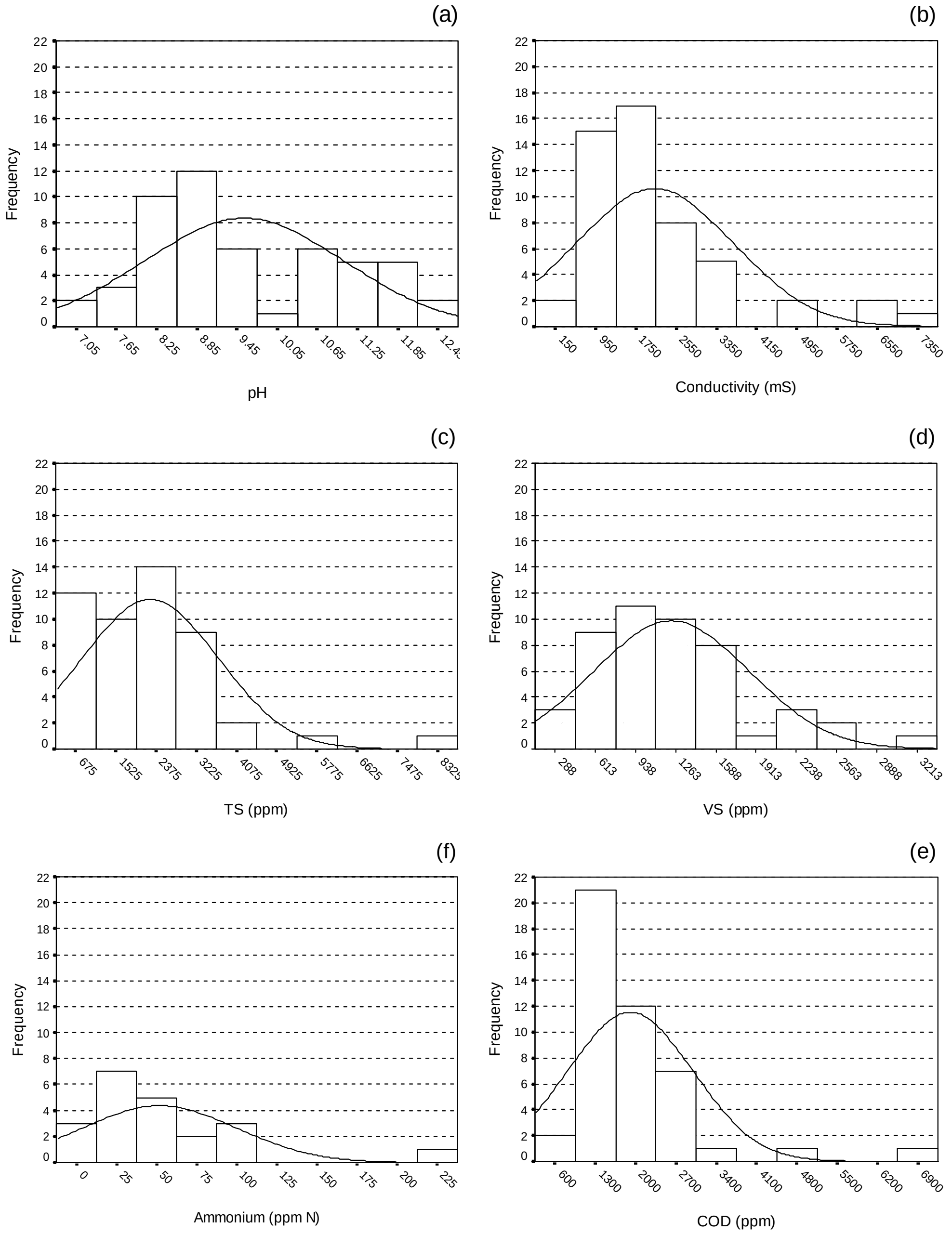


Figure 5.2: Histogram representation of (a) pH, (b) conductivity, (c) total solids, (d) volatile solids, (e) ammonium, and (f) total COD for received wastewaters prior to being added to the storage tank. Continuous line corresponds to a Gauss distribution according to mean values and standard deviations are gathered in Table 5.2.

Figure 5.3 shows the COD evolution in all the operational periods of the textile wastewater (storage tank) and the SBR effluent. During Period 1 a mixture of urban wastewater and industrial wastewater was introduced to the SBR in order to adapt the biomass to the new wastewater. Initially, in Period 1, the exchange ratio was 0.20 (5:25 of V_F/V_T, see Table 5-1). The SBR effluent COD started to reduce down to values of around 300 mg/l. On the 13th day of the operation, the influent COD increased up to 1600 mg/l, and a slight increase in the effluent COD of up to 500 mg/l. Afterwards, from the day 16th the proportion of textile wastewater was increased to 75% in volume, with the remaining 25% being urban wastewater. The COD efficiency of the period ranged from 50 to 72%.

During Period 2 of the operation the SBR was fed only with textile wastewater. In order to minimise the impact of changing to pure textile effluent, a slightly lower applied carbon load was selected (reducing exchange ratio from 0.20 to 0.17). The SBR behaviour during this period was similar to the precedent. The effluent COD presented a continuous decrease associated to the diminution of influent COD obtaining COD efficiency values of between 65 and 77%.

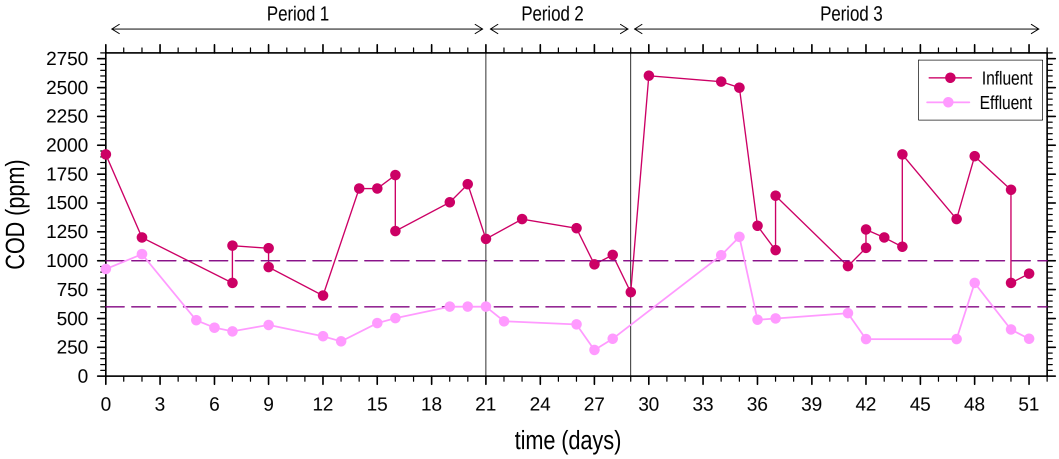


Figure 5.3: Total COD evolution in all operational periods of the raw and treated wastewater.

Another requirement, in this case, to comply with the legislation was that of the maximum peak flow discharge into the municipal sewage. Therefore, during the last operational period, Period 3, the total cycle time was reduced from 8 to 6 hours in order to adjust the peak flow discharge of treated wastewater to comply with the regulations. Thus, the number of cycles per day was increased from 3 to 4. Such an increase in the number of cycles per day concluded with a lower overall reaction time per day due to the presence of an additional settling and draw event (1.5 hours) for the new added cycle and so less effective time (aerobic reaction time) was applied. This reduction was compensated with a reduction in the applied carbon load modifying the exchange ratio from 0.17 to 0.13. Nevertheless, this change was coupled with a COD increase of received wastewaters, feeding the SBR with COD values of up to 2500 mg/l (Days 30 to 35 of operation). In spite of this high influent COD increase, the SBR was able to rapidly adapt to such changing conditions and, when returning to normal influent COD values of around 1500 mg/l, the effluent COD recovered its efficiency observed at the end of the previous period.

From the 36th day of operation until the end of the experiment, the SBR presented enough efficiency for the treated wastewater to be discharged into the urban sewer (lower than 1000 mg/L COD), with the mean COD removal percentage of 58%.

5.5.3 SBR PERFORMANCE: OUR EVOLUTION

During whole periods, Oxygen Uptake Rate (OUR) was tracked in order to evaluate the treatability of the wastewater and so, the biodegradability of the textile wastewater could be determined. At the same time, the step-feed strategy was a useful tool to analyse the processes of famine (feed off) and COD loading or feast (feed on) events in cycle reaction times during the OUR profile evolution.

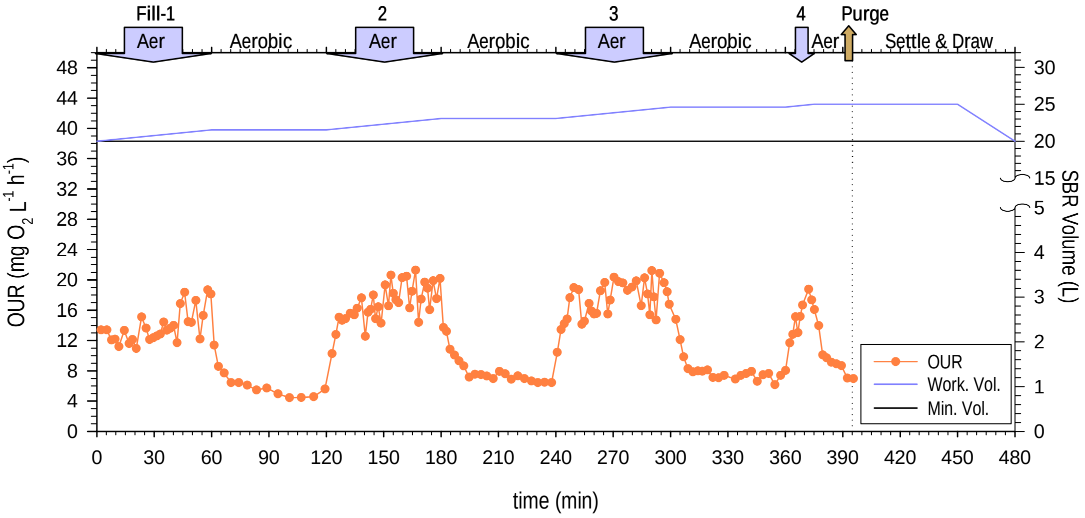


Figure 5.4: OUR evolution and the SBR volume evolution for one operational cycle in Period 1 on the 19th day.

Figure 5.4 presents the OUR profile and the SBR volume evolution on the 19th day of operation in Period 1. Feed events are distinguished by an increase of OUR values of up to 20 mg/l·h. Nevertheless, when feed was switched off the OUR presented a sudden reduction down to values lower than 7 mg/L·h and staying around this value until another filling event when the OUR value increased again. Such OUR behaviour could lead to a supposition that there was a complete adaptation of the SBR to textile effluent by verifying the absence of inhibition substances because the OUR increased with the filling events. On this day, the COD concentration in the effluent was around 600 mg/L, while the influent of 1505 mg/L COD, with the removal percentage being 60%. The remaining COD corresponding to a low and constant OUR value was due to endogen respirometry (Johansen *et al.*, 1997, Dircks *et al.*, 1999). This means that the remaining COD corresponded to a non-biodegradable or slowly biodegradable organic matter.

At the end of Period 2 (28th day of operation), when the SBR was working under stable conditions, the cycle OUR profile (Figure 5.5) presented a similar profile as in Period 1. During the feed events the OUR increased until values of up to 20 mg/l·h resulted. Meanwhile, when feed was switched off the OUR presented a sudden reduction up to values of around 5 mg/L·h. The COD concentration in the influent was 1049 mg/L, while the effluent was 323 mg/L, obtaining a removal percentage of 70% on this particular day.

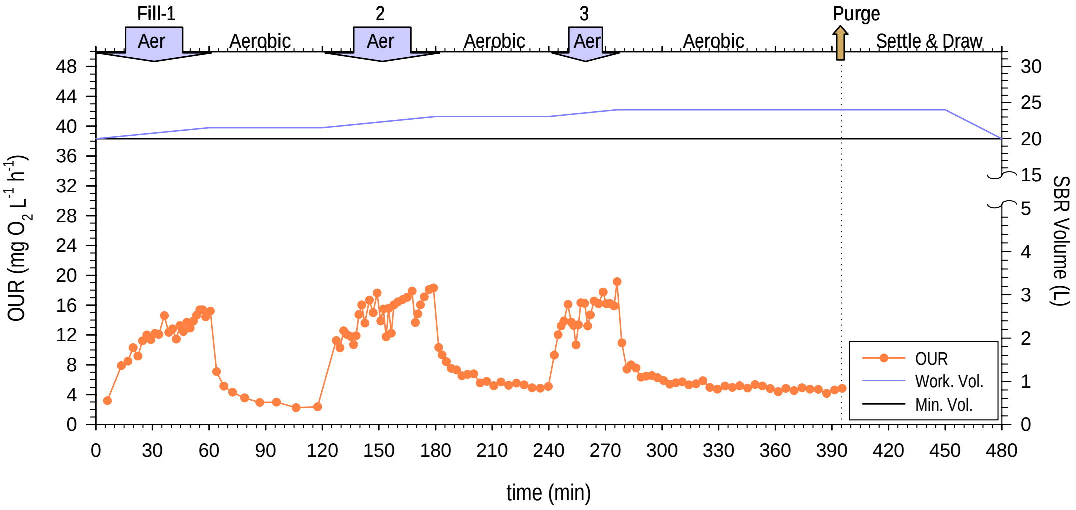


Figure 5.5: OUR evolution and the SBR volume evolution for one operational cycle in Period 2 on the 28th day.

Figure 5.6 presents the OUR profile on the 50th day of operation, where again the difference between the feed events of the cycle (OUR values around 30 mg/l·h) and the famine events with lower OUR values can be clearly observed. However, during these last days of operation a higher final OUR value was observed (around 10 mg/l·h) due to the increase of mixed liquor suspended solids (MLSS). On this particular day the COD concentration in the effluent was around 323 mg/L, while the influent was 887 mg/L COD, with the removal percentage being 64%.

Finally, in order to assure that effluent COD was mainly composed of non biodegradable or slowly biodegradable organic matter, BOD_5 analyses were performed, in an external laboratory, and in fact did obtain values lower than 5 mg/L.

The OUR profiles obtained throughout the study proved to be an easy and fast way to determine the SBR status.

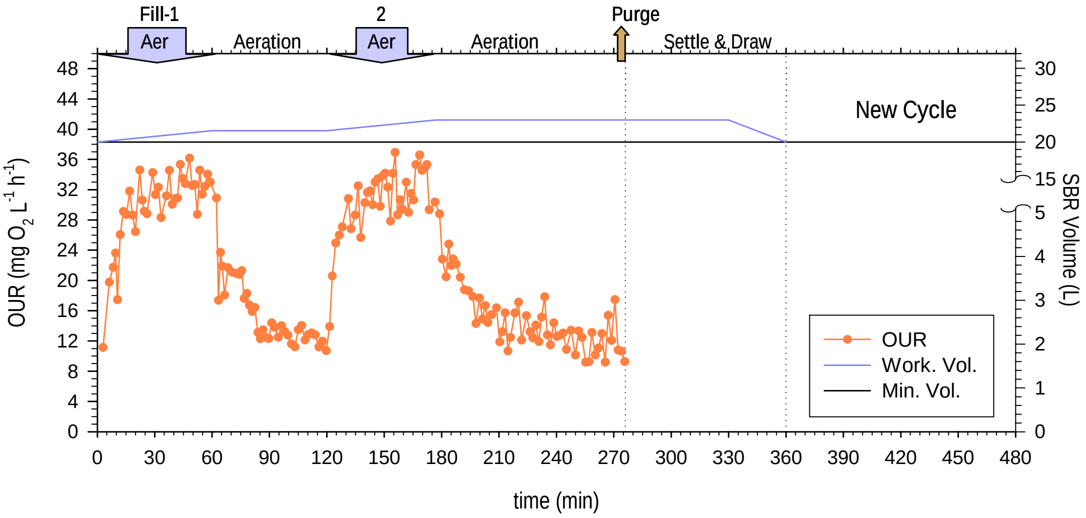


Figure 5.6: OUR evolution and the SBR volume evolution for one operational cycle in Period 3 on the 50th day.

5.6 Conclusions

The conclusions obtained in this chapter are related below:

- Treated textile wastewater presented a high variation mainly due to production planning. Such variations mainly affected pH values, always with a strong basic characteristic, and a high variation in COD contents (ranging from 700 to 7000 mg/L COD).

- The step-feed strategy has proved to be an efficient operational procedure in dealing with such high COD variations. The operation of the SBR using a number of filling events (M) of 2 and exchange ratio (V_F/V_T) of 0.13 in a 6 hour cycle to comply with maximum peak flow requirement, has concluded with an effluent mainly lower than 600 mg/L COD and being basically non-biodegradable organic matter.

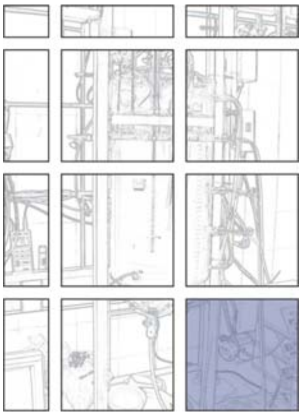
- The simple DO control applied, based on a compressed air ON/OFF strategy, proved to be enough to determine the OUR profile during aerobic reactions times.

- Following the OUR profiles during aerobic reaction times, proved to be a good tool to identify the endogenous conditions reached after each feeding event. Such endogenous conditions presented a low and constant OUR value of between 5-12 mg

O_2/L·h depending on the operation period considered.

- On-line OUR profiles must be used together with a control of possible inhibition effects, mainly affecting pH values or nutrients deficiency. As a control of endogenous respiration reached at the end of SBR reaction time, a BOD_5 analysis could serve as a proof that lower biodegradable matter levels are in fact achieved.

- The effluent quality could be improved through a chemical treatment such as Fenton in order to decrease the COD concentration.



6

APPLICATION OF STEP-FEED STRATEGY FOR CARBON AND NITROGEN REMOVAL. A CASE STUDY WITH LANDFILL LEACHATE WASTEWATER

6.1 Summary

In this chapter sequencing batch reactor (SBR) technology is applied to treat a landfill leachate composed of a mixture of young and matured leachate. The experimental study was carried out with a lab-scale SBR over four different operational periods: 1) adaptation, 2) raw leachate, 3) young leachate and 4) matured leachate treatment. Process efficiency was evaluated by following influent and effluent composition such as COD, ammonia and nitrate. However, because of low COD removal efficiencies, investigations about the possible presence of non biodegradable compounds were performed by following the on-line oxygen uptake rate (OUR) data. Such presence of non biodegradable compounds was stated after process analysis

for on-line OUR. Complete nitrification could be easily achieved by avoiding some pH inhibition events. Nevertheless, the presence of non biodegradable organic matter reduced the denitrification efficiency concluding with the nitrate presence in the treated leachate.

6.2 Introduction

Landfill leachate is a complex mixture of water, organic and inorganic compounds generated by the decomposition of landfill organic wastes and supplemented by rainwater percolating through the waste material. Landfill leachate is generally characterized by high variability from one site to another, mainly because of the nature of wastes from landfill, methodology applied during landfill life term, structure of the site or climatic characteristics of the location. Nevertheless, landfill leachates are characterised by high levels of organic compounds, (ammonia plus organic nitrogen), and high levels of inorganic salts; making it a difficult to treat with conventional biological treatment facilities stream. On the other hand, leachate generation may occur over several decades even after the landfill has been capped and closed. Thus, selection of the leachate treatment technology for the landfill operational period and during the long period after closure (i.e. up to 30 years depending on administrative requirements) must be considered in terms of leachate quality, treatment efficiency, stability and operational cost.

The evolution over time of landfill leachate composition induces to a primary classification of leachates as that of young and matured. Whilst young leachates are characterised by high concentrations of organic matter, basic pH values and low nitrogen concentrations, during landfill maturation the leachate characteristics change to low pH values, low organic matter contents and high nitrogen levels. Such leachate evolution over time from young to mature also affects to the organic matter quality, which evolves from easily to slowly biodegradable and with an significant increase of non biodegradable compounds (Horan *et al.*, 1997). In addition to leachate composition evolution, leachate flow generation presents a clear evolution over time with different superposed patterns: i) rainy-dry weather periods and, ii) a characteristic leachate volume reduction over time after landfill closure.

SBR technology has been proven to be a cost effective and energy efficient option for removing organic compounds in industrial wastes, soils, and leachates from landfills (Yalmaz and Örtürz, 2001).

The results presented in this chapter were obtained during the investigation to evaluate the performance of a lab-scale SBR processing the leachate from a Mutiloa (Basque Country, Spain) landfill site. The treatment performance was focused on organic matter and nitrogen removal (biological nitrification and denitrification) by means of applying aerobic and anoxic phases during the reaction time of the SBR cycle. Because of the site morphology, two different leachates were collected in a common pond: a matured leachate that comes from a closed landfill and, a young leachate from the actual operating landfill.

6.3 Objectives

The main objective of this chapter is to study the application of the step-feed strategy for the treatment of a landfill leachate wastewater, which a focus on achieving organic matter and nitrogen removal. Thi is done through determining the operational conditions and by the application of the OUR advantages as a tool in studying the biodegradability efficiency of the treated wastewater. These objectives are specified in:

- Study the suitable biological carbon and nitrogen removal of the different sources (mixture, young and matured) of leachate present in the same landfill.
- Study the suitable operational conditions related to exchange ratio (V_F/V_T) and number of filling events (M) for carbon and nitrogen removal
- Application of oxygen uptake rate (OUR) to identify the biologicasl activity.

6.4 Materials and Methods

6.4.1 ANALYTICAL METHODS

Throughout the operational study, raw and treated leachates were analysed for: Total Solids (TS), Volatile Solids (VS), Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Chemical Oxygen Demand (COD), ammonium ($N\text{-}NH_4^+$), nitrites ($N\text{-}NO_2^-$, 3.3.9I) and nitrates ($N\text{-}NO_3^-$, 3.3.9I) according to section 3.3.

6.4.2 RAW LEACHATE CHARACTERISTICS

Once a week between 25 and 150 litres of leachate from the Mutiloa landfill site was received to our laboratory. Because of high iron contents (Fe^{3+}), an initial precipitation with sodium hydroxide of up to pH 8.5 was conducted. After precipitate removal, the leachate was analysed and stored in 150 litres stainless steel tank and refrigerated at 4ºC to avoid degradation before SBR treatment. From initial analyses, phosphate adjustment, (by the addition of phosphate buffer) was carried out due to a low phosphorus content and a high pH values obtained after iron precipitation. A phosphorus concentration of around 20 mg/L of this buffer (including KH_2PO_4, K_2HPO_4 and, Na_2HPO_4) was added maintaining a pH value of between 7-7.5. During the study, some nitrification inhibition by pH was detected and corrected with the addition of a sodium bicarbonate solution (0.35-0.60 g/L). The main characteristics presented by the young leachate were around 8.2 pH, COD 1400 mg/L and, 95 mg/L $N\text{-}NH_4^+$; while for the matured leachate the pH was around 6.5, COD 260 mg/L and, 85 mg/L $N\text{-}NH_4^+$.

6.4.3 EXPERIMENT SET-UP

A cylindrical vessel with a maximum working volume of 30 litres was used as the SBR pilot plant. A full description of the SBR is presented in section 3.1.1. During the adaptation period the reactor was seeded with a nitrifying activated sludge from the wastewater treatment plant of Sils (Girona, Spain) and fed with urban watewater from the wastewater treatment plant of Girona (Girona, Spain). An 8 hour cycle was conducted in the SBR, treating between 10 and 1.5 L of wastewater per cycle. The dissolved oxygen supply was controled at 2.0 mg/L O_2 through a set point OD.

The SBR was operated by means of an in-house developed data acquisition and control software program developed by Lab-View. The software was able to repeat, over time, a previously defined operational cycle which controlled the on/off switch of all electrical devices (i.e. peristaltic pumps, electro-valves and mixing units). On-line mean values of pH, ORP, DO and Temperature signals were sampled every 10 milliseconds and every 15 seconds mean values were stored in a simple text file for further processing.

6.4.4 OPERATIONAL CONDITIONS

The study was carried out over four operational periods as described in Table 6-1 and Figure 6.1. As a common feature of all periods, the SBR was operated with an 8 hour cycle (480 minutes) composed of a fill and reaction phase (390 min.), a settling phase (60 min.) and a draw phase (30 min.) (see Figure 6.1). During the filling events (conducted one or several times during a cycle) the reactor was always under anoxic conditions in order to enhance biological denitrification.

The first period, Period 1 was basically to adapt the biomass to the leachate wastewater. This period was operated under two different conditions: Period 1a with a six filling phases and Period 1b with a sole filling event. Initially, the SBR operated for 25 days with urban wastewater during the Period 1a. On day 25, a 17% portion of leachate mixture (vol.:vol.) was added to the feed. After that a progressive increase was executed until a 75% of leachate mixture was reached at the end of Period 1a. Due to the high COD concentration of the landfill leachate, the filling volume was reduced from 10 to 5 L on day 25. At the same time, during the whole period the cycle was adjusted to the new wastewater and its characteristics such as decrease the aerobic time to increase the anoxic reaction time which initially was 50% anoxic and 50% aerobic, arriving to 67 and 33% respectively, in order to enhance the nitrogen removal.

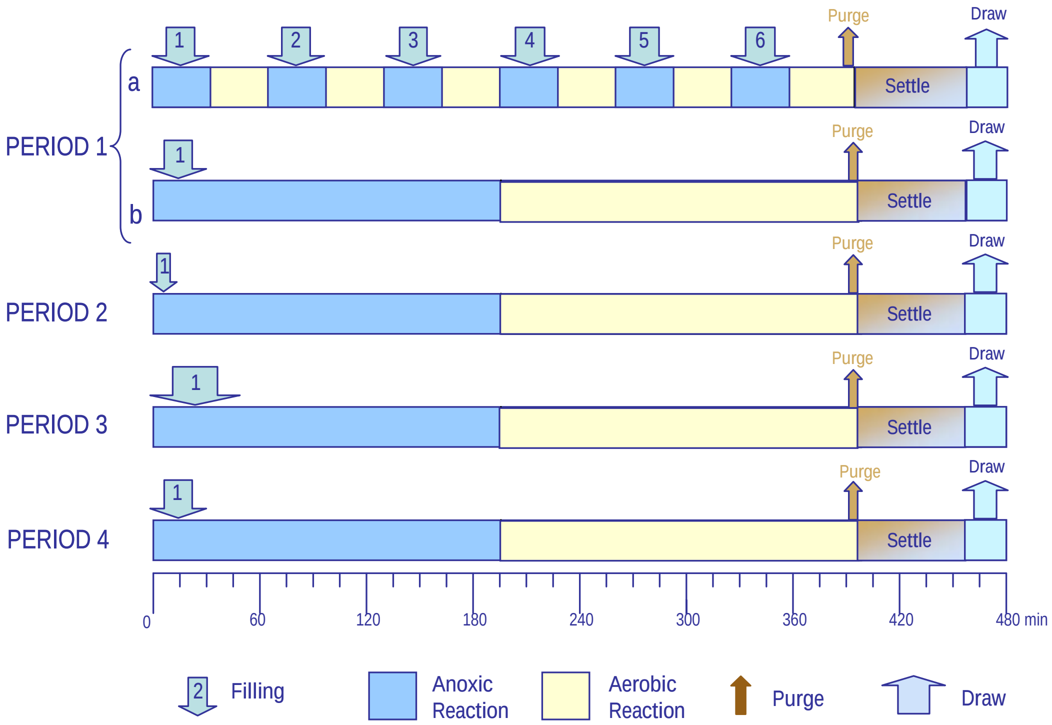


Figure 6.1: Operational periods during SBR operation showing SBR cycle strategy.

In Period 1b, the SBR operated with a sole filling event. In addition the filling volume was decreased from 5 to 2.5 L and the minimum volume increased from 20 to 25 L. These changes were made due to the slowly biodegradabilty of the organic matter and to denitrification at the beginning of the cycle and dilute the rest of the nitrates obtained. The SBR was fed with a 77% of mixture of leachate and a 23% mixture of urban wastewater throughout the period except from day 75 to day 84 where no leachate was received by the lab (due to operational problems in the landfill) and so urban wastewater with a portion of synthetic wastewater was used as a feed. On the 84th day the SBR was fed again with a 77% (vol.) of leachate mixture.

Table 6-1: Main operational conditions applied during all the operational periods. *% Anoxic and Aerobic reaction time are calculated over the reaction time.

Description	Symbol	Units	Period 1		Period 2	Period 3	Period 4
			1a	1b			
Total cycle time	tc	h	8				
Effective fraction	f_E	-	0.82				
Minimum Volume	V_{MIN}	L	20	25			
Number of filling events	M	-	6	1			
Effective time	$t_E= t_F+t_R$	h	6.58	6.54			
Anoxic reaction time*	%ANOXIC	%	50-67	50			
Aerobic reaction time*	%AEROBIC	%	50-33	50			
Wastewater ratio (UW:Leachate)	-	-	1:0-3	1:3	0:1		
Exchange ratio	V_F/V_T	-	0.3-0.2	0.1		0.06	0.11
Flow	Q	L/d	30-15	7.5		4.5	9
Hydraulic retention time	HRT	d	1	1.67	3.67	5.89	3.11
Effective hydraulic retention time	HRT_E	d	0.82	1.37	3.01	4.83	2.55
Period length	-	days	66	28	65	21	14

During Periods 2, 3 and 4, full concentration leachates were treated maintaining a sole filling event and 25 L as a minimum volume. Meanwhile in Period 2 a mixture of young and matured leachate was fed, in Period 3 was only fed with young leachate and Period 4 with matured leachate. Due to the different COD concentrations applied the filling volumes were 2.5 L, 1.5 L and 3 L for Periods 2, 3 and 4, respectively.

6.4.5 METHODOLOGY

The reactor performance was monitored throughout the experiment at least twice a week though the determination of the COD, solids and nitrogen ($N\text{-}NH_4^+$, $N\text{-}NO_3^-$ and $N\text{-}NO_2^-$) in the influent and the effluent. The samples were obtained from the storage tank and at the end of the cycle from the withdrawn wastewater. Mixed-liquor suspended solids (MLSS) and mixed-liquor volatile suspended solids (MLVSS) were analysed at the end of the aerobic phase twice a week.

General reactor maintenance was routinely performed, involving tasks such as checking and testing the probes, checking the pump flow rates, replacing tube connections and cleaning the reactor.

6.4.6 ON-LINE OUR DETERMINATION

As stated above, the aerobic phases of the SBR cycles were conducted by injection of compressed air into the reactor and controlling the DO around 2.0 mg O_2/L by an ON/OFF strategy. Such alternated sequence of air ON/OFF events were automatically conducted by the developed software, with the oxygen uptake rate data (OUR, mg $O_2 \cdot L^{-1} \cdot h^{-1}$) as the slope of the decreasing dissolved oxygen trend (see section 5.4.5).

6.5 Results and Discussion

SBR technology was applied to treat leachate from the Mutiloa landfill. The experimental study was carried out over four different operational periods. First of all, the SBR was operated with urban wastewater which was progressively substituted by provided leachate Period 1. From this point, the SBR was operated with a mixture of young and matured leachate (Period 2). Afterwards, in order to identify non biodegradable carbon sources, two more operational periods with separate young and matured landfill leachate were operated during Periods 3 and 4, respectively.

6.5.1 COD REMOVAL EFFICIENCY.

During all of the operational periods, a comparison between influent and effluent COD was performed in order to identify organic matter removal efficiency (Figure 6.2). Period 1, when biomass adapted from urban to leachate wastewater, different cycle adaptations were performed in order to achieve the carbon and nitrogen removal. During Period 1a, COD removal presented high values (up to 90%) up to day 25 because the SBR was only fed with urban wastewater. From day 25, the influent contained a 17% (vol.:vol.) of leachate and progressively increased up to day 66 where 75% (vol.:vol.) of leachate was used. The trend of COD influent and effluent was increased as the percentage of leachate. The average COD removal when leachate was introduced as a feed was 77%.

In the rest of the period, Period 1b where one filling event was realized, the influent contained 77% of leachate, except between days 75 and 84 in which urban wastewater with a synthetic compound to maintain the carbon load was fed in. During these days the COD in the effluent decreased. After the 84th day, when the feed was composed of 77% of leachate, low values of COD in the influent were found. However, the concentration of organic matter in the effluent increased to 250 mg/L COD.

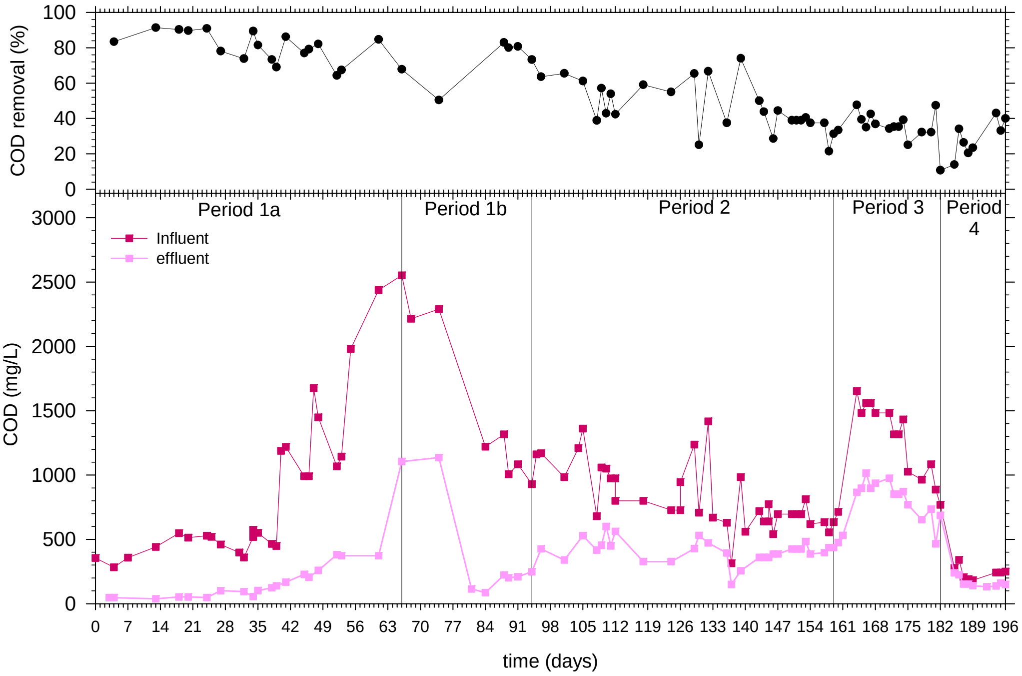


Figure 6.2: Evolution of COD removal efficiency (upper graph) and influent and effluent COD concentrations (lower graph) during all the operational periods.

Throughout Period 2 (days 95 to 160), the SBR treated a mixture of young and matured leachate COD removal efficiency decreased to 40-45% and effluent COD around 400 mg/L. Thus, such lowered COD removal efficiency could cause supposition of different causes: i) nutrient deficits or, ii) the COD leaving the reactor is mainly composed of non-biodegradable compounds. Analytical data indicated suficient nitrogen and phosphorus concentrations and OUR data (presented in the following section 6.4.6) suggested a high content of non biodegradable compounds were present in the landfill leachate. As the treated leachate in Period 2 was composed of a mixture of young and matured leached, two more periods (Periods 3 and 4) were operated with only young and matured leachate to test the biodegradability of each pond independently.

During Period 3 (161st to 182nd day), when treating young leachate the influent COD increased up to 1500 mg/L achieving an initial COD removal efficiency of around 35%. After 15 days of operation, a process stabilisation was observed at around a COD removal efficiency of 40%. Again such lowered COD removal indicated that the young leachate contained a high fraction of non biodegradable compounds which concluded with an effluent COD concentration around 800 mg/L.

Period 4 (starting at day 182) was operated only with matured leachate. A suddenly decrease of influent COD could be observed (from 1000 to 250 mg/L). Nevertheless, even with such lower influent COD, the SBR was still not able to increase COD removal efficiency by more than 40%, concluding with an effluent COD of around 150 mg/L.

6.5.2 NITROGEN REMOVAL

Taking into account nitrogen removal efficiencies, two different aspects must be studied: i) nitrification of influent ammonia and, ii) denitrification of nitrate to nitrogen gas. Figure 6.3 presents the evolution of nitrogen compounds (influent ammonia, effluent ammonia and nitrate and, in the upper graph the ammonia removal efficiency) through all the operational periods.

During Period 1 the cycle was modified to achieve nitrogen removal. Initially, in Period 1a, a complete nitrification was achieved around day 25, when 17% (vol.:vol.) leachate was introduced as a feed and maintained until the 49th day, when the reactor operated with 70% leachate. Meanwhile a partial denitrification was found on the 25th day, when leachate was introduced and nitrate concentration increased to 45 mg/L on the 33rd day. The sudden increase was reduced by means of synthetic organic matter, thus in this way maintaining the nitrate concentracions of between 15 and 25 mg/L N until day 47. As a result, a poor denitrification was achieved. On the 47th day, in order to improve the denitrification under anoxic conditions, aerobic time was reduced to increase the anoxic time (from initially 50% of anoxic time to 67% and from 50% of aerobic time to 33%).

On the 50th day of operation, a suddenly increase of influent ammonia (from 80 to 130 mg $N\text{-}NH_4^+$/L) concluded with an increase of effluent ammonia of up to 30 mg $N\text{-}NH_4^+$/L. Such reduced nitrification efficiency was caused by the high concentrations of ammonia, pH inhibition (caused by the nitrification process), and the progressive reduction of aerobic time. From this point, first of all, enough alkalinity (i.e. sodium bicarbonate) was added at the influent in order to maintain reactor pH values above 6.5. However, this action was not enough to recover the nitrification, so, in the next period it was decided to increase again the aerobic time and redesign the operational strategy.

In Period 1b, on the 66th day, the aerobic time was increased from 33 to 46% decreasing the anoxic time from 67 to 54%, in order to recover nitrification. In addition, the filling volume was reduced from 5 to 2.5 litres and the minimum volume was increased from 20 to 25 litres with the purpose of diluting the nitrates. And finally, the number of filling events was reduced from six to one. This would ensure that, during the anoxic phases, the organic matter available would be used to denitrify the nitrates at the beginning of the cycle and by increasing the minimum volume the nitrates remaining would be diluted.

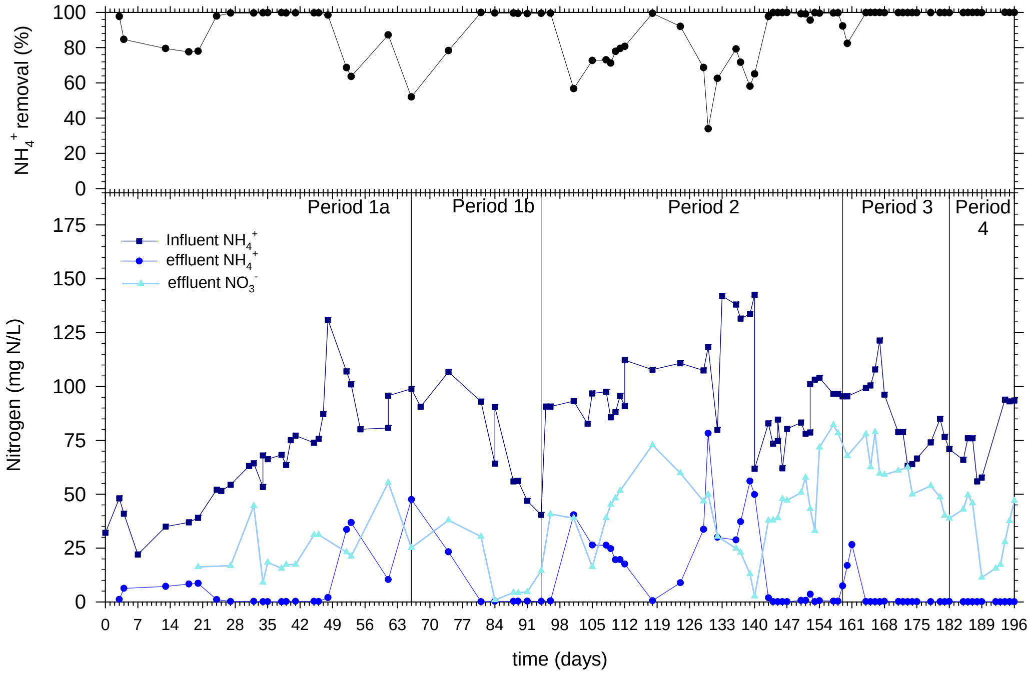


Figure 6.3: Evolution of nitrogen compounds (ammonium and nitrate) and ammonium removal.

After fifteen days, (i.e. from the 80th day of operation), the nitrification was consolidated up to the end of Period 1b. At the same time nitrates were reduced because some urban wastewater with a synthetic compound fed the reactor between days 75 and 84. When a 75% of leachate mixture was fed some nitrate concentration began to increase maintaining a complete nitrification. In spite of the denitrification process being enhanced by conducting the filling events under anoxic conditions, denitrification was only partially achieved, indicating the presence of a non suitable organic matter for denitrification purposes, as presented in the following section 6.5.3.

During period 2, when treating a mixture of young and matured leachate, the nitrification was initially reduced but, after influent alkalinity adjustments, nitrification efficiency reached values of up to 99%. It was clearly stated that, when treating high ammonia wastewaters, pH inhibition events could be solved by the addition of external bicarbonate. The concentration of the external bicarbonate was increased from 0.35 g/L initially on day 104 to 0.6 g/L on day 140, when the nitrification was completely recovered. On the other hand, during this Period denitrification efficiency was reduced, concluding with a high nitrate effluent concentration (up to 60 mg $N\text{-}NO_3^-/L$). Such reduced denitrification was caused by the non presence of suitable organic matter for denitrification in the mixture of landfill leachates. On days 104 and 132 synthetic organic matter was added to reduce the nitrate concentration.

Finally, when treating young and matured landfill leachates (Periods 3 and, 4, respectively) similar results where obtained: a complete ammonia nitrification, but a high effluent nitrate concentration caused by low denitrification efficiency.

6.5.3 EVIDENCE OF NON-BIODEGRADABLE COMPOUNDS

As stated above, when discussing COD removal and denitrification efficiencies, it seems that treated leachates (young and matured) can contain a high proportion of non-biodegradable compounds (800 and 125 mg/L for young and matured leachate, respectively). Figure 6.4 presents the evolution of dissolved oxygen and OUR of the aerobic reaction phase (from the 200th to the 390th minutes of cycle time) for Periods 3 and 4. The ON/OFF control strategy with a dissolved oxygen set-point of 2.0 mg O_2/L is clearly observed.

For both leachates, young (Figure 6.4.A) and matured (Figure 6.4.B), the OUR profile follows a similar trend. In both figures, a first and constant plateau (1) was observed due to high consumption of DO to degrade the organic matter and, afterwards, a slight decrease (between 220-230 minutes) was observed up to a new lower plateau (2). These plateaus are reflected in the DO profile also, and with the extension during the DO slopes. Finally, the OUR values were reduced to OUR values lower than 4 mg $O_2 \cdot L^{-1} \cdot h^{-1}$ (from the 280th minute until the end of the aerobic phase).

The first plateau reflects the nitrification of ammonia, while the second originates from metabolism of residual biodegradable organic matter. Finally, such a low final OUR was clearly evidence of endogenous conditions (Dircks *et al.*, 1999). It allowed assurance that the effluent COD was mainly composed of non biodegradable organic matter.

On these particular days, the COD concentration in the effluent was 735 and 140 mg/L respectively for young leachate (Figure 6.4.A) and matured leachate (Figure 6.4.B), being 1084 and 183 mg/L COD concentration in the influent. The efficiency of these days was 32% and 23% respectively, while a complete nitrification was achieved (99.9%) in both cases, that being the ammonia influent of 85 and 58 mg/L N-NH_4^+, respectively for young and matured leachate (Period 3 and Period 4).

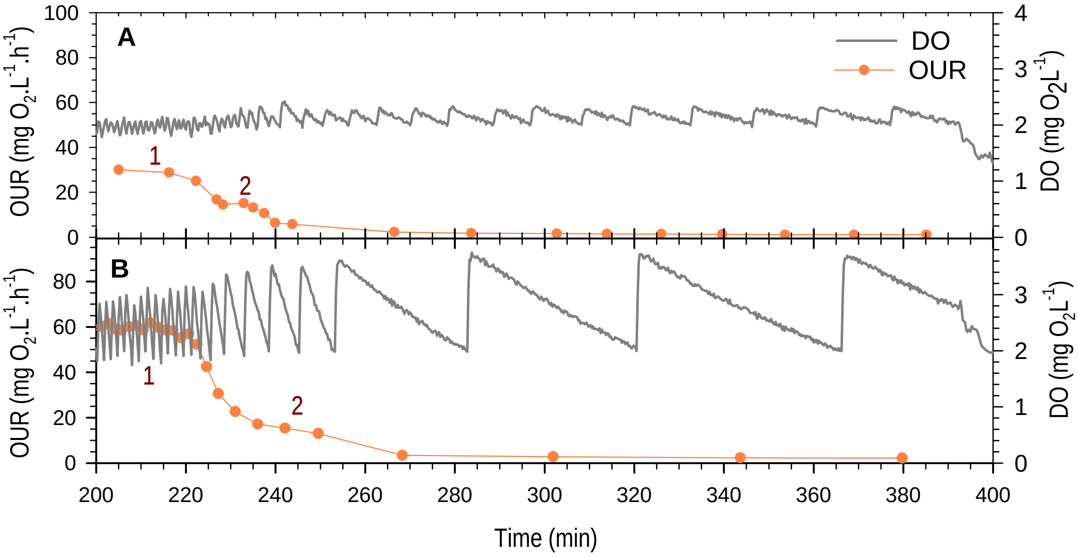


Figure 6.4: OUR (circle-line) and DO (single line) profiles obtained during the aerobic phase of an 8 hour cycle treating young (A) or matured (B) leachate.

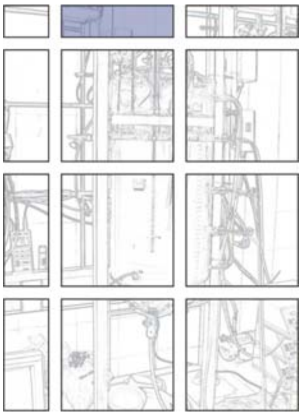
6.6 Conclusions

The conclusions obtained in this chapter are related below:

- In spite of this, biological process has proved useful for treating some landfill leachates, in each case a biodegradability study must be conducted in order to ensure proper organic matter reductions.
- In our case, nitrification was easily achieved if pH inhibition was avoided by adjusting treated leachate with enough bicarbonate.
- The ability of calculate an on-line value of the OUR is a useful tool in order to identify a the possible presence of non-biodegradable compounds by avoiding the use of

biological oxygen demand (BOD_5) essays which are extremely time consuming (up to 5 days).

- Evolution of landfill leachate over time (from young to mature) indicates a reduction of in organic matter by keeping or slightly increasing the ammonia contents. Nevertheless, such a low COD content is mainly composed of non biodegradable matter.
- Thus, the biological treatment of a leachate landfill could be considered as part of, but not the only part of the leachate treatment. When high contents of non biodegradable organic matter are detected other chemical or physical treatments (i.e. chemical oxidation with hydrogen peroxide or inverse osmosis) must be considered.



7

OPERATIONAL CONDITIONS FOR NITROGEN AND PHOSPHORUS REMOVAL USING STEP-FEED STRATEGY.

7.1 Summary

A step-feed strategy was applied in a Sequencing Batch Reactor (SBR) for a nitrogen and phosphorus removal treating urban wastewater. As well as the anoxic and aerobic alternation to achieve nitrogen removal, an initial anaerobic phase was introduced to allow phosphorus removal in the SBR. Different feed strategies were used, long and short filling phases and a different number of filling events from six to three to test these performances in the nitrogen and phosphorus removal. The information supplied for the on-line monitoring pH, ORP and DO data was used to get to know the process and to identify the critical points for the nitrification and denitrification, because no critical points of phosphorus were observed.

7.2 Introduction

The progressive application of more severe regulations (EU Directive 91/271/EEC limiting the discharge of total nitrogen and phosphorus to 15 mg/L N and 2 mg/L P, respectively) is demanding the updating of conventional nutrient removal technologies to fulfil these discharge limits. The basic benefits of biological nutrient removal include relatively low cost for removing nitrogen and phosphorus, monetary savings through reduced aeration capacity, less sludge production, the avoid expense for chemical reagents, enhanced removal of BOD_5 and TSS, and added process stability and reliability (Janssen (2002)).

Enhanced Biological Phosphorus Removal (EBPR) is the name that receives the accumulation of phosphorus inside the cell for the Phosphorus Accumulating Organisms (PAO). PAOs are able under anaerobic conditions to take up the volatile fatty acids (VFA) and store them inside the cell as polyhydroxyalkanoates (PHA). At the same time the polyphosphate pool is consumed releasing phosphate into the liquid media. Under aerobic or anoxic conditions, PAO take up soluble phosphate to recover the intracellular polyphosphate pool levels by the oxidation of stored PHA. Furthermore, the energy provided by PHA is also used for growth. The final result is a net phosphate removal from the wastewater (Smolders *et al.*, 1994, Figure 1.1)

Phosphorus is taken up either under anoxic or aerobic conditions by utilizing nitrates or oxygen as the final electron acceptor (Stevens *et al.*, 1999). The advantage of the anoxic phosphate removal is that both the amount of COD and the oxygen required for nutrient removal can be significantly reduced, since as stored PHA is used simultaneously for denitrification and phosphate uptake (Kuba *et al.*, 1996).

This chapter presents the study of nitrogen and phosphorus removal using a step-feed strategy in a sole SBR treating urban wastewater. The SBR cycle has been adapted from previous carbon/nitrogen removal experiences to get a suitable nutrients removal according to biological nutrient removal requirements and by applying a step-feed strategy. Following similar methodologies from previous chapters, the on-line data obtained from pH, DO and, ORP probes has been analysed to identify the main characteristic points related to nutrient removal.

7.3 Objectives

The main objective of this chapter is to evaluate different step-feed strategies for removing nitrogen and phosphorus from an urban wastewater through the definition of the number and the length of the phases for a cycle, the number and the duration of filling events. And also, it is studied the identification of the critical points following the on-line pH, DO and ORP data. These objectives are specified in:

- Define the number of filling events (6 and 3) and length of phases (anoxic-aerobic pairs) for a cycle
- Study the influence of nitrates in the phosphorus removal during the anaerobic phase
- Follow the status of the process through the critical points by means of the on-line pH, DO and ORP measurements.

7.4 Materials and Methods

7.4.1 ANALYTICAL METHODS

During all the operational study, synthetic and treated wastewaters were analysed for: Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Total Chemical Oxygen Demand (COD), ammonium ($N\text{-}NH_4^+$), Total Kjeldahl Nitrogen (TKN), nitrites ($N\text{-}NO_2^-$) and nitrates ($N\text{-}NO_3^-$), and phosphate ($P\text{-}PO_4^{3-}$) according to methodologies presented in section 3.3.

7.4.2 RAW WASTEWATER

The SBR was fed with real urban wastewater from the treatment plant of Cassà de la Selva-Llagostera (Girona, N.E. Spain). Twice a week 150 litres of fresh wastewater was transported (i.e. a 1 hour trip) to the laboratory and stored at 4ºC in a stainless-steel mixing tank to minimise microbiological activity. In order to increase the concentration of the easily biodegradable organic matter and to stimulate the phosphorus removal, around 200 mg/L of synthetic carbon source was added to the fresh wastewater. Table 7-1 shows the composition of the synthetic carbon source, mainly composed of volatile fatty acids (acetate and propionate), ethanol and some complex carbon sources as starch and tryptone.

Table 7-1: Composition of the synthetic carbon source used to add the fresh wastewater.

Name	Formula	Concentration
Sodium acetate	CH_3COONa	1.75 mg/L
Sodium propionate	CH_3CH_2COONa	1.75 mg/L
Starch	$(C_6H_{10}O_5)_n$	1.75 mg/L
Tryptone	-	1.75 mg/L
Ethanol	CH_3CH_2OH	0.13125 mL/L

After the addition of the synthetic carbon source to fresh wastewater, the resulting wastewater was analysed throughout the operational study, presenting the composition show in Table 7-2. This wastewater was the influent used to feed the SBR.

Table 7-2: Main components analysis of wastewater user for the experimental period.

Description	Symbol	Units	Mean Value $\pm \sigma$	Range
Chemical Oxygen Demand	COD	mg/L	637.3 ± 232.8	322.6-1485.0
Total Kjeldahl Nitrogen	TKN	mg/L N	51.7 ± 18.4	22.0-89.7
Ammonium Nitrogen	NH_4^+	mg/L N	33.9 ± 13.0	6.9-62.2
Nitrite Nitrogen	NO_2^-	mg/L N	0.25 ± 0.48	0.00-1.86
Nitrate Nitrogen	NO_3^-	mg/L N	0.23 ± 0.59	0.00-2.33
Phosphate	PO_4^{3-}	mg/L P	8.29 ± 5.03	1.61-26.65
Mixed Liquor Suspended Solids	MLSS	mg/L	201 ± 105.5	12.0-568.0
Mixed Liquor Volatile Suspended Solids	MLVSS	mg/L	190 ± 100.2	12.0-540

7.4.3 EXPERIMENT SET-UP

The SBR, a cylindrical reactor with a working volume of 30 L and a minimum volume of 20L, was seeded with nitrifying activated sludge from the wastewater treatment plant of Sils (Girona, N.E. Spain) and operated over four months under nitrogen removal conditions. A full description of the SBR is shown in 3.1.1. After that, the operational conditions were adapted to achieve nitrogen and phosphorus removal, introducing an initial anaerobic phase and later alterning aerobic and anoxic phases. The total length of the cycle was kept at 8 hours treating 10 L of wastewater per cycle with an exchange ratio of 0.33. The wastewater was introduced via the bottom of the reactor to improve the formation of volatile fatty acids (Keller *et al.*, 1997). The hydraulic retention time was 24 hours, while the sludge retention time (SRT) was around 20 days.

The SBR was operated by means of an in-house developed data acquisition and control software program developed by LabView. The software was able to repeat over time a previously defined operational cycle which controlled the on/off switch of all electrical devices (i.e peristaltic pumps, electro-valves and mixing units). The dissolved oxygen (DO) concentration was controlled at 2 mg/L using an on/off control valve that was connected to a compressed air supply. On-line mean values of pH, ORP, DO and Temperature were obtained every 5 seconds and stored in a simple ASCII file for further processing.

7.4.4 OPERATIONAL CONDITIONS

The experimental study was conducted over two different operational periods: Period 1 with six filling events and, Period 2 where the filling events were reduced from six to three, as presented in Figure 7.1 and summarized in Table 7-3. As a common characteristic to all operational periods, total cycle time was 8 hours divided into reaction (393 minutes), settling (60 minutes) and discharge (27 minutes) phases. In every cycle 10 litres of wastewater was added to the reactor and filling periods of each cycle were always conducted under anaerobic or anoxic conditions. Figure 7.1 shows the distribution over the cycle time of anaerobic, anoxic and aerobic phases, as well as the wastewater filling, purge and draw phases.

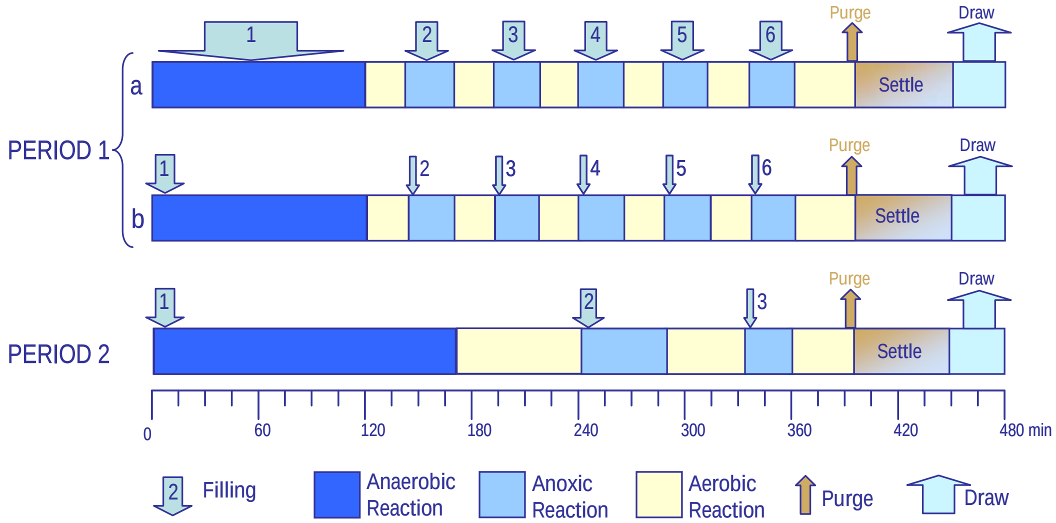


Figure 7.1: SBR cycles definition during periods 1a-b (six filling events) and 2 (three filling events).

Period 1, composed of six filling events, was operated under two different conditions: Period 1a with long filling phases (i.e. 110 minutes for the first filling and 20 minutes for each one of the others filling phases) and Period 1b where wastewater filling was conducted over a short time (i.e. 15 minutes the first filling and the rest of 3 minutes each). Nevertheless, in both operational Periods 1a and 1b, the total wastewater added per cycle was distributed in the same way: 5 litres during the first filling event and 1 litre for each one of the subsequent filling events (from 2nd to the 6th); concluding with 10 litres of wastewater treated per cycle. The reaction time distribution was also maintained during Periods 1a and 1b, as 39.9% aerobic and 61.1% anaerobic-anoxic, as presented in the Figure 7.1.

Period 2 was characterised by a reduction of the number of filling events from 6 to 3. The distribution of wastewater feed during the cycle was of 5, 3 and 2 litres for the first, second and third filling event, respectively, while a fast filling was realized for each filling phase (15, 9 and 6 minutes). As a consequence of this distribution, anoxic and aerobic phases of Period 1 were joined in Period 2, as it is shown in Figure 7.1. Observing this cycle, a slight decrease of aerobic reaction time fraction from 38.9 to 37.7% was detected, while anaerobic+anoxic fraction increased from 61.1 to 62.3%.

Table 7-3 presents a summary of the operational conditions for each period. While the conditions were kept constant, the operational strategy was modified in order to improve the phosphorus removal.

Table 7-3: Operational conditions applied during Periods 1 and 2. *% Aerobic and Anaerobic-Anoxic reaction time are calculated over reaction time.

Operational Condition	Symbol	Units	Period 1		Period 2
			1a	1b	
Exchange ratio	V_F/V_T	-	0.33		
Minimum Volume	V_{MIN}	L	20		
Flow	Q	L/d	30		
Total cycle time	tc	h	8.00		
Effective time	$t_E= t_F+t_R$	h	6.55		
Effective fraction	f_E	-	0.82		
Hydraulic retention time	HRT	d	1.00		
Effective hydraulic retention time	HRT_E	d	0.82		
Anaerobic-Anoxic reaction time	%AN-ANOX *	%	61.1		62.3
Aerobic reaction time	%AEROBIC *	%	38.9		37.7
Sludge retention time	SRT	d	24	28	28
Mixed liquor suspended solids	MLSS	mg/L	3941	4518	4293
Period Length	-	days	32	101	60

7.4.5 METHODOLOGY

The reactor performance was monitored throughout the experiment at least twice a week though determination of the COD, solids, nitrogen (TKN, N-NO_3^-, N-NO_2^- and N-NH_4^+) and phosphorus in the influent and the effluent. The samples were obtained from the storage tank and at the end of the cycle from the withdrawn wastewater. In addition, every time that fresh urban wastewater was collected and stored in the refrigerated tank, it was analysed before and after the addition of the synthetic carbon source solution.

Once per period, a cycle was performed to obtain nitrogen and phosphorus profiles, by taking samples every few minutes over an 8 hour cycle. Mixed-liquor suspended solids (MLSS) and mixed-liquor volatile suspended solids (MLVSS) were analysed at the end of aerobic phase at least once a fortnight.

General reactor maintenance was routinely performed, involving tasks such as checking and testing the probes, checking the pump flow rates, replacing tube connections and cleaning the reactor.

7.5 Results and discussion

7.5.1 SBR PERFORMANCE: COD, N AND P EVOLUTION

After the nitrogen removal period presented in chapter 4 (4.6), the operational cycle was adapted in order to achieve a joined nitrogen and phosphorus removal. The main difference with previous operational cycles was the addition of an initial anaerobic phase followed by an aerobic phase to induce the biological phosphorus removal process, as presented in Figure 7.1. The performance of COD, N and P evolution was followed throughout the experimental study during the different periods exposure in Figure 7.1: Period 1, when the SBR was operated with six long (Period 1a) or short (Period 1b) filling events and, Period 2 where the filling events were reduced to three and conducted under short filling events.

Figure 7.2 shows the COD evolution in all operational periods of the real wastewater (adjusted with carbon solution) and the treated effluent. Throughout the experimental time, influent COD had a high variability ranging from 77 to 2475 mg/L with a mean influent COD around 529 mg/L. Such high variability was a consequence of the influence of rainy and dry weather as well as some industrial contribution. In spite of such significant variation, effluent COD was always achieved values lower than 125 mg/L in accordance with to European Directive 91/217/CEE.

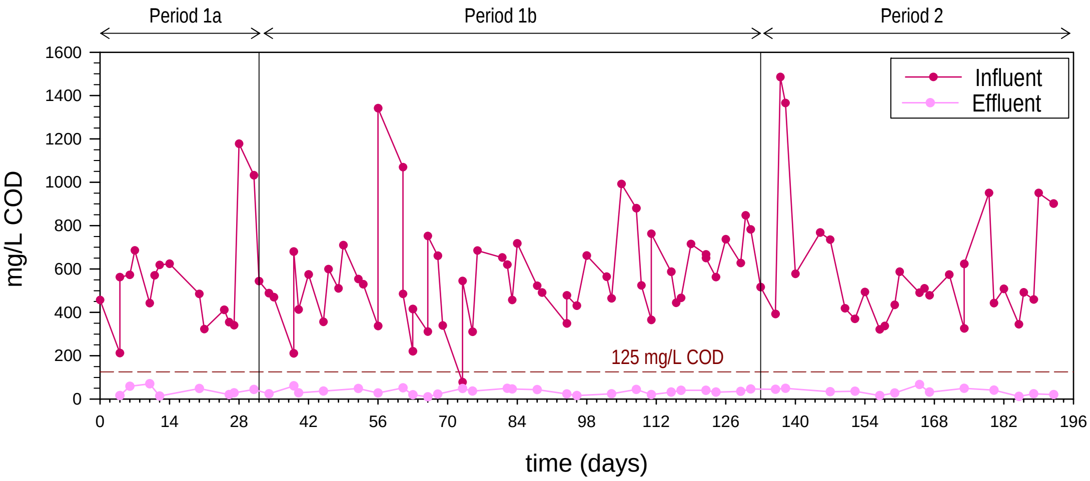


Figure 7.2: Total COD evolution in all operational periods of the influent and the treated wastewater.

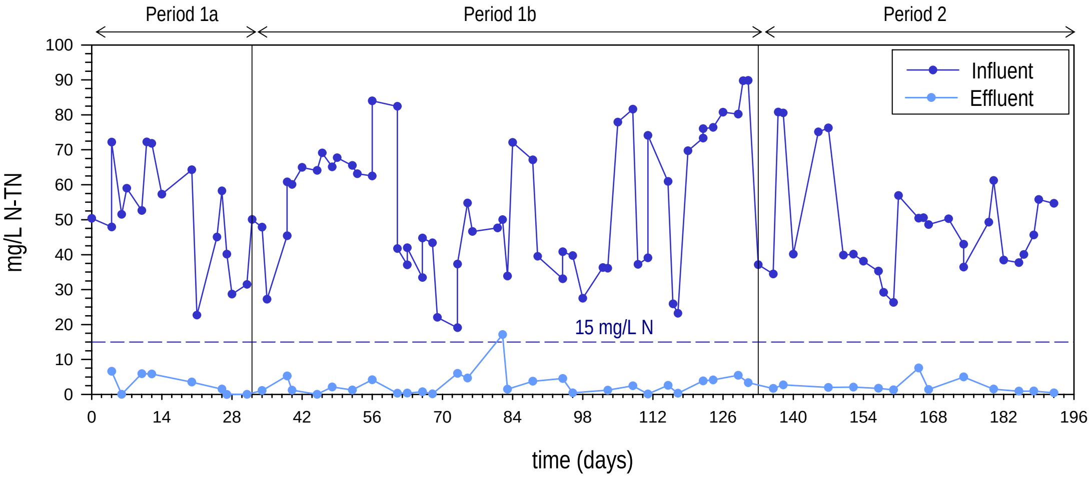


Figure 7.3: Total Nitrogen evolution in all operational periods of the influent and the treated wastewater.

Total nitrogen, influent and effluent, evolution during all the operational periods are presented in Figure 7.3. Influent total nitrogen presented a similar variability as influent COD as stated before in the Figure 7.2. Influent concentration ranged from 5 to 90 mg/L N. Throughout the experimental time (Periods 1 and 2) total nitrogen concentration in the effluent was lower than 15 mg/L N in accordance with the nitrogen dump limit of the European Directive

91/217/CEE, in whichever operational strategy applied (Figure 7.1). Only on one day (82nd day), was nitrogen concentration higher than the legislative limit. Such concentration was a consequence of some oxygen supply problems.

Whereas organic matter and nitrogen evolution always presented a suitable nitrogen and organic matter removal, general phosphorus evolution presented a randomised behaviour as presented in Figure 7.4. Similar to nitrogen and COD influent, soluble phosphorus influent presented a high variation ranging from 0 to 26.7 mg/L P. A similar variation was observed in effluent soluble phosphorus from 0 and 7 mg/L P. Only on a few occasions was the effluent soluble phosphorus lower than 2 mg/L P, the limit of the European Directive 91/217/CEE.

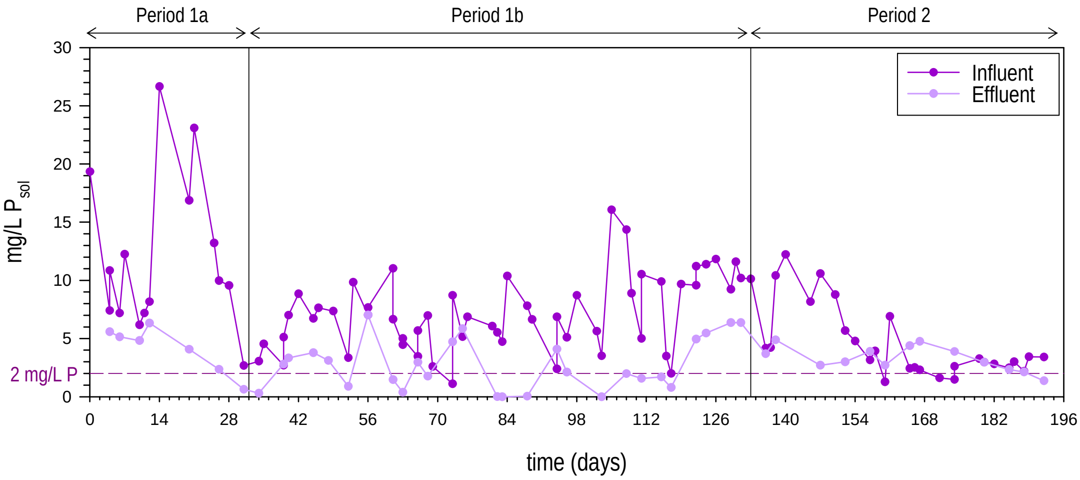


Figure 7.4: Soluble P evolution in all operational periods of the influent and the treated wastewater.

In spite of different operational strategies being applied throughout the experimental time, no significant improvement was achieved in phosphorus removal. In order to understand the biological phosphorus removal behaviour and dynamics, a complete operational cycle of each operational period was studied.

7.5.2 COMPARISON BETWEEN LONG (PERIOD 1A) AND SHORT (PERIOD 1B) FILLING EVENTS

During Period 1 two different filling strategies were applied, the first one with long and slow fillings (Period 1a) and the second one with short and faster fillings (Period 1b). To understand the behaviour of all the compounds during the different periods, a specific cycle study was conducted for each operational period. Phosphorus evolution in a typical cycle of the SBR was followed by analysis of phosphorus and the recording of the on-line values of pH, DO and, ORP to detect the possible critical points.

Figure 7.5 presents the phosphorus evolution and on-line monitoring of pH, DO and ORP measurements during one cycle of Period 1a. In the phosphorus evolution figure the calculated phosphate (P_{calc}) which corresponds to the calculated soluble phosphorus inside the reactor assuming only dilution effects of the phosphorus contents of wastewater, neither chemical nor biological reaction, is also plotted. This calculation is the result of the SBR volume increasing during the cycle time because of the different additions of wastewater during the cycle in order to observe the phosphorus release and uptake during anaerobic and aerobic phases.

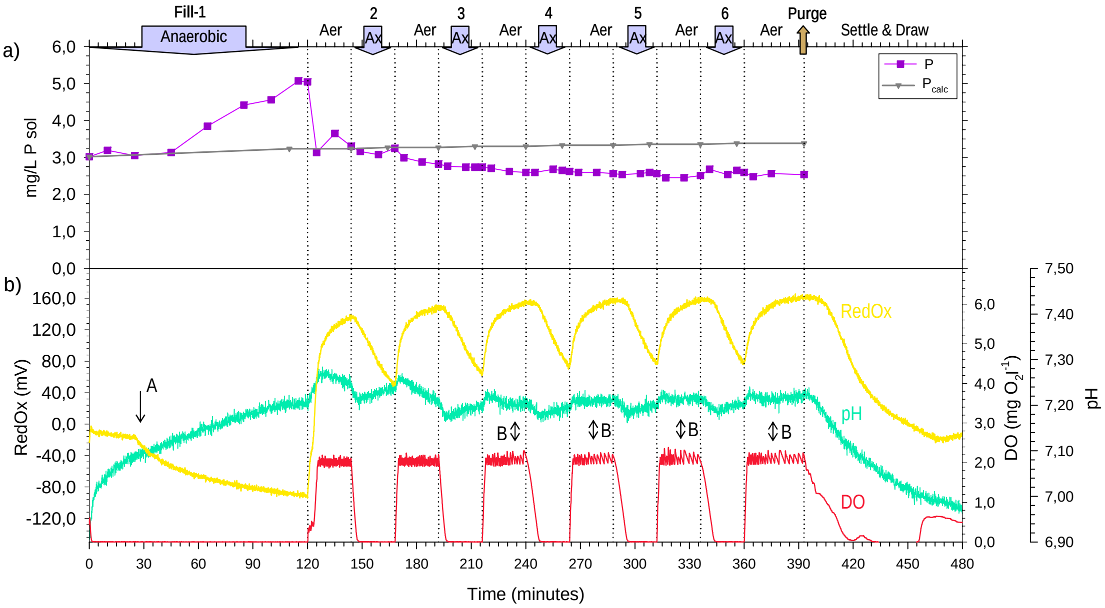


Figure 7.5: Typical cycle profile during Period 1a. The experimental phosphate (P) and the calculated phosphate assuming no reaction (P_{calc}) are shown at the top graph (a), while the bottom graph (b) shows the evolution of pH, DO and ORP after process stabilisation.

The Period 1a operated under long and slow filling events where the first filling phase was carried out over 110 minutes. Initially, phosphate concentration remained constant at around 3.1 mg/L P (Figure 7.5a), due to the denitrification of the nitrate present in the reactor. This fact was reflected in the ORP curve which was maintained around -12 mV until the apparition of Nitrate Knee in minute 30 (point A, Figure 7.5b) obtaining anaerobic conditions. Then, under anaerobic conditions, phosphate was released due to the biological activity, increasing the concentration of phosphate from 3.1 to 5.1 mg/L P at the end of the anaerobic phase in minute 120. The P release value was 1.8 mg/L P, calculated as the difference between experimental phosphate and calculated phosphate assuming no reaction. The pH was maintained with a slight increase as a consequence of the continuous fill during 110 minutes and only in the last 10 minutes of the anaerobic phase when no feed was added was the pH flat. Meanwhile during this phase the pH should decrease due to the formation of volatile fatty acids (VFA).

Under aerobic conditions the dissolved oxygen was controlled at under 2.0 mg/L O_2 (Figure 7.5b). During the first aerobic phase of 19 minutes, phosphorus decreased from 5.1 mg/L P to 3.3 mg/L P, it meant a P uptake of 1.8 mg/L P (Figure 7.5a).

After the first two phases designed for phosphorus removal, the rest of the cycle was designed for nitrogen removal. However, under aerobic phases phosphorus decreased slightly, concluding with a final phosphorus concentration of 2.7 mg/L P-PO_4^{3-}. The overall P uptake of this cycle was 2.4 mg/L P higher than P release.

Analysing the monitoring of on-line data (pH, ORP and DO) was not able to clearly identify the critical points, especially the end of nitrification (point B, minutes 230, 275, 320 and 370) because of the oxygen control strategy. As a result of this, the calculation of Oxygen Uptake Rate (OUR) was made possible following the methodology previously defined in 5.4.5. The OUR gives information about organic matter removal and nitrification all processes with oxygen presence. Figure 7.6 presents the OUR evolution during all aerobic phases and the evolution of the working volume in the reactor throughout the cycle.

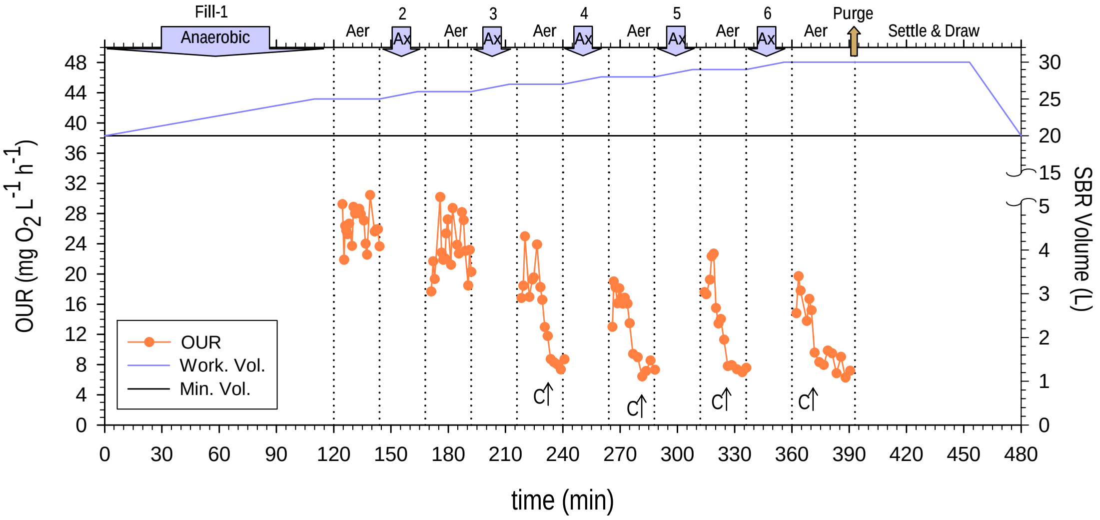


Figure 7.6: Evolution of the OUR in the Period 1a when set-point of DO was applied. At the top the increase in the volume due to the filling strategy is presented.

Under the first two aerobic phases, OUR values remained constant as a consequence of the microbiological activity because the nitrification and/or the COD removal were not completed. On the other hand the rest of four aerobic phases, initially OUR was kept at a high values, but when the substrate was finished a significant decrease was observed until endogenous values (point C, Figure 7.6). These values could possibly mark the end of the nitrification. These points appeared in the minutes 230, 275, 320 and 370 and coincide with longer intervals in the DO curve, so a complete nitrification is achieved in this cycle. On the other hand, observing the ORP and pH profiles during the anoxic phase, neither Nitrate knee nor Nitrate Apex were detected. Then the denitrification was partial. The ammonia, nitrite and the nitrate values in the effluent were of 0 mg/L N-NH_4^+, 0.6 mg/L N-NO_2^- and 1.5 mg/L N-NO_3^-, respectively.

The Period 1b was characterized by short and fast filling events. Figure 7.7 presents the phosphorus evolution, nitrites and nitrates evolution, and on-line monitoring of pH, DO and ORP during one cycle of Period 1b.

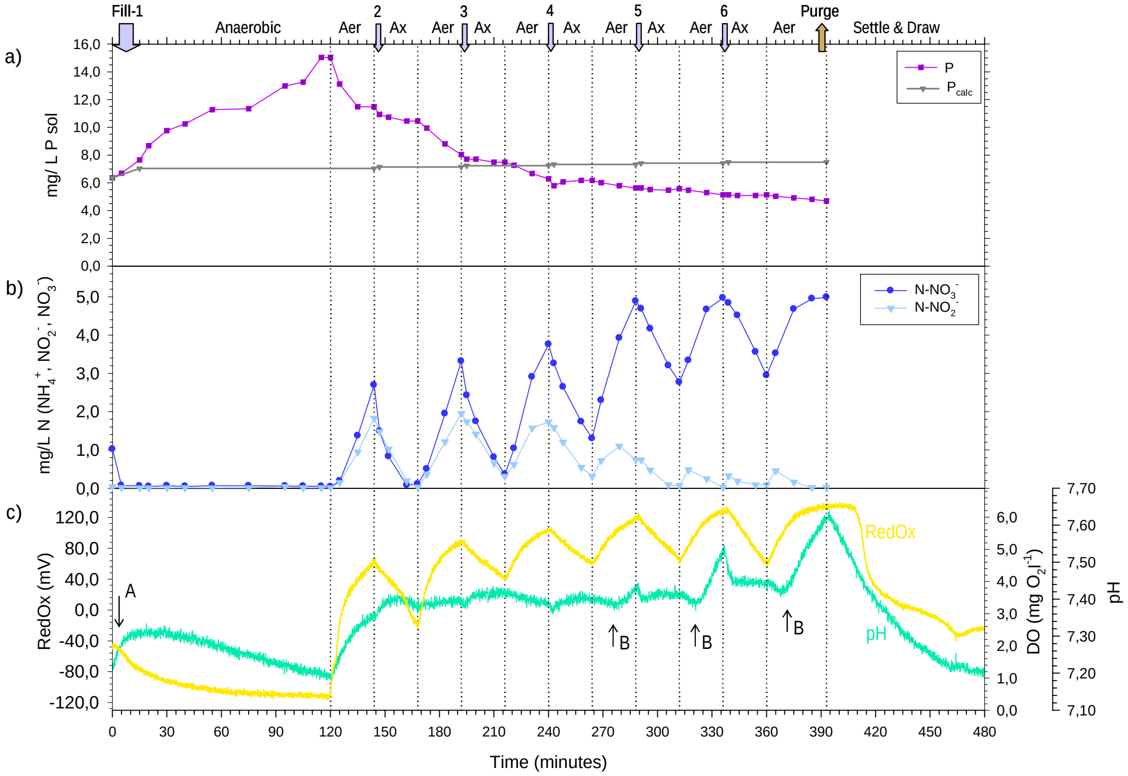


Figure 7.7: Typical cycle profile during Period 1b. The experimental phosphate (P) and the calculated phosphate assuming no reaction (P_{calc}) are shown at the top (a), while in the middle (b) shows the nitrite and nitrate evolution and the bottom (c) shows the evolution of pH, DO and ORP after process stabilisation.

Period 1b operated with fast filling where the first filling phase was executed over 15 minutes instead of 110 minutes of Period 1a. At the beginning, the trends of experimental and calculated phosphate assuming no reaction were similar and had the same tendency (Figure 7.7a) due to the denitrification process. In less than 5 minutes a complete denitrification (Figure

7.7b) occurred and Nitrate Knee and Nitrate Apex (point A, Figure 7.7c) appeared in ORP and pH curves, respectively. After this, pH and ORP decreased due to the production of volatile fatty acids and phosphate released, and the anaerobic conditions. At the end of this phase phosphate concentration reached 15 mg/L P. Thus, P release value was 8 mg/L P, calculated as the difference between experimental and calculated phosphorus.

Under aerobic conditions a constant oxygen supply was applied during all aerobic phases due to operational problems with the DO probes during some days in the Period 1b. During the first aerobic phase, phosphate was taken up partially from 15 to 11.5 mg/L in 24 minutes, being the P uptake of 3.5 mg/L P. At the same time, nitrate and nitrite were formed due to nitrification of the ammonia but no Ammonia Valley or other critical points were detected.

In the rest of the cycle, with the purpose of nitrogen removal, the phosphate trend was kept flat under anoxic conditions and slightly descended under aerobic conditions, as in Period 1a (Figure 7.5a). However, at the end of the cycle, 4.8 mg/L P-PO_4^{3-} was found, making the P uptake of 10.2 mg/L P higher than P release 8 mg/L P.

The focus on the nitrogen part of the cycle, as a sequence of anoxic phase (including the first three minutes of filling) and the aerobic phase was repeated in five times. Critical points can be explained by nitrate and nitrate evolution (Figure 7.7b) and on-line parameters (Figure 7.7c). Under the first anoxic phases, Nitrate Apex and Nitrate Knee (point A, Figure 7.7c) were observed. In the second aerobic phase, no critical points were detected so the nitrification was not complete. During the rest of the sequences (anoxic, aerobic), a decrease of nitrate was observed under anoxic phases, while a gradual increase of nitrates was achieved under aerobic phases ((Figure 7.7b). Whereas the general tendency of nitrates was accumulative throughout the cycle, an opposite tendency was detected for the nitrites. Only in the last three aerobic phases was the nitrification considered complete due to the apparition of Ammonia Valley (point B, Figure 7.7b, minutes 275, 320 and 370) but a partial denitrification occurs in the anoxic phases. At the end of the cycle 4.1 mg/L N-NO_3^-, 0.06 mg/L N-NO_2^- and 0 mg/L N-NH_4^+ were found. In analysing the values of P uptake and P release obtained in Figure 7.5a and Figure 7.7a, it seems that the fast fill is more efficient than the slow fill. However, to make an accurate comparison between both cycles (Period 1a and Period 1b), different parameters such as the wastewater composition and the biomass characteristics for each cycle, as presented in Table 7-4 should be taken into account.

Table 7-4: Comparison of analytical characterization (wastewater and biomass) for studied cycles in Periods 1a and 1b.

Description	Symbol	Units	Period 1a	Period 1b
Chemical Oxygen Demand	COD	mg/L	340	562
Total Nitrogen	TN	mg/L	41.5	76.4
Phosphate	P	mg/L	4.2	9.7
Ratio COD/TKN	COD/TKN	-	8.48	7.36
Ratio COD/P	COD/P	-	80.95	57.94
Ratio COD:TKN: P	COD:TKN:P	-	81:10:1	58:8:1
Mixed Liquor Suspended Solids	MLSS	mg/L	3600	4783
Mixed Liquor Volatile Suspended Solids	MLVSS	mg/L	2888	3892

From the results gathered in Table 7-4, the cycle studied in the Period 1b presented a higher concentration of COD, TN and P than in Period 1a, while the ratio COD/TKN and COD/P were lower than in Period 1a. At the same time, the COD:TKN:P ratios are higher in the Period 1a than Period 1b. So it could be concluded that a higher efficiency would be found for the Period 1a. Nevertheless, the efficiency depends on the wastewater characterization and the biomass present in the reactor. As both cycles had a different suspended solids concentration, Period 1b higher than Period 1a, in order to compare them both it is necessary to express the results with respect to the volatile suspended solids. For this reason, Figure 7.8 shows the difference between experimental phosphate and calculated phosphate assuming no reaction per unit of volatile suspended solid (VSS) with respect to the time. This value could be defined on the net phosphorus balance, positives values indicate a net P release, while negative values are indicative of a net phosphorus uptake indicating that there are phosphorus accumulating inside the cell.

After the comparison of wastewater and biomass characteriscs for both cycles, the easiest way to compare both phosphorus removals is through the difference between experimental and calculated phosphate assuming no reaction with respect to the biomass for each specific cycle in Period 1a and 1b, as presented in the Figure 7.8.

The profiles of (P-P_{calc})/VSS in the anaerobic phase (P realise per unit of VSS) had different tendency for both periods. The rate of Period 1b was higher than Period 1a. This fact could be explained by the fact that during the fast fill the concentration of organic matter available inside the reactor is higher than in the slow fill. Then, as microorganisms follow Monod kinetics, a low concentration of substrates means a low rate of the microorganisms. As a consequence, a high phosphate release rate was found in the fast fill period. At the same time, when the fast fill is applied, more organic matter is available to denitrify in less time, and the rest of the anaerobic time is available to produce and take up the volatile fatty acids responsible for the phosphorus removal.

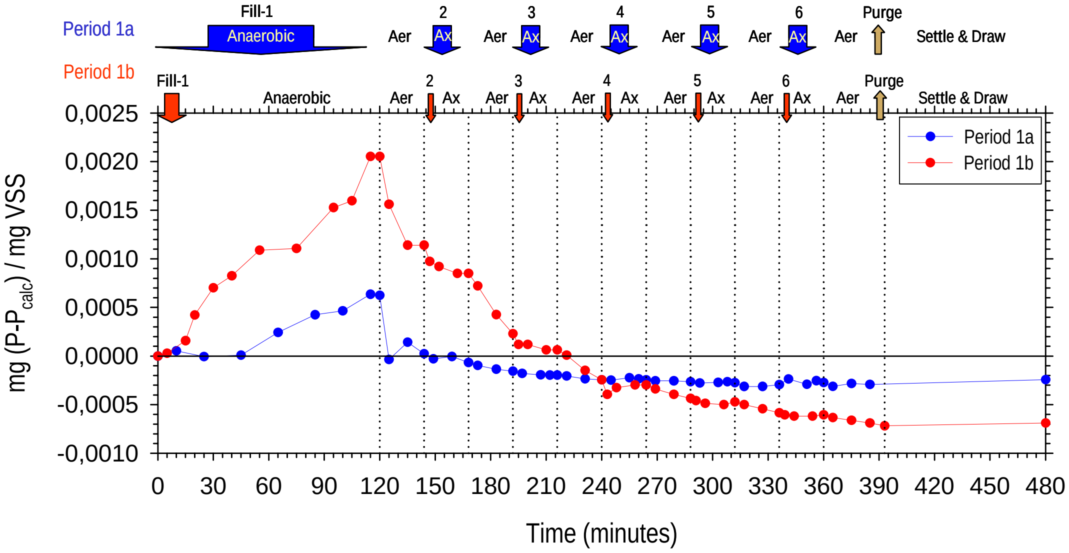


Figure 7.8: Comparison between experimental and calculated results for the phosphate of Period 1a and Period 1b with reference to volatile suspended solid.

In the aerobic phase the phosphate was taken up for the PAOs and the ratio P/VSS decreased. At the beginning, both plots had the same tendency of taken up the phosphate per volatile suspended. In Period 1a, this ratio crossed the line of zero earlier than in Period 1b, minutes 155 and 220, respectively. But Period 1b took more time to cross the zero line because more phosphorus was released and more phosphorus could be taken up later. Finally the difference between experimental and calculated phosphorus assuming no reaction per volatile suspended solids was higher in that of Period 1a than in Period 1b. The overall P release and P uptake were higher in Period 1b than in a fast fill. Thus, fast fill has demonstrated advantages over slow fill for the phosphorus removal.

7.5.3 PERIOD 2

After the results obtained during Period 1, some modifications were carried out in order to improve the phosphorus removal. In Period 1b (Figure 7.7), at the end of the anaerobic phase phosphorus, the tendency was increasing. It seemed that P release had not in fact finished and a longer anaerobic phase was required. So with this in mind, the anaerobic phase was increased from 120 to 170 minutes in the Period 2. The rest of effective time (fills plus reaction) was reduced because of the length of the cycle and the settle and draw phases were maintained at the same time as the earlier period. Thus, less time was required to perform the five remaining filling events with anoxic and aerobic phases. So, different strategies could be executed in order to keep or decrease the nitrogen concentration at the end of the cycle. Firstly, if the number of filling events was maintained at five equal filling phases, the final nitrogen concentration would increase because the remaining time was not enough to achieve the nitrogen removal. Secondly, if the number of equal filling events was reduced the final concentration of nitrogen in the effluent would also increase also (see Table 4-1). Therefore, if neither the maintenance nor the reduction of the number of filling events could be carried out because of the increase of nitrogen effluent, another strategy could be applied by reducing the number of filling events but feeding different volumes (more volume in the first filling events and less in the last one). This strategy was adopted and consisted of decreasing the number of filling events from 6 to 3 being the feeding volumes 5, 3 and 2 litres, respectively for the first, the second and third filling event. In that way, the nitrates of the others phases could be removed and leave a low concentration of nitrogen in the effluent.

In summary, Period 2 differed to Period 1b in the number of filling events (6 to 3), the total time of the anaerobic phase (120 to 170 minutes) and as a consequence of these, in the time of the aerobic and anoxic phases (Figure 7.1, Period 2).

After process stabilization a new operational cycle was analysed to understand the behaviour of all compounds inside the reactor. The phosphorus, nitrite and nitrate and on-line monitoring of pH, DO and ORP probe evolution along the cycle during the Period 2 are presented in Figure 7.9.

During the first 15 minutes of the anaerobic phase, the feed was introduced into the reactor. Due to the influent phosphate concentration, the trends of experimental phosphate and calculated phosphate assuming no reaction were similar and had the same tendency (Figure 7.9a) as a consequence of the denitrification process (Figure 7.9b). Nitrate Apex in the pH and Nitrate Knee in the ORP were detected around minute 20 (point A, Figure 7.9c) when complete denitrification was achieved. After this point, under anaerobic phase, pH and ORP decreased due to anaerobic conditions and a progressive release of phosphate was detected from 7 mg/L P to 11.7 mg/L P, being the P release of 5 mg/L P at the end of the anaerobic phase.

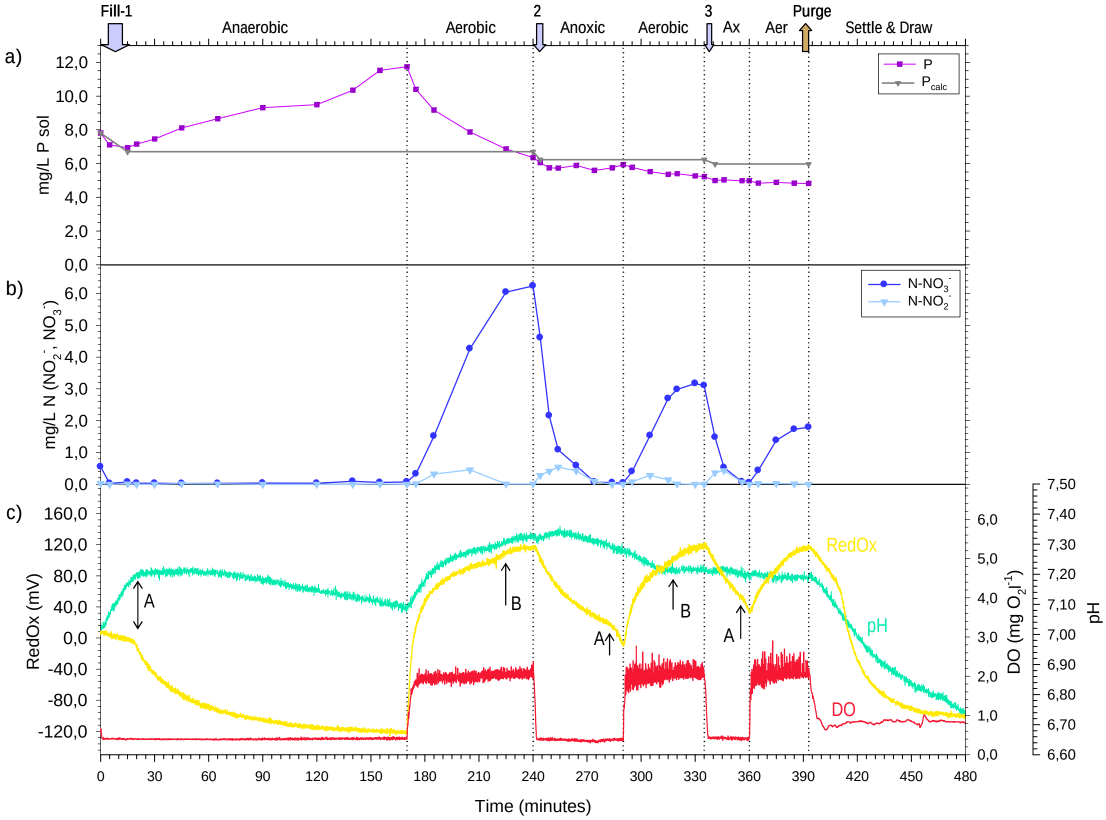


Figure 7.9: Typical cycle profile during Period 2. The experimental phosphate (P) and the calculated phosphate assuming no reaction (P_{calc}) are shown in the top (a), while at the middle (b) shows the nitrite and nitrate evolution and at the bottom (c) shows the evolution of pH, DO and ORP after process stabilisation.

Under aerobic conditions the dissolved oxygen was controlled to under 2.0 mg/L O_2 (Figure 7.9c), as in Period 1a. The phosphate was taken up by the microorganisms obtaining a value of 6.0 mg/L P at the end of the first aerobic phase. Then, the P uptake value at this point was 5.4 mg/L P higher than P release. At the same time, the ammonium was oxidized to nitrate and nitrite reaching a final concentration of 6.2 and 0.0 mg/L N, respectively. When a set-point of DO is used as a control, the typical critical points to detect the end of the nitrification are more difficult to observe. However, oxygen uptake rate (OUR) can be an alternative as in the Period 1a. Figure 7.10 presents the Oxygen Uptake Rate (OUR) evolution during all aerobic phases and the evolution of the working volume in the reactor throughout the cycle. In the first aerobic phase, OUR achieved a minimum value at minute 225 (point C, Figure 7.10) indicating the end of the nitrification. At the same time, the α_{ORP} in the ORP curve (point B, Figure 7.9c) was identified.

In the rest of the cycle (basically to remove nitrogen), phosphate had a slightly decreased tendency obtaining a value of 4.7 mg/L P in the effluent, being the final P uptake of 7 mg/L P.

During the second filling event three litres of wastewater were introduced during the first nine minutes of the anoxic phase. In approximately 25 minutes all nitrates and nitrites were reduced from 6.2 mg/L N-NO$_3^-$ to near zero. Some nitrites were detected under the denitrifying phase. In the posterior aerobic phase the current ammonia inside the reactor was nitrified. Nitrate concentration was lower during the second aerobic phase than during the first one due to a low volume of feed being introduced in the second filling event. In the last anoxic phase, two litres of wastewater were added and the nitrates were denitrified. Then in the aerobic phase, nitrification occurred. At the end of the cycle 1.4 mg/L N nitrogen concentration was found corresponding to 1.3 mg/L N-NO$_3^-$ and 0.1 mg/L N-NH$_4^+$ less than in Period 1b.

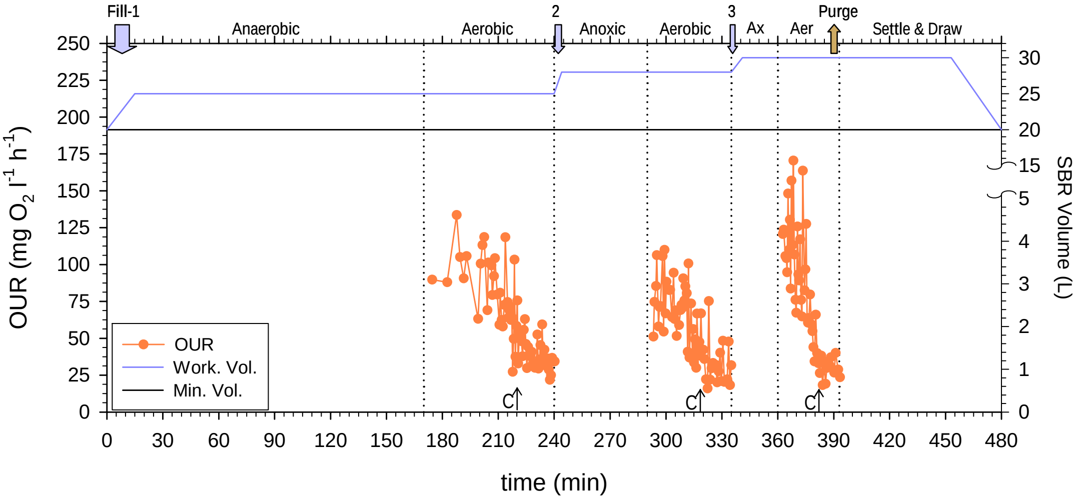


Figure 7.10: Evolution of the OUR in Period 2 when the DO set-point was applied. At the top the increase in the volume due to the filling strategy is presented.

In the second and third anoxic phase, Nitrate Knee was observed in the minutes 285 and 355 (point A, Figure 7.9c), while Nitrate Apex was more difficult to detect. Under the rest of aerobic conditions, the α_{ORP} in the ORP were detected in minute 320 and marked as point B (Figure 7.9c). While in the OUR profile, point C (Figure 7.10) appeared in the minutes 320 and 380 thus indicating the end of the nitrification.

The results obtained in Period 2 was consequence of the strategy applied (as previously explained) and the wastewater composition and the biomass characteristics. These parameters are presented in Table 7-5.

From the results gathered in Table 7-5, the cycle studied a low concentration of phosphorus in the influent is shown in Period 2. In addition of organic matter and phosphorus concentration, volatile suspended solids play an important role in the phosphorus removal. For this reason, Figure 7.11 shows the difference between experimental and calculated soluble phosphate respect the suspended solid.

Table 7-5: Analytical characterization (wastewater and biomass) for studied cycle in the Period 2.

Description	Symbol	Units	Period 2
Chemical Oxygen Demand	COD	mg/L	476
Total Nitrogen	TN	mg/L	48.6
Phosphate	P	mg/L	2.3
Ratio COD/TKN	COD/TKN	-	9.79
Ratio COD/P	COD/P	-	206.06
Ratio COD:TKN: P	COD:TKN:P	-	207:21:1
Mixed Liquor Suspended Solids	MLSS	mg/L	3974
Mixed Liquor Volatile Suspended Solids	MLVSS	mg/L	3310

At the beginning of the cycle, the (P-P_{cal})/VSS value remained close to zero (Figure 7.11) until minute 10 due to the presence of nitrates and the dilution effect, as before mentioned. After this, the phosphate was released linearly until minute 120 where it was stabilized to increase again.

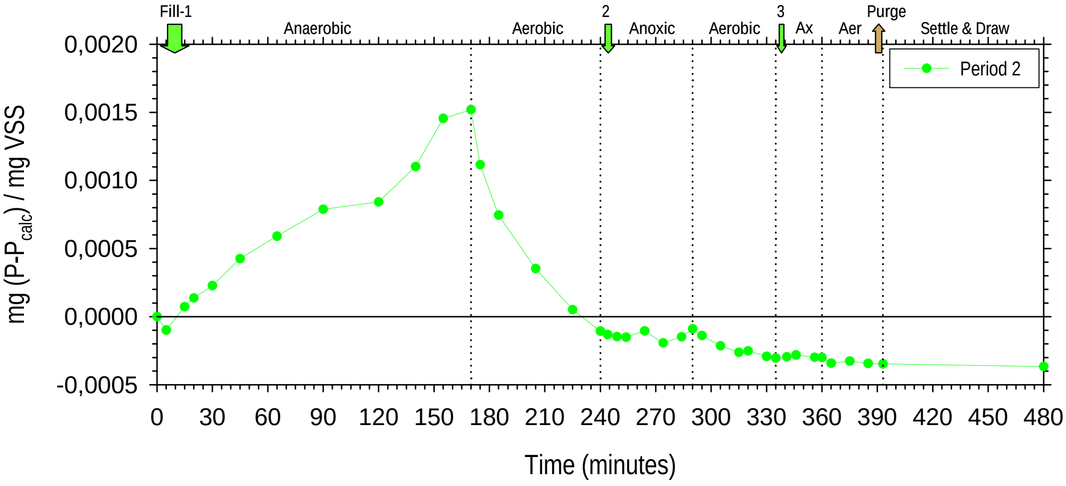


Figure 7.11: Evolution of experimental and calculated results for the phosphate of Period 2 reference to volatile suspended solid.

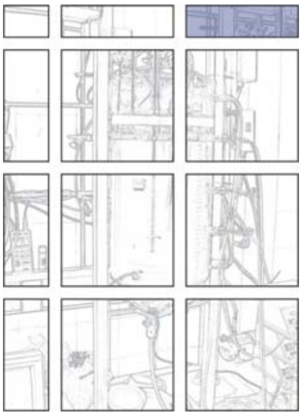
Under the aerobic phase the phosphate was taken up for the PAOs and the ratio (P-P_{cal})/VSS decreased. This ratio crossed the line of zero earlier, namely in minute 230, only 60 minutes were necessary. This means that all the phosphorus release was taken up and the system was able to remove more phosphorus. Throughout the rest of the cycle, the slope had a different, or rather, flatter tendency. Finally, at the end of the cycle the difference between experimental and calculated phosphorus respect de volatile suspended solids was close to

0.0004 mg P/mg VSS.

7.6 Conclusions

The conclusions obtained in this chapter are related below:

- The addition of an initial anaerobic-aerobic pair is necessary to implement the biological phosphorus removal in a SBR. After this, the sequenced anoxic-aerobic pair must be used for nitrogen removal.
- The different step-feed strategy applied in this study has demonstrated to be able to remove organic matter and nitrogen obtaining effluent lower than 90 mg/L COD and 8 mg/L N according with the legislation.
- Instead of the strategies used for phosphorus removal, a low value of efficiency has been obtained.
- With respect to phosphorus removal, the presence of nitrate at the beginning of the anaerobic phases caused the competition between denitrifier organisms and phosphorus accumulating organisms (PAO) for the organic matter available.
- The use of short filling phase against a long filling phase has been favourable in order to quickly decrease the nitrate concentration at the beginning of the cycle.
- When the anaerobic phase is increased, the number of anoxic-aerobic pairs must be reduced. Nevertheless, in order to maintain the same nitrogen removal efficiency volumes of wastewater added during the filling events in the anoxic-aerobic pairs must be different and the filling volume added in the last filling event must be lower than the previous.
- The difference between P experimental and P calculated assuming volume changes and the VSS has proved a useful methodology to identify phosphorus uptake and release in a EBPR process using a step-feed strategy in a SBR.



8

INFLUENCE OF PH AND CARBON SOURCE IN THE PHOSPHORUS REMOVAL

8.1 Summary

In lab-scale reactors fed with acetate and propionate respectively, two different operational parameters were changed in order to improve the poor levels of phosphorus removal in these systems. These strategies consisted of increasing the pH of the media and changing the carbon source.

High phosphorus removal levels were found using both strategies, with the best results achieved in the propionate-fed reactor. Large enrichments of PAOs were achieved in a high pH and with propionate as the carbon source after operational periods of competition between

PAOs and GAOs for VFA.

8.2 Introduction

Nutrient discharged into the receiving waters are mainly responsible for the accelerated aging of lakes and estuaries due to excessive plant and algal growth (i.e. eutrophication). This is why it is necessary to remove phosphorus from wastewaters by chemical or biological processes. In comparing both processes, the main advantages of the biological process include reduced costs and lower sludge production (Metcalf and Eddy (2003)). However, biological phosphorus removal may be unstable at times, and is prone to occasional failure.

Enhanced biological phosphorus removal (EBPR) is based on the incorporation of phosphorus from the influent into cell biomass, which subsequently is removed from the process as a result of sludge wasting. Incorporation of the phosphorus into cell biomass is achieved through alternating anaerobic and aerobic conditions in the activated sludge process. The organisms responsible for this task are known as Phosphorus Accumulating Organisms (PAOs).

Under anaerobic conditions the influent is introduced into the reactor and PAOs are able to take up volatile fatty acids (VFAs) from the influent and convert them to Poly-β-HydroxyAlkanoates (PHAs). The energy and reducing power required for these transformations is obtained through the hydrolysis of their intracellular stored polyphosphate (poly-P) and glycogen (Mino *et al.*, 1998, Smolders *et al.*, 1994). During aerobic conditions, PAOs oxidise PHA to gain energy for growth, glycogen replenishment and phosphorus uptake.

VFA can also be taken up anaerobically by another group of microorganisms, known as Glycogen Accumulating Organisms (GAOs). Like PAOs, GAOs are also able to convert VFA into PHA. However, GAOs are not able to release phosphorus under anaerobic conditions and do not take up phosphorus under aerobic conditions. Hence GAOs do not contribute to the phosphorus removal; GAOs are only competitors for often-limited VFA substrates.

Thus, in order to enhance biological phosphorus removal, it is desirable to maximise the VFA uptake by PAOs and minimise the VFA uptake by GAOs. Previous studies have suggested the importance of pH in the competition between PAOs and GAOs. (Bond *et al.*, 1999b, Filipe *et al.*, 2001c, Filipe *et al.*, 2001b, Jeon *et al.*, 2001, Schuler and Jenkins, 2002, Serafim *et al.*,

2002) and propose that a higher pH is more beneficial for PAOs and less favorable for GAOs. Assuming that the internal pH of the cells is kept constant, if there is an increase in the ambient the pH corresponds to an increase in the pH gradient and a corresponding increase in the potential difference across the cell membrane (Smolders *et al.*, 1994). Thus, more energy is required for VFA transport through the cell membrane when the external pH is high. For PAOs the energy is generated through an increase in polyphosphate hydrolysis and released as orthophosphate. Indeed many studies have shown that a higher pH induces higher anaerobic P release in enriched PAO cultures (Bond *et al.*, 1999a, Filipe *et al.*, 2001a, Liu *et al.*, 1996et al. 1996, Smolders et al. 1994). However, batch studies performed in reactors fed with acetate as the sole carbon source show that the acetate uptake rate is independent of pH over the range of 6.5 and 8.0 (Filipe *et al.*, 2001a, Liu *et al.*, 1996, Smolders *et al.*, 1994). In the case of GAOs, glycogen is the only source of energy for VFA uptake, and an increase in pH has been observed to yield a higher glycogen degradation (Filipe *et al.*, 2001b). In contrast, the acetate uptake rate by GAOs, in short term tests, decreased significantly when the pH of the medium increased (Filipe *et al.*, 2001b), suggesting that a high pH negatively affects the ability of GAOs to take up the acetate.

Some studies suggest that propionate could potentially be very useful in controlling the growth of GAOs in EBPR systems. It is well known that acetate is the main fraction of VFA present in most full-scale EBPR systems and because of this previous experimental studies in this field have focused largely on the use of acetate as the sole VFA substrate (Filipe *et al.*, 2001b, Smolders *et al.*, 1994, Zeng *et al.*, 2003). However, other VFA substrates are also present in wastewater plants, primarily propionate. Recently some studies have suggested that propionate is a more favourable substrate than acetate for EBPR providing an advantage to PAOs over GAOs (Chen *et al.*, 2004, Oehmen *et al.*, in preparationa, Oehmen *et al.*, in preparationb, Pijuan *et al.*, 2004, Thomas *et al.*, 2003). Previous study by Oehmen *et al.* has revealed that a culture of GAOs enriched with acetate was virtually incapable of propionate uptake during short-term testing. In contrast, similar batch tests with an acetate enriched PAO culture immediately showed a high level of propionate uptake.

This chapter presents the study of two different strategies in two PAO reactors using synthetic wastewater in order to improve the EBPR performance when competition between PAOs and GAOs exist. These strategies are the increase of pH and the change of carbon source. While, in the acetate fed reactor the effect of carbon source change from acetate to propionate and the effect of the pH is studied, in the propionate fed reactor only the effect of the pH is studied.

8.3 Objectives

The main objective of this chapter is to evaluate the influence of pH and carbon source to remove phosphorus for a synthetic wastewater through the study of the effect of increasing the pH in two different carbon sources and studying the effect of carbon source change. These objectives are specified in:

- Study the phosphorus removal process under controller conditions
- Study the pH increase (from 7 to 8) in two reactors using different carbon sources (acetate and propionate)
- Study the effect of change of carbon source from actate to propionate.

8.4 Materials and Methods

8.4.1 ANALYTICAL METHODS

Orthophosphate (PO4-P) and volatile fatty acids (VFA) were analysed according to the methods 3.3.10III and 3.3.4, respectively. These analyses were executed for the laboratory of Advanced Wastewater Management Centre (AWMC) in Brisbane (Queensland, Australia).

8.4.2 SYNTHETIC WASTEWATER

The synthetic wastewater was composed of two different solutions, a carbon-rich solution and a phosphorus-rich solution. These two solutions were prepared once a week in different tanks in order to avoid any microbiological contamination. During feeding, 0.3L of the carbon-rich solution and 1.7L of the phosphorus-rich solution were mixed prior to being pumped into the

SBR.

Table 8-1: Synthetic wastewater composition.

Name	Formula	Concentration	Solution
Sodium acetate [1]	CH_3COONa	11.3 mg/L	Carbon solution
Propionic Acid [2]	CH_3CH_2COONa	3.5 mL/L	
Sodium Hydroxide 5M [2]	NaOH	10.5 mL/L	
Ammonium chloride	NH_4Cl	710 mg/L	
Peptone	-	320 mg/L	
Magnesium sulphate heptahydrate	$MgSO_4.7H_2O$	1140 mg/L	
Calcium chloride dihydrate	$CaCl_2.2H_2O$	530 mg/L	
Allyl-N Thiourea	ATU	14 mg/L	
Nutrient Solution (Smolders et al.1994)	-	3.8 mL/L	
Potassium dihydrogen phosphate	KH_2PO_4	187 mg/L	Phosphorus solution
Dipotassium hydrogen phosphate	K_2HPO_4	146 mg/L	

[1] Only for the acetate feed

[2] Only for the propionate feed

The carbon-rich solution consisted of either acetate or propionate and other nutrients similar to previous studies (Smolders *et al.*, 1994) as shown in Table 8-1. When acetate was used as the sole carbon source, 11.3 mg/L sodium acetate was added in the carbon solution, while 3.5mL/L propionic acid and 10.5mL/L of 5M NaOH (to adjust the pH to 7.5) was used when propionate was the sole carbon source. This carbon-rich solution was autoclaved and later cooled and stored at room temperature. The phosphorus solution was prepared separately in a 55 L tank and was made up according to Table 8-1. The two combined streams resulted in 800mg/L COD and 53.3mg/L P-PO_4^{3-} during steady state operation, giving a COD/P ratio of 15 mg COD/mg P-PO_4^{3-}.

8.4.3 EXPERIMENTAL SET-UP

Three cylindrical sequencing batch reactors with a working volume of 8 L and a minimum volume of 6 L, were seeded with activated sludge from the wastewater treatment plant andwith phosphorus removal (EBPR) in Noosa (Queensland, Australia). A full description of the SBRs is shown in 3.1.2. The total length of cycle was 6 hours, treating 2 L of synthetic wastewater per cycle with an exchange ratio of 0.25. Each reactor was fed with a sole and different carbon source, acetate and propionate. The hydraulic retention time (HRT) was maintained at 24h. At the end of the aerobic period 250 mL of mixing liquor was removed from the reactor maintaining a sludge retention time (SRT) of 8 days. Nitrogen gas was bubbled into the reactor during the anaerobic period to maintain strict anaerobic conditions. In the aerobic period, the dissolved oxygen (DO) concentration was controlled at 3 ± 0.2 mg/L using an on/off control valve that was connected to a compressed air supply. The pH was controlled during the anaerobic and aerobic phases at a maximum value of 7 ± 0.1 by using one-way controller that dosed 0.5M HCl when the pH was above the set-point.

8.4.4 OPERATIONAL CONDITIONS

The experimental study was conducted in three reactors from day 0, when the different changes were made. Before day 0, two of the reactors were run under identical operating conditions. Each reactor was fed with a sole and different carbon source, acetate or propionate. A 6h cycle was conducted for each SBR consisting of around a 2 h anaerobic react phase, 3 h 10 min aerobic react phase and a 50 min of settle and draw phase. During the first 6 minutes of the anaerobic phase 2 L of synthetic wastewater was introduced into each reactor.

Two strategies were adopted during the whole experimental part: namely to increase the maximum pH and to change carbon source. While in the acetate-fed reactor (SBR-A) both strategies were applied splitting the reactor in two reactors (SBR-A1 and SBR-A2), in the propionate-fed reactor (SBR-P) only the pH strategy was applied (Figure 8.1)

The maximum pH was increased from 7 to 8 adding a base inside the reactor on day 0. To maintain this pH for the other cycles, the influent pH was increased by adding NaOH to the phosphorus tank. In addition, the pH controller was changed to pH 8 and acid added when pH was higher than 8.

The change of carbon source occurred gradually from acetate to propionate. On day 0 a mixture of 50%:50% (vol.:vol.) fed the reactor. The total concentration of COD was maintained at 800 mg/L COD, as before. On the 8th day the reactor was fed with propionate as a sole carbon source but the COD concentration was lower, 600 mg/L COD. Finally, on day 16 the full concentration of propionate (800 mg/L COD) as the sole carbon source fed the reactor. The pH was controlled at 7 at all moment.

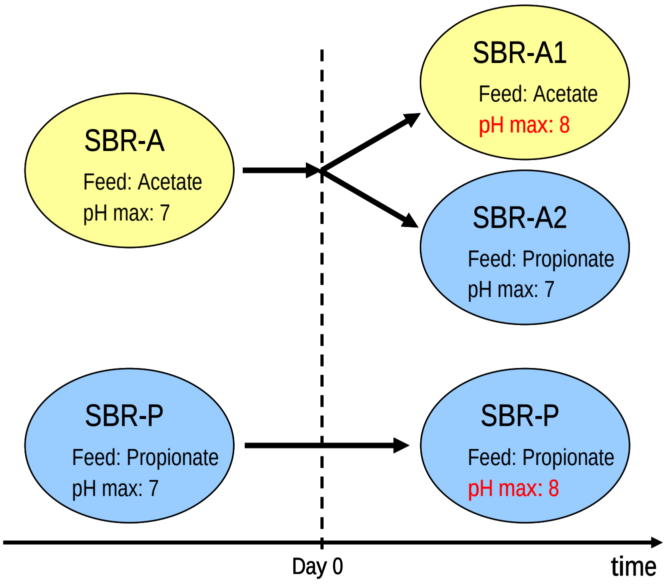


Figure 8.1: Scheme of the operational conditions. In yellow the reactors fed with acetate and in blue the ones fed with propionate. Notably reactor SBR-A was split into SBR-A1 and SBR-A2. SBR-A1 was allowed to reach at maximum pH of 8, whereas SBR-A2 received no change in the limit of pH but was fed with propionate. SBR-P reactor's conditions changed to allow a maximum pH of 8.

8.4.5 METHODOLOGY

The reactor performance was monitored throughout the esperimental period at least twice a week thought determination of P release, P uptake, and VFA uptake. The samples were taken at the beginning of each cycle before the feeding of soluble COD, at the end of the anaerobic phase and at the end of the aerobic phase. In addition, a cycle study was performed once per week by taking samples every few minutes to obtain a phosphorus profile. At these times glycogen, PHA and FISH samples were also obtained.

Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were analysed at the end of aerobic phase in triplicate at least once a week.

General maintenance routinely involved tasks such as checking the pump flow rates, replacing tube connections and cleaning the reactor.

8.5 Results and discussion

After a period of time where acetate and propionate reactors were kept under stable conditions with a poor phosphorus removal, different strategies were applied for each reactor in order to improve the phosphorus removal.

8.5.1 ACETATE-FED REACTOR: COMPARISON BETWEEN PH EFFECT AND CHANGE OF CARBON SOURCE.

In order to improve phosphorus removal in the acetate-fed SBR (SBR-A), this reactor was split into two separate reactors where different strategies were applied for each one: the maximum pH was increased from 7 to 8 in one reactor (named SBR-A1), and in the other one, the carbon source was changed from acetate to propionate (named SBR-A2).

I Acetate-fed reactor: pH effect (SBR-A1)

In the reactor fed with acetate as the sole carbon source, the maximum pH was increased from 7 to 8 in an attempt to improve the phosphorus removal. Figure 8.2 presents the ratio of MLVSS/MLSS (top) and the P release, P uptake and effluent phosphorus concentration (bottom) throughout the entire study.

For more than 40 days, where the maximum pH was set at 7, the performance of the reactor was stable with a P release and P uptake average of 18 and 24 mg/L P, respectively. The phosphorus concentration in the effluent during this time was around 44 mg/L P, which was a very high value because the influent concentration was 53.3 mg/L P. On day 0, the maximum pH was increased from 7 to 8. After the change in pH the reactor gradually improved. The P effluent initially increased, but quickly stabilized and dropped slowly thereafter. Five weeks later, the P effluent was maintained at approximately 17 mg/L P, while P release and P uptake were around 70 and 83, respectively.

The ratio of MLVSS/MLSS (Figure 8.2), decreased from 0.89 during poor P removal to 0.65 after the reactor performance had improved (approximately 5 weeks). This is likely to be due to an increase of phosphorus content in the biomass caused by an increase in the polyphosphate storage inside the PAOs cells. When the polyp proportion increased in the cells, a higher inorganic portion is found in the biomass, causing a decrease in the MLVSS/MLSS ratio.

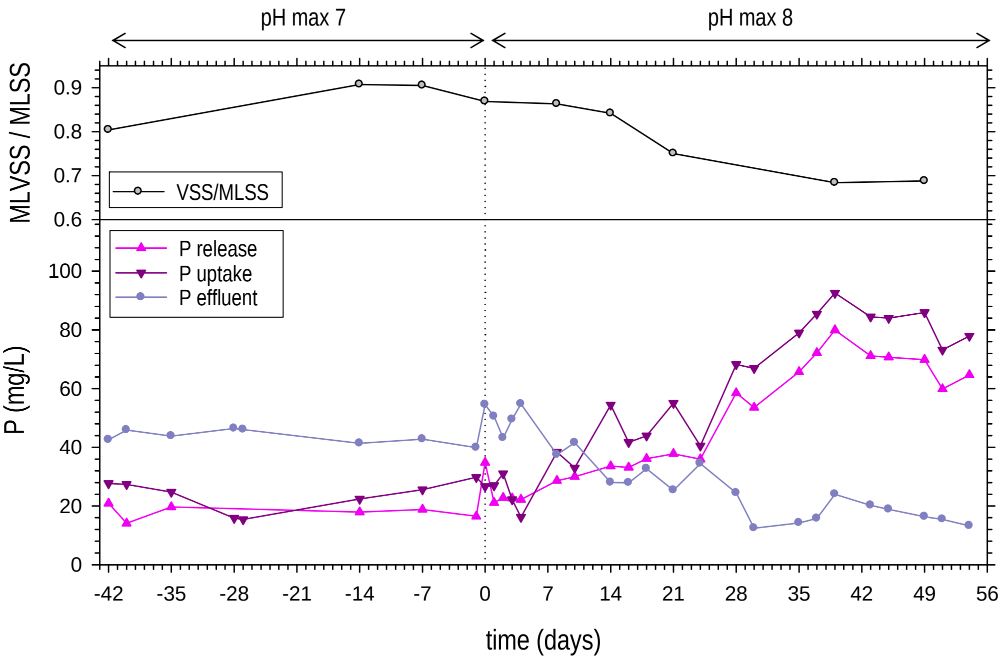


Figure 8.2: The P release, P uptake and P effluent throughout the experiment when the maximum pH was increased from 7 to 8 for the acetate-fed reactor.

In order to study the phosphorus behaviour inside the reactor, two typical cycle studies are presented below. Figure 8.3 and Figure 8.4 show the pH and DO profiles (top) as well as the corresponding P and VFA transformations (bottom) for the typical cycles in the acetate-fed SBR at pH 7 and pH 8, respectively.

In Figure 8.3 where the maximum pH was controlled at 7, all the acetate was taken up within the first 30 minutes. This could be caused by PAOs or GAOs, because both of them are able to take up and store volatile fatty acids anaerobically. When observing the phosphorus transformations inside the reactor, it was seen that the phosphate was released until acetate was taken up 30 minutes later. After that, phosphate was kept constantly around 70 mg/L P, yielding a P release of approximately 20 mg/L P. Under aerobic conditions the phosphate in the effluent was around 44 mg/L, yielding a P uptake of 25 mg/L. Thus, a poor phosphorus removal was achieved. Altogether, this suggested competition between PAOs and GAOs for the VFA.

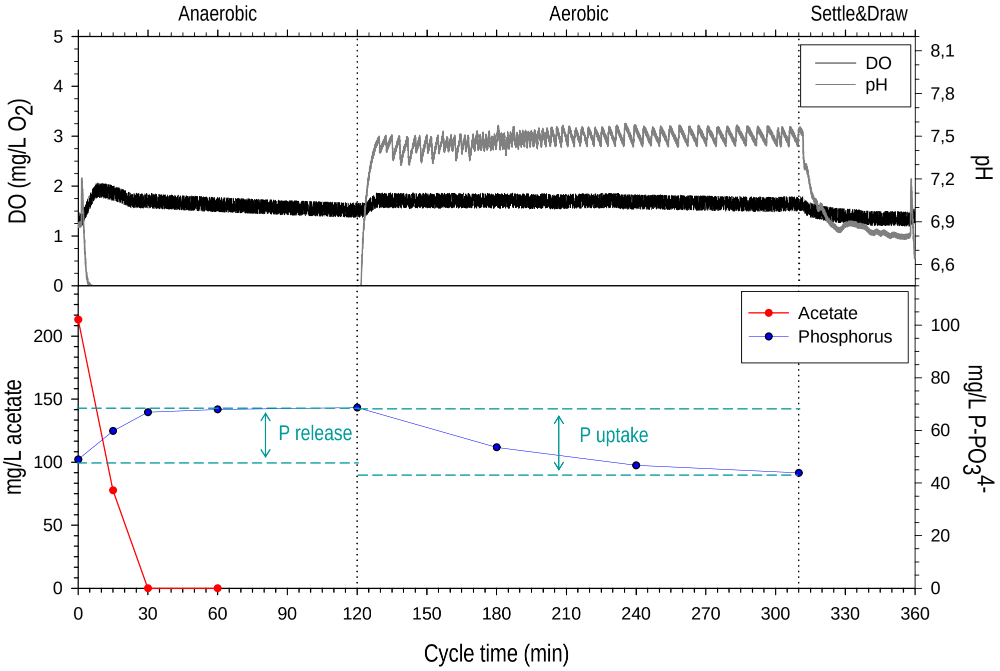


Figure 8.3: Typical cycle during maximum pH 7. The pH and DO profiles are shown at the top, while at the bottom the VFA and P transformation inside of the acetate-fed reactor is shown.

On-line monitoring of pH and DO profiles (Figure 8.3, top) show that DO was maintained at zero under anaerobic conditions due to nitrogen gas bubbling inside the reactor, while under aerobic the DO was controlled at a maximum of 3 mg/L O_2. The pH ranged between 6.85 and 7.10 units.

During the first few minutes of the anaerobic phase the pH increased slightly. When the pH was higher than 7, HCl was added to decrease the pH as shown in Figure 8.3. After that the pH decreased slowly until 6.90 at the end of the anaerobic phase. This decrease in the pH is likely due to the degradation of polyphosphate, stored in the cells, realising protons (Henze (2002). During aerobic conditions the pH increased because during the reaction uptake the phosphate releases hydroxyl ions and CO_2 production (Henze (2002)). However, from minute 250 the microbiological activity decreased as shown in the DO profile because the DO control was more spaced.

The phosphorus transformation and pH and DO profiles at a high pH are presented in Figure 8.4. A complete acetate uptake was achieved in 60 minutes when the maximum pH was controlled at 8, while the phosphate concentration at the end of the anaerobic phase was 102 mg/L P, yielding a P release of approximately 70 mg/L P. Under the aerobic phase phosphorus removal was improved decreasing the phosphate in the effluent to 16 mg/L P and a yielding P uptake of 86 mg/L P.

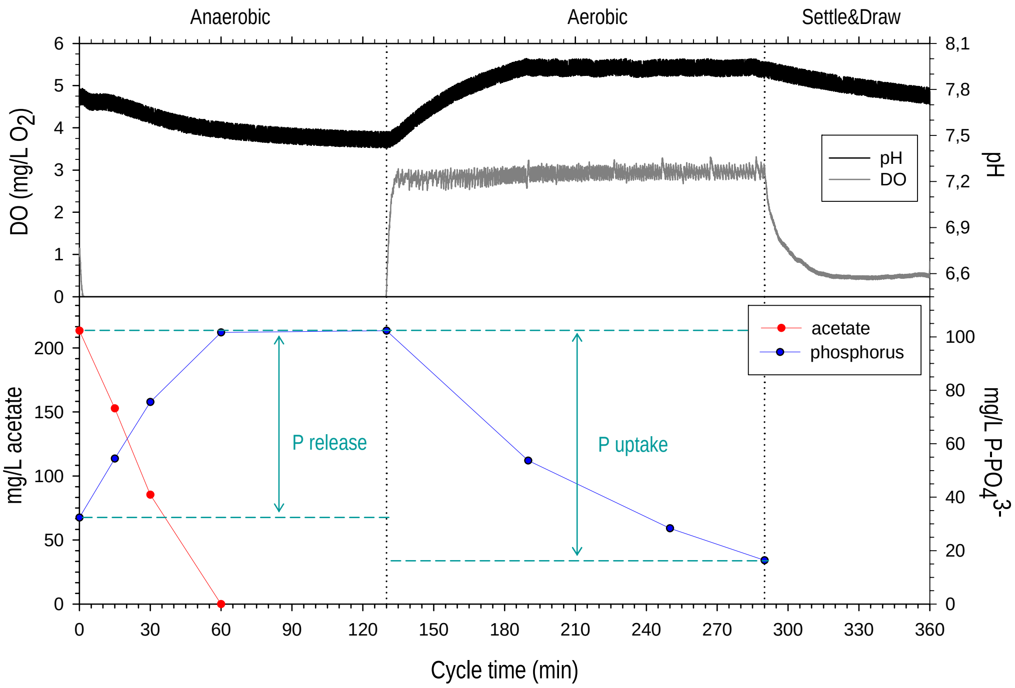


Figure 8.4: Typical cycle during maximum pH 8. The pH and DO profiles are shown at the top, while the bottom shows the VFA and P transformation inside the acetate-fed reactor.

The on-line profiles, pH and DO (Figure 8.4, top) show that DO was maintained at zero under anaerobic conditions, while under aerobic the DO was controlled at a maximum of 3 mg/L O_2. The pH ranged between 7.40 and 8.00 units.

During the first few minutes of the anaerobic phase the pH was kept constant, while decreasing later from 7.80 to 7.40 (Figure 8.4).

Under aerobic conditions the pH increased to 8, where the controller began to add acid after the 190th minute. After that, the pH was maintained at 8 during the rest of the aerobic phase. The microbiological activity began to decrease after the 250th minute as indicated by the reduced rate of oxygen uptake shown in the DO profile.

In comparing both cycles, a higher P release and a higher P uptake were achieved in a high pH. At the same time lower phosphorus concentration was found in the effluent with at a high pH although not complete P removal was achieved. Then, using the same concentration of the carbon source (acetate) a high yield was achieved at a higher pH. This could be due to a high pH being more favourable than a low pH for PAO enrichment. This fact is reflected in the ratio of MLVSS/MLSS that decreased with a high pH.

II Acetate-fed reactor: Change of carbon source (SBR-A2)

As stated before, two strategies were applied to the acetate-fed reactor (SBR-A). While one reactor (SBR-A1) ran with a high pH, the other reactor (SBR-A2) ran in parallel with a different strategy. This acetate-fed reactor ran at a maximum pH of 7 throughout the whole study, but the sole carbon source was changed from acetate to propionate gradually in an attempt to improve the phosphorus removal. Figure 8.5 presents the ratio of MLVSS/MLSS (top) and the P release, P uptake and effluent phosphorus concentration (bottom) throughout the entire study.

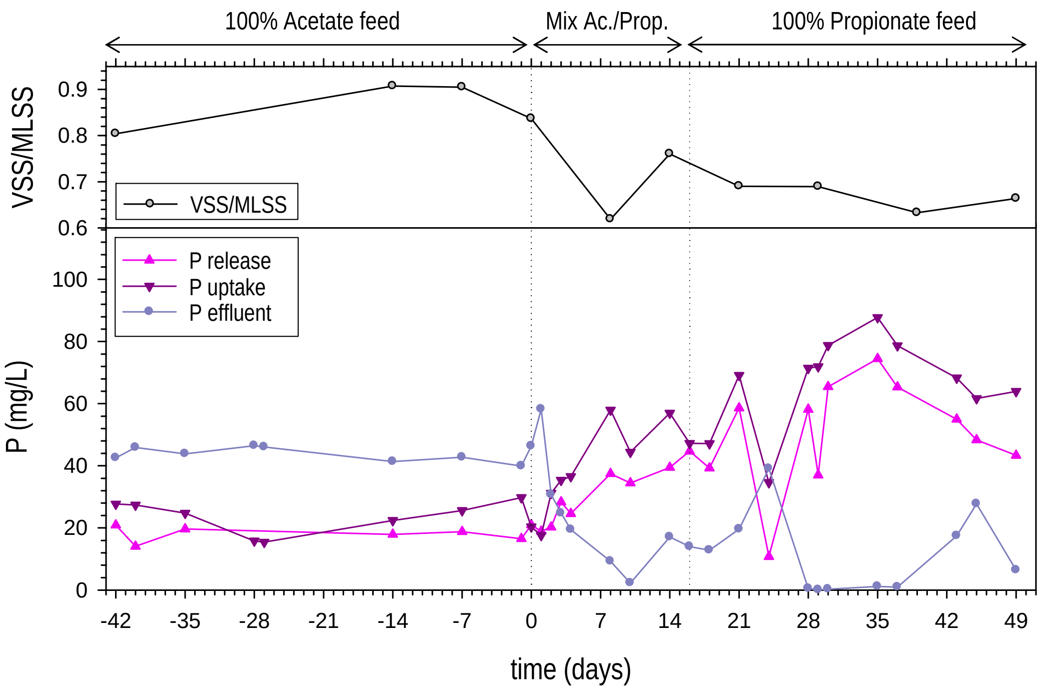


Figure 8.5: The P release, P uptake and P effluent throughout the experiment when acetate was progressively changed on the day 0 for propionate.

The performance of the first 40 days to day 0 is the same as in Figure 8.2 with P release, P uptake and P effluent averaging at around 18, 24 and 40 mg/L P respectively, as before mentioned. From day 0 the carbon source was changed from acetate to propionate finally getting a full and sole propionate concentration on the 16th day. During these days of adaptation the P effluent decreased while P release and P uptake improved slightly (Figure 8.5). After day 16, where propionate was used as the sole carbon source, some fluctuations joined together with the improvement of phosphorus removal kept the reactor instable. While on some days the P effluent was 0 mg/L P, on other days it reached 39 mg/L P. The P release and P uptake ranged from 11 to 75 mg/L P and from 35 to 88 mg/L P. In spite of these variations, the average of these values was 54, 70 and 9.9 mg/L P respectively for P release, P uptake and P effluent.

The ratio of MLVSS/MLSS (Figure 8.5) decreased from 0.89 during poor P removal to 0.63 after the reactor performance had improved approximately 3 weeks after day 16th. This is likely due to an increase in the P content of the biomass, then, a higher P inorganic portion is found in the biomass causing a decrease in the MLSS/MLVSS ratio.

III Comparison between pH effect and change of carbon source

An improvement in phosphorus removal was achieved in both strategies, of increasing the pH of the reactor and of changing the carbon source for the acetate-fed reactor (SBR-A). While the best performance in a high pH (SBR-A1) P release and P uptake were 70 and 83mg/L P, changing the carbon source (SBR-A2) meant these results were 75 and 88 mg/L P. Meanwhile, phosphate effluent for the high pH was kept at around 12 mg/L P, in the carbon strategy complete phosphorus removal was obtained on some days. Therefore, the carbon strategy was more efficient in phosphorus removal than in the pH strategy; nevertheless some fluctuations did influence the yields.

8.5.2 PROPIONATE-FED REACTOR: PH EFFECT (SBR-P)

In order to improve phosphorus removal in the propionate-fed reactor the maximum value of the pH was increased from 7 to 8. In this way, the pH and propionate effect together was able to be analysed. Figure 8.6 presents the ratio of MLVSS/MLSS (top) and the P release, P uptake and effluent phosphorus concentration throughout the entire study.

For more than 20 days, the performance of the reactor was stable with a P release and P uptake of approximately 14 and 24 mg/L P, respectively. The phosphorus concentration in the effluent during this time was around 25 mg/L P. On day 0, the maximum pH was increased from 7 to 8. One day after the change in the pH the reactor performance got worsened decreasing in P release and P uptake and increasing the P effluent until 80 mg/L P. Afterwards this turbulence, the P effluent decreased while the P release and the P uptake were recovering. On the 14th day, two weeks after the change, no phosphorus was found in the effluent. This performance of obtaining P release, P uptake and P effluent results around 85, 100 and 0.5

mg/L P, respectively, was maintained until the end of this study.

The ratio of MLVSS/MLSS (Figure 8.6) decreased from 0.79 during the poor P removal to 0.57 when the reactor reached a good performance, two weeks later. This means that the sludge was in fact constituted by a higher fraction of inorganic sludge, polyp.

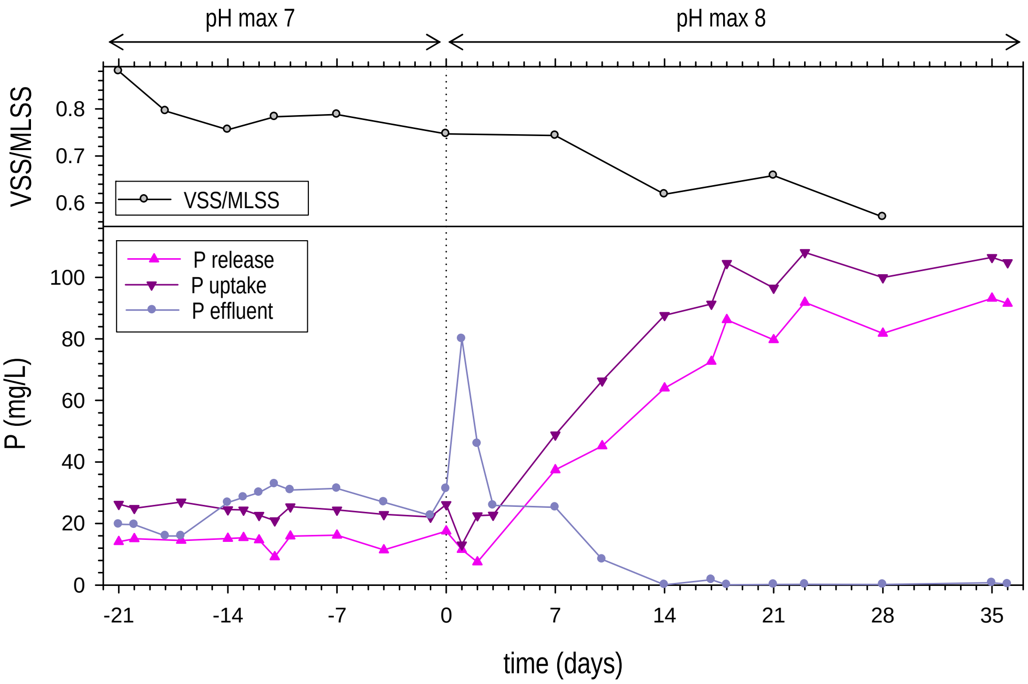


Figure 8.6: The P release, P uptake and P effluent throughout the experiment when the maximum pH was increased from 7 to 8 for the propionate reactor.

In order to understand the phosphorus behaviour inside the reactor, two typical cycle studies are presented below. Figure 8.7 and Figure 8.8 show the pH and DO profiles (top) as well as the corresponding P and VFA transformations (bottom) for the typical cycles in the propionate-fed SBR at pH 7 and pH 8, respectively.

In Figure 8.7 where the maximum pH was controlled at 7, all the propionate was taken up from the media by the microorganisms (PAOs or GAOs) in the first 15 minutes, while the phosphate was released until 50 mg/L P, yielding a poor P release of 15 mg/L P under anaerobic conditions. In the aerobic conditions 25 mg/L P was taken up, ensuring a phosphate effluent of 27 mg/L P. These low levels of phosphorus removal could be a consequence of the competition for the propionate from PAOs and GAOs.

On-line monitoring of pH and DO profiles from Figure 8.7 shows that DO was maintained at zero under the anaerobic conditions due to nitrogen gas bubbling inside the reactor, while under the aerobic phase the DO was controlled at a maximum of 3 mg/L O_2. The pH ranged between 6.65 and 7.00. The pH increased during the first few minutes of the anaerobic phase due to the wastewater being introduced to the reactor. After this, the pH was kept stable for 30 minutes and later decreased to 6.65 as in the acetate reactor. Under aerobic conditions the pH recovered because in the reaction of uptake the phosphate releases hydroxyl ions and CO_2 production (Henze (2002)), and were controlled at 7.

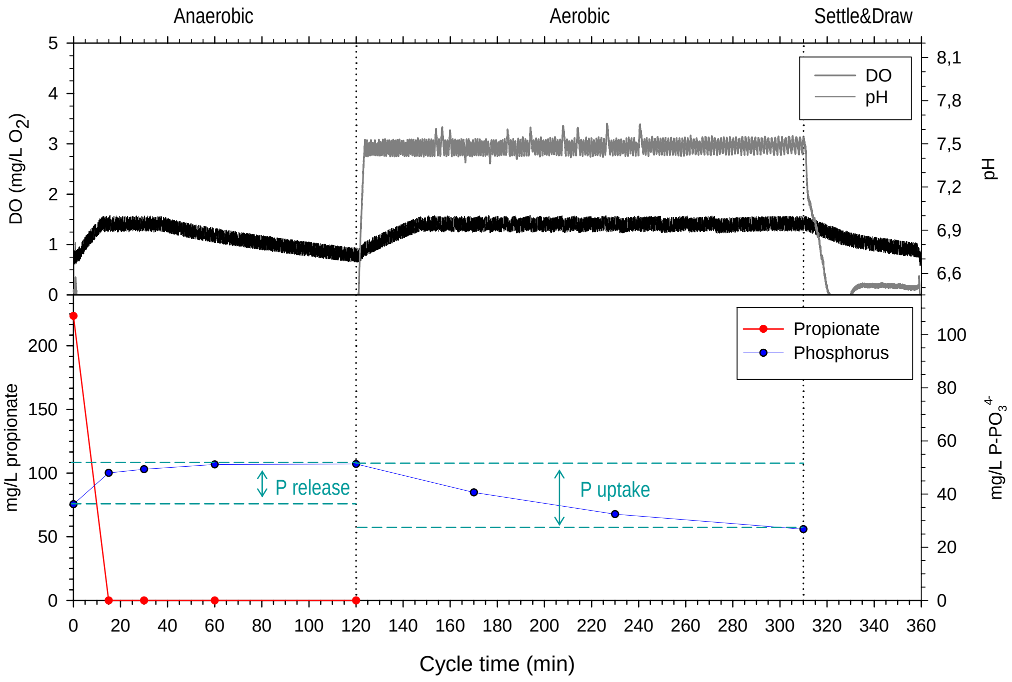


Figure 8.7: Typical cycle during a maximum pH 7. The pH and DO profiles are shown at the top, while the bottom shows the VFA and P transformation inside the propionate-fed reactor.

In Figure 8.8 where the maximum pH was controlled at 8, propionate was taken up in the first 15 minutes anaerobically, as at low pH. An important increase of phosphorus transformation was achieved in the reactor with a phosphate concentration at the end of the anaerobic phase of 97 mg/L P, yielding a P release of 80 mg/L P. Under aerobic conditions, all phosphate was taken up until complete phosphorus removal in 100 minutes. The P uptake was 97 mg/L while the phosphorus concentration in the effluent was zero. So, it seems that PAOs were able to take up the propionate in a high pH, whereas high pH was less favourable for the GAOs.

On-line monitoring of the pH and DO profiles from Figure 8.8 shows that the DO was maintained at zero under the anaerobic conditions due to nitrogen gas bubbling inside the reactor, while under the aerobic phase the DO was controlled at a maximum of 3 mg/L O_2. The pH ranged between 7.00 and 8.00.

As previously stated, during the first minutes of the anaerobic phase (Figure 8.8) the pH increased because wastewater was introduced to the reactor. After the filling phase the pH went down to 7.0. The most important slope was found at the same time of the phosphate was released. Later, in aerobic conditions the pH quickly recovered (Henze (2002)) and kept constant at 8. When the phosphate was removed in the minute 190, the pH had a decreasing tendency.

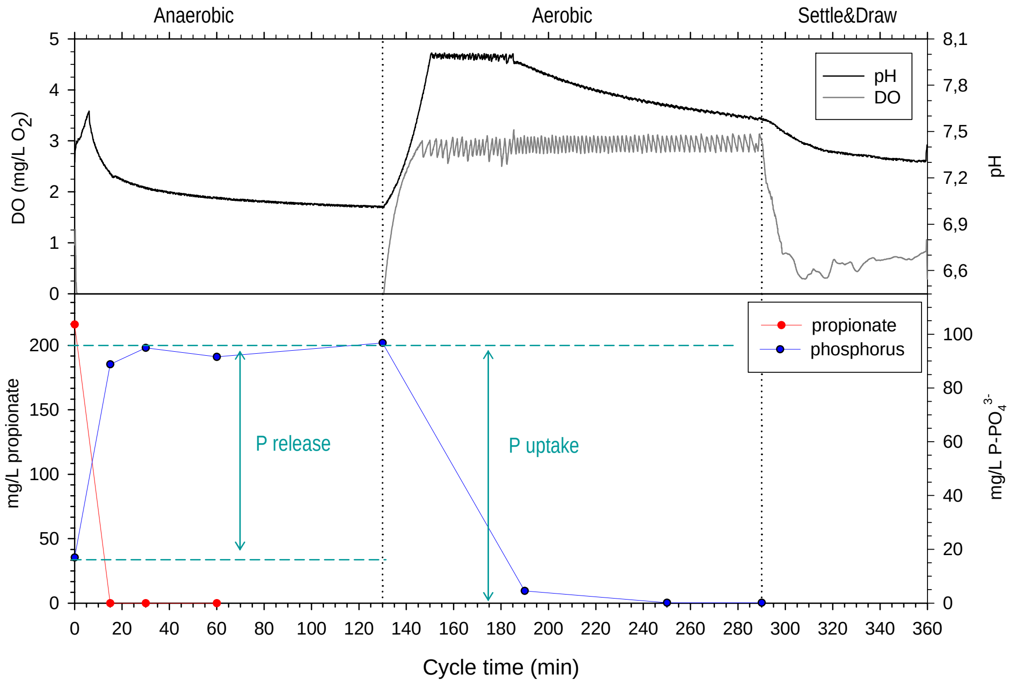


Figure 8.8: Typical cycle during maximum pH 8. The pH and DO profiles are shown at the top, while the bottom shows the VFA and P transformation inside the propionate-fed reactor.

In comparing both pHs, using the same concentration of carbon source, in both pHs the propionate was taken up in 15 minutes, but in a high pH more phosphorus was released than in a low pH during the anaerobic phase under the same conditions. This change in the phosphorus behaviour can only be explained by the benefits that a high pH has for the PAO microorganisms as opposed to the GAOs.

I Comparison of pH effect between the reactor fed with acetate and the reactor fed with propionate as a sole carbon source.

The low levels of P release and uptake, coupled with high levels of anaerobic acetate or propionate uptake, indicated a high level of GAO activity when the reactors operated at the pH maximum of 7. Nevertheless, the high levels of P release and uptake, coupled with the high levels of anaerobic acetate or propionate uptake indicated a level of PAO activity when the reactors operated at pH maximum of 8. Those hypotheses were corroborated by the glycogen, PHA and FISH analyses (Oehmen *et al.*, in preparation).

While in acetate and propionate reactors at a low pH they had the same wide of range (0.30 units of pH), at high pH the variation between both reactors were more significant. The acetate reactor had fluctuations between 7.4 and 8, and the propionate reactor varied from 7.0 to 8.0 despite the initial pHs inside the reactor being equals. This difference could explain for the higher P release in the propionate reactor or the different metabolic routes of these VFA.

At the same time the fastest to recover was only two weeks for the propionate reactor (in only two weeks), against the five weeks required by the acetate reactor, present the propionate as a carbon more favourable to the PAOs rather than GAOs.

8.6 Conclusions

The conclusions obtained in this chapter are related below:

- An improvement of phosphorus removal was achieved in both strategies as much as in increasing the pH of the reactor as in changing the carbon source for the acetate reactor.
- While in the acetate fed reactor both strategies, pH and the carbon source, achieved a good removal, only in the case of the change of carbon source was the phosphorus completely removal. However, the trend of that reactor was more instable than the reactor with the increase of pH whose phosphorus effluent was around 12 mg/L P.
- Higher level of phosphorus removal resulted in the acetate and propionate reactors

when a high pH was applied. While in propionate reactor only two weeks were required to reach a good removal, five weeks were necessary for the acetate reactor. Then, when propionate as a carbon source and high pH were applied the results were better than when acetate was the carbon source.

- The best results have been obtained in a high pH and propionate as a carbon source.
- The two strategies applied to improve the phosphorus removal have obtained a good yield. Both strategies demonstrated were more favourable to the PAO population for the uptake of VFA than the GAOs, when competition between PAOs and GAOs was present.
- It would be necessary to corroborate these results with real wastewater.

9

CONCLUSIONS

This pHD thesis has proved that the SBR is a system with a high flexibility treating different kinds of wastewaters (synthetic or real, urban or industrial) and for different requirements (carbon, nitrogen or phosphorus removal).

Also, step-feed strategy has demonstrated a high versability in the different required treatments.

9.1 Operational conditions for nitrogen removal using step-feed strategy

- The step-feed methodology applied in this study has proved useful for nitrogen removal. The number of filling events (M) and the exchange ratio (V_F/V_T) has demonstrated themselves to be useful parameters to identify the nitrogen concentration in the effluent.

- The operation in a SBR using a number of filling events (M) of 2 and exchange ratio (V_F/V_T) of 0.33 in a 8 hour cycle, and treating a synthetic wastewater with a mean values of 600 mg/L COD and 70 mg/L N-NH_4^+ has concluded with an effluent of 55 mg/L COD and 14.6 mg/L N mainly as nitrate (13.6 mg/L N-NO_3^-).

- A step-feed strategy based on six filling events (M=6), V_F/V_T of 0.33 in a 8 hours cycle and promoting use of organic matter for denitrification purposes, has concluded with an effluent of 55 mg/L COD and 5.8 mg/L N mainly as nitrate (5.3 mg/L N-NO_3^-). During this period most of the time, the effluent concentrations have been lower than 5 mg N/L avoiding the rising problems.

- By on-line monitored pH, ORP and DO values, the process status and performance can be followed in real time by the detection of critical points. Ammonia Valley coupled with α_{O2} can be the critical points which determine the end of the nitrification. Meanwhile Nitrate Knee coupled with Nitrate Apex show the end of the nitrification. All these critical points could be used for further work to optimise the process.

9.2 Application of step-feed strategy for organic matter removal. A case study with textile wastewater.

- Treated textile wastewater presented a high variation mainly due to production planning. Such variations mainly affected pH values, always with a strong basic characteristic, and a high variation in COD contents (ranging from 700 to 7000 mg/L COD).

- The step-feed strategy has proved to be an efficient operational procedure in dealing with such high COD variations. The operation of the SBR using a number of filling events (M) of 2 and exchange ratio (V_F/V_T) of 0.13 in a 6 hour cycle to comply with maximum peak flow requirement, has concluded with an effluent mainly lower than 600 mg/L COD and being basically non-biodegradable organic matter.

- The simple DO control applied, based on a compressed air ON/OFF strategy, proved to be enough to determine the OUR profile during aerobic reactions times.

- Following the OUR profiles during aerobic reaction times, proved to be a good tool to identify the endogenous conditions reached after each feeding event. Such endogenous conditions presented a low and constant OUR value of between 5-12 mg $O_2/L \cdot h$ depending on the operation period considered.

- On-line OUR profiles must be used together with a control of possible inhibition effects, mainly affecting pH values or nutrients deficiency. As a control of endogenous respiration reached at the end of SBR reaction time, a BOD_5 analysis could serve as a proof that lower biodegradable matter levels are in fact achieved.

- The effluent quality could be improved through a chemical treatment such as Fenton in order to decrease the COD concentration.

9.3 Application of step-feed strategy for carbon and nitrogen removal. A case study with landfill leachate wastewater

- In spite of this, biological process has proved useful for treating some landfill leachates, in each case a biodegradability study must be conducted in order to ensure proper organic matter reductions.

- In our case, nitrification was easily achieved if pH inhibition was avoided by adjusting treated leachate with enough bicarbonate.

- The ability of calculate an on-line value of the OUR is a useful tool in order to identify a the possible presence of non-biodegradable compounds by avoiding the use of biological oxygen demand (BOD_5) essays which are extremely time consuming (up to 5 days).

- Evolution of landfill leachate over time (from young to mature) indicates a reduction of in organic matter by keeping or slightly increasing the ammonia contents. Nevertheless, such a low COD content is mainly composed of non biodegradable matter.

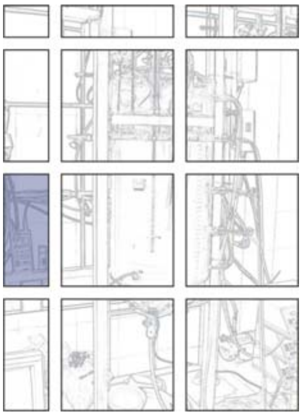
- Thus, the biological treatment of a leachate landfill could be considered as part of, but not the only part of the leachate treatment. When high contents of non biodegradable organic matter are detected other chemical or physical treatments (i.e. chemical oxidation with hydrogen peroxide or inverse osmosis) must be considered.

9.4 Operational conditions for nitrogen and phosphorus removal using step-feed strategy

- The addition of an initial anaerobic-aerobic pair is necessary to implement the biological phosphorus removal in a SBR. After this, the sequenced anoxic-aerobic pair must be used for nitrogen removal.
- The different step-feed strategy applied in this study has demonstrated to be able to remove organic matter and nitrogen obtaining effluent lower than 90 mg/L COD and 8 mg/L N according with the legislation.
- Instead of the strategies used for phosphorus removal, a low value of efficiency has been obtained.
- With respect to phosphorus removal, the presence of nitrate at the beginning of the anaerobic phases caused the competition between denitrifier organisms and phosphorus accumulating organisms (PAO) for the organic matter available.
- The use of short filling phase against a long filling phase has been favourable in order to quickly decrease the nitrate concentration at the beginning of the cycle.
- When the anaerobic phase is increased, the number of anoxic-aerobic pairs must be reduced. Nevertheless, in order to maintain the same nitrogen removal efficiency volumes of wastewater added during the filling events in the anoxic-aerobic pairs must be different and the filling volume added in the last filling event must be lower than the previous.
- The difference between P experimental and P calculated assuming volume changes and the VSS has proved a useful methodology to identify phosphorus uptake and release in a EBPR process using a step-feed strategy in a SBR.

9.5 Influence of pH and carbon source in the phosphorus removal

- An improvement of phosphorus removal was achieved in both strategies as much as in increasing the pH of the reactor as in changing the carbon source for the acetate reactor.
- While in the acetate fed reactor both strategies, pH and the carbon source, achieved a good removal, only in the case of the change of carbon source was the phosphorus completely removal. However, the trend of that reactor was more instable than the reactor with the increase of pH whose phosphorus effluent was around 12 mg/L P.
- Higher level of phosphorus removal resulted in the acetate and propionate reactors when a high pH was applied. While in propionate reactor only two weeks were required to reach a good removal, five weeks were necessary for the acetate reactor. Then, when propionate as a carbon source and high pH were applied the results were better than when acetate was the carbon source.
- The best results have been obtained in a high pH and propionate as a carbon source.
- The two strategies applied to improve the phosphorus removal have obtained a good yield. Both strategies demonstrated were more favourable to the PAO population for the uptake of VFA than the GAOs, when competition between PAOs and GAOs was present.
- It would be necessary to corroborate these results with real wastewater.



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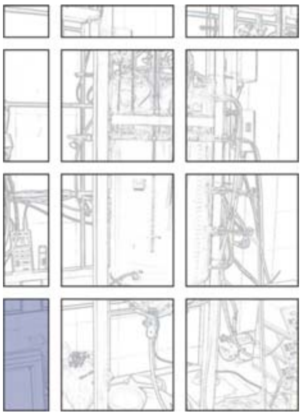

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ANNEX

11.1 Publications

Oehmen, A, **Vives M.T**, Lu, H, Yuan, Z, Keller J. (2004, in preparation). The effect of pH on enhanced biological phosphorus removal performance. *Biotechnology and Bioengineering*.

Oehmen, A, Saunders, A.M, **Vives M.T**, Yuan, Z, Keller J. (2004, in preparation). Improvement of Enhanced Biological Phosphorus Removal Performance with Propionate as Carbon Source. *Biotechnology and Bioengineering*.

Puig, S., **Vives, M.T.**, Corominas, Ll., Balaguer, M.D., Colprim, J. (2004, accepted) Wastewater nitrogen removal in SBRs, applying a step-feed strategy: From Lab-Scale to Pilot Plant operation. *Water Science and Technology*.

Vives, M.T., Balaguer, M.D., García, S., García, R., Colprim, J. (2003) Textile dyeing wastewater treatment in a sequencing batch reactor system. *Journal of Environmental Science and Health. Part A-Toxic/Hazardous Substances & Environmental Engineering*, **A38**, 2089-2099.

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11.2 Conferences

POSTER titled: "Step-feed optimization for wastewater carbon and nitrogen removal in SBRs: process robustness and adjustment to wastewater quality" by **Vives M.T.**, Balaguer M.D, Colprim J, *in the 3rd International Specialised Conference on Sequencing Batch Reactor Technology,* 22-26 February 2004, Noosa, Queensland, Australia.

POSTER titled: "On-line optimisation of step-feed operation of an urban wastewater nitrogen removal SBR by on-line OUR determination and ORP analysis " by Corominas Ll, Rubio M, Puig S, **Vives M.T**, Melendez J., Colomer J, Balaguer M.D, Colprim J, *in the 6th Specialised Conference on Small Water and Wastewater Treatment Systems*, 12-14 February 2004, Perth, Western Territory, Australia.

POSTER titled: "Treating real landfill leachate for carbon and nitrogen removal. Is the biological process suitable for all landfill life term?" by **Vives, M.T.**, López, H., Balaguer M., Elorduy M, Colprim, J., *in the 6th Specialised Conference on Small Water and Wastewater Treatment Systems*, 12-14 February 2004, Perth, Western Territory, Australia.

ORAL PRESENTATION titled:" Textile dyeing wastewater treatment in a sequencing batch reactor system" by **Vives, M.T.**, Balaguer, M.D., García, S., García, R., Colprim, J., in the 5th Specialised Conference on Small Water and Wastewater Treatment Systems, 24-26 Septembre 2002, Istambul, Turkey.

Assistance to the "2nd International Symposium on Sequencing Batch Reactor Technology" 10-12 July 2000, Narbone, France.

11.3 Proceedings

Puig, S., **Vives**, M.T., Corominas, Ll., Balaguer, M.D., Colprim, J. Wastewater nitrogen removal in SBRs, applying a step-feed strategy: From Lab-Scale to Pilot Plant operation. *Proceedings of the 3rd International Specialised Conference on Sequencing Batch Reactor Technology*, 22-26 February 2004, Noosa, Queensland, Australia

Vives M.T., Balaguer M.D, Colprim J. Step-feed optimization for wastewater carbon and nitrogen removal in SBRs: process robustness and adjustment to wastewater quality. *Abstract in the proceedings of the 3rd International Specialised Conference on Sequencing Batch Reactor Technology*, 22-26 February 2004, Noosa, Queensland, Australia

Corominas Ll, Rubio M, Puig S, **Vives** M.T, Melendez J., Colomer J, Balaguer M.D, Colprim J. On-line optimisation of step-feed operation of an urban wastewater nitrogen removal SBR by on-line OUR determination and ORP analysis. *Proceedings of the in the 6th Specialised Conference on Small Water and Wastewater Treatment Systems*, 12-14 February 2004, Perth, Western Territory, Australia.

Vives, M.T., López, H., Balaguer M., Elorduy M, Colprim, J. Treating real landfill leachate for carbon and nitrogen removal. Is the biological process suitable for all landfill life term? *Proceedings of the in the 6th Specialised Conference on Small Water and Wastewater Treatment Systems*, 12-14 February 2004, Perth, Western Territory, Australia

Vives, M.T., Balaguer, M.D., García, S., García, R., Colprim, J. Textile dyeing wastewater treatment in a sequencing batch reactor system. *Proceedings of the 5th Specialised Conference on Small Water and Wastewater Treatment Systems,* 24-26 Septembre 2002, Istambul, Turkey, vol. 1, pp.437-445.

ACKNOWLEDGEMENTS

Des que un dia una decideix fer la tesi, fins el dia que la defensa, al cap de cinc anyets, la vida dóna moltes voltes. (Qui m'havia de dir que aniria a Austràlia!)

Al llarg de la tesi hi ha bons moments i també de dolents, especialment quan es treballa amb reactors, tenen vida pròpia i molts cops les seves accions no coincideixen amb la teva voluntat. Però els mals moments s'esborren quan arriben els bons, per sort de tots ☺.

Durant aquests anys en el LEQUIA ha passat molta gent per la meva vida, gent que m'ha ajudat a fer més senzill el meu pas per la tesi, entre aquesta gent hi ha directors, companys, amics de sempre i de nous, i especialment la família. A tots vosaltres vull tenir un record en aquest apartat de la tesi, per deixar una part de vosaltres en mi i espero jo haver deixat una part de mi en vosaltres.

En primer lloc, als meus directors, Jesús i Marilós, sense el vostre suport això no hagués estat possible. Per ser tant diferents i alhora tant complementaris, això ens ha portat moltes discussions que han enriquit molt aquesta tesi. Sense vosaltres no hagués estat el mateix, però sobretot gràcies per confiar amb mi i per fer ciència!

Al LEQUIA per haver-me acollit i fer-me de segona casa. De cada un podria dir alguna cosa, però semblaria una segona tesi, en lloc d'uns agraïments. Manel, Miquel, Ignasi, Quim, Jaume, August tots vosaltres m'heu ensenyat alguna cosa. Maria, amb tu a més a més vaig començar el treball experimental i tu vas ser qui em va animar a continuar amb el camí de la recerca, sinó potser no m'hagués embrancat en aquesta aventura.

No podria pas continuar sense parlar dels meus companys de despatx, Clàudia, Anna, Mireia, Montse, Gemma, Sebastià, Helio, Lluís, Francesc, Peter, Xavi i Moi, per cada un podria dir alguna coseta com... per esperar-me per anar a dinar i mentre dinava, per acompanyar-me a busca aigua residual més d'un cop, per fer-me classes de conducció, per ajudar-me a fregar (quan s'inundava el laboratori), per oferir-se a ajudar-te sense demanar res a canvi,... per aquells cafès de matí i després de dinar, pels dinars del divendres...i per moltes coses més.

També recordar a tota la gent que ha passat per la guarderia, els que ja han marxat ja doctors (Estefi, Christian, Elvira, Núria, Jordi, Oriol, Esther) i els que no (Aumatell) que donen aquells consells que només pot donar qui ja ha passat per això.

En el laboratori, he passat la major part del meu temps, per tant, no podria faltar un record a tota la gent que un dia hi ha entrat per ajudar, ja sigui fent treballs experimentals o pràctiques en empresa: la Núria M., la Mª José G., en Tomàs C, la Samantha A., en Ramon, l'Ariadna, la Gemma petita, la Tamara. Però les que han portat durant molt de temps el pes dels laboratoris han estat l'Anna Mª i la Gemma Rustullet, a les que més tard va unir-se per poc temps l'Anna Moreno.

Alda, en Tomàs P. i l'Israel per fer-me la vida una miqueta més fàcil, ja sigui amb tota la paperassa o amb el programa informàtic.

I would like to thank to Jürg Keller and Zhiguo Yuang to give the opportunity to work in the AWMC and improve my knowledge about phosphorus removal. To Adrian, to share with me your knowledge and let me take care of your reactors.

In Australia I discovered a world of sensations, new landscape, new experiences, new friend and a new family. To Victoria, Linda and Jimmy, my Chinese family for their friendship and make me feel at home. To my Aussie mates, Aaron, Rikke, Chris and my travel mates Adrian, Valeria, Valerio, because without all you Australia is not Australia!!

A mi Gildinha, en las antípodas encontré una amiga, una alma gemela, una compañera de viajes y de consejos, por ser así. Maitinha, la meva lleidana preferida a la terra d'Oz, llàstima que no surti Ivars a la Lonely Planet!

A les ja doctores del cafè, encara que al final ja fèiem moltes campanes, sempre vam trobar un momentet, amb mi es tanca la saga del cafè, l'última doctora, esperem. Que em comprareu el cuixot ara??

A tots aquells amics o familiars que em seria impossible d'anomenar ara, que em cada gest, cada trucada o tant sols un somriure et fan la vida més agradable.

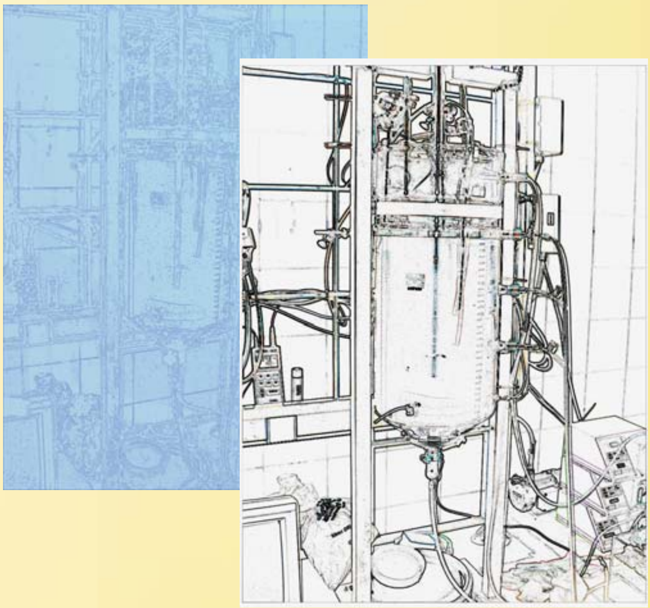
A les meves dues mosqueteres, Imma i Montse, per totes les histories compartides en aquelles nits inacabables, que són moltes, podria explicar moltes coses, però no vull fer la competència a la Montse. Així que, només dir-vos que els amics són com les estrelles a vegades no les veus, però sempre hi són, com vosaltres.

A la meva família, als meus pares, Josep i Josefina, i al meu germanet, Carles, per estar sempre al meu costat. Sé que us va ser difícil entendre què era el doctorat i més què feia cada dia a la universitat, fins i tot vau arribar a pensar que era normal arribar sempre amb l'últim tren. Però encara us va ser més difícil entendre perquè marxava a l'altre punta de món per sis mesos, però va valer la pena, de veritat. Perquè per molt lluny que marxi, qualsevol lloc ara és més proper que Austràlia. A en Tap per fer-me companyia cada dia mentre escrivia la tesi, no importava l'hora sempre allà mirant-me, i jo amb l'ordinador.

I finalment a en Marc, per recordar-me que hi ha un altre món fora d'aquí. Pel teu suport incondicional, encara que això representés està allunyat de mi durant més de sis mesos. Pels teus petits consells, molts cops no seguits. Per fer-me riure, per ser tant dolç i no provocar càries ☺, per ser a vegades la meva consciència, per ser el meu amic i el meu company, pel temps dedicat a la tesi, per la portada, per l'estil... per tot plegat i encara està al meu costat.

... a tots vosaltres MOLTES GRÀCIES de tot cor!!!!

Si amb aquestes paraules he aconseguit dibuixar un somriure a la teva cara, quin agraïment millor puc rebre?



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