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Sidestream treatment for improved BNR process performance

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Abstract

The removal of nutrients from the wastewaters through biological processes is a cost effective and environmentally sound alternative to chemical treatment. The primary driver for the success of the biological nutrient removal (BNR) processes is the availability of suitable carbon sources in the influent wastewater. Unfortunately, in the UK the wastewaters considered being weak for the BNR carbon limited processes and hence many methods have been examined in the past for the enhancement of BNR.

In this project an internal carbon source was proposed and examined. The carbon was produced from the disintegration of activated sludge by a mechanical process, which was explored and its impact on the BNR carbon limited processes was evaluated. The equipment used in this study for mechanical sludge disintegration was a deflaker, which was able to cause significant increase in chemical oxygen demand and volatile fatty acids (VFA) in the soluble phase of sludge. Laboratory scale tests revealed that this carbon source can improve the phosphorus release and denitrification process and hence the phosphorus and nitrogen removal.

These results led us to investigate the carbon source produced from disintegration in pilot scale and two BNR reactors were used for this purpose. The mechanical disintegration of 5.8% of return activated sludge was able to increase the concentration of VFA in the influent wastewater by 2.5-7 mg l^{-1} and successfully replace the equivalent amount of acetic acid, which is normally considered to be the best carbon source for biological phosphorus removal. The performance of the test reactor in terms of nitrogen, suspended solids and chemical oxygen demand was also unaffected. In addition, the sludge disintegration affected the bacteria growth yield, which combined with the longer sludge age by 6 days compared to the control reactor caused a 20-26% reduction in sludge production. In order to examine whether this process could be used by the water utilities a cost analysis took place, which revealed that the operational cost of the specific disintegration process and under the conditions examined in this study outweighs the savings from the produced carbon source and reduced amount of sludge.

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Chapter 1 Introduction

1. Introduction

1.1 Project background

The reduction and control of nutrients in effluents is becoming an important factor in design and operation of wastewater treatment works, with increasing use of biological treatment for nitrogen (N) and phosphorus (P) removal being applied (European Union Urban Waste Water Treatment Directive 91/271 and 98/15). In Severn Trent Water and Thames Water areas there are ~20 biological nutrient removal (BNR) plants, which serve ~15% of the population and this number is expected to increase over the next few years. A significant factor in the success of any BNR plant is the quality of the wastewater it receives and in particular the carbon to nitrogen and carbon to phosphorus ratio, as carbon is used by the microorganisms to enhance the nitrogen and phosphorus removal. The quantity of carbon is not the only issue as the form of carbon in wastewaters will determine the performance of the process (Abu-ghararah and Randall, 1991).

Wastewater in the UK is considered too weak for BNR processes and all the successful BNR sites in Severn Trent Water and Thames Water area receive an extra carbon source such as industrial wastes or products of primary sludge fermentation. These methods along with wastewater pre-fermentation have been implemented in many countries (Munch and Koch, 1999; McCue *et al.*, 2003; Llabres *et al.*, 1999). However, some significant drawbacks of these methods such as the size enlargement (tanks to accommodate the fermentation process) and the difficult applicability of the industrial wastes (transportation and high concentration of nutrients) has led water utilities to look for alternative methods to enhance BNR.

At the same time the treatment and disposal of the produced sludge of a wastewater treatment plant is a major environmental and economical issue (Strunkmann *et al.*, 2006). Sludge disintegration, which can significantly increase the soluble organic matter, has been used in the past to reduce sludge production and/or to enhance sludge stabilization (Muller, 2000). The chemical disintegration (ozonation) of activated sludge has been examined for the production of soluble carbon for the enhancement of denitrification process alone (Ahn *et al.*, 2002; Dytczak *et al.*, 2007). Any research conducted to examine sludge disintegration as a carbon source for biological phosphorus removal process, was in lab scale and with synthetic wastewater (Saktaywin *et al.*, 2006). The challenge of this project was to examine the disintegration of activated sludge sources, for the production of useful internal organic matter and then to investigate its impact on the BNR process performances and sludge growth. The selected equipment was the deflaker, an "off the shelf" technology (used in the paper industry), which was compared to ultrasound processes and the source of the sludge was a proportion of the return activated sludge (RAS) after being thickened up to ~6% TS.

1.2 Project development

The increasing number of BNR plants in Severn Trent Water and Thames Water area and the lack of sufficient and suitable carbon in the wastewater led the companies to examine alternative methods to increase the available carbon sources for the BNR processes. As a result the idea behind this thesis was developed. Previous work by Withey (2003) had shown that the deflaker could disintegrate sludge prior to anaerobic digestion, but here we have compared the carbon release to two ultrasound disintegration systems. Batch laboratory predictive tests were developed to allow simulation of phosphorus release and denitrification process and were used to evaluate the carbon produced from disintegration. The positive results from those tests led us to examine the mechanical sludge disintegration as method for the production of carbon source for BNR at pilot scale.

1.3 Aims and objectives

The aim of this project was to investigate whether a mechanical sludge disintegration process can be used for the production of an internal carbon source for the carbon limited BNR processes.

Consequently a series of objectives were identified:

- To examine the performance of the mechanical device proposed for sludge disintegration (deflaker) and compare it to ultrasound equipment in terms of carbon release and energy input.
- To investigate the mechanism of mechanical sludge disintegration.
- To develop a series of batch predictive tests, and use these tests for rapid assessment of the usefulness of any released carbon.
- To examine the application of the mechanical disintegration on a pilot scale BNR reactor and evaluate its impact on the performance of the system in terms of nutrient removal and sludge production.

1.4 Thesis plan

This thesis is presented in a paper format. All papers were written by the first author Pantelis Kampas and edited by Prof Simon A. Parsons and Dr Elise Cartmell (supervisors). Apart from the paper 1 (Chapter 3) where the experimental work is a result of the collaboration of the first author and another PhD student (second author), the rest experimental work was undertaken exclusively by the first author.

The links between the various phases of experimental work are presented in Figure 1.1. The work begins with a review of the literature on biological nutrient removal, methods to enhance the process performance and methods to predict the performance.

Chapter 3 compares three disintegration processes in terms of carbon release and energy input. The equipments compared are a deflaker, an ultrasound radial horn and a dual frequency ultrasound processor. *(Chapter 3 – P. Kampas, D. Minervini, C. Caccamo, S. A. Parsons and E. Cartmell. Carbon release from activated sludge – A comparison of three disintegration processes. Ultrasonics Sonochemistry (Submitted)).*

Chapter 4 explores in depth the disintegration by the deflaker and specifically the carbon release in terms of VFA, SCOD, proteins and carbohydrates as well as the energy required and the mechanism of disintegration. (*Chapter 4 - Kampas P., Parsons S. A., Pearce P., Ledoux S., Vale P., Churchley J. and Cartmell E. Mechanical sludge disintegration for the production of carbon source for biological nutrient removal. Water Research (2007)).*

Chapter 5 covers the development of the predictive batch tests (P and N) found in the literature in order to be used for the evaluation of potential carbon sources for BNR. (*Chapter 5 - Kampas P., Parsons S. A., Pearce P., Ledoux S., Vale P., Churchley J., and Cartmell E. Rapid evaluation of carbon sources for biological nutrient removal. In Young Researchers 2006 edited by Richard Stuetz and Lim Teik-Thye. IWA Publishing, London (2006)).*

Chapter 6 uses the findings from Chapter 5 and uses the adapted predictive tests in order to evaluate the carbon produced from deflaker. (*Chapter 6 - Kampas P., Parsons S. A., Pearce P., Ledoux S., Vale P., Churchley J., and Cartmell E. An internal carbon source for improving biological nutrient removal. Water Research (Submitted)).*

Finally, taking into account the results from Chapter 6, Chapter 7 moves on and examines the overall impact of mechanical disintegration by deflaker on BNR process performances and sludge growth in pilot scale reactors. *Chapter 7 - Kampas P., Parsons S. A, Pearce P., Ledoux S., Vale P. and Cartmell E. Disintegration of sludge recycles and its impact on BNR process performance. Water Research (Submitted)).*

A combination of data produced from the experimental work undertaken for Chapters 4, 5 and 6, but not appeared in these chapters, was presented in the International IWA conference in Nutrient Management in Wastewater Treatment, Krakow Poland, September 2005 as a poster, which was awarded as the best poster presentation and a paper was asked for publication. *(Appendix - Kampas P., Parsons S. A., Pearce P., Ledoux S., Vale P., Churchley J., and Cartmell E. Mechanical sludge disintegration: Providing an alternative carbon source for nutrient removal. Environmental Technology (In Press)).*

In Chapters 8 and 9 the practical implications for the water utilities and the conclusions of this project are presented. A cost analysis is conducted for the examined disintegration process providing useful information for the water utilities.

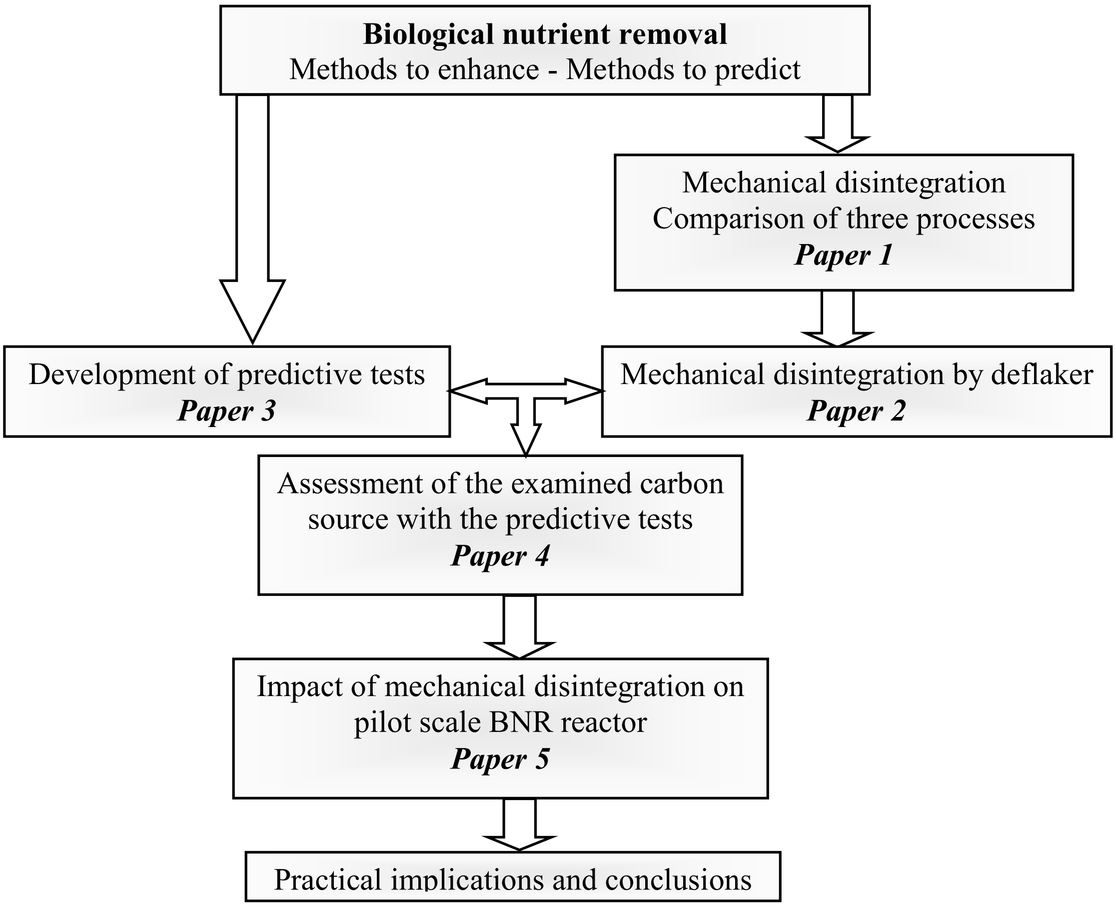

Figure 1.1 The thesis as a flow chart

1.5 References

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Chapter 2 Literature review

Chapter 2: Literature Review

2.1 Biological nutrient removal

Biological nutrient removal is the process of removing nutrients (carbon, nitrogen and phosphorus) by the cultivation and growth of microorganisms in the wastewaters. Processes have been developed for biological phosphorus removal only, nitrogen removal by biological nitrification and denitrification only, and removal of both nutrients in dual or combined systems.

In raw wastewater, phosphorus and nitrogen occur in many different chemical forms. Nitrogen may be present as organic nitrogen, ammonium, nitrite or nitrate. Phosphorus may occur as organic phosphorus, polyphosphate or orthophosphate. Efficient denitrification for nitrogen removal requires all forms of nitrogen to be converted to nitrate nitrogen. Likewise, for efficient phosphorus removal, all forms of phosphorus must be biologically converted to orthophosphate. Both design and operation need to provide for optimization of these biochemical reactions (Water Environment Federation, 1998).

2.1.1 Process

Nitrogen can occur in many forms in wastewaters and undergo numerous transformations in wastewater treatment (Figure 2.1). The two principal mechanisms for the removal of nitrogen are assimilation and nitrification-denitrification. In biological nitrogen removal nitrification-denitrification is the dominant mechanism and is accomplished in two conversion steps. The first step, nitrification is achieved in a two stages process involving two genera of microorganisms, *Nitrosomonas* and *Nitrobacter*. In the first stage ammonium is converted to nitrite and in the second stage nitrite is converted to nitrate. The conversion process is described as follows:

First step,

$$NH4^{+} + 3/2O_2 \xrightarrow{Nitrosomonas} NO_2^{-} + 2H^{+} + H_2O$$

Second step,

$$NO_2^{-} + 1/2O_2 \xrightarrow{Nitrobacter} NO_3^{-}$$

The second step is the denitrification, where the nitrogen in the form of nitrate is removed by conversion to nitrogen gas under anoxic conditions. Two types of enzyme systems are involved in the reduction of NO_3^{-} - N: assimilatory and dissimilatory. In the assimilatory, nitrate reduction process, NO_3^{-} - N is converted to ammonia nitrogen to be used by he cells in biosynthesis and occurs, when NO_3^{-} - N is the only form of nitrogen available. In the dissimilatory nitrate reduction process, nitrogen gas is formed from NO_3^{-} - N. In most biological nitrification-denitrification systems, the wastewater must contain sufficient carbon (organic matter), to provide the energy source for the conversion of nitrate to nitrogen gas by the bacteria. The reactions for nitrate reduction are:

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

The last three compounds are gaseous products and can be released to the atmosphere.

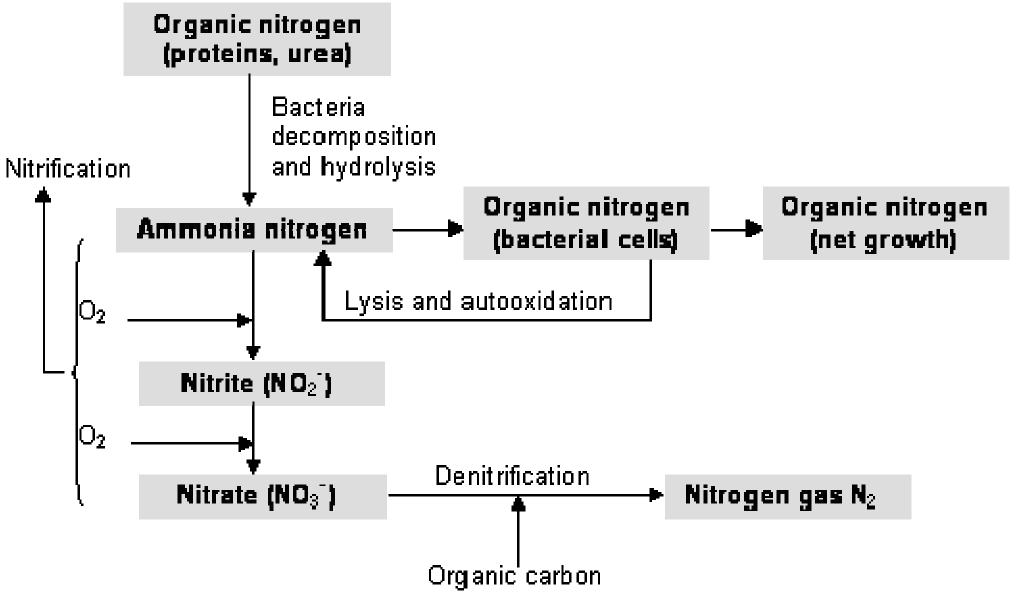

Figure 2.1 Nitrogen transformations in biological treatment processes (Metcalf and Eddy, 2003)

In biological removal of phosphorus, the phosphorus in the influent wastewater is incorporated into cell biomass, which subsequently is removed from the process as a result of sludge wasting. Phosphorus accumulating organisms (PAOs) are encouraged to grow and consume phosphorus in systems that use a reactor configuration that provides PAOs with a competitive advantage over other bacteria (Figure 2.2).

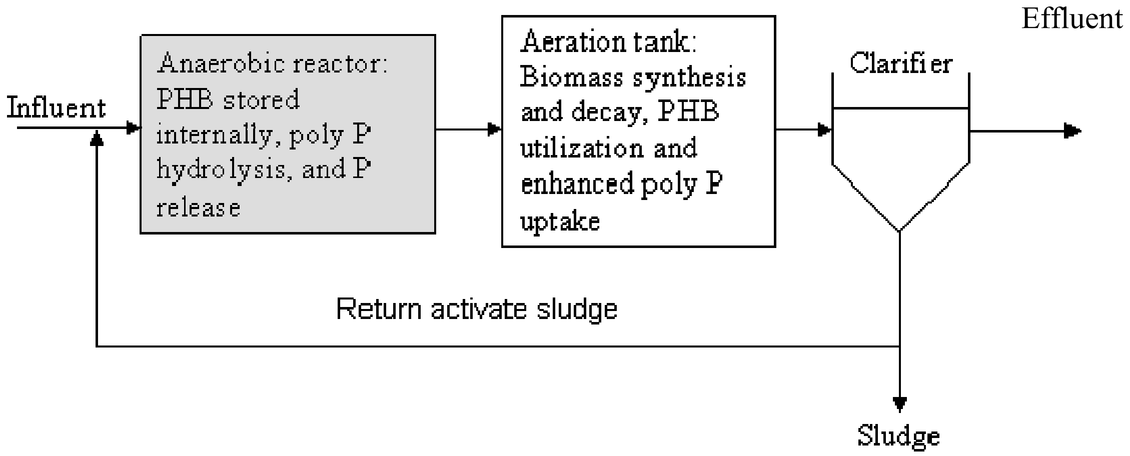

Figure 2.2 Biological phosphorus removal: typical reactor configuration (Metcalf and Eddy, 2003)

In a treatment plant with biological phosphorus removal several groups of heterotrophs are active and competing for the substrate, especially for low molecular fatty acids that are needed for the phosphorus storage mechanism. Many of the competitors are not PAOs. The result of this competition and fatty acid availability, determines the success or failure of the bio-P process. Apart from PAOs, other key groups of microorganisms involved are DPAOs (Denitrifying Polyphosphate Accumulating Organisms) and GAOs (Glycogen Accumulating Organisms). The PAOs and DPAOs are beneficial for biological phosphorus removal whereas the GAOs compete with them and as a consequence, they inhibit the process.

Hu *et al.*, (2002) found that DPAOs show a significantly lower enhanced biological phosphorus removal (EBPR) performance under anoxic conditions and use the influent readily biodegradable chemical oxygen demand (RBCOD) less “efficiently” compared with PAOs. It is generally accepted that poly-P microorganisms, are unable to directly utilize glucose under anaerobic condition in the EBPR system and moreover, glucose is even detrimental to the EBPR unless it is first converted to short chain volatile fatty acids (SCVFAs) by non-poly-P microorganisms (acidogenic bacteria) (Randall *et al.*, 1994)

Processes occurring in the anaerobic zone: The PAOs, using energy available from stored polyphosphates assimilate acetate or other short chain fatty acids and produce intracellular polyhydroxybutyrate (PHB) storage products. Some glycogen contained in the cell is also used. At the same time the release of orthophosphate (O-PO_4) takes place. The PHB content in the PAOs increases while the polyphosphate decreases.

Processes occurring in the aerobic/anoxic zone: Stored PHB is metabolized, providing energy from oxidation and carbon for new cell growth and producing some glycogen. The energy released from PHB oxidation is used to form polyphosphate bonds in cell storage so that soluble orthophosphate (O-PO_4) is removed from solution and incorporated into polyphosphates within the bacteria cell. Cell growth also occurs due to PHB utilization and the new biomass with high polyphosphate storage accounts for phosphorus removal.

Figure 2.3 illustrates the proposed mechanism for the three main groups of microorganisms (PAOs, DPAOs, GAOs).

2.1.2 Design

The principal biological processes used for wastewater treatments can be divided into two main categories: suspended growth and attached growth processes. In suspended growth processes, the microorganisms responsible for treatment are maintained in liquid suspension by appropriate mixings methods. The most common suspended growth process used for municipal wastewater treatment is the activated sludge process (Metcalf and Eddy, 2003).

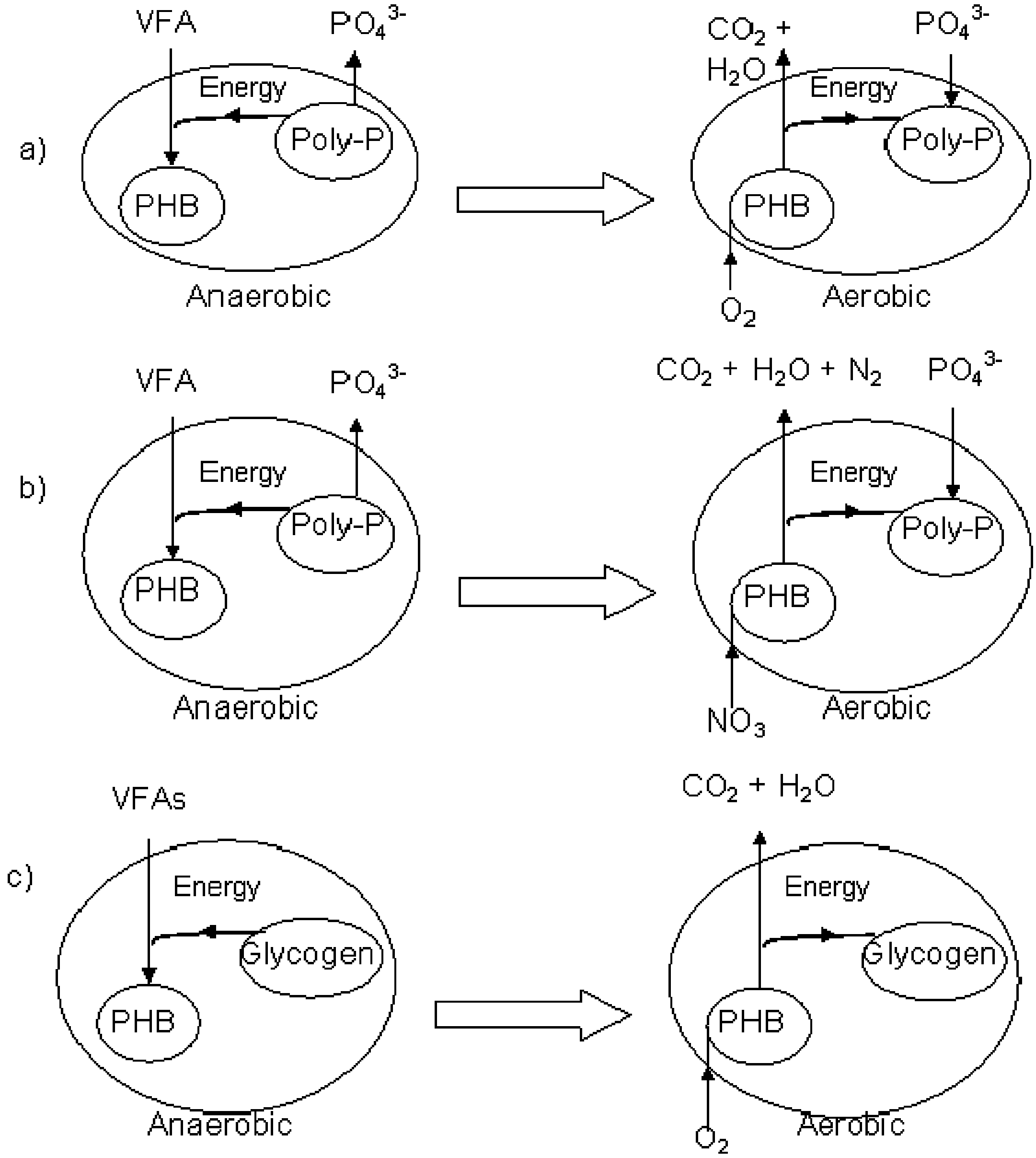

Figure 2.3 Proposed mechanisms for phosphorus release and uptake with different groups of microorganisms: a) PAOs, b) DPAOs, c) GAOs

In attached growth process, the microorganisms responsible for the conversion of organic material or nutrients are attached to an inert packing material. Packing materials used in attached growth processes include rock, gravel, slag and a wide range of plastic or other synthetic materials. The most common attached growth process is the trickling filter. In suspended growth biological process nitrification can be achieved along with BOD removal in a single-sludge process or separately in a two sludge process (Figure 2.4).

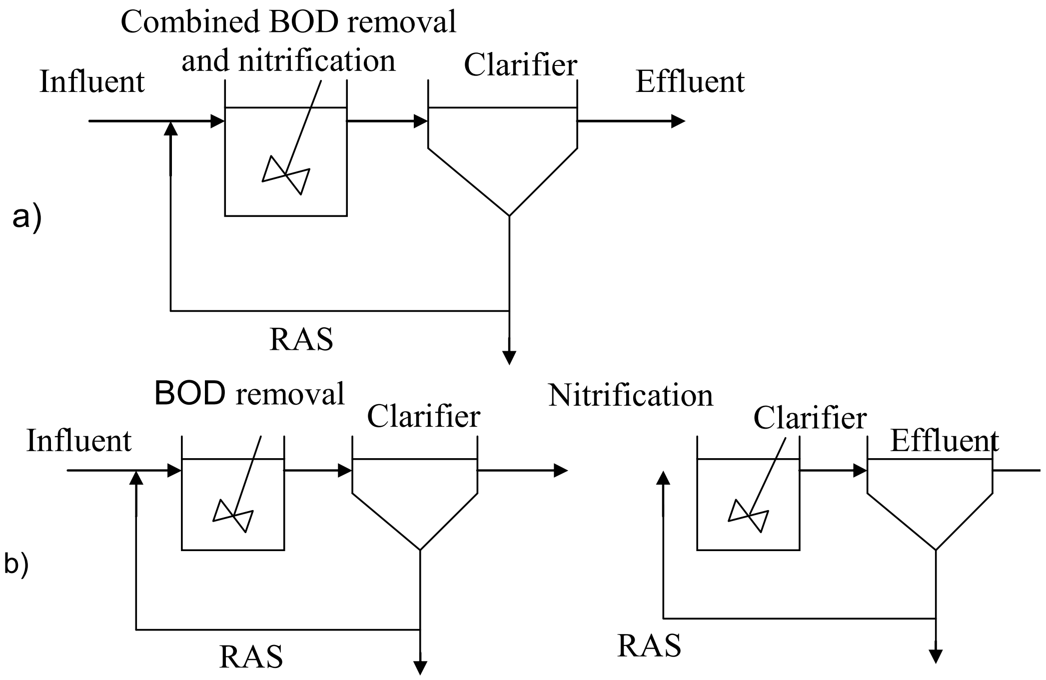

Figure 2.4 a) single-sludge process, b) two-sludge process

The technology for biological phosphorus removal is divided into two approaches. One approach can be called *mainstream* processes and the other *sidestream* processes. The most common mainstream processes are the Phoredox (A/O) process, the A^2O and the University of Cape Town processes (UCT) (Figure 2.5) and the most common sidestream process is the PhoStrip process (Figure 2.6).

The main difference between the Phoredox (A/O) and the A^2O processes is that A/O is used only for phosphorus removal and nitrification does not occur. The other two processes are able to remove both phosphorus and nitrogen. The difference between them is that in the UCT process, the activated sludge recycle is directly before the anoxic zone (Figure 2.6). The PhoStrip^{TM} sidestream process combines biological and chemical processes for phosphorus removal.

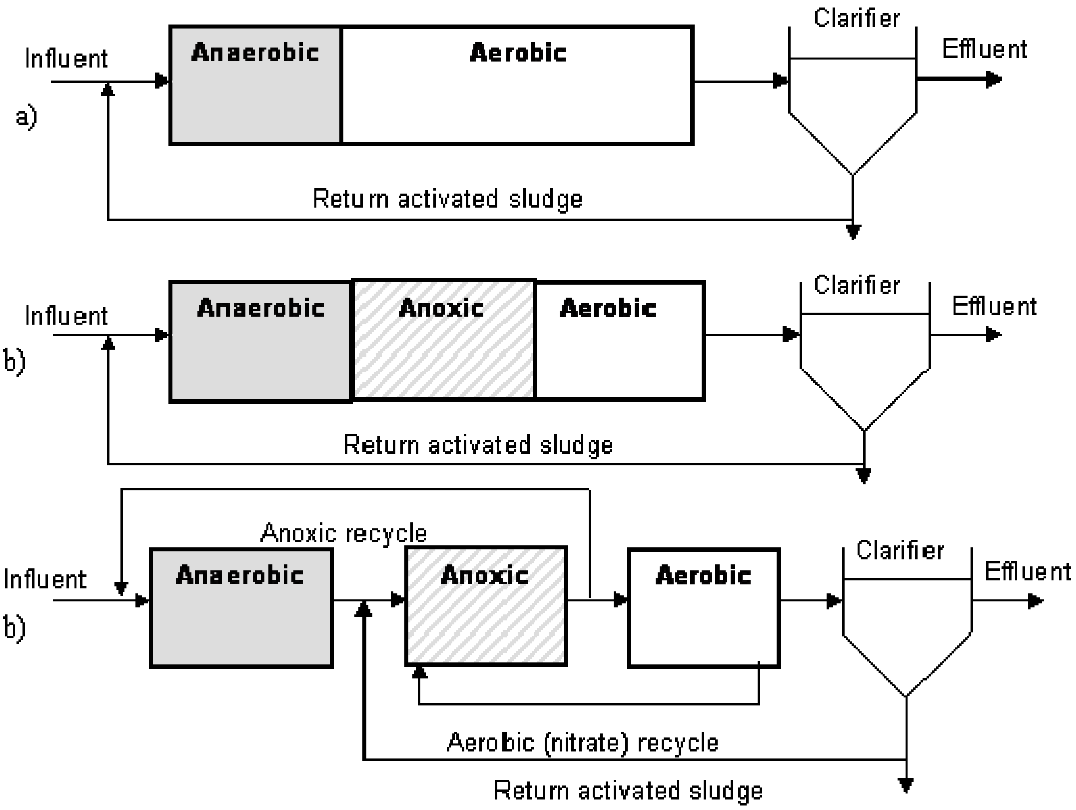

Figure 2.5 Typical mainstream biological phosphorus removal processes: a) Phoredox (A/O), b) A^2O and c) University of Cape Town (UCT) (Metcalf and Eddy, 2003)

2.1.3 Requirements

A number of environmental factors are able to influence the biological nitrogen removal. Nitrification capability can be adversely affected by low temperature if the retention time is not properly maintained. In theory, the lower the temperature, the higher the retention time must be for complete nitrification. At a temperature of 10°C the Solid Retention Time (SRT) theoretically should be about three times greater than the SRT at 20°C. Denitrification is also affected by low temperatures with the rates to decrease significantly at temperatures less than 10°C (Water Environment Federation, 1996). Denitrification can also occur at thermophilic temperatures of 50-60°C (Henze *et al.*, 2002).

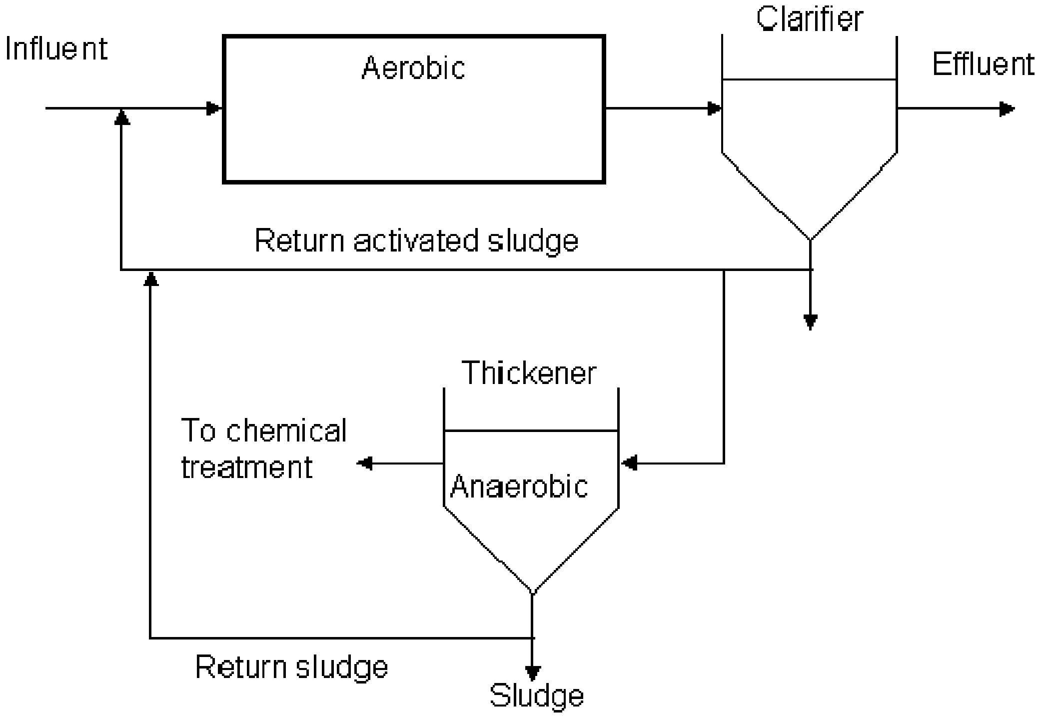

Figure 2.6 PhoStrip sidestream biological phosphorus removal process (Metcalf and Eddy, 2003)

Reports on the effect of dissolved oxygen (DO) concentration on nitrification rates vary widely in the literature with the minimum requirement for complete nitrification to be 0.3 mg l^{-1}, but with nitrification rates doubling as the DO concentration increases from 1 to 3 mg l^{-1}. On the other hand, dissolved oxygen can inhibit nitrate reduction by repressing the nitrate reduction enzyme. A DO concentration of 0.2 mg l^{-1} and above is reported to inhibit denitrification (Randal *et al.*, 1992).

The nitrification process is pH dependent with an optimum in the 7.5-8 range. At pH values of 5.8 to 6, the nitrification rates may be 10 to 20 percent of the rates at pH 7. The alkalinity is reduced in water during the nitrification process. For every mole of NH_4^+ - N, which is oxidised to NO_2^- - N, approximately two moles of HCO_3 are consumed and this corresponds to two equivalents of alkalinity. Alkalinity may have to be added if the influent wastewater has insufficient alkalinity to maintain pH. It is reported that alkalinity requirements for nitrification have been estimated at approximately 6-7.2 g $CaCO_3$ g^{-1} NH_4 - N (Metcalf and Eddy, 2003; Randall *et al.*, 1992). Fortunately, the denitrification reaction produces alkalinity. For every mole of nitrate converted, one equivalent alkalinity is produced. This release of alkalinity reduces the initial demand to 3.57 g $CaCO_3$ g^-1 NH_3 - N (Metcalf and Eddy, 2003). The optimum pH is around 7-9, but with variations depending on local conditions (Water Environment Federation, 1996).

The nitrification process in activated sludge plants can be inhibited by many different substances, since nitrifying organisms are sensitive to a wide range of organic and inorganic compounds. In many cases, nitrification rates are inhibited even though bacteria continue to grow and oxidise ammonia and nitrate, but at significantly reduced rates. In some cases, toxicity may be sufficient to kill the nitrifying bacteria. Compounds that are toxic include solvent organic chemicals, proteins, amines, phenolic compounds, alcohols, ethers, carbamates, and benzyne. Metals also inhibit nitrification. Finally, nitrification can be inhibited by un-ionized ammonia (NH_3) or free ammonia and un-ionized nitrous acid (HNO_2) (Henze *et al.*, 2002).

Another important factor that can influence nitrogen removal is the energy sources. Denitrifying bacteria can utilize a broad spectrum of energy sources. Internal energy sources are from the wastewater and sludge and the external carbon sources include acetic acid and methanol.

According to the stoichiometry of denitrification reaction 2.6 g COD are needed for the denitrification of 1 g NO_3^- - N. In reality the carbon, which is necessary for denitrification, is greater. In the literature influent TCOD:KN ratio was the most important factor to be considered for successful nitrogen removal and a wide range of COD/N ratios can be found which ensure complete denitrification (Choi and Eum, 2002). In practice, 4-15 g COD g^{-1} N are required for different wastewaters and a minimum ratio of 3.5-4 is mentioned (Henze, 1991; Kujawa and Klapwick, 1999; Bolzonella *et al.*, 2001). Randall *et al.*, (1992) recommend the use of external carbon source, when the ratio COD:TKN in a given wastewater is under 9. Minimum quantities of readily biodegradable influent carbon required for complete denitrification plus assimilative uptake range from 2.9-5 g COD g^{-1} TN, with practical quantities typically twice this range, have been reported (Henze *et al.*, 2002). Finally, the same authors have reported that the required influent C:N ratio for complete denitrification using biofilters was 5-6 g COD g^{-1} NO_3-N. Table 2.1 shows the expected nitrogen removal efficiency for different organic matter to nitrogen ratios.

Another carbon source for denitrification can be the PHB stored by the PAOs during the phosphorus release process. During the initial years of the development of BNR technology, it was assumed that the P-bacteria could not use nitrates as a final electron acceptor and could thus not denitrify (Stevens *et al.*, 1999). Recent research has shown that denitrification can occur using the carbon that was taken up by the P-bacteria with the simultaneous uptake of phosphates. That results to reduction in the total demand of carbon source (Kuba *et al.*, 1996; Jonsson *et al.*, 1996 and Ostgaard *et al.*, 1997). However, the denitrification with simultaneous phosphorus uptake takes place only when the nitrate load in the anoxic zone is more than the denitrification potential of the heterotrophic bacteria. That means that the denitrifying PAOs (DPAOs) will appear to denitrify the "excess" nitrates only after the depletion of any other carbon sources (Hu *et al.*, 2002).

Table 2.1 Relationship between expected biological nitrogen removal efficiency and influent organic matter to nitrogen ratios (Grady *et al.*, 1999)

Nitrogen removal efficiency	**COD/TKN**	**BOD_5/NH_3-N**	**BOD_5/TKN**
Poor	<5	<4	<2.5
Moderate	5-7	4-6	2.5-3.5
Good	7-9	6-8	3.5-5
Excellent	>9	>8	>5

Similar to nitrogen removal, successful operation of biological phosphorus removal processes requires the consideration of several environmental factors. The recommended DO concentration is 0-0.2 mg l^{-1} and 3-4 mg l^{-1} for anaerobic and aerobic zone, respectively (Shehab *et al.*, 1996). Temperature generally affects significantly the biological processes, but for BPR the research has shown conflicting results. It has been reported that higher temperatures of 20-37°C caused higher BPR efficiency (McClintock *et al.*, 1993), but also higher efficiency has been reported for lower temperatures of 5-15°C (Florentz *et al.*, 1987). The drop of temperature might not affect directly the P removal but can play a significant role in nitrification and denitrification, which can affect the BPR process (Randall *et al.*, 1992 and Mulkerrins *et al.*, 2004).

Several studies have shown that the removal efficiency is greatly reduced at pH values below 6.5 and the BPR mechanisms do not function with pH at less than 5.4. It is also known that BPR can operate in the pH range 8.5-9 (Water Environment Federation, 1998). In addition, another study showed that the phosphorus release process was enhanced as the pH was increased (Smolders *et al.*, 1994).

Desirable Solid Retention Time (SRD) values from 4 to 5 d for phosphorus removal only, but has to be increased for combined systems, where nitrification has to be achieved. A research comparing the nutrient removal at SRTs of ranging from 5 to 30 days demonstrated similar results at 10 and 15 days with higher P removal at 10 days (Kargi and Uygur, 2002).

The redox potential is a key factor determining the rate of anaerobic phosphorus release. The lower the redox potential, the more phosphates are released in the anaerobic zone and that means more phosphorus to be taken up under anoxic or aerobic conditions (Metcalf & Eddy, 2001)

In biological phosphorus removal systems, sufficient cations associated with polyphosphate storage must be available. For an influent soluble phosphorus concentration of 10 mg l^{-1}, the recommended concentration of Mg, K, and Ca is 5.6, 6.3 and 3.2 mg l^{-1}, respectively. However, calcium seemed not to be required for BPR (Pattarkine and Randall, 1999). Brdjanovic *et al.*, (1996) showed that when the biological phosphorus removal system was exposed to a severe shortage of potassium in the influent, the performance of P removal was negatively affected. Fortunately, the requirements are considerably less than the quantities of these cations found in most wastewaters (Randall *et al.*, 1992).

The concentration of biodegradable organic matter relative to the phosphorus concentration in an influent wastewater can dramatically affect the performance of BPR. Enhanced BPR cannot be accomplished without sufficient bio-P-available organic substrate, preferably measured as Volatile Fatty Acids (VFAs) and RBCOD, but also as approximated by either COD or BOD. It is reported that 1 mg of phosphorus to be removed, requires 6-10 mg of VFAs (Wentzel *et al.*, 1989; Pitman *et al.*, 1992). Abu-ghararah and Randall (1991) suggested that at least 20 mg COD equivalent of acetic acid is needed for the removal of 1mg phosphorus. Moreover, Carlsson *et al.*, (1996) reported that at neutral pH the ratio of phosphorus release to COD was 0.35-0.4 at laboratory scale and 0.5 on the pilot plant.

Randall *et al.*, (1997) investigated the effect of different carbon sources on EBPR. They found that iso-valeric acid was the most consistent and efficient substrate and acetic acid gave slightly higher overall removal, only at significantly greater concentrations. Propionic acid was the only C_2-C_5 VFA, which was not beneficial to EBPR. Moreover, they found that branched isomers were significantly more beneficial than their linear counterparts and alcohols had small or negligible effects compared to VFA with the same carbon chain length. Finally, synthetic wastewater and glucose, were the most consistently and significantly detrimental substrates to P removal.

The effect of VFAs on biological phosphorus removal was also investigated by Abu-ghararah and Randall (1991). The results were similar to the previous authors and the most effective acids to P release and uptake were the acetic and iso-valeric acid. Branched VFAs enhanced phosphorus removal compared to VFAs with the same number of carbons. Table 2.2 shows the required COD for the removal of P for all VFAs, separately.

On the contrary, Thomas *et al.*, (2003) reported that GAOs, which are not able to remove phosphorus, have a competitive advantage to use acetate and PAOs have a competitive advantage to use propionate. Hence, they concluded that contrary to popular belief acetate may not be the optimum VFA for biological phosphorus removal. Furthermore, Moser-Engeler *et al.*, (1998) found that acetate and propionate are taken up much faster than the C_4-C_5 acids and PAOs preferentially consume linear fatty acids, when they are exposed to equimolar mixture of SCFAs. This statement is in contradiction with the previous authors.

Table 2.2 Ratios of mg COD utilized per mg phosphorus removed (Abu-gharah and Randall, 1991)

Volatile fatty Acid	mg COD utilized / mg P removed
Valeric acid	94.0
Butyric acid	39.0
Isobutyric acid	36.1
Propionic acid	31.5
Isovaleric acid	23.5
Acetic acid	18.8

2.1.4 Possible operational problems for biological phosphorus removal

BNR is a complex process with the phosphorus removal to depend on some factors, which were not examined in the previous section and if they are not taken into account can lead in BPR deterioration or even failure.

For applications where nitrification is needed to meet discharge requirements, it is necessary for the process to include biological denitrification to prevent excessive amounts of nitrate from entering the anaerobic reactor by the way of the RAS recycle. Heterotrophic bacteria responsible for denitrification will use nitrate to consume carbon food source and firstly the RBCOD in the anaerobic zone, which then leaves less RBCOD available for PAOs, thus decreasing biological phosphorus treatment efficiency (Metcalf and Eddy, 2003). Sometimes, even the presence of anoxic zone does not resolve the problem, when there is not complete denitrification thus a continuous monitoring of the nitrates is advised to prevent their concentration in anaerobic reactors to be over 5 mg l^{-1} (Water Environment Federation, 1996).

The glycogen accumulating organisms (GAOs) are very similar to PAOs, as both can accumulate PHA anaerobically. However, GAOs use only glycogen as an energy source, contrary to PAOs which use phosphorus. That leads to a competition with PAOs for the available carbon source under anaerobic conditions without releasing phosphates and of course without taking phosphates up under aerobic conditions. As a consequence there is not enough available carbon for the PAOs (Cech and Hartman, 1993; Mino *et al.*, 1998 and Saunders *et al.*, 2003). It has been shown that GAOs are mesophilic bacteria, while the PAOs are phycrophilic and at temperatures 10°C or less have a growth advantage (Pansward *et al.*, 2003 and Erdal *et al.*, 2003). In addition, the pH affects the competition of the two types of bacteria. It was reported that when the pH in the anaerobic zone was less than 7.25 the GAOs were able to consume acetate faster than PAOs and full BPR was achieved when the minimum pH allowed in the system was 7.25 (Filipe *et al.*, 2001b). The same authors (Filipe *et al.*, 2001a) determined, in agreement with previous research that GAOs are present at temperatures above 30°C, at low pH values, when feed with glucose or a sugar rich waste or acetate alone. A system fed with a combination of acetic and propionic acid can achieve more stable operation (Barnard and Steichen, 2006). The ratio of phosphorus to total organic carbon (P:TOC) can also play a role in the domination of GAOs. High ratios encourage the growth of PAOs and low feeding ratios the growth of PAOs is suppressed by the domination of GAOs (Liu *et al.*, 1997).

The phosphorus release that occurs in the absence of VFA is defined as secondary release and this form of phosphorus release is detrimental to the BPR process (Danesh and Oleszkiewicz, 1997)**.** This phenomenon takes place usually under anaerobic conditions and as is not associated with PHB storage, there is no energy in the aerobic zone for the uptake of the released phosphorus. Actually was reported that only 40 to 60% of the secondary released phosphorus can be taken up during aeration (Stephens and Stensel 1998). The anaerobic conditions required for the secondary P release can be found in prolonged anaerobic zones, in anoxic zones with the absence of nitrates and in secondary clarifiers (Mulkerrins *et al.*, 2004; Carlsson *et al.*, 1996 and Urbain *et al.*, 2001).

Finally, another common problem in BNR systems is the incomplete partitioning of the different sections, which results in backflows between the compartments. As a consequence, nitrates might enter the anaerobic zone, different from the initially designed hydraulic retention time occurs in each compartment and DO might be transferred to the oxygen free zones. All of them can lead to a significant deterioration of P removal (Barnard and Abraham, 2006).

2.1.5 BNR summary

Biological nutrient removal systems may be categorized according to their nutrient removal capabilities as nitrogen removal processes, phosphorus removal processes and systems that remove both nitrogen and phosphorus. The last systems incorporate anaerobic, anoxic and aerobic zones. Table 2.3 summarizes the biochemical transformations occurring in the various zones of a BNR process. Many factors can affect BNR processes and extra attention is needed not only during the design of the process but also during its operation. The most important issue for the biological nutrient removal is the available substrate with the presence of easily biodegradable organic matter. For this reason, all methods that have been used to improve biological nutrient removal try to increase the appropriate organic matter in the wastewater.

Table 2.3 Summary of biological nutrient removal processes zones (Graddy *et al.*, 1999)

Zone	Biochemical transformations	Functions	Zone required for
Anaerobic	● Uptake and storage of VFAs by PAOs ● Fermentation of readily biodegradable organic matter by heterotrophic bacteria ● Phosphorus release	● Selection of PAOs	● Phosphorus removal
Anoxic	● Denitrification ● Alkalinity production	● Conversion of NO_3-N to N_2 ● Selection of denitrifying bacteria	● Nitrogen removal
Aerobic	● Nitrification ● Metabolism of stored and exogenous substrate by PAOs ● Metabolism of exogenous substrate by heterotrophic bacteria ● Phosphorus uptake ● Alkalinity consumption	● Conversion of NH_3 to NO_3-N ● Nitrogen removal through gas stripping ● Formation of polyphosphate	● Nitrogen removal ● Phosphorus removal

2.2 Enhanced Biological Nutrient Removal

Since Environmental Agencies under the Urban Wastewater Treatment Directive demand lower consents from sewage works, water companies try to find methods to enhance BNR in order to reach lower quantities of nutrients in the effluent. Most of these methods increase the available organic matter for denitrification and P removal. The best energy sources are fermentation products, in particular the short-chain carboxylic acids (i.e. volatile fatty acids). For denitrification alcohols and glucose may also be used. In addition Jonsson *et al.*, (1996) found that in plants, which remove both nitrogen and phosphorus, PHB can be used as one of the major carbon sources for denitrification. That leads to the conclusion that any methods used to enhance BPR will cause a positive effect to denitrification as well. As has already been mentioned denitrifying PAOs can play a significant role to both EBPR and denitrification, because they can relieve the competition of carbon source between them, by using nitrate for electron acceptors (Wanner *et al.*, 1992 and Shoji *et al.*, 2003).

2.2.1 Pre-treatments

The enhanced biological nutrient removal can be achieved by using different kinds of pre-treatments. The most popular are the pre-fermenters (the entire wastewater stream is treated) and the side-stream (only primary clarifier underflow is treated), which consisted of sludge hydrolysis and acidogenesis. The hydrolysis can be biological, chemical and thermal. Generally, chemical and thermal hydrolysis products contain very little VFA, compared with biological (Metcalf and Eddy, 2003; Barlindhaug and Odegaard, 1996a, 1996b). The performances of P and N removal and the denitrification rates for different pre-treatments are summarised in Table 2.4.

McCue *et al.*, (2003) made a comparison of two BNR systems, one operated with and the other without on-line pre-fermenter. The conclusions were that prefermentation increased RBCOD and VFA content of domestic wastewater. VFAs were increased almost 25%. This led to an increase of BNR process performance of 30 and 5% for P and N removal, respectively. Nutrient removal in a sequencing batch reactor (SBR) with the use of a SBR fermenter was investigated by German *et al.*, (1998). This pre-treatment brought a 437 %

increase in SCOD and a significant VFA content (223 mg l^{-1}) resulting in good N and P removal (88% and 98%, respectively). Furthermore, Danesh and Oleszkiewicz (1997) using the same system with two SBRs, attained a very good VFA production rate and uptake by bio-P bacteria. The phosphorus removal was 92% with a 53% increase. Rustrian *et al.*, (1997, 1999) and Delgenes *et al.*, (1998) used a SBR connected with a two-step anaerobic digestion system. They found that this process had the benefit of saving carbon source for denitrification and P removal with the highest performances for nitrogen and phosphorus removal to be 78% and 95%, respectively.

Table 2.4 Performances of P and N removal and denitrification rates for several pre-treatments

PRE-TREATMENT	Nitrogen removal %	Phosphorus removal %	Denitrification rate	**REFERENCE**
On line prefermenter	64	77		McCue *et al.*, (2003)
	88	98		German *et al.*, (1998)
		92		Danesh and Oleszkiewcz (1997)
	78	95		Rustrian *et al.*, (1999)
Primary sludge fermentation			6 mg NO_3-N g^{-1} COD h^{-1}	Moser-Engeler *et al., (1998)*
	87	87		Charlton (1994)
Primary sludge hydrolysis	80			Kristensen *et al.*, (1992)
			4.1 mg NO_3-N g^{-1} VSS h^{-1}	Isaacs and Henze (1995)
			9 mg NOx-Ng^{-1}MLSS h^{-1}	Hatziconstantinou *et al.*, (1996)
Ozonated waste activated sludge			0.45 - 3.4 mg NO_3-N g^{-1} VSS h^{-1}	Ahn *et al.*, (2002)
Mechanically disintegrated sludge			15 mg NO_3-N g^{-1} VSS h^{-1}	Muller *et al.*, (2000a)

Fermentation of primary sludge has been widely examined as it can produce VFA and increase the carbon sources for EBNR (Urbain *et al.*, 2001; Bixio *et al.*, 2001; Skalsky and

Daigger, 1995). The addition of the supernatant of raw sludge fermentation can cause up to 1500% increase in VFA content of wastewater (Pitman *et al.*, 1992; Thomas *et al.*, 2003). Moser-Engeler *et al.*, (1998) reported a denitrification rate of 6 g NO_3-N kg^{-1} COD h^{-1}, when the substrate was fermentation products, which is much higher than denitrification rate based on the single substrate acetate or propionate (3.8 and 1.7 g NO_3-N kg^{-1} COD h^{-1}, respectively). A comparison with methanol, the best cheap alternative, shows that fermentation products are better in practice, since methanol needs an adaptation time of several days in order to be used by the microorganisms (Purtschert *et al.*, 1996) and cannot be used for EBPR. Charlton (1994) investigated the application of a primary sludge fermenter for the BNR of weak sewage. The results were 87% removal for both phosphorus and nitrogen.

Kristensen *et al.*, (1992) used biological sludge hydrolysate as the carbon source for nitrogen removal. The hydrolysate COD was consisted mainly of VFA resulting in high denitrification rates and an overall nitrogen removal 80%, almost 15% more. Isaacs and Henze (1995) used the same carbon source and reported a maximum denitrification rate of 4.1 mg NO_3-N g^{-1} VSS h^{-1}. The biological hydrolysate employed in this study had a COD:TKN ratio of about 18, much higher than the COD requirements for N removal. Hatziconstantinou *et al.*, (1996) reached to the same conclusion that primary sludge hydrolysis is a valuable process for the production of readily biodegradable soluble organics, which can be utilized for BNR and found a maximum denitrification rate of 9 mg NO_x g^{-1} MLSS h^{-1}.

Finally, mesophillic hydrolysis of primary sludge can increase RBCOD or short chain fatty acids (Canziani *et al.*, 1995). This internal carbon source is able to increase denitrification efficiency by 4-10 %. On the other hand, thermal hydrolysis can produce a C:N ratio of 8 but the VFA content increases marginally. Barlindhaug and Odegaard (1996a & 1996b). Mechanically disintegrated sludge by Stirred Ball Mills (SBM) and High Pressure Homgenizers (HPH) was also used as carbon source for the denitrification process with a maximum denitrification rate at 15 NO_3-N g^{-1} VSS h^{-1} (Muller, 2000a & 2000b).

2.2.2 Addition of external carbon source

The addition of external carbon source for denitrification and phosphorus removal has been widely examined and can be separated into two main categories. In the first, the organic carbon in the form of alcohols, volatile acids or glucose is directly added to the wastewater and in the second the carbon source is industrial wastes rich in organic matter.

2.2.2.1 Addition of alcohols, volatile acids or glucose

Takai *et al.*, (1997) and Eilersen *et al.*, (1995) examined the effect of volatile fatty acids on denitrification. The denitrification rate, when acetic acid was used as a carbon source was 2.42 mg N g^{-1} MLSS h^{-1}, while propionic acid was not used effectively for denitrification. Naidoo *et al.*, (1998) reported a range of 3.2-7.3 mg N g^{-1} VSS h^{-1} for denitrification rate with acetate as external carbon source. Fass *et al.*, (1994) compared the short chain fatty acids, with butyrate to give the maximum denitrification rate. The rate when the mixture of VFA was used was 19.9 mg N-NO_x mg g^{-1} SS h^{-1}. Constantin and Fick (1997) made a comparison between ethanol and acetic acid as carbon source for denitrification. Their experiments have shown that the development of the microorganisms was higher on ethanol, but on acetic acid the specific denitrification rate was higher. That can be explained by the fact that ethanol must be first transformed into acetate.

Many authors have made comparisons between methanol and ethanol as carbon sources for denitrification (Christensson *et al.*, 1994; Nyberg *et al.*, 1996; Carrera *et al.*, 2003). Ethanol has been proved to be more efficient, as the growth rate of denitrifiers with ethanol was 2-3 times higher than with methanol. The denitrification rates were around 10 and 3 mg N g^{-1} VSS h^{-1} for ethanol and methanol, respectively. Moreover, methanol requires longer adaptation period than ethanol, before full effect of the carbon source added, is reached. The same conclusions were reached by Carrera *et al.*, (2003), who reported the maximum denitrification rate with ethanol about six times higher than with methanol. Hasselblad and Hallin (1998) investigated the intermittent addition of ethanol and their results suggest that is possible to use an intermittent strategy when adding ethanol, with denitrification rate between 3 and 4 mg N g^{-1} VSS h^{-1}. However, methanol addition can substantially increase denitrification efficiency and the total nitrogen removal can be improved from 52 to 72%.

Glucose and its influence on enhanced biological phosphorus removal was examined by many authors (Tasli *et al.*, 1997; Maurer *et al.*, 1997; Carucci *et al.*, 1997; Jeon and Park, 2000). Phosphorus removal is much lower when glucose is the available substrate in comparison with acetate. That is expected since glucose can enhance the dominance of G-bacteria (GAOs), when EBPR is mostly accomplished by PAOs and DPAOs. In some cases glucose can be detrimental to EBPR. The BNR performances, when external carbon source is used, are demonstrated in Table 2.5.

Table 2.5 Performances of BNR for different carbon source

CARBON SOURCE	Nitrogen removal %	Phosphorus removal %	Denitrification rate	**REFERENCE**
Methanol			3 mg N g^{-1} VSS h^{-1}	Nyberg *et al.*, (1996)
	66	80		Tam *et al.*, (1992)
Ethanol			10 mg N g^{-1} VSS h^{-1}	Nyberg *et al.*, (1996)
			3-5 mg N g^{-1} VSS h^{-1}	Hasselblad and Hallin (1998)
Acetic acid	89	84		Tam *et al.*, (1992)
			3.2 - 7.3 mg N g^{-1} MLSS h^{-1}	Naidoo *et al.*, (1998)
			2.42 mg N g^{-1} MLSS h^{-1}	Takai *et al.*, (1997)
Mixture VFA			19.9 mg N-NO$_x$ g^{-1} SS h^{-1}	Fass *et al.*, (1994)
Glucose	61	40		Tam *et al.*, (1992)
Glucose/ acetate (50/50)	85	90		Kargi and Uygar (2003)

2.2.2.2 Addition of industrial wastes

There are many different kinds of industrial wastes that include organic matter, which can be useful for biological nutrient removal. Table 2.6 shows some of them with the quantities of the useful organic substrate.

The main disadvantage of the addition of external carbon in the form of volatile acids or alcohols is the high operational cost. The best alternative could be industrial wastes, which comprise readily biodegradable organic matter. Pavan *et al.*, (1998), Llabres *et al.*, (1999) and Bolzonella *et al.*, (2001), examined the addition of fermented Organic Fraction of Municipal Solid Waste (OFMSW) to the wastewater. The first authors found that the addition of that waste can increase the RBCOD in the wastewater approximately 580% and the denitrification rate from 0.41 to 2.5 mg $N\text{-}NO_3$ g^{-1} VSS d^{-1}. The overall nitrogen removal was increased by 33%. The second authors reached an overall nitrogen and phosphorus removal of 80 and 84% respectively and a maximum denitrification rate of 2.5 mg $N\text{-}NO_3$ g^{-1} VSS d^{-1}, by using hydrolysis products of OFMSW. A comparison of these performances with those of acetate addition showed that they are slightly lower, since acetate addition resulted in 86% and 95% for N and P removal. Bolzonella *et al.*, (2001) reached a maximum denitrification rate of 5.5 mg N mg^{-1} VSS h^{-1}.

Table 2.6 Industrial wastes and their organic content

INDUSTRIAL WASTE	TCOD g l^{-1}	SCOD g l^{-1}	VFA g l^{-1}	**REFERENCE**
Fermented OFMSW*	80		29.3	Llabres *et al.*, (1999)
OFMSW	60-80	35 - 50	7 - 25	Bolzonella *et al.*, (2001)
Fermented food waste (TS=2%wv)		13	7.2	Lim *et al.*, (2000)
AFLFW**	37.2	29	9.5	Lee *et al.*, (2002)
Fermented swine wastes	22.8			Lee *et al.*, (1997)
Septic sludge	21.5	1.12		Morling (2001)
Wine distillery effluent	45.8	22.5	5.6	Bernet *et al.*, (1996)
Winery	19.7	17.5		Ruiz *et al.*, (2002)
Piggery	37.9 - 52.7		10 - 19.6	Choi and Eum (2002)
Farm dairy	6.6 - 9.9	3.7	0.27	Elwood and Mason (2003) Mason and Mulcachy (2003)
Distillery slopes (apple)	32	13.2		Baier and Schmidheiny (1997)
Brewery	1.8	1.5	0.074	Curto, (2001)
Peat wet carbonized	9.3 – 13.6	8.3 - 12.7	0.6 - 0.9	Ghosh *et al.*, (2001)
Nightsoil	53	79		Choi *et al.*, (1996)
Textile and domestic (4:1)	1	0.6		Bortone *et al.*, (1994)
Fermented vegetable market wastes			6	Lata *et al.*, (2002)
Milkpowder/butter	2.05			Donkin and Russel (1997)
Fermented farm dairy			1.96	Elwood and Mason (2003),

*Organic Fraction of Municipal Solid Waste

**Anaerobic Fermented Leachate of Food Waste

The production of VFA from food waste fermentation and their application to BNR in a SBR was investigated by Lim *et al.*, (2000). The removal of nitrogen and phosphorus improved from 44 and 37 % to 92 and 73%, respectively. Lee *et al.*, (2002) used the anaerobically fermented leachate of food waste (AFLFW) as an external carbon source for BNR in both domestic and synthetic wastewater. The removals of N and P were 74-77% and 67-68%, respectively. The denitrification rate of AFLFW was 8.2 mg NO_3-N g^{-1} VSS h^{-1}, smaller than that of acetate, but AFLFW has economical and environmental advantages. Table 2.7 summarizes the performances of P and N removal for processes with several industrial wastes as carbon source.

Table 2.7 BNR performances with different industrial wastes as the carbon source

CARBON SOURCE	Nitrogen removal %	Phosphorus removal %	Denitrification rate	**REFERENCE**
Fermented OFMSW	80	84	2.5 mg N g^{-1} VSS h^{-1}	Pavan *et al.*, (1998)
			2.2 mg N g^{-1} VSS h^{-1}	Llabres *et al.*, (1999)
			5.5 mg N g^{-1} VSS h^{-1}	Bolzonella *et al.*, (2001)
Fermented food waste	92	73		Lim *et al.*, (2000)
AFLFW	77	68	8.2 mg N g^{-1} VSS h^{-1}	Lee *et al.*, (2002)
Fermented swine wastes	90	89	3.2 - 7.3 mg N g^{-1} MLSS h^{-1}	Lee *et al.*, (1997)
Septic sludge	73	97.4	2.42 mg N g^{-1} MLSS h^{-1}	Morling (2001)
Wine distillery effluent	61	40	35.2 mg N g^{-1} VSS h^{-1}	Bernet *et al.*, (1996)
Nightsoil	53	79		Choi *et al.*, (1996)

Lee *et al.*, (1997) compared fermented swine wastes with acetate for supplementation on SBR for enhanced BNR. Both achieved a total nitrogen removal of 90% and total phosphorus of 89%. The denitrification rates with fermented swine wastes were similar to those with acetate. On the other hand, reactors with no supplementation achieved total N and P removals of 76 and 75%, respectively. Morling (2001) used septic sludge as a carbon source in a SBR plant, with P and N removal to be 97.4 and 73%, respectively. The use of a wine distillery effluent in a high strength wastewater was reported by Bernet *et al.*, (1996). The denitrification rate they reached was 35.2 mg N-NO_x g^{-1} VSS h^{-1}, which is comparable with results obtained with pure volatile fatty acids as the carbon source (Fass *et al.*, 1994). Nightsoil application to return activated sludge (RAS) showed significant improvements in nitrogen and phosphorus removal both in municipal and piggery wastes (Choi *et al.*, 1996).

Finally, the enhanced biological nutrient removal can be achieved by the combination of pre-treatments and addition of external carbon source. Banerjee *et al.*, (1999) and Maharaj and Elefsiniotis (2001) investigated the effect of the addition of potato-processing wastewater on the acidogenesis of primary sludge. The addition of that starch-rich wastewater, considerably improved the performances of the system, resulting in an increase in the net VFA and soluble COD (SCOD) concentrations, proving that the starch-rich wastewater has a positive effect on acidogenesis. The mean value of VFA concentration was 500 mg l^{-1}, which could be enough for EBPR. Thomas *et al.*, (2003) examined the addition of acetic acid or molasses in the primary sludge fermenter. The VFA production and phosphorus removal were greater with the molasses dosing, though acetate was expected to give better performances, since is considered as the best carbon source for the micoorganisms.

2.3 Sludge disintegration

During the biological step of activated sludge processes between 40 and 50% of the original pollution load in the influent wastewater is assimilated into new cellular biomass, turning a water pollution control problem into a solid waste disposal problem (Weemaes and Verstraete, 1998). A lot of interest has been devoted to sludge disintegration as a pre-treatment for the enhancement of further processing of sludge, which is aimed to reduce sludge mass production, reduce odours and increase biogas production. Sludge disintegration was introduced to solubilise and convert slowly biodegradable, particulate organic materials to low molecular weight, readily biodegradable compounds. A range of mechanical, thermal, chemical and biological pre-treatments of sludge to improve digestibility have been investigated. All of these methods are able to increase SCOD and VFA content. However, there is little information about the application of the treated sludge to BNR in order to improve P and N removal performances.

In the previous section it was mentioned that pre-fermentation of primary sludge can increase VFAs, which are the most suitable substrate for denitrification and EBPR.

Unfortunately, the use of pre-fermenters is not an easy solution, as they are not easy to be monitored and not easy to be modified if the performance is not the expected (Munch and Koch, 1999). In addition, during the pre-fermentation processes nutrients are also released and consequently, there is more P and N to be removed (Rossle and Pretorius, 2001).

On the other hand, mechanical disintegration of sewage sludge has a positive effect on various steps of sludge treatments. It is reported that mechanical disintegration can increase soluble COD, increase digestion efficiency and reduce sludge volume. Moreover, Muller (2000a and 2000b) has reported that disintegrated sludge can be a suitable carbon source for denitrification. The same author made a comparison of mechanical, thermal and chemical sludge treatment. The highest degree of disintegration was reached by the chemical (ozone) treatment, with the mechanical methods reaching medium degrees of disintegration with a relatively low energy input.

Chiu *et al.*, (1997) reported that with the chemical (alkaline) pre-treatment of waste activated sludge a 16 and 8 fold increase in soluble COD and VFAs, respectively, was reached. When a combination of alkaline pre-treatment and ultrasonic vibration, was used, a 41.5 soluble COD and 28 VFA fold was reached. The maximum solubilization in COD has been identified by ultrasound equipment with 50 fold increase in SCOD (Wang *et al.*, 1999). Withey (2003) used a deflaker technology from paper industry for sludge disintegration and reported a 10 fold increase in SCOD. The effect of different sludge disintegration processes on SCOD and VFA content is summarized in Table 2.8.

The mechanical disintegration can be separated into two categories. The first one is when the disintegration takes place with low energy input and causes floc-destruction and the second when high energy disintegration is used and causes cell-disruption. Hence, different kind of disintegration can be used, dependent on sludge application. When sludge is used as carbon source to enhance BNR, the floc-destruction will probably be enough for the increase of suitable substrate without releasing nutrients. When the main goal is mass reduction, the disintegration can go further to cell-disruption. The main and essential advantages of mechanical disintegration are that needs little information for design, is applicable in every wastewater treatment plant and can be used for a variety of purposes. On the other hand the main drawbacks are the energy consumption and the release of nutrients in the liquid phase.

Table 2.8 Sludge treatments and their effect to SCOD and VFAs

Treatment type	Soluble COD increase	VFA increase	REFERENCE
Chemical	19 fold		Lin *et al.*, (1997)
Alkaline	16.5 fold	8 fold	Chiu *et al.*, (1997)
Alkaline with ultrasonic vibration	41.5 fold	28 fold	Chiu *et al.*, (1997)
Ozonation	26 fold		Weemaes *et al.*, (2000)
Fermentation of food waste + ozonation	3 fold	11 fold	Kim *et al.*, (2005)
Thermal	30 fold	9 fold	Wang *et al.*,(1997)
Hydrothermal	7.6 fold		Shanableh (2000)
Thermochemical		5 fold	Tanaka and Kamiyama (2002)
Mechanical (jet smash technique)	6.5 fold		Choi *et al.*, (1997)
Mechanical (jet smash technique)	7 fold		Nah *et al.*, (2000)
Mechanical (Ball mill)	15 fold		Baier and Schmidheiny (1997)
Mechanical (stirred ball mill)	26.5 fold		Muller *et al.*, (2000a)
Mechanical (deflaker)	10 fold		Withey (2003)
Mechanical (lysate centrifuge)	5 fold		Doyanos *et al.*, (2000)
Mechanical (ultrasound)	7 fold		Zhang *et al.*, (2007)
Mechanical (ultrasound)	50 fold		Wang *et al.*, (1999)
Mechanical (ultrasound)	34.5 fold		Tiehm *et al.*, (1997)

2.4 Predictive tests

As it has been noted in section 2.1 the most important factor affecting biological nutrient removal is the available substrate with the presence of easily biodegradable organic matter. That means that the BNR process performance is directly dependent on the influent wastewater characteristics. In the past, many researchers tried to find key parameters for the prediction of the BNR performances of a site. The carbon content of the wastewater and its relation to the influent nitrogen and phosphorus concentration are the most frequently used.

2.4.1 EBPR prediction

The parameters that have been used for EBPR are the COD, BOD and VFA potential to influent total P ratios and their minimum requirements are presented in Table 2.9. The best ratio indicator to date is the VFA potential to influent total P (Curto, 2001). Unfortunately, the calculation of VFA potential requires a test that is completed in 15 days. Moreover, the sample potential (SP) developed by Thames Water could be the best current indicator according to Alvarez (2002) and Avendano (2003). The sample potential is a unitless number defined as the theoretical phosphorus release divided by the total incoming phosphorus concentration. The theoretical P release can be predicted by multiplying the VFA fractions by the appropriate constants, as have been shown by Abu-gararah and Randall (1991), (Table 2.11). According to Alvarez (2002) and Avendano (2003) the minimum value of SP for successful EBPR is 4.4.

Based on data found in the literature, the actual P removal from BNR reactors with the respective predictive parameter is demonstrated in Figure 2.7. There is no correlation between P removal and total COD to total incoming P ratio, as the two greatest values of TCOD:TP ratio (68 and 58) gave the highest and lowest P removal (97.4% and 68%, respectively). As above, VFA:P ratio is not able to predict the best EBPR performance with 67 and 21 of VFA:P ratio to give 98 and 95% of P removal, respectively. Furthermore, after calculating the SP, it was concluded that the highest SP will not give the highest P removal, but still can be considered as a good predictive parameter.

Table 2.9 Predictive parameters and their minimum requirements for EBPR

Reference	Ratio		Value
Carlson *et al.*, (1996)	COD:P	>	**50-70**
Randall *et al.*, (1992)	BOD:P	>	**20**
Cooper *et al.*, (1995)	BOD:P	>	**20**
Jeyanaygam (2000)	BOD:P	>	**20-25**
Alvarez (2002)	BOD:P	>	**20**
Alvarez (2002)	RBCOD	>	**11.5-13**
Abu-gararah and Randall (1991)	VFA_{pot}:P	>	**20**
Merseth and Stensel (1996)	VFA_{pot}:P	>	**16.5**
Johnsson *et al.*, (1996)	VFA_{pot}:P	>	**14**
Curto (2001)	VFApot:P	>	**14**
Stephens and Stensel (1998)	Acetate: $P_{removed}$	>	**16.5**

Table 2.10 Examples demonstrating that predictive ratios are not reliable indicators for EBPR.

Ratio	Value	P removal (%)	Reference
TCOD:P	21.6	95	Llabres *et al.*, (1999)
BOD:P	18.2	93.5	Avendano (2003)
VFA_{pot}:P	15	98	German *et al.*, (1998)

Table 2.11 Ratios of phosphorus released and fatty acids utilised under anaerobic conditions (Abu-gararah and Randall, 1991)

Volatile Fatty Acid	mg phosphorus released per mg COD utilised
Acetic	0.37
Propionic	0.12
Butyric	0.15
Valeric	0.22

Another method used for the prediction of EBPR is a laboratory test simulating the phosphorus release process, which is the carbon limited process for P removal (Park *et al.*, 2001; Tykesson *et al.*, 2002, Vale *et al.*, 2005). According to this test the anaerobic conditions were simulated and the concentration of released phosphorus from a mixture of PAOs-containing sludge and wastewater was measured for 2 hours. The phosphorus that can be removed was predicted by the relationship proposed by Wentzel (1985). Based on that test Avendano (2003) proposed a predictive parameter, which is the ratio of released phosphorus after 2 hours to the incoming phosphorus. If the value of the ratio is over 2 the wastewater is likely to be suitable for EBPR. This test could also be used to evaluate the effect of different carbon sources on EBPR process. However, the information available on this test is limited and requires further examination.

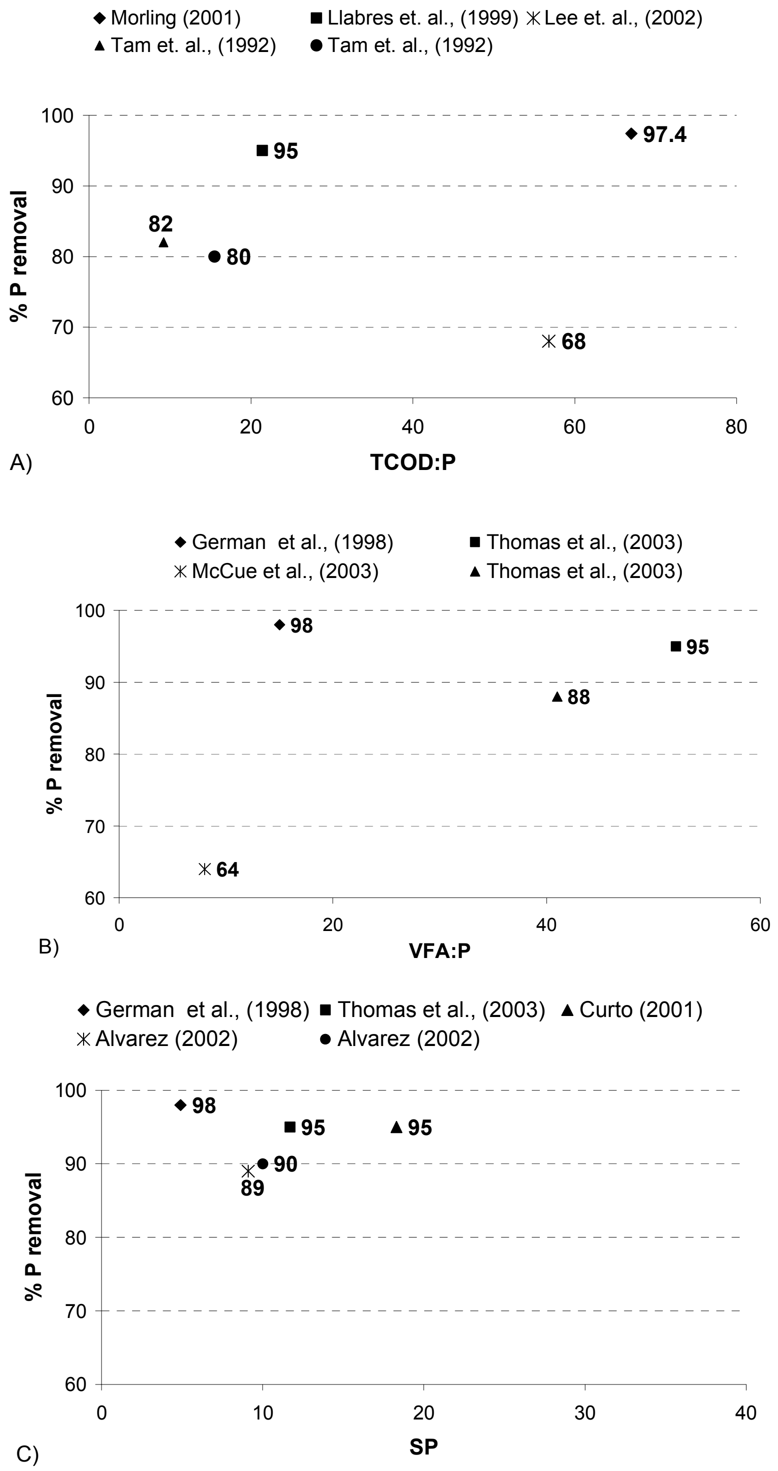

Figure 2.7 Phosphorus removal against A) TCOD:P ratio, B) VFA:P ratio and C) Sample Potential

Industrial wastes have been shown to enhance BNR process performances. The addition of a range of wastes with high organic matter to TP ratio into the incoming wastewater will cause an increase to the overall ratios, which means that the wastewater will be more suitable for EBPR (here we have compared industrial wastes in terms of their predictive ratios (Table 2.12)). The highest TCOD:P ratio was found to be at peat wet-carbonized wastewaters (652) and the highest VFA:P ratio at the fermented food wastes (162). The same wastes have the highest sample potential as well (25.9).

Table 2.12 The EBPR predictive parameters in different industrial wastes

Industrial wastes	TCOD:P	VFA:P	SP	Reference
Nightsoil	57	6.9	1.9	Choi *et al.*, (1996)
Fermented food waste		162	25.9	Lim *et al.*, (2000)
OFMSW*	243	55		Bolzonela *et al.*, (2001)
MSW	494			Llabres *et al.*, (1999)
Farm dairy	121	4	0.98	Mason and Mulcachy (2003)
Fermented farm dairy		23.4	11.7	Elwood and Mason (2003)
AFLFW**	200	51	7.86	Lee *et al.*, (2002)
Piggery	67.6	23		Choi *et al.*, (1996)
Peat wet-carbonized	633	50	18.8	Ghosh *et al.*, (2001)

* Organic Fraction of Municipal Solid Waste

**Anaerobic Fermented Leachate of Food Waste

2.4.2 Prediction of nitrogen removal

Contrary to EBPR, no predictive parameters have been suggested for biological nitrogen removal. Based on data from the literature we compared the N removal from wastewater with different TCOD to N ratio (Figure 2.9). This ratio was not able to predict the performance in terms of N removal. The key processes for nitrogen removal are nitrification-denitrification, of which the denitrification is carbon limited. For that reason, the test that could best indicate the success of nitrogen removal and has been used by many researchers is the Nitrate Utilization Rate (NUR) test, where the anoxic conditions are simulated (Naidoo *et al.*, 1998; Kujawa and Klapwijk, 1999; Lee *et al.*, 2002). The reduction rate of nitrates (denitrification rate) could be an indicator whether the wastewater is suitable for biological nitrogen removal. In addition, this test could be successfully used to compare different external carbon sources for the enhancement of denitrification

As with phosphorus, we compared the ratios of organic matter in terms of COD and VFA to nitrogen of some industrial wastes (Table 2.13). The highest TCOD:TKN and VFA:TKN have been found in the Organic Fraction of Municipal Solid Waste (OFMSW), 200 and 45 respectively. The addition of a waste with high TCOD:TKN ratio to the influent wastewater will increase the available organic matter for the denitrification process.

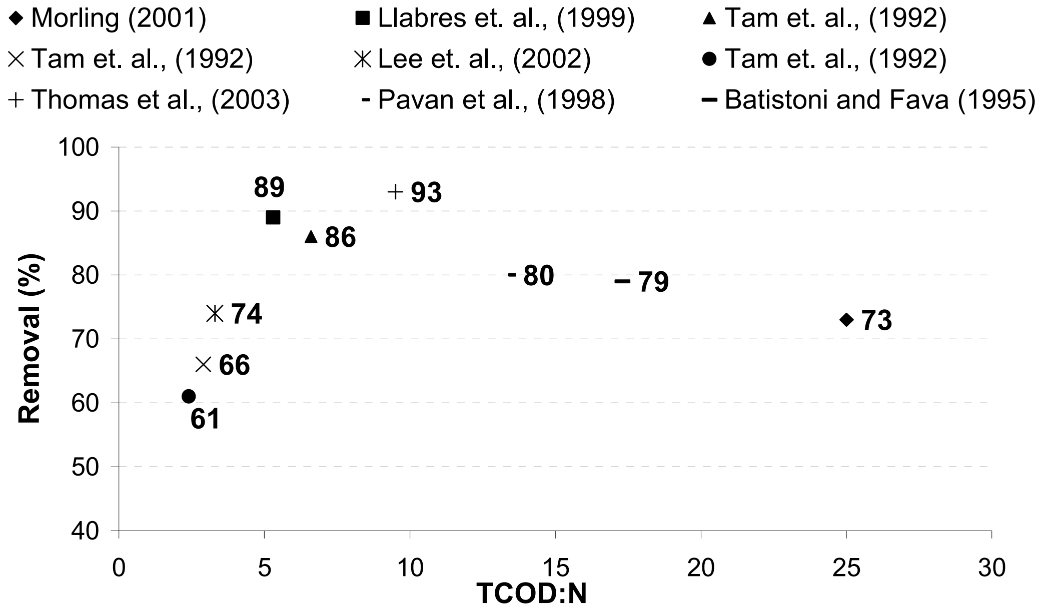

Figure 2.8 Nitrogen removal to TCOD:N ratio

Table 2.13 Predictive parameters for nitrogen removal in different industrial wastes

Industrial wastes	TCOD:TKN	VFA:TKN	Reference
Nightsoil	57	1.25	Choi *et al.*, (1996)
OFMSW*	200	45	Bolzonela *et al.*, (2001)
MSW	68		Llabres *et al.*, (1999)
Farm dairy	25.4	0.8	Mason and Mulcachy (2003)
Fermented farm dairy		2.6	Elwood and Mason (2003)
AFLFW**	19.7	5	Lee *et al.*, (2002)
Piggery	6.9	2.31	Choi *et al.*, (1996)
Meat processing	9		Thayalakumaran *et al.*, (2003)
Peat wet-carbonized	44.1	2.2	Ghosh *et al.*, (2001)

* Organic Fraction of Municipal Solid Waste

**Anaerobic Fermented Leachate of food Waste

2.5 Summary

Phosphorus and nitrogen are the key nutrients that cause eutrophication and therefore their concentrations in sewage effluents must be reduced. Biological nutrient removal is the most commonly used method to remove nutrients from wastewaters and since the nutrient content must be very low in sewage effluent water companies look for methods to improve the performances of BNR processes.

BNR is strongly affected by wastewater characteristics. It is necessary that wastewaters have enough carbon and in the appropriate form to be used by the microorganisms. To enhance BNR the carbon substrate typically needs to be increased and made more bioavailable. The most suitable carbon sources are the volatile fatty acids, which can improve both EBPR and denitrification.

During sludge pre-treatment processes a significant amount of COD is released in the liquid phase. The lack of carbon in the influent wastewater on one side and the extra carbon produced from sludge pre-treatments on the other makes us consider the disintegrated sludge as a potential carbon source. The idea of applying processed sludge to both carbon limited BNR processes (P release and denitrification) as an internal carbon source has not been examined.

The prediction of BNR potential has also been investigated. The carbon to phosphorus and carbon to nitrogen ratios have been found unreliable for indicating BNR potential. Batch laboratory tests simulating the phosphorus release process could be an alternative way for EBPR prediction. Similarly, nitrogen removal can be predicted by tests simulating the denitrification process under anoxic conditions. Both tests have the potential to be used for the comparison of external carbon sources.

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Chapter 3 Carbon release from activated sludge – A comparison of three disintegration processes

Ultrasonics Sonochemistry (Submitted)

3. Carbon release from activated sludge – A comparison of three disintegration processes

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Abstract

Mechanical disintegration of sewage sludge has a positive impact in various processes of wastewater sludge treatment. This research investigates three different mechanical devices including two ultrasound reactors and one mechanical homogenizer, which are compared in terms of carbon release and mechanism of disintegration related to energy input. The disintegration processes are examined on return activated sludge (RAS) and thickened surplus activated sludge (SAS) samples. The increase in soluble chemical oxygen demand (SCOD) during the disintegration varied from 50 to 1300 mg l^{-1} for RAS and from 550 to 9100 mg l^{-1} for thickened SAS, depending on the equipment and the energy input. All the devices were able to cause particle size reduction (the final median particle size was ~40 and ~21 μm for RAS and thickened SAS samples, respectively) and differences in their performance appeared due to the temperature and the different ultrasound generators.

Keywords mechanical disintegration, activated sludge, ultrasound, deflaker, pretreatment, particle size, SCOD, specific energy

3.1 Introduction

During the biological step of activated sludge processes between 40 and 50% of the original pollution load in the influent wastewater is assimilated into new cellular biomass, turning a water pollution control problem into a solid waste disposal problem (Weemaes and Verstraete, 1998). Excess sludge production in a wastewater treatment plant (WWTP) usually represents only 1-2% of the total flow of sewage but the cost of excess sludge treatment for subsequent disposal or reuse can account up to 30-60% of the total running cost of the works (CIWEM, 1995; Wei *et al.*, 2003). Changing and more restrictive legislation has made sludge disposal more difficult and expensive (Campbell, 2000), as a consequence there is a great interest in developing methods for improving the recycling and reuse of excess sludge (Muller, 2000a).

Sludge disintegration induces structural changes, floc and cell breakage, intra and extra cellular solubilisation and stress on microbial community and hence can reduce bulking and foaming, enhance dewatering, provide extra carbon source for biological nutrient removal, reduce sludge growth and enhance biodegradability during anaerobic digestion (Boehler and Siegrist, 2006; Lehne *et al.*, 2001; Yin *et al.*, 2004).

Many studies have investigated a variety of methods based on different disintegration technologies such as mechanical (including ultrasound) (Muller 2000b; Mason 2000; Lehne *et al.*, 2001; Neis *et al.*, 2001; Kampas *et al.*, In Press (Chapter 4)), chemical (Chiu *et al.*, 1997; Yeom *et al.*, 2002; Dytczak *et al.*, 2007), thermal (Kepp *et al.*, 2000) and biological (Barjenbruch and Kopplow, 2003).

The efficiency of the disintegration techniques can be evaluated in terms of the increase in chemical oxygen demand in soluble phase (SCOD). The high release in organic material in combination with economical energy consumption is essential for the beneficial use of disintegration in sludge treatment. Mechanical disintegration has been proved to be efficient due to sufficient SCOD release and their relatively low capital cost and energy consumption (Muller 2000a).

In this paper a mechanical device is investigated and compared with two different types of ultrasonic systems. The mechanical device under study, a deflaker, has already been used is the paper industry. The potential to be adapted as an ‘off-the–shelf’ technology and their simple and flexible design makes deflakers a promising method (Withey, 2003). The two sonicators under study, a high intensity radial horn and low intensity dual frequency processor, are good examples of the variety of different designs available. The three systems are compared in terms of sludge solubilisation, energy input and mechanism of action.

3.2 Materials and Methods

3.2.1 Activated sludge

Both RAS and thickened SAS used in this study were grab samples collected from the RAS line and immediately after the belt thickener for RAS and SAS, respectively, from a WWTP that operates in biological nutrient removal (BNR) mode. The total solid (TS) concentration was ~9 g l^{-1} for RAS and ~ 56 g l^{-1} for thickened SAS. The comparison of the performance of the three equipment in terms of mechanical disintegration was carried out in the same fresh (less than three hours storage time) RAS and thickened SAS samples.

3.2.2 Equipment

Three different equipments were examined in this study in terms of release of organic matter investigating the original sources of the released carbon, taking into account the role of temperature and energy input. For that reason, each equipment was used with three different energy doses, which correlates to three different retention times of treatment for both RAS and thickened SAS samples.

The first is a dual frequency sonicator with two magnetostrictive transducers, purchased from Advanced Sonic Processing Systems (USA). It operates with the frequencies of 16 kHz and 20 kHz, the power input varies from 0 to 100% of 2.4 kW and is considered a low intensity sonicator. The different frequencies make the device more efficient due to minimisation of "dead" spots in the system. That means that the biomass is very likely to get close to a bursting cavitation bubble, which will cause disintegration (Feng *et al.*, 2002). During the experiments it was always operated at the maximum energy input. In addition, the system is temperature controlled thanks to cooling manifolds underneath the transducer covers where cold water is injected and flows off by gravity. The ultrasound reactor was a rectangular narrow (6.3 mm width) pipe with 0.205 l active volume. The RAS and thickened SAS samples pass from that pipe to be sonicated by a peristaltic pump delivering different flow rates equivalent to three different retention times (30, 60, and 180 seconds). These experiments were conducted with the temperature control on. Finally, the sonication of RAS and thickened SAS was repeated at retention time of 60 seconds and without the temperature being controlled. All the equipments are summarised and described in Table 3.1.

The second ultrasonic reactor was the radial ultrasound probe SONIX^{TM} manufactured by Purac Ltd and provided for this research by Anglian Water (Table 3.1). The specific probe used in this study was a prototype and not the developed latest version that currently is on market by Purac Ltd. This ultrasonic processor, which is consisted of a piezoelectric transducer and a titanium probe, operates at 20 kHz frequency and 3 kW maximum power. During the experiments the power input was 2.2 kW. The experiments were conducted in a beaker with the RAS and thickened SAS samples to cover the radial horn. The volume of the samples was 1.5 l and the sonication time 30, 60 and 120 seconds.

Finally the third mechanical device used in this study was a 10” Pilao DTD Spider Deflaker with a 30 kW motor fitted with 230 mm discs with 3 active cell layers (Table 3.1). The gap distance between stator and rotor was 0.6-0.9 mm and the rotation speed 3000-3600 rpm, (Withey 2003). The disintegration process was conducted as a batch with five litres of thickened SAS to be treated each time at three different retention times, 2, 5 and 10 minutes.

To quantify maximum carbon release from the samples a thermal extraction method was used, which was a modification of a method reported by Zhang *et al.*, (1999) for the extraction of extracellular polymers. The thermal extraction method could give similar results to other methods for complete disintegration, destroying not only flocs but also cells (Lehne *et al.*, 2001; Muller 2000b). During that method RAS or thickened SAS was left for an hour under the conditions of 1bar and 105^{o}C.

Table 3.1 The equipments used in this study with their characteristics

Equipment type	**Radial horn**	**Dual frequency processor**	**Deflaker**
Manufacturer	Purac Ltd (UK)	Advanced Sonic Processing Systems (USA)	PILAO (Austria)
Transducer type (Frequency)	Piezoelectric (20 kHz)	Magnetostrictive (16 & 20 kHz)	NA
Power input (Maximum power)	2.2 kW (3 kW)	2.4 kW (2.4 kW)	5.7 kW (30 kW)
Reactor volume	1.5 l	0.205 l	5 l
Power intensity	38 W cm^{-2}	5 W cm^{-2}	NA
Power density	1.46 W ml^{-1}	11.7 W ml^{-1}	1.14 W ml^{-1}
Temperature control	No	Yes/No	No

3.2.3 Analysis

Particle size analysis was carried out using a Malvern Mastersizer 2000 (Malvern, UK). The Mastersizer uses an optical unit to detect the light scattering pattern of sludge particles dispersed in deionised water. High performance size exclusion chromatography (HPSEC) was carried out using high performance liquid chromatography (HPLC) (Shimadzu VP Series, Shimadzu, UK) with UV detection set at 254 nm and a BIOSEP-SEC-S300 column (Phenomenex, UK). For each sample a chromatogram of absorbance against time was produced. Larger molecular size compounds were eluted from the column first and smaller molecules later.

The temperature was measured immediately after the completion of the test. Apart from the total solids all the other analysis were carried out in the filtered (0.45 μm) supernatant of the untreated and treated sample after centrifugation (10500 g, 7°C). The concentration of Total Solids (TS), volatile fatty acids (VFAs) and soluble COD (SCOD) was measured according to APHA Standard Methods (1998). The soluble protein content was determined according to standard protein method by Branford (1976) with a protein diagnostic kit (Sigma, England). The concentration of soluble proteins was determined from a standard curve constructed using bovine serum albumin (P0914 Sigma – Aldrich, Gillingham, UK) in deionised water, as the standard. Soluble carbohydrate concentrations were determined using the phenol sulphuric method introduced by Dubois *et al.*, (1956). Carbohydrate concentration was calculated from a calibration curve constructed using a glucose standard.

3.3 Results – Discussion

This study investigates the performance of three different equipments used for activated sludge disintegration. The comparison was made in terms of carbon release and energy input, where the results are separated for RAS and thickened SAS due to the significant difference in solid concentration (9 and 56 g l^{-1} for RAS and thickened SAS, respectively) and also in terms of the mechanism of disintegration for the three processes.

3.3.1 Carbon release and energy input

RAS samples

Initially the effect of temperature increase on the concentration of SCOD was examined (Figure 3.1). The dual frequency processor operated with temperature control and hence the temperature even after 180 seconds of sonication increased only by 6^{o}C. On the contrary, the radial horn caused an increase in temperature of 28^{o}C and the deflaker increased the temperature by 75^{o}C. A similar temperature increase (~50^{o}C) was observed during sonication by a 20 kHz probe of a RAS sample with a solid concentration similar to this study (8.2 g l^{-1}) (Chu *et al.*, 2001). The increase in temperature during disintegration by the deflaker is a result of friction between the active layers and the sample. When the dual frequency processor operated without temperature control the temperature increased by 40^{o}C due to cavitation effects and also due to low energy efficiency of the magentostrictive transducers (Horst and Hoffman, 1999).

The highest increase of SCOD (1515 mg l^{-1}) was reported for the dual frequency processor operated without temperature control. The amount was similar to the maximum release produced by the thermal extraction method (1998 mg l^{-1}), which is expected as the combination of thermal and ultrasound treatment is very effective for disintegration. The temperature makes bacterial cells more susceptible to cavitational forces, most likely by weakening bacteria cell walls (Save *et al.*, 1994). Grönroos *et al.*, (2005) examined the effect of temperature on sludge, with and without ultrasound treatment and observed a 90% higher SCOD when the sludge (1.5 % TS) was disintegrated by the combination of thermal (50°C) and ultrasound (20 kHz for 30 min) than thermal alone (50°C). The mechanical shear forces of deflaker were not able to cause the same SCOD increase as the cavitational forces, even when the temperature of the sludge reached 93°C.

The results from the disintegration in terms of SCOD by the three equipments compare well with previous reports on a mechanical device increasing the pressure of the sludge up to 50 bar with a pressure pump and then sends it through a nozzle (diameter of 2.45 mm) to a collision plate located 29.5 mm away from the nozzle (Choi *et al.*, 1997; Nah *et al.*, 2000). Although the solid concentration of the sludge was around 20 g l^{-1}, which is higher that the solid concentration of sludge tested in this study (9 g l^{-1}), the SCOD increase was similar (100-650 mg l^{-1}).

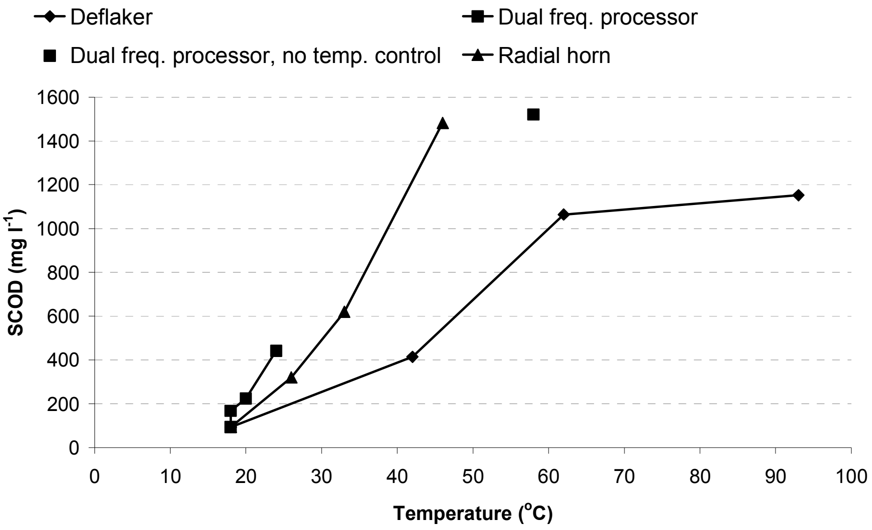

Figure 3.1 The SCOD increase in RAS as a function of temperature for the three disintegration processes

Alongside SCOD the concentration of VFA, proteins and carbohydrates was also measured (Table 3.2). Again the longer disintegration times gave the greatest release of organic material and the combination of ultrasound treatment with high temperature was very effective for sludge disintegration.

Table 3.2 VFA, proteins and carbohydrates release from RAS (0.9% TS) treated with dual frequency processor, radial horn and deflaker for different retention times, compared with untreated samples and thermal extraction method

	Untreated	**Dual frequency processor**				**Radial horn**			**Deflaker**			**Thermal Extraction**
		30 sec	60 sec	180 sec	No temp. control 60 sec	30 sec	60 sec	120 sec	2 min	5 min	10 min	
RAS												
VFA (mg l^{-1})	7	26	37	54	95	59	72	151	25	58	76	110
Proteins (mg l^{-1})	12	18	21	91	560	124	298	457	72	326	438	734
Carbohydrates (mg l^{-1})	1.3	13	18	23	271	19	37	130	19	155	145	458

The energy input in correlation with SCOD increase and particle size reduction was examined for all three processes. The release of 280 mg l^{-1} SCOD required 210000, 15000 and 5000 kJ kg^{-1} TS from the dual frequency processor, the deflaker and the radial horn, respectively (Figure 3.2). According to Gronroos *et al.*, (2005) the application of 2000-15000 kJ kg^{-1} TS ultrasound from a 27 kHz reactor in activated sludge with 2.45% TS caused an increase of 150-3200 mg l^{-1} in SCOD concentration, which compares well with the results from the radial horn in this study despite the difference in solid concentration.

The dual frequency processor requires much more energy (42 and 14 times more than the radial horn and the deflaker, respectively) for the same release of SCOD, compared to the other equipments, even though the power density was 8 and 10 times higher than the density in the radial horn and the deflaker, respectively. The first reason is that the dual frequency processor is the only equipment that was operated with temperature control. When the dual frequency processor was also operated without temperature control, SCOD release is 1515 mg l^{-1} at around 75500 kJ kg^{-1} TS, which is higher than both the deflaker and the radial horn. Another reason is that the magnetostrictive transducers of the dual frequency processor although there are reliable and durable (Hunicke, 1990) are less efficient than the piezoelectric of the radial horn as a consequence of the extra conversion step required to generate the magnetic field and of the magnetic hysteresis effects (Horst and Hoffmann, 1999; Keil and Swamy, 1999).

Finally, intensity plays a major role in sludge biomass disintegration performances: the higher the intensity the higher the degree of disintegration. Sludge disintegration is due to hydromechanical shear forces and requires high energy inputs and at a specific energy input, better results can be obtained using higher powers for shorter periods, i.e. higher power densities and, hence, intensities (Grönroos *et al.*, 2005; Neis *et al.*, 2001). Moholkar *et al.*, (1999) on the base of mathematical simulations, showed that, by increasing the intensity, the amplitude of ultrasound is increased together with the magnitude of the pressure pulse generated by the imploding cavitational bubbles and hence the magnitude of the hydromechanical forces, causing floc and cell disrupture. Tiehm *et al.* (2001) reported a 12% increase in the degree of disintegration between 1.0 and 1.5 W cm^{-2} of intensity, when using the same system of 40000 kJ kg^{-1} TS. Neis *et al.*, (2000) found that the release of SCOD was doubled when intensity increased from 6 to 8 W cm^{-2} using a 31 kHz frequency sonicator (3.8 kW). It is reminded that the power intensity of the radial horn is 7.6 times greater than the intensity of the dual frequency processor (38 and 5 W cm^{-2}, respectively). The difference in performances found between a low and high intensity system in this paper is in agreement with the data produced by Nickel (2005), where the SCOD release at ~1500 kJ kg^{-1} TS was four times greater in the high intensity system equipped with five horns along the flow path than the low intensity system equipped with multiple disk transducers mounted on the walls of a tube shaped reactor.

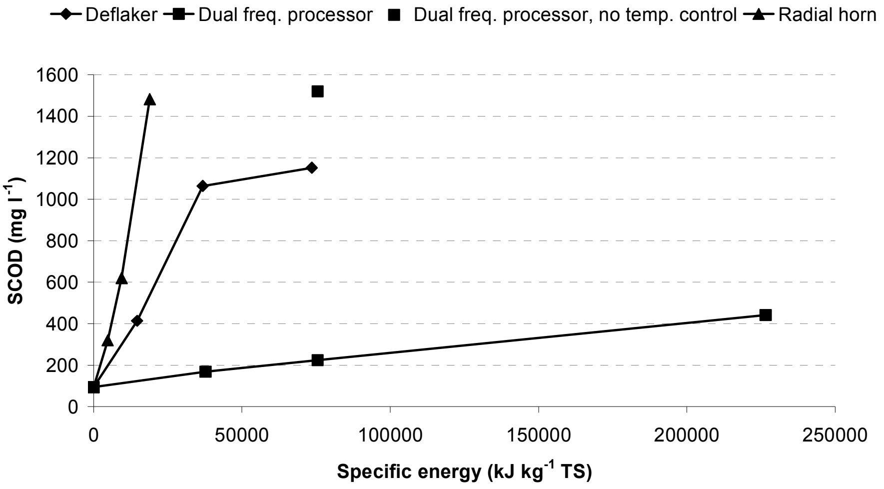

Figure 3.2 The SCOD increase in RAS as a function of the energy input for the disintegration processes

The reduction in particle size shows that all the equipment can initially reduce the size of the particles in the sludge with the radial horn giving the smallest median particles (35 µm) (Figure 3.3). The longer disintegration in the deflaker and in the dual frequency processor does not cause any further reduction compared to the radial horn. Wastewater sludge consists of porous flocs (120µm) and microflocs (13µm) (Jorand *et al.*, 1995). In this study the size of the porous flocs in raw sludge was lower (~52 µm) and these flocs were not totally destroyed leading to a median particle size of 40 µm after disintegration by the dual frequency processor and the deflaker and 35 µm after disintegration by the radial horn, requiring 226000, 73000 and 19000 kJ kg^{-1} TS, respectively. A 25% reduction in particle size achieved by all processes, but with the consumption of 75000, 36000 and 9000 kJ kg^{-1} TS for the dual frequency processor, the deflaker and the radial horn, respectively. Mao *et al.*, observed that for the same particle size reduction (25%) using an ultrasound reactor (20 kHz, 200 W), ~14000 kJ kg^{-1} TS was required. In addition, when an ultrasonic homogenizer (200 kHz) disintegrated sludge with similar solid concentration to this study (11.4 g kg^{-1}) reached the same degree of particle size reduction (25%) with the specific energy consumption of 1500 kJ kg^{-1} TS (Lehne *et al.*, 2001).

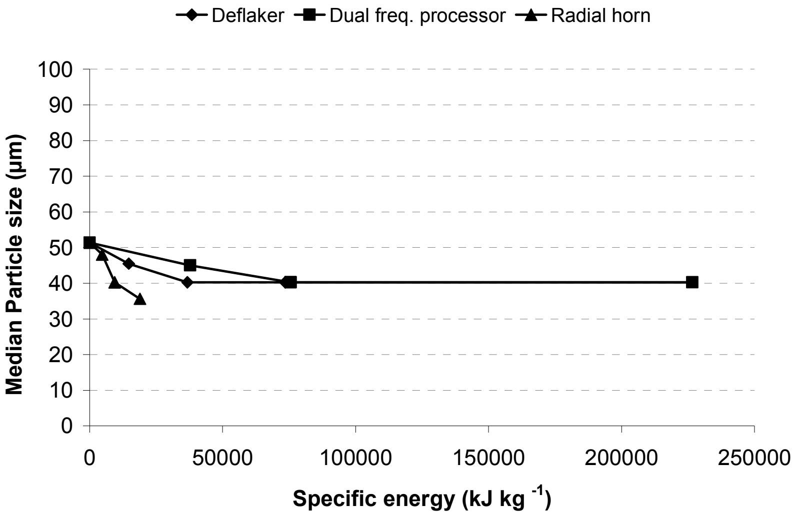

Figure 3.3 The mean particle size reduction in RAS in correlation with the energy input for the three disintegration processes

Thickened SAS samples

The thickened SAS samples disintegrated by the three processes contained a solid concentration of 56.7 g l^{-1}. The carbon release was evaluated in terms of SCOD, VFA proteins and carbohydrates (Table 3.3). The SCOD was also examined as a function of temperature for the three disintegration processes (Figure 3.4). The temperature increase was the same as the one that took place under the same conditions for RAS samples for the dual frequency processor and the radial horn but significantly lower for the deflaker (37°C compared to 93°C). Again here the temperature appears to play a major role in disintegration of biosolids as according to the results from the dual frequency processor 3 times longer disintegration with steady temperature released 6630 mg l^{-1} of SCOD (or 71%) less than when the temperature was controlled.

The SCOD released in this research (from 200 to 2600-9300 mg l^{-1}) compares well with the release reported in other studies. For example, Wang *et al.*, (2006) reported a SCOD release from a 3% TS sludge, ranging from 2000 to 10000 mg l^{-1} for a long disintegration time of 5 to 30 minutes with an ultrasound probe at 20 kHz and ultrasonic density lower than the one used in this study, at 0.96 W ml^{-1}. In addition, Mao *et al.*, (2004) using a 20 kHz ultrasound probe at ultrasonic density of 3 W ml^{-1} from 1 to 20 minutes sonication reported an increase in SCOD from 1000 to 4000 mg l^{-1}. In this study the radial horn, the deflaker and the dual frequency processor were operated at power density of 1.46, 1.14 and 11.4 W ml^{-1}, respectively. Finally, Kampas *et al.*, (In Press) (Chapter 4) examined the disintegration of thickened SAS by the deflaker for a wide range of disintegration time. The 10 minutes disintegration gave higher SCOD release than observed in this study, which is explained by the lower solid concentration of thickened SAS here (5.6 compared to 7.1% TS).

Table 3.3 VFA, proteins and carbohydrates release from thickened SAS (5.6% TS) treated with dual frequency processor, radial horn and deflaker for different retention times, compared with untreated samples and thermal extraction method

	Untreated	**Dual frequency processor**				**Radial horn**			**Deflaker**			**Thermal Extraction**
		30 sec	60 sec	180 sec	No temp. control 60 sec	30 sec	60 sec	120 sec	2 min	5 min	10 min	
						Thickened SAS						
VFA (mg l^{-1})	15	30	65	140	440	74	184	728	80	140	210	651
Proteins (mg l^{-1})	18	134	274	750	1788	415	1015	1952	325	557	793	3868
Carbohydrates (mg l^{-1})	20	49	156	400	581	133	277	602	199	298	407	667

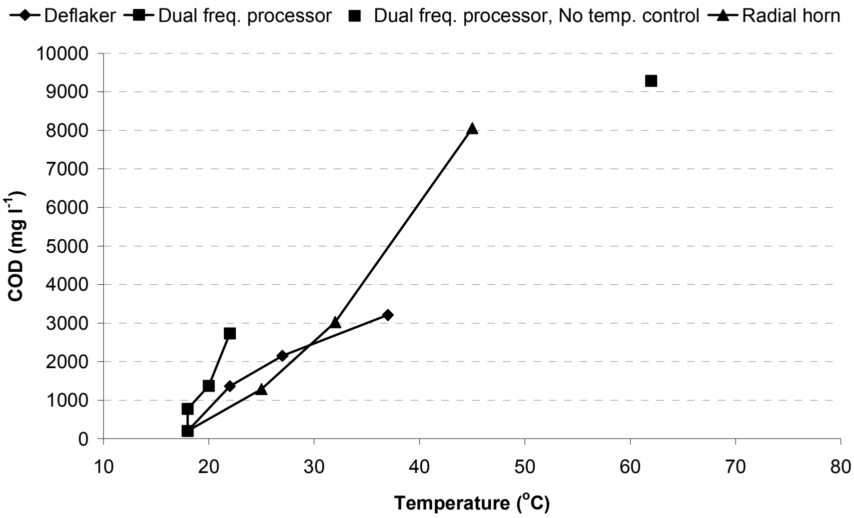

Figure 3.4 The SCOD increase in thickened SAS as a function of temperature for the three disintegration processes

The radial horn appeared to be the most energy efficient among the three equipments with the specific energy of 3000 kJ kg^{-1} TS to give a SCOD concentration of 8000 mg l^{-1} (Figure 3.5). For the same amount of specific energy the concentration of SCOD was

1500 and 400 mg l^{-1} for the deflaker and the dual frequency processor, respectively. These results compare well with the maximum concentration of SCOD that observed by Gronroos *et al.*, (2005), when an ultrasonic reactor (27 kHz) was used to disintegrate sludge (2.45% TS). The SCOD concentration was ~4000 mg l^{-1}, consuming 14500 kJ kg^{-1} TS. In this study, the radial horn disintegrated thicker sludge (5.6% TS) and the maximum SCOD concentration was 8000 mg l^{-1}, while it required 4700 kJ kg^{-1} TS. The dual frequency processor caused less SCOD release (2685 mg l^{-1}) with higher energy input (37000 kJ kg^{-1} TS). This significant difference between the two ultrasonic devices tested in this study can be explained by the lower power intensity of the dual frequency processor (5 W cm^{-2}) compared to the radial horn (38 W cm^{-2}) and also by the different transducer type, as was previously explained.

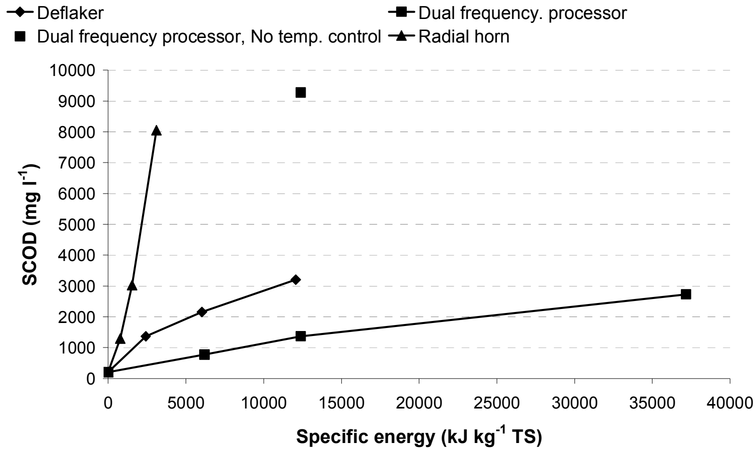

Figure 3.5 The SCOD increase in thickened SAS in correlation with the energy input for the three disintegration processes

The particle size reduction as a function of energy input was also investigated in the thickened SAS samples (Figure 3.6). The particle size of the raw thickened SAS was 3 times higher than the one in RAS due to the flocculation and thickening process. There was a rapid reduction in the particle size even for low energy input. The radial horn reduced the particle size from ~155 μm down to ~31 μm when operated at 60 seconds or using 1500 kJ kg^{-1} TS of specific energy. The deflaker caused even further reduction (~21 μm) but with 2400 kJ kg^{-1} TS. The dual frequency processor caused the least reduction in sludge particle size (~45 μm) with the higher energy input (37000 kJ kg^{-1} TS), All the above results are in agreement with the data reported in the literature for particle size reduction due to mechanical disintegration (Jorand *et al.*, 1995; Muller 2000a; Lehne *et al.*, 2001; Chu *et al.*, 2001; Mao *et al.*, 2004 and Kampas *et al.*, In Press (Chapter 4). In particular Mao *et al.*, (2004) reported that for the reduction of the particle size of sludge (2.88% TS) to 15 μm with an ultrasonic reactor (20 kHz, 200 W), 64800 kJ kg^{-1} TS was required. Similarly Lehne *et al.*, (2001) reported that the floc size reduction (15 μm) of 1.1% TS sludge with an ultrasonic homogenizer (200 kHz) occurred with energy input of 3000 kJ kg^{-1} TS.

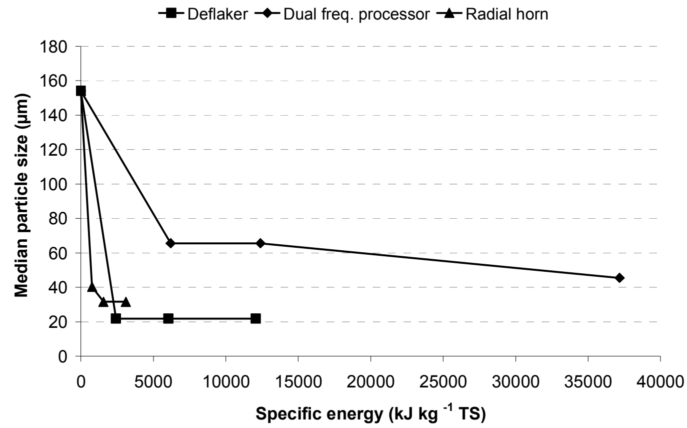

Figure 3.6 The mean particle size reduction in thickened SAS in correlation with the energy input for the three disintegration processes

3.3.2 Mechanism of disintegration

The disintegration by the three processes has been evaluated in terms of carbon release and particle size reduction. However, is not clear if this is a result of defloculation or cell lysis. In order to investigate this further we have attempted to "fingerprint" the organic released in terms of molecular size using the high performance size exclusion chromatography (HPSEC). The chromatographs are shown in Figure 3.7 and the large molecular materials appear first (lower time) in the produced graphs, while the smaller ones come later. The large materials are polymeric substances and are typically found outside of the cells and the smaller compounds considered being intracellular and appear in liquid phase as a result of cell lysis (Jorand *et al.*, 1995). Based on that technique, longer disintegration produced intracellular material, while shorter disintegration times produced only large molecular size compounds (extracellular).

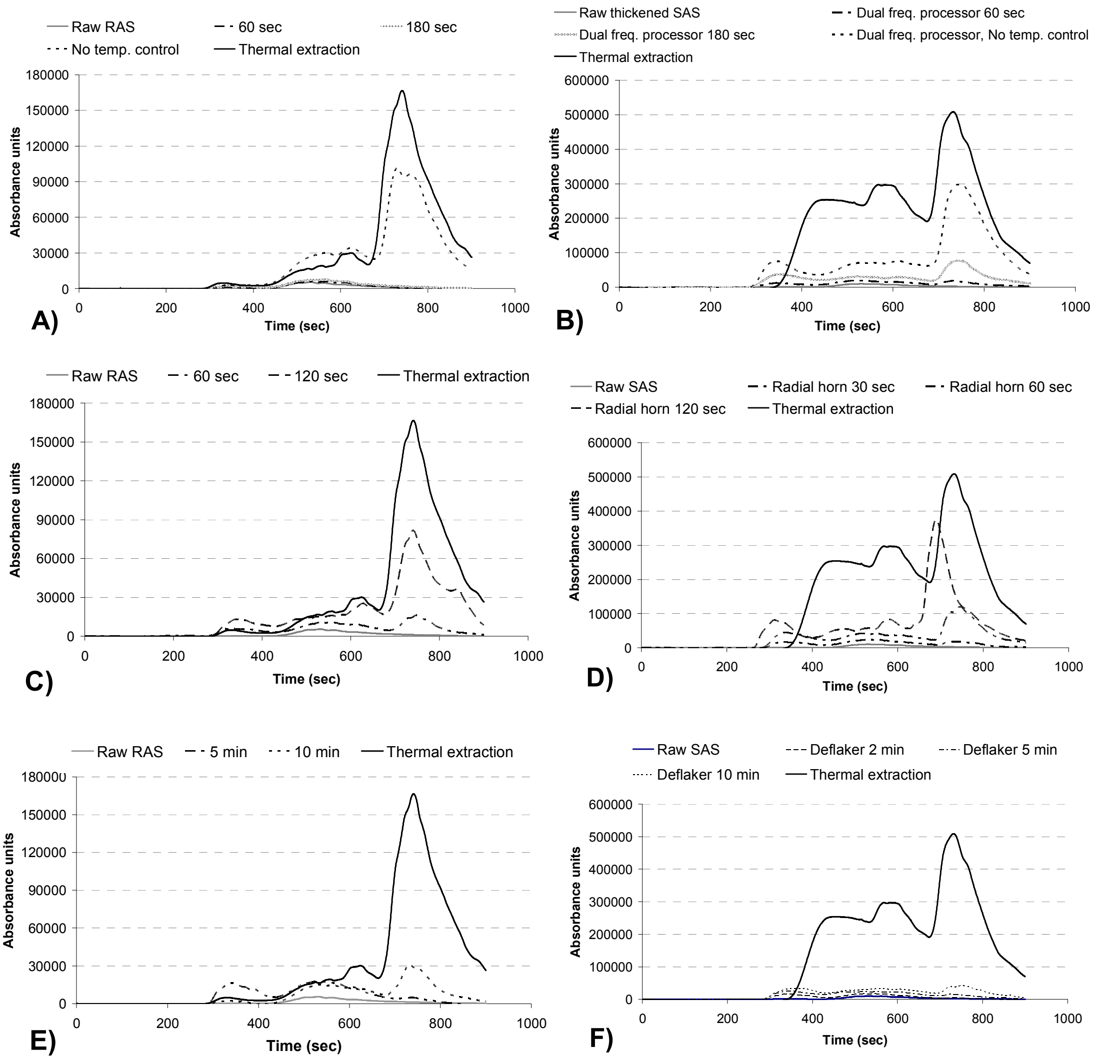

Figure 3.7 HPSEC results for RAS and thickened SAS A) and B) disintegration from the dual frequency processor, C) and D) disintegration from the radial horn and E) and F) disintegration from the deflaker

The thermal extraction method, which does cause cell lysis was confirmed here by the significant peak at ~800 seconds in the graph from HPSEC. It can also been seen that the extracellular material has not been destroyed by the thermal extraction method and their absorbance is similar with the extracellular compounds produced by mechanical disintegration. This is an indication that the late peak in the graphs (Figure 3.7) for the different equipment is not because of the destruction of the polymeric compounds, but due to the cell lysis, which releases material with smaller molecular size. It can been seen that cell lysis takes place at the no temperature control test for the dual frequency processor, at the disintegration of 120 seconds for the radial horn and to a smaller degree at the 10 minutes disintegration in the deflaker. This is in agreement with the carbon release data, when the longer disintegration gave more organics material produced, which initially comes from floc destruction and then from the breakage of the cell walls, as many researchers have reported (Wang *et al.*, 1999; Mao *et al.*, 2004 and Wang *et al.*, 2006).

Comparing the three equipments the radial horn is able to cause cell lysis, the dual frequency processor can cause cell lysis mainly when is operated without temperature control and finally the deflaker destroys the flocs but cell lysis is not as obvious.

3.4. Summary – Recommendations

All the equipment tested was able to cause sludge disintegration the degree of which depends on the energy that was consumed and the solid concentration of the sludge. The dual frequency processor performed better in terms of SCOD release when operated without temperature control. The deflaker was more efficient in terms of carbon release when was used on the thicken SAS samples. The radial horn required the least specific energy among the three devices for the production of the same amount of SCOD for both RAS and thickened SAS samples. Finally, all the examined processes were able to decrease the particle size of sludge and to cause similar mechanism of disintegration, but with different energy requirements.

They have been used under conditions, which were as close as possible to those used in full scale applications and comparisons with devices used in laboratory scale are not fair. For example Mao *et al.*, (2004) reported a good performance in terms of solubilisation and reduction in particles for a lab scale ultrasound reactor with low power output (0.4 kW) disintegrating 50 ml of sludge for 10 to 50 minutes. Alike, Kampas *et al.*, (In Press) (Appendix) reported a ~40 times increase in SCOD disintegrating the sludge with a 550 W lab sonicator for 30 to 70 minutes.

The solid concentration in sludge plays significant role in the performance of the devices used for disintegration. Comparing the results from disintegration of RAS and thickened SAS, is clear that all the equipments need 6 times less energy to cause higher degree of disintegration in thickened SAS than in RAS (2.9-7.8 times more SCOD released from thickened SAS than RAS samples). Many researchers have reported that the high energy ultrasound and short retention time is more efficient than the low energy and long retention time, for the same energy consumption (Gronoos *et al.*, 2005 and Zhang *et al.*, 2007). In this study we showed that the temperature and the type of the ultrasound generator in terms of transducer type and power intensity are very important factors and can determine the performance of the equipment. The temperature effect though has to be ignored for full scale applications, as the high flows will not cause any temperature increase. In addition, is well known that the piezoelectric transducer is more effective than the magnetostrictive. The factor that appeared in this research to play a major role in sludge disintegration by ultrasound is the power intensity of the ultrasonic equipment, which can decide its efficiency.

Finally, we have to take two other parameters into account in order to complete the comparison such as the capacity and the cost. Indisputably, all the equipments have to pass through the optimization process before they can be used in full scale application at a wastewater treatment plant, which can affect their performance either way. In Table 3.4 an evaluation of the three examined equipment is presented in terms of four different factors. The ability to solubilize the sludge and the energy requirements based on the results from this study and the capacity (amount of sludge can treat) and the costs based on calculations and market research, respectively (data not shown). Definitely, each factor has a different gravity dependant on the purpose of the application, which cannot be taken into account at this phase. The dual frequency processor was evaluated for the temperature controlled operation, as the high flows in full scale will not allow the temperature to rise.

Table 3.4 Evaluation of the three equipments in terms of sludge solubilisation, energy input, capacity and cost

	Solubilisation	Energy input	Capacity	Cost	
				Capital	Maintainance
Dual frequency processor	+	+	++	++	++
Radial horn	+++	+++	+++	+	+
Deflaker	++	++	+	+++	+++

Most efficient among the three = +++, ++, + = least efficient among the three

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Chapter 4 Mechanical sludge disintegration for the production of carbon source for biological nutrient removal

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4. Mechanical sludge disintegration for the production of carbon source for biological nutrient removal

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ABSTRACT

The primary driver for a successful biological nutrient removal (BNR) is the availability of suitable carbon source, mainly in the form of volatile fatty acids (VFA). Several methods have been examined to increase the amount of VFAs in wastewater. This study investigates the mechanism of mechanical disintegration of thickened surplus activated sludge (SAS) by a deflaker technology for the production of organic matter. This equipment was able to increase the soluble carbon in terms of VFA and soluble chemical oxygen demand (SCOD) with the maximum concentration to be around 850 and 6530 mg l^{-1}, for VFA and SCOD, respectively. The particle size was reduced from 65.5 μm to 9.3 μm after 15 minutes of disintegration with the simultaneous release of proteins (1550 mg l^{-1}) and carbohydrates (307 mg l^{-1}) indicating floc disruption and breakage. High performance size exclusion chromatography (HPSEC) evaluated the disintegrated sludge and confirmed that the deflaker was able to destroy the flocs releasing polymeric substances that are typically found outside of cells. When long disintegration times were applied (≥10 minutes or ≥9000 kJ kg^{-1} TS of specific energy) smaller molecular size materials were released to the liquid phase, which are considered to be found inside the cells indicating cell lysis.

Keywords activated sludge, biological nutrient removal, carbon source, cell lysis, mechanical disintegration, particle size, polymers

4.1 Introduction

Biological nutrient removal (BNR) is widely used in modern municipal and industrial wastewater treatment plants. A significant factor in the success of the BNR process is the availability of a suitable carbon source. Many authors have reported a specific ratio of carbon to phosphorus (P) and carbon to nitrogen (N), which can indicate the suitability of the wastewater for BNR treatment (Johnsson *et al.*, 1996; Randall *et al.*, 1992; Grady *et al.*, 1999 and Curto 2001). The most common methods for increasing these ratios and hence make the wastewater treatable by a BNR process, are the pre-treatment of the wastewater (McCue *et al.*, 2003) or the addition of extra carbon. The extra carbon can either be organic carbon in the form of methanol, ethanol, acetic acid and glucose, hydrolysed primary and secondary sludge or industrial wastes rich in readily biodegradable organic matter and volatile fatty acids (VFAs) (Charlton 1994 and Llabres *et al.*, 1999).

The online fermentation of wastewater is able to increase the concentration of VFAs (by 25 %) and improve the performance of the process (McCue *et al.*, 2003). Likewise sludge fermentation can increase the available carbon and improve nutrient removal (Hatziconstantinou *et al.*, 1996 and Charlton 1994). Unfortunately, the application of these methods is not a straightforward procedure. The fermenters require site enlargement and usually are prepared for permanent use without being flexible to any modifications (flows, retention times etc.) (Munch and Koch, 1999). In addition, nutrients are also released from sludge during the fermentation process, increasing the overall amount of nutrients that have to be removed. Industrial wastes, such as the fermented organic fraction of municipal solid waste, fermented leachate of food waste and nightsoil have been shown to contain rich organic substrate in terms of VFA and soluble chemical oxygen demand (SCOD) (Llabres *et al.*, 1999; Bolzonella *et al.*, 2001 and Choi *et al.*, 1996). The addition of the above wastes in BNR process has been reported to have a positive impact increasing the removal of nitrogen (~ 28-109 % increase) and phosphorus (~ 97-410 % increase) (Lim *et* *al.*, 2000 and Lee *et al.*, 1997). For instance, in the UK the wastewater treatment plants in Derby and Reading in Severn Trent Water and Thames Water areas, respectively, are successful BNR sites with domestic sewage being mixed with industrial effluent. When the additional carbon is in the form of methanol or acetic acid, there is an improvement in BNR performances (Tam *et al.*, 1992; and Fass *et al.*, 1994). The only important disadvantage of the addition of direct organic carbon is the high operational cost. Similarly, the industrial wastes are not always applicable to a given wastewater treatment plant since transportation requirements may result in extra costs. Moreover, the content of nutrients in some industrial wastes is high, increasing the load to the process.

Researchers investigating alternative carbon sources, which can easily be used without high operational cost, observed that sludge disintegration used in sludge treatment processes is able to increase the SCOD and VFA content. The ultimate goals of these methods are foam control, increase in biogas production and sludge mass reduction (Muller 2000b). However, there is little information about the application of the disintegrated sludge to BNR in order to improve P and N removal. Muller (2000a and 2000b), made a comparison of mechanical, thermal and chemical sludge treatment. The highest degree of disintegration was reached by the chemical (ozone) treatment (52%) with the mechanical methods reaching medium degrees of disintegration (20-37%) with a relatively low energy input (1000-10000 kJ kg^{-1}). Stirred ball mills and high pressure homogenizers were used for sludge disintegration by Muller (2000b), to produce a carbon source for denitrification. According to their experiments the maximum denitrification rate was up to 15 mg NO_3-N g^{-1} VSS h^{-1}. Chiu *et al.*, (1997) reported that the combination of alkaline treatment with ultrasound vibration brought an increase in SCOD and VFA at 41.5 and 28 times, respectively. The maximum increase in SCOD was reported by Wang *et al.*, (1999) at 50 times with ultrasound equipment of 400 W treating 100 ml of surplus activated sludge (SAS) for 40 minutes.

This study examines mechanical sludge disintegration using a deflaker, a technology designed for processing the pulp in paper industries. The main goal of this study was to examine whether this equipment is capable of producing extra carbon from SAS and to investigate the mechanisms of disintegration. The suitability of the carbon produced for improving biological nutrient removal will be investigated in further research.

4.2 Material and methods

The SAS used in this study was collected immediately after the belt thickener with the total solid (TS) concentration in the range of 4-7%, from wastewater treatment plants (WWTPs) that operate in BNR (BNR SAS) (Derby WWTP) or standard activated sludge mode (non BNR SAS) (Barnhurst WWTP) (Table 4.1).

Table 4.1 Summary of the samples collected from different WWTPs with different solid content

	Solid concentration (%) for different samples of thickened SAS						
BNR WWTP	5.8	5.9	4.3	6.3	5.2	7.2	6.1
Non BNR WWTP	4.3	6.2	5.6	5.2			

4.2.1 Disintegration

The equipment used for sludge disintegration was a 10” Pilao DTD Spider Deflaker with a 30 kW motor fitted with 230 mm discs with 3 active cell layers (Figure 4.1). The gap distance between stator and rotor was 0.6-0.9 mm and the rotation speed 3000-3600 rpm, (Withey 2003). The disintegration process was conducted as a batch with five litres of thickened SAS to be treated each time at four different retention times, 2, 5, 10 and 15 minutes. The maximum monitored temperature of disintegrated sludge was 35 ^{o}C and considered to have negligible effect on disintegration (Wang *et al.*, 2005). To quantify maximum carbon release in SAS a thermal extraction method was established, which was a modification of a method reported by Zhang *et al.*, (1999) for the extraction of extracellular polymers. This method was used only for comparative reasons as was assumed that thermal extraction could indicate the absolute carbon release causing cell lysis. During that method thickened SAS was left for an hour under the conditions of 1bar and 105^{o}C.

Figure 4.1 Pilao 10" spider deflaker

4.2.2 Analytical methods

Particle size analysis was carried out using a Malvern Mastersizer 2000 (Malvern, UK). The Mastersizer uses an optical unit to detect the light scattering pattern of sludge particles dispersed in deionised water. High performance size exclusion chromatography (HPSEC) was carried out using high performance liquid chromatography (HPLC) (Shimadzu VP Series, Shimadzu, UK) with UV detection set at 254 nm and a BIOSEP-SEC-S300 column (Phenomenex, UK). For each sample a chromatogram of absorbance against time was produced. Larger molecular size compounds were eluted from the column first and smaller molecules later.

Apart from the total solids all the other analysis were carried out in the filtered (0.45 μm) supernatant of the untreated and treated sample after centrifugion (10500 g, 7^{o}C). The concentration of Total Solids (TS), soluble COD, VFA, NH_4 and P was measured according to APHA Standard Methods (1998). The soluble protein content was determined according to standard protein method by Branford (1976) with a protein diagnostic kit (Sigma, England). The concentration of soluble proteins was determined from a standard curve constructed using bovine serum albumin (P0914 Sigma – Aldrich, Gillingham, UK) in deionised water, as the standard. Soluble carbohydrate concentrations were determined using the phenol sulphuric method introduced by Dubois *et al.*, (1956). Carbohydrate concentration was calculated from a calibration curve constructed using a glucose standard.

4.3 Results-Discussion

The mechanical disintegration of thickened SAS by the deflaker was evaluated in terms of soluble carbon release, and its correlation with energy input. In addition, the mechanism of the process was investigated in order to identify whether the deflaker is able to cause floc erosion, floc breakage or cell lysis.

4.3.1 Carbon and phosphorus release and energy input

The initial concentration of VFA and SCOD in thickened SAS was always dependant on the WWTP source (BNR or non BNR). In BNR thickened SAS the VFA and SCOD was ranged from 0 to 19 mg l^{-1} and 120 to 342mg l^{-1}, respectively and in non BNR from 186 to 311 mg l^{-1} and 752 to 1180 mg l^{-1}, respectively. The results from mechanical disintegration of BNR thickened SAS at four different retention times in the deflaker are summarized in Table 4.2. As expected, the increase in VFA and SCOD was related to the disintegration time. The maximum concentration of VFA and SCOD measured were 530mg l^{-1} and 6180 mg l^{-1} for 10 and 15 minutes retention time, respectively. Additionally, phosphorus release also occurred, again increasing with the retention time in the equipment with the maximum concentration measured to be 480 mg l^{-1} for 15 minutes of disintegration. The ammonium was not frequently measured and only a few measurements have been taken in the disintegrated sludge by deflaker for 15 minutes, which showed that there is an increase reaching the concentration of ~60 mg l^{-1}.

Table 4.2 VFA, SCOD and P release from thickened BNR SAS (4.3-7.2 % T.S.) treated with deflaker for different retention times

	Raw		**2 minutes**		**5 minutes**		**10 minutes**		**15 minutes**	
	Ave	Max	Ave	Max	Ave	Max	Ave	Max	Ave	Max
VFA (mg l^{-1})	3	19	113	113	185	263	205	299	403	530
SCOD (mg l^{-1})	176	342	1525	1845	2383	2780	3060	4175	4440	6180
Sol. P (mg l^{-1})	107	159	216	216	232	242	253	300	326	480

The results from disintegration of non BNR SAS followed the same trend as the BNR sludge, although here the initial concentrations of VFA and SCOD were higher (Table 4.3). This is expected as in the non BNR WWTP the soluble available carbon is not totally consumed and can still be found in surplus sludge. Phosphorus release was much lower with the maximum concentration to be 135 mg l^{-1}, as in non BNR WWTP the biologically stored phosphorus content in sludge is lower than in sludge from BNR WWTP. The maximum concentration of the released P was 135 mg l^{-1} for 15 minutes of disintegration, much lower than the respective concentration after disintegration of BNR sludge (480 mg l^{-1}).

Table 4.3 VFA, SCOD and P from thickened non-BNR SAS (4.3-6.2% T.S.) treated with deflaker for different retention times

	Raw		**2 minutes**		**5 minutes**		**10 minutes**		**15 minutes**	
	Ave	Max	Ave	Max	Ave	Max	Ave	Max	Ave	Max
VFA (mg l^{-1})	236	311	486	486	541	772	611	611	852	852
SCOD (mg l^{-1})	1004	1180	3745	3745	4110	5500	6040	6410	5810	6530
Sol. P (mg l^{-1})	46	69	59	59	62	77	78	78	100	135

The energy consumption of the deflaker was 5.7 kW for each 5 L of sludge. After 15 min of disintegration at 1.14 W ml^{-1} the SCOD was increased by 20 times. This compares well to the increase in SCOD by 7.7 times reported by Mao *et al.*, (2004) with a sonication of 20 kHz frequency and at 4 W ml^{-1}. The performance of disintegration by the deflaker can also be compared with other disintegration techniques by using specific energy, which can be defined as the amount of mechanical energy that stresses a certain amount of sludge (Muller 2000a). The effect of specific energy from the deflaker on SCOD shows as expected, that greater energy input gave higher release in SCOD (Figure 4.2). The rate of SCOD release is higher for the first 2500 kJ kg $^{-1}$ TS, than when more energy is applied. This rate (specific energy <2500 kJ kg^{-1} TS) is the same for the two sludges with different solids concentration, but with higher energy input the more thickened sludge proved to be more efficient as with the same energy gives higher SCOD release. The degree of disintegration for COD (DDCOD) was also taken into account, which was calculated by the equation below:

$$DDCOD = [\ (COD_d - COD_u) / (COD_{th} - COD_u)\ ] \cdot 100 \qquad [\%],$$

Where COD_d, COD_u, and COD_{th} are the SCOD values for the disintegrated (COD_d), untreated (COD_u) and thermal extracted (COD_{th}) sample (Muller 2000a). The maximum degree of disintegration was taken as being released by a thermal extraction method, which gives similar results with other methods used in literature for the same purpose (Lehne *et al.*, 2001, Muller 2000b, Tiehm *et al.*, 2001).

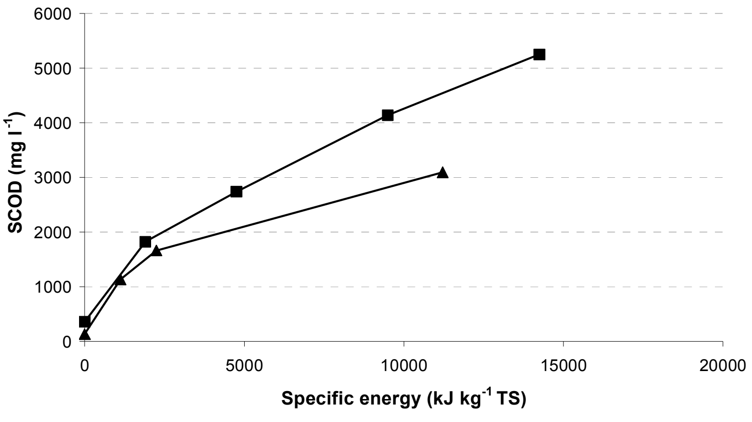


Figure 4.2 Effect of specific energy on SCOD for BNR sludge with two different solid concentrations (■ 7.2 % TS, ▲6.1% TS)

The degree of disintegration by the deflaker as a function of specific energy is shown below (Figure 4.3). Stirred ball mills (SBM), which are a similar type of mechanical equipment to the deflaker and an ultrasonic homogenizer (UH) were tested by Muller

(2000a). A comparison of deflaker to the other equipment showed that to achieve a 25% degree of disintegration SBM, deflaker and UH required 3000, 4000 and 10400 kJ kg^{-1} TS of specific energy, respectively.

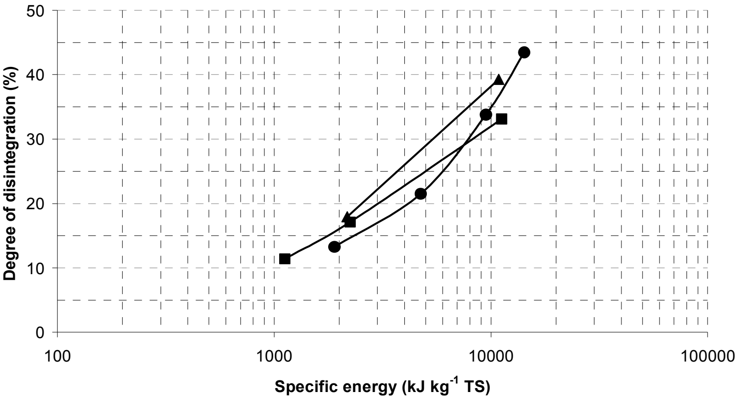
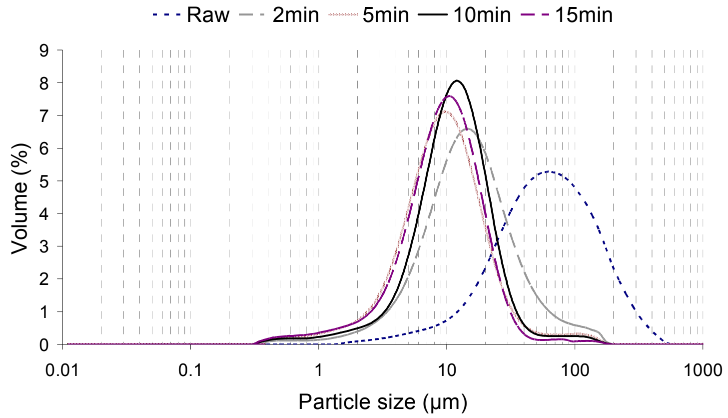


Figure 4.3 Degree of disintegration by the deflaker as a function of specific energy for three different sludge samples (● BNR SAS 7.2 % TS, ■ BNR SAS TS 6.1% TS, ▲non BNR SAS 6.2% TS)

4.3.2 Mechanisms of disintegration

The results from the particle size distribution from both sludges showed that the deflaker was able to decrease the size of the particles (Figures 4.4 and 4.5). The median size of the raw BNR sludge was around 65.5 μm and was reduced to 9.3 μm after 15 minutes of disintegration. Similarly, the size of particles in raw non BNR sludge was 45.6 μm and after 10 minutes of disintegration with the deflaker was 9.3 μm. The formation model of floc consists of primary particles (~2.5 μm), microflocs (~13 μm) and porous flocs (~100 μm) (Jorand *et al.*, 1995). Particle size distribution shows that after disintegration not only most of the porous flocs are destroyed, but also some of the microflocs with the simultaneous release of polymeric compounds which link the microflocs to each other (Jorand *et al.*, 1995). That is in agreement with Chu *et al.*, (2001) who reported a porous floc destruction at an ultrasonic treatment of 20 kHz frequency at 0.44 W ml^{-1} and can be confirmed by the fact that the reduction in particle size takes place with the increase in organic matter (SCOD, VFA).



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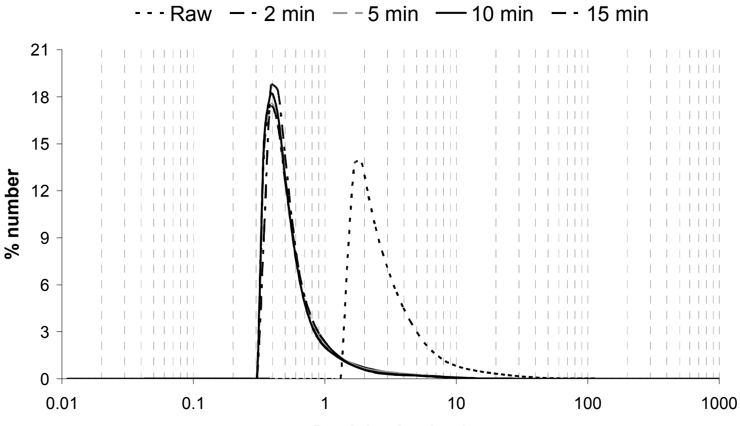
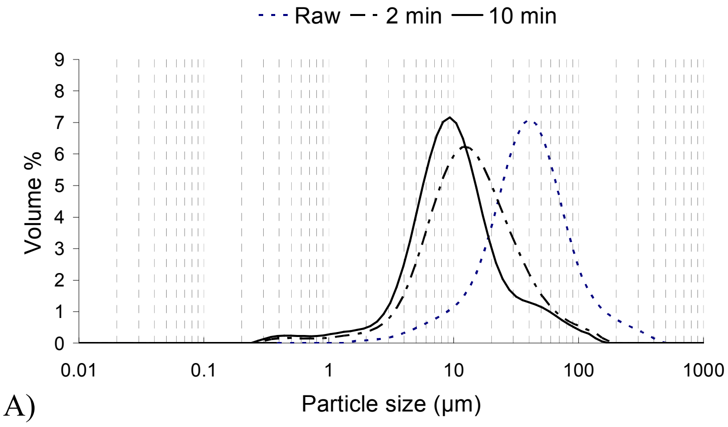


B)

Figure 4.4 Particle size distributions for raw and disintegrated thickened BNR SAS. A) particle size against volume and B) particle size against number



A)

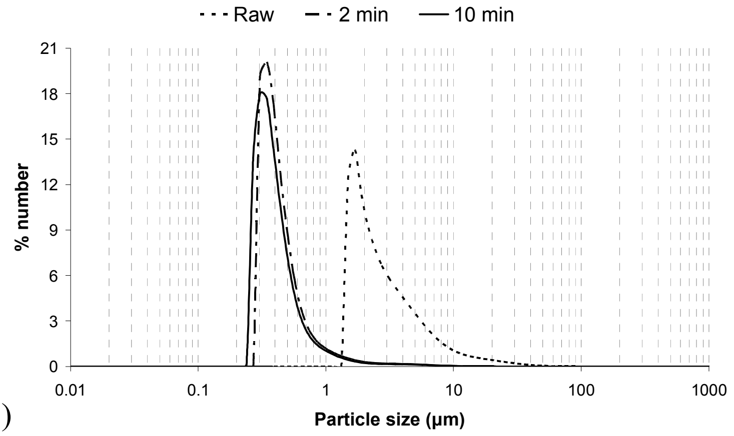


Figure 4.5 Particle size distributions for raw and disintegrated thickened non BNR SAS. A) particle size against volume and B) particle size against number

According to Lehne *et al.*, (2001) 3000 kJ kg^{-1} TS are required for floc size reduction and decrease the median size of the particles down to 10-15 μm. They reported that further disintegration caused a smaller decrease in particle size, from 10-15 μm to 3 μm with high amount of specific energy (from 3000 to 100000 kJ kg^{-1} TS). Here the deflaker was able to cause porous floc disruption as the median particle size is decreased to approximately 10 μm and for similar specific energies (~2500 kJ kg^{-1}TS) (Figure 4.6). In addition, as mentioned above the SCOD release follows a different rate between the first 2500 kJ kg^{-1} TS applied and the rest specific energy added. The release in SCOD is faster for the first 2500 kJ kg^{-1} TS of specific energy and around 0.96 mg SCOD per kJ kg^{-1} TS of specific energy added, when also particle size is significantly reduced and then the rate is decreased to 0.36 mg SCOD per kJ kg^{-1} TS of specific energy added with almost no reduction in the particle size (Figure 4.7). That means that during the floc breakage, a big amount of organic matter is released in the liquid phase (1500-1900 mg l^{-1} in terms of SCOD) and for further disintegration and energy input organic matter is also released, but without any difference in particle size indicating that is not coming from the disruption or breakage of flocs.

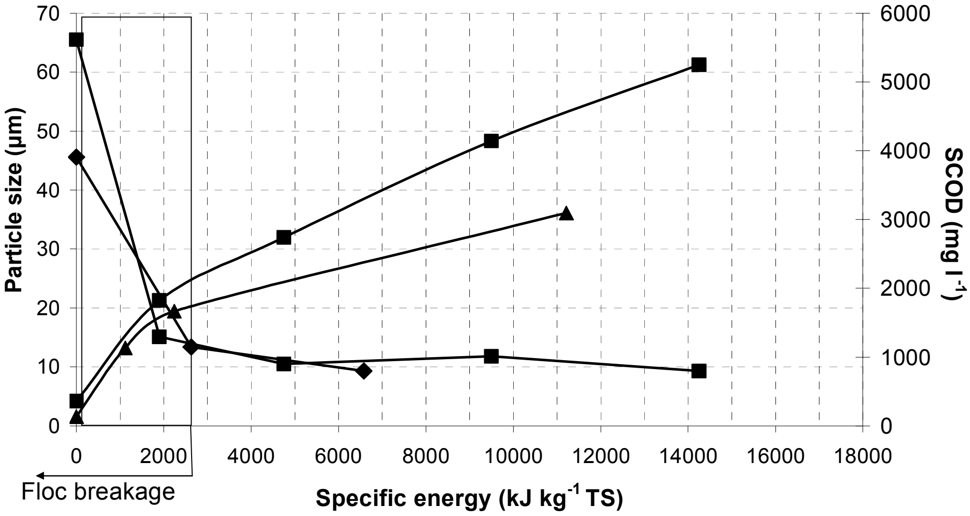


Figure 4.6 Effect of specific energy of disintegration on particle size and SCOD by deflaker for three sludge samples (■ BNR SAS 7.2 % TS, ▲BNR SAS 6.1 % TS and ♦ non BNR SAS 5.2 % TS)

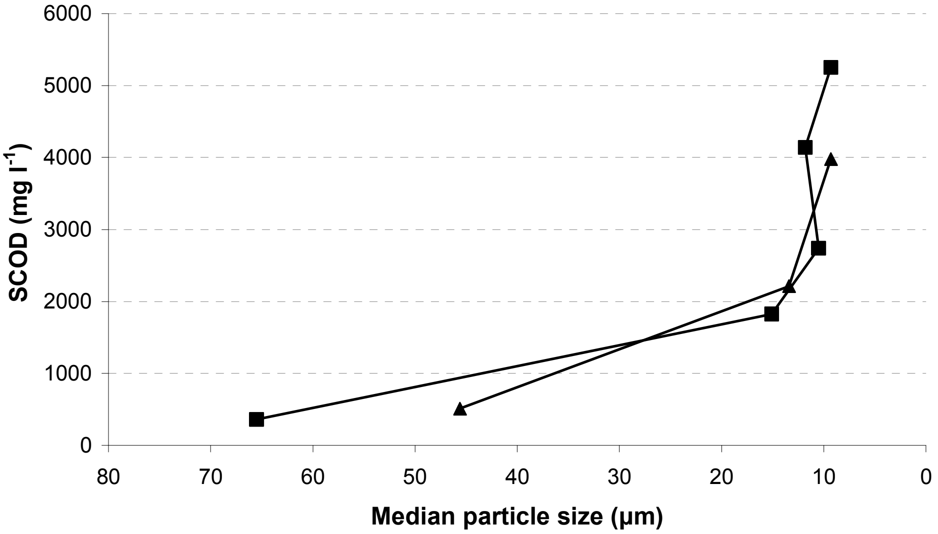


Figure 4.7 Correlation between SCOD release and particle size reduction (■ BNR SAS 7.2 % TS, ▲BNR SAS 6.1 % TS)

It is still not certain though, whether cell lysis takes place as the released organic matter after 2500 kJ kg^{-1} TS of specific energy could be not due to cell lysis, but due to further floc breakage. The concentrations of soluble proteins and carbohydrates in the supernatant before and after disintegration were also examined in order to evaluate disintegration. Protein analysis has been reported as another method for assessing disintegration showing that can be a relatively quick and effective method (Schmitz *et al.*, 2000). The concentrations of proteins, carbohydrates, SCOD and VFA after disintegration were related to the retention time (Figures 4.8 and 4.9). Here, disintegration was compared with the thermal extraction method, as an estimation of maximum release. The predominant component of the released material is SCOD, which includes the proteins, carbohydrates and volatile acids. The protein concentration indicates that a part of the extracellular polymeric substances (EPS), which link the microflocs to each other, have been destroyed (Jorand *et al.*, 1995, Wang *et al.*, 2005). The concentration of proteins increased approximately 27 and 5 fold for BNR and non BNR sludge, respectively. This increase is significantly higher than the one reported by Nah *et al.*, (2000) from mechanical treatment using a high pressure pump and a nozzle (2.5 times), but lower than the increase reported for ultrasound treatment (200 W and 9 kHz) for 40 minutes (~48 times) (Wang *et al.*, 1999). The results agree with Wang *et al.*, (2005) who reported an increase in SCOD, proteins, polysaccharide and DNA after disintegration by ultrasound (300-1200 W, 20 kHz and 0-30 minutes retention time).

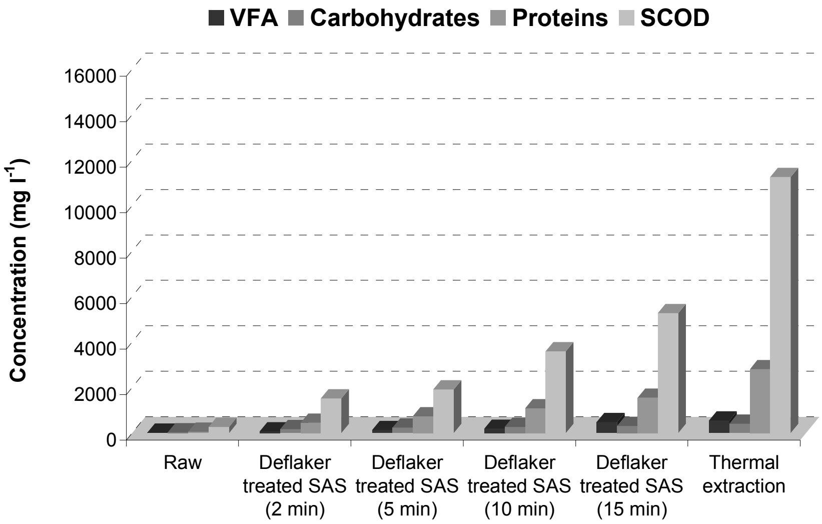


Figure 4.8 Disintegration results for BNR thickened SAS (7.1 % TS)

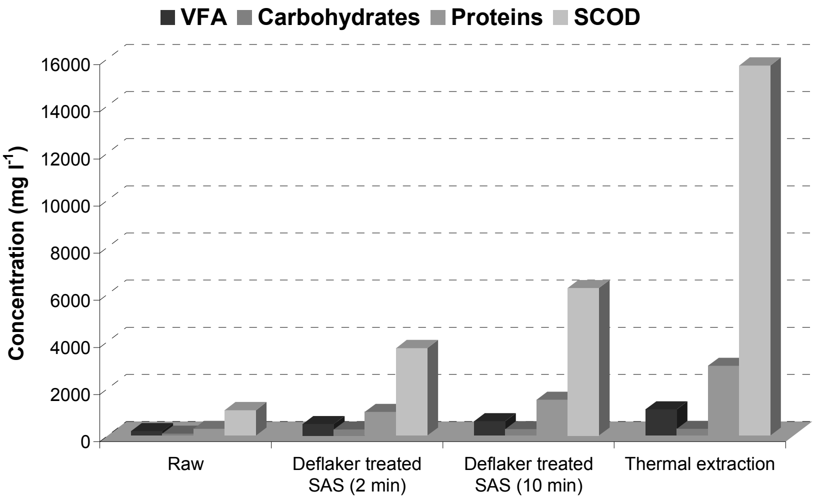


Figure 4.9 Disintegration results for non BNR thickened SAS (6.2 % TS)

To summarize, the particle size distribution showed that disintegration caused a decrease in particle size with the simultaneous release of organic matter in the form of proteins and carbohydrates. The breakage of flocs released the polymeric substances used for the formation of flocs in the aqueous phase. But, to determine whether cell lysis takes place further information was required.

The high performance size exclusion chromatography (HPSEC) was used as a "fingerprint" technique for the organic materials that are produced during disintegration. The results showed that during short retention time (<10 minutes) large molecular size materials (first peaks in the graph) are released, which are thought to be polymeric substances and typically found outside of the cells (extracellular) (Figure 4.10) (Jorand *et al.*, 1995). At longer retention time (≥10 minutes) the release not only of the extracellular, but also of smaller molecular size materials (last peak in the graph) can be observed. These materials can either be disrupted extracellular polymers or intracellular material after cell lysis. On the other hand the thermal extraction method seems to have released small molecular size materials without destroying the polymeric substances (Figure 4.10c). Taking also into account that the destruction of polymers would not have caused an overall increase of the soluble organic matter as was observed (Figures 4.8 and 4.9), we consider that the appearance of smaller compounds in BNR SAS disintegration are mainly material that have been released due to cell lysis. Moreover, after the destruction of the flocs and the removal of the polymeric substances from the cell walls the shear forces from the deflaker would be able to break the cell walls (Wang *et al.*, 2005). Results from HPSEC confirmed the data from particle size distribution proving that during mechanical disintegration with the deflaker, firstly flocs are disrupted decreasing the particle size and releasing extracellular material and then cell lysis starts taking place releasing some extra organic matter, for longer periods of disintegration (≥10 minutes or ≥9000 kJ kg^{-1} TS of specific energy).

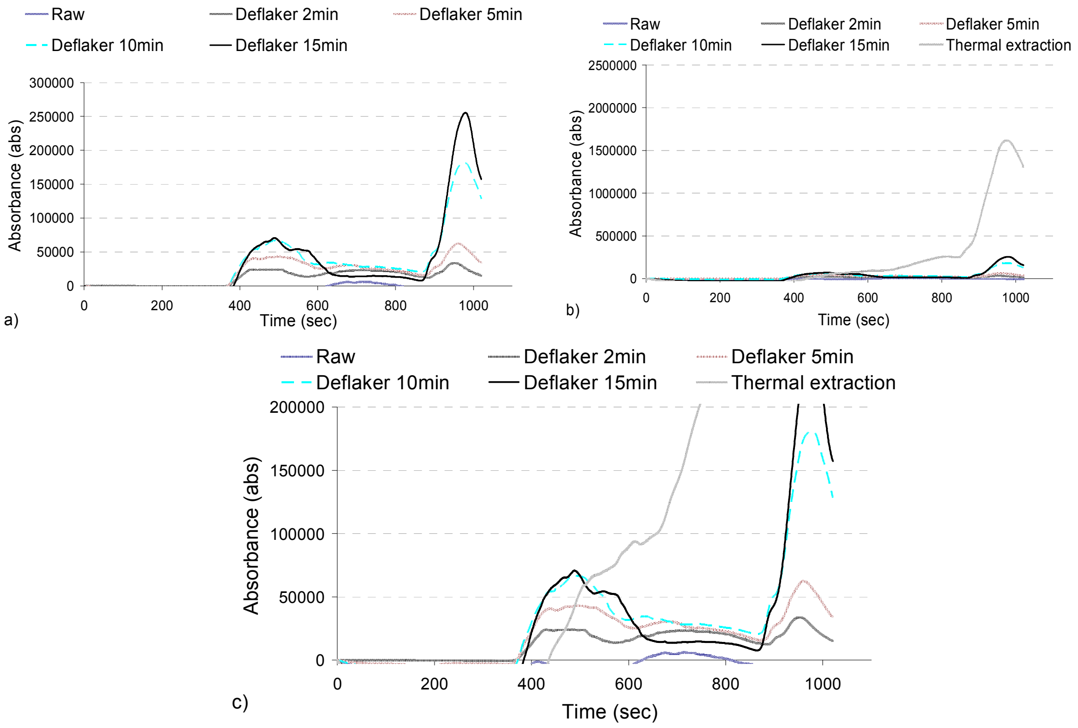


Figure 4.10 HPSEC results for BNR thickened SAS a) disintegration from deflaker, b) disintegration from deflaker compared with thermal extraction and c) the same as b) in different scale observing the absorbance of the large molecular size material.

After the particle size distribution it was suspected that the increase in organic matter after 2500 kJ kg^{-1} TS of specific energy added, with the simultaneous steady size of the particles is due to cell lysis. The HPSEC results showed that cell lysis appears when more energy is added (9000 kJ kg^{-1} TS), proving that the extra SCOD released for energies between 2500 and 9000 kJ kg^{-1} TS is because of further damages on the flocs, without reducing the size of the particles and without cell lysis. Using the 9000 kJ kg^{-1} TS of specific energy as a threshold for cell lysis we can estimate the proportion of SCOD that comes from floc breakage and cell lysis (Figure 4.2). For a total energy input of 14250 kJ kg^{-1} TS and 4900 mg l^{-1} of SCOD released the 73 % or 3900 mg l^{-1} SCOD comes from floc disruption or breakage and the remaining 27 % from cell lysis. The above could be verified by confirming the threshold of cell lysis by doing an assay for DNA, where the significant increase in the concentration means cell lysis.

The lack of available soluble carbon is a major problem in the BNR process. This study shows that the deflaker process can be used to disintegrate the sludge and release trapped organic material to the liquid phase. Unfortunately, there is little information in the literature about the application of disintegrated sludge in BNR, as an extra carbon source. Most of the applications of sludge disintegration to date have consisted of improving anaerobic digestion and reducing sludge production. Muller (2000b) has reported some exemplary results of how denitrification rate can be improved by different disintegration methods. As reported by the same author mechanical disintegration on adapted biomass gave a higher denitrification rate compared with thermal disintegration (no relation with thermal extraction method mentioned above) and biological hydrolysis.

A comparison has been made between the available carbon produced and phosphorus released by disintegration in the form of SCOD to P ratio (Table 4.4). The ratios are low (7-13 for BNR sludge) compared to the ratios found in the literature for successful BNR plants (40-60) (Randall *et al.*, 1992; Carlson *et al.*, 1996), but with longer disintegration giving higher ratio. That means that mechanical disintegration releases more phosphorus than the produced carbon is theoretically able to remove. The ratios for non BNR sludge are higher than the ones produced from BNR sludge (77 and 13.6 for non BNR and BNR sludge, respectively), but are expected to decrease, when the WWTP be converted to BNR and the phosphorus being removed biologically. This is an indication that the addition of mechanically disintegrated sludge in a BNR process could cause deterioration instead of improvement. The sidestream removal of the released phosphorus (i.e. struvite or calcium phosphate precipitation) before being added to the process could permit disintegration by deflaker to have a positive impact on BNR. On the other hand, the increase of ammonium was not significant enough to affect negatively the SCOD:NH_4 and this ratio was increased (250 %) to ~70 which is much higher than the theoretical requirements for nitrogen removal (8-14 for TCOD:TKN) (Carlson *et al.*, 1996, Grady *et al.*, 1999). Whether the extra soluble carbon produced by the deflaker can be utilised by the bacteria and improve both denitrification and phosphorus removal needs to be examined experimentally in further research.

Table 4.4 SCOD:P and SCOD:NH_4 mass ratios produced in sludge by disintegration for different retention times

	Raw	2 minutes	5 minutes	10 minutes	15 minutes
			BNR SAS		
SCOD:P	1.6	7	10	12	13.6
SCOD:NH_4	20				70
			Non BNR SAS		
SCOD:P	21	63	66	77	58.1

4.4 Conclusions – Future work

- The examined disintegration technique, the deflaker proved to be able to increase the soluble carbon in the form of VFA and SCOD.
- The increase in concentration of VFA, SCOD, proteins and carbohydrates was related to the time of disintegration and the source of the sludge, with non BNR SAS resulting in higher values, with the maximum concentration of VFA and SCOD at 852 mg l^{-1} and 6530 mg l^{-1}, respectively.
- The increase in the concentration of phosphorus during the disintegration of BNR SAS reaching 480 mg l^{-1} for 15 minutes of retention time led to a relatively low ratio of SCOD:P (~13), which indicated that the addition of disintegrated sludge would deteriorate the process. The sidestream stripping of phosphorus immediately after the disintegration is considered essential in order to have an improvement of BNR performances.
- Particle size distribution showed that the deflaker decreased and destroyed the porous flocs and microflocs releasing the organic matter that links particles together.

- High performance size exclusion chromatography (HPSEC) confirmed that at short disintegration time (<2 minutes or <2000 kJ kg^{-1} TS) the deflaker was able to release the extracellular material (floc breakage). During disintegration of 2-10 minutes retention time or 2000-8000 kJ kg^{-1} TS of specific energy, a release of extracellular material mainly took place, with also the first indications of cell lysis. Disintegration for longer period (≥10 minutes or 9000 kJ kg^{-1} TS of specific energy) caused cell lysis. No cell lysis was observed for the non BNR sludge.
- The addition of 15000 kJ kg^{-1} TS of specific energy increased SCOD significantly, from which 73 % probably came from floc disruption and breakage and the rest from cell lysis.
- Further research will examine the application of disintegrated sludge on BNR, as extra carbon source. Firstly, lab scale tests will investigate the suitability of the released carbon on BNR enhancement and then tests on a pilot plant will examine the conditions under which this internal carbon can be applied.

Acknowledgments

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Chapter 5 Rapid evaluation of carbon sources for biological nutrient removal

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5. Rapid evaluation of carbon sources for biological nutrient removal

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Abstract Biological nutrient removal (BNR) is a complex process that is strongly affected by the characteristics of wastewater. The lack for available carbon is a major issue for a successful BNR. The need of a reliable predictive parameter is essential for testing not only the wastewater characteristics but also different carbon sources that can possibly be applied. This study examines the application of disintegrated sludge on phosphorus release and denitrification process. Batch laboratory scale tests were conducted to measure the phosphorus release and the reduction of nitrates under anaerobic conditions. The phosphorus (P) release test (P test) was developed to become more suitable for examining the application of the external carbon source by minimizing the storage time between sampling and experiment. Similarly the denitrification test (N test) was modified to assess the impact of the addition of extra carbon by adding the solid free fraction of disintegrated sludge which contains the organic matter that can be utilized. According to these tests the comparison of the results with and without addition of carbon showed that there was higher phosphorus release (460 %) and higher denitrification rates (244 %) when the carbon was added.

Keywords biological nutrient removal, carbon source, denitrification rate, disintegrated sludge, phosphorus release, predictive test, wastewater

5.1 Introduction

Biological nutrient removal (BNR) is a well documented wastewater treatment process that has been implemented in many countries (Pavan *et al.*, 1998 and Jonsson *et al.*, 1996). BNR processes have increasingly gained more importance and become more widely applied over recent years. The key for successful BNR is the availability of carbon in wastewater that has to be assimilated during the phosphorus release and denitrification processes. The most suitable carbon source for BNR has been found to be volatile fatty acids (VFA) and readily biodegradable chemical oxygen demand (RBCOD) (Abu-ghararah and Randall, 1991; Randall *et al.*, 1997).

The need for a predictive parameter for examining the suitability of wastewaters for BNR became essential the recent years, when more standard activated sludge plants have been converted to BNR plants. The most popular predictive parameters that have been used were the carbon to phosphorus and carbon to nitrogen ratios. The carbon can be represented either as biological oxygen demand (BOD), COD or VFA. It was reported that for a successful BNR process a ratio of COD: P above 50 (Carlson *et al.*, 1996) or BOD: P above 20 (Randall *et al.*, 1992; Cooper *et al.*, 1995) was necessary. Another ratio used for examining the wastewater carbon availability was the VFA potential to phosphorus, which has to be above 14-20 in order to be suitable for BNR (Abu-gararah and Randall, 1991; Johnsson et al., 1996; Curto 2001). Similarly, for nitrogen the higher the carbon to nitrogen ratio (COD: N) in wastewater the more likely the wastewater is able to give good nitrogen removal (Henze, 1991; Kujawa and Klapwick, 1999; Henze, 2002).

Unfortunately, these parameters proved to be unreliable for indicating BNR potential as in many cases although, the initial indications showed successful BNR, the performance was poor or the reverse (German *et al.*, 1998; Llabres *et al.*, 1999; Avendano 2003). Therefore, further tests were developed, which instead of recycling on the stoichiometric ratios to predict phosphorus and nitrogen removal, batch laboratory scale tests were used, such as the phosphorus release test (Park *et al.*, 2001; Vale *et al.*, 2005) for phosphorus and the nitrate utilization rate (NUR) test for nitrogen (Kujawa and Klapwijk 1999). The basic idea of the phosphorus test is to monitor the phosphorus release under anaerobic conditions, with and without acetate addition. High phosphorus release (~30 mg l^{-1}) without any acetate addition and similar to the release with acetate, can indicate high uptake under aerobic conditions and hence efficient phosphorus removal. The reduction of nitrates was observed in NUR tests with the fast and complete denitrification to be a good indicator for a satisfactory nitrogen removal.

All the above predictive parameters and tests were used to examine the potential of wastewater for successful BNR and how the results correlate with the wastewater characteristics. On the other hand, the aim of this study was to investigate the quality and suitability of an external carbon source for improving BNR performances. The modifications and the overall development of these tests in order to make them appropriate for assessing the impact of an external carbon source to BNR process are presented in this paper.

5.2 Materials and methods

Grab samples of wastewater were collected and used in this study from four different wastewater treatment plants (WWTPs) (Table 5.1). Sites 3 and 4 are successful BNR sites with the domestic wastewater mixed with industrial effluent rich in organic matter (~500 mg l^{-1} VFA), while sites 1 and 2 are standard activated plants that have to be converted to BNR the next few years. The wastewater from sites 3 and 4 was domestic as was collected before the inputs of industrial sources. Moreover, for the completion of phosphorus release tests bio-P sludge (return activated sludge, RAS) was sampled from a successful BNR site (site 4). Initially, the wastewater was stored at 4 ^{o}C for one day and RAS stored at 4 ^{o}C and aerated. The experiment was then modified and a minimum storage time (2-3 hours) for RAS was applied under aerobic conditions. The external carbon source tested in this research was mechanically disintegrated sludge (surplus activated sludge, SAS) with carbon one and carbon two appeared in the following graphs to correspond to the sludge, disintegrated by the same equipment but on different retention times and hence different carbon release (Kampas *et al.*, In Press (Chapter 4)). This carbon source was also compared to industrial wastewater (brewery effluent) when the phosphorus release test was conducted for site 3.

Table 5.1 Collection of samples and number of test completions

	Site 1	Site 2	Site 3	Site 4
BNR mode			✓	✓
Non BNR mode	✓	✓		
Settled sewage	✓	✓	✓	✓
RAS				✓
SAS	✓	✓	✓	✓
Phosphorus release test	1	2	2	1
Denitrification test	-	2	1	4

5.2.1 Phosphorus release test

The phosphorus release test consisted of four plastic vessels with 1L of wastewater and 1L of return activated sludge (RAS) that were kept under anaerobic conditions for 2 hours. During the test there was no inhibition by the presence of nitrates as their concentration was always very low (<1 mg l^{-1}) (Kuba *et al.*, 1994). The first vessel was the control one without any amendment. The second and third were operated with the addition of external carbon source (disintegrated sludge) and the fourth with the addition of sodium acetate. In every reactor the same amount of carbon was added, as all the carbon sources were matched in terms of VFA or SCOD (25 mg COD l^{-1}) and with a limit in volume for disintegrated sludge (100 ml). When 100 ml of the added sludge contained less than 25 mg COD l^{-1}, the match of carbon for the three reactors was on the minimum concentration of COD. All vessels were sealed and a nitrogen blanket was over the solution, which was mixed by magnetic stirrers. Moreover, all the vessels were inside a water bath with a heater and circulation pump to keep the temperature constant (20 ^{o}C). During the experiment pH and dissolved oxygen (DO) were observed taking measurements every 30 minutes. The experimental rig is demonstrated in Figure 5.1. Samples were taken every 30 minutes, filtered immediately with a syringe filter (0.45 μm) and the concentration of phosphates (PO_4) was measured.

5.2.2 Denitrification test

The above experimental rig was also used for the denitrification test with the difference here that 2L of wastewater was used in the reaction vessels. Again, the first vessel was unamended with carbon, the second and third with the addition of external carbon and the fourth one with sodium acetate. The carbon was matched again in terms of VFA or SCOD (25 mg l^{-1}) and with the limit of 100 ml as well. Moreover, the same amount of nitrate (30 mg l^{-1} N-NO_3) in the form of KNO_3 was added in all reactors. Samples were taken every 30 minutes, filtered immediately with syringe filter (0.45 μm) and the concentrations of nitrate (NO_3) and nitrite (NO_2) were measured. The volatile suspended solids (VSS) were also measured from the solution of each vessel.

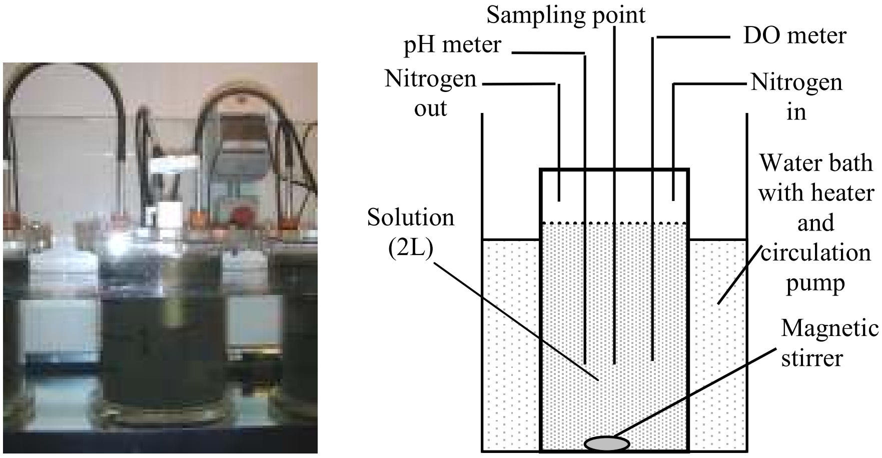

Figure 5.1 A picture and a schematic of the experimental rig

5.2.3Analytical methods

The concentration of soluble COD, VFA, total solids (TS), VSS, and PO_4 was measured according to APHA Standard Methods (1998). Analysis of nitrates (NO_3) and nitrites (NO_2) from the denitrification tests was carried out using ion exchange chromatography (IEC) system, (Dionex, DX500 series, UK).

5.3 Results and discussion

5.3.1 Phosphorus release test

In phosphorus release test (P test) the release of phosphorus, when there was no external carbon source available was compared to the release, when external carbon sources were present. Moreover, the additional external carbon was compared to acetate, which as mentioned above is believed to be the most suitable for P release. Our expectations were to receive a higher release in the reactor with the added carbon, equivalent to the release in acetate reactor. Unfortunately, not only we did not observe that, but also instead of seeing a release under anaerobic conditions, phosphorus was taken up in one of the reactors despite the fact that soluble carbon was available (Figure 5.2, site 2). Failure in the phosphorus release process has been observed in laboratory tests and full scale operation. In our case the conditions were not anoxic, where it is possible phosphorus uptake to take place (Kern-Jespersen and Henze 1993), but anaerobic. Other possible reasons are the presence of glycogen accumulating organisms (GAOs), which compete for the carbon with polyphosphate accumulating organisms (PAOs), responsible for phosphorus release (Cech and Hartman 1993) and the shortage of potassium and other elements (Brdjanovic *et al.*, 1998). Taking into account that a normal domestic sewage contains sufficient amount of the required inorganic elements and the WWTP that RAS was taken from was operated under normal and usual conditions (without any GAOs interference), was assumed that the awkward results from phosphorus release process were due to the storage of RAS for 24-48 hours under aeration before the experiment. Moreover, the higher phosphorus release observed in the control reactor than the reactor with the added carbon (Figure 5.2, site 1) can be characterized as secondary phosphorus release, which takes place after prolonged aeration and lack of available carbon (Metcalf and Eddy 2003). For all these reasons it was decided that the time between sampling and experiment had to be minimized.

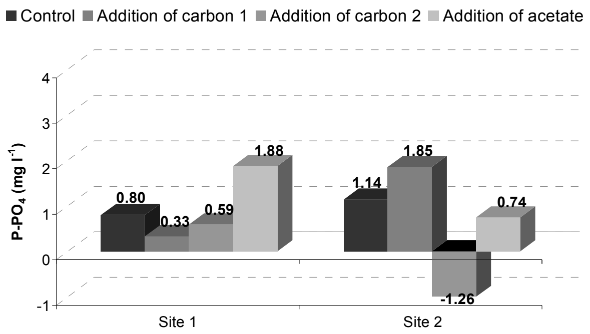

Figure 5.2 Phosphorus release when the test was conducted with RAS being stored 24-48 h after sampling from site 1 and site 2

The next step was to compare P releases from two tests with the same wastewater and RAS and the storage time of RAS varying only, expecting to see different amount of phosphorus to be released. Indeed, the amount of phosphorus released was much higher when "fresh" RAS was used (Figure 5.3). However, the results were following the same trend and as expected the control reactor gave the lowest release. The examined external carbon source was able to be taken up by the PAOs releasing more phosphates than the control, but still lower than the reactor with acetate addition.

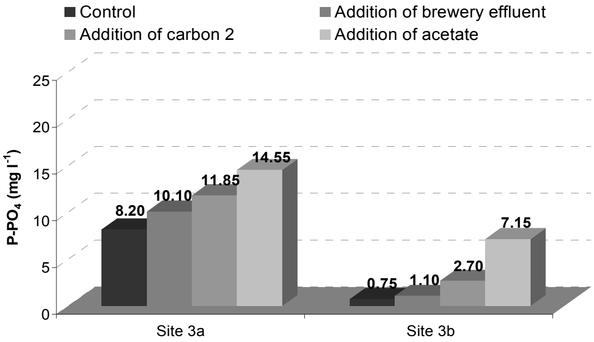

Figure 5.3 Results from phosphorus release test from site 3. a: test immediately after sampling, b: RAS stored for 24-48 h after sampling

The amended P test (minimum RAS storage) was conducted again for sites 2 and 4, testing the same carbon sources and comparing them with acetate by adding the same amount in terms of VFA or SCOD investigating which is the most preferable to the microorganisms (Figure 5.4). The test for site 2 took place with the external carbon to be matched in terms of VFA (25 mg COD l^{-1}) and for site 4 in terms of SCOD (25 mg COD l^{-1}). In first case the SCOD concentration of the acetate was 25 mg COD l^{-1} and for the disintegrated sludge was 214 and 442 mg l^{-1}. A comparison between the results presented in Figure 5.4 shows primarily the different wastewater quality in these two WWTPs and also the preference of PAOs bacteria to the external carbon (disintegrated sludge) rather than the acetate in the test with wastewater from site 2, despite that the carbon was matched in terms of VFA. This is a strong indication that VFA is not the only carbon that can be utilized by the bacteria, but also a proportion of SCOD produced from sludge by the disintegration.

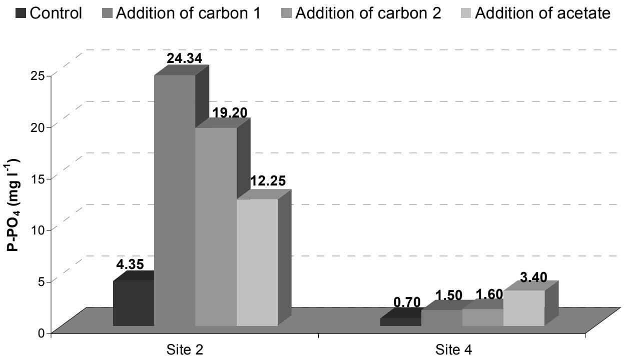

Figure 5.4 Phosphorus release when test was conducted immediately after sampling

5.3.2 Denitrification test

The denitrification tests (N test) were carried out to examine whether the external carbon source could be assimilated by the denitrifying bacteria. It was assumed that the N test could take place without any biomass but using only the bacteria that are available in wastewater. Initially the extra carbon, which was always matched in terms of VFA or SCOD (25 mg COD l^{-1}), was added in the form of sludge resulting in rapid denitrification in these reactors much faster than the control and acetate reactor (Figure 5.5). That happened because of the addition of extra biomass. It was assumed that the disintegrated sludge contained enough active microorganisms, which with the presence of organic carbon gave immediate denitrification.

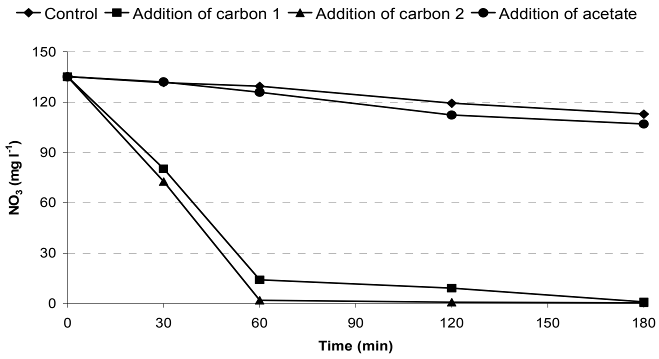

Figure 5.5 Reduction of nitrates against time when the additional carbon was sludge (site 4)

The N test was modified and the solid free fraction of disintegrated sludge was applied. In this case the VSS concentration was equal in all reactors (~100 mg l^{-1}) and the reduction of nitrate was almost similar (Figure 5.6). The denitrification rates as mg N-NO_3 reduced in the first hour of experiment per g of VSS available could reveal the importance of the external carbon source (Figure 5.7). Comparing the denitrification rates produced from the modified N test and with different wastewaters the application of the examined carbon source was always beneficial to denitrification process with those reactors to give higher rates than the control and most of the times higher than the acetate reactor. These rates were higher than the rates reported in literature using a range of carbon sources, such as primary sludge hydrolysate (4.1 mg NO_3-N g^{-1} VSS h^{-1}) (Isaacs and Henze 1995), methanol (3 mg NO_3-N g^{-1} VSS h^{-1}) (Nyberg *et al.*, 1996), ethanol (10 mg NO_3-N g^{-1} VSS h^{-1}) (Nyberg *et al.*, 1996), acetic acid (7.3 mg NO_3-N g^{-1} MLSS h^{-1}) (Naidoo *et al.*, 1998), fermented solid waste (2.5 mg NO_3-N g^{-1} VSS h^{-1}) (Pavan *et al.*, 1998), fermented swine wastes (7.3 mg NO_3-N g^{-1} VSS h^{-1}) (Lee *et al.,* 1997) and septic sludge (2.4 mg NO_3-N g^{-1} VSS h^{-1}) (Morling 2001). That may be due to the different solid concentration on the substrate used, where the extra carbon source was added, as in all the above cases biomass was used instead of wastewater and also due to the different initial concentration of NO_3. Similar rates were reported when wine distillery effluent (35.2 mg NO_3-N g^{-1} VSS h^{-1}) (Bernet *et al.*, 1996) and mixture of VFAs (31.9 mg NO_3-N g^{-1} SS h^{-1}) (Fass *et al.*, 1994) were the carbon source. At this point has to be mentioned that we do not expect to see these rates in full scale denitrification process as the conditions will be completely different. There will not be the same initial high concentration of nitrates and the substrate will be mixed liquors suspended solids, (MLSS) and not wastewater only. However, the difference in denitrification rates when the examined carbon sources were added, the ability to compare them to the rates produced from the addition of acetate (an excellent carbon source) and the overall applicability of the test, made us conclude that the N test is an efficient tool for evaluating external carbon sources for denitrification.

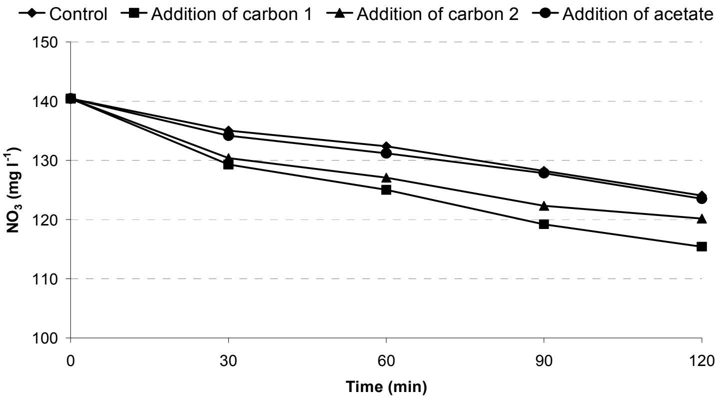

Figure 5.6 Reduction of nitrates against time when additional carbon was solid free fraction of sludge and the substrate was wastewater (site 2)

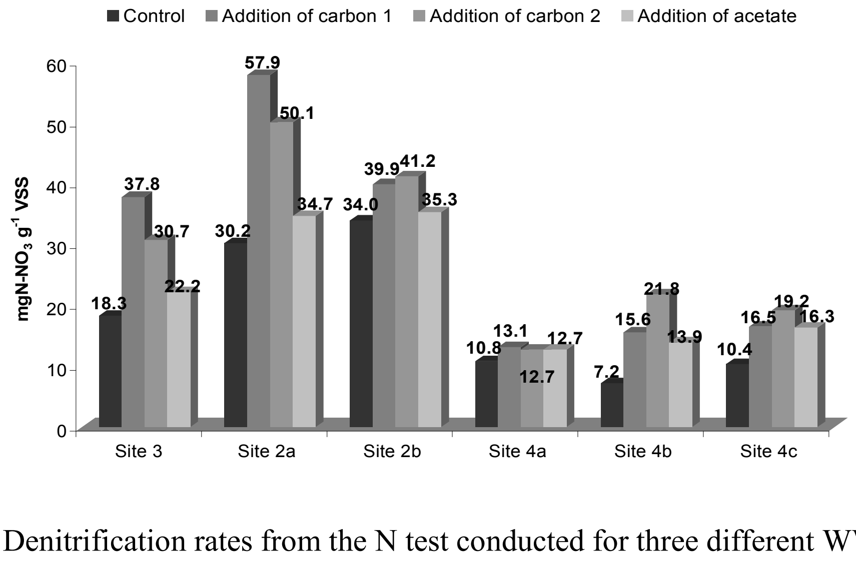

Figure 5.7 Denitrification rates from the N test conducted for three different WWTP. (a, b and c represent different sampling times)

5.4 Conclusions - Recommendations

- The phosphorus release test described here can be used for comparing carbon source suitability of enhanced biological phosphorus removal (EBPR), but the time between the sampling and test should be kept as short as possible. The higher phosphorus release in the reactor with the added carbon than the control one, is a strong indication that the carbon source tested is likely to be able to improve EBPR.
- The denitrification test described here can be used for carbon source comparison when the substrate used contains a similar amount of active bacteria measured as VSS. The denitrification rates produced indicate whether the examined carbon can improve denitrification.
- Overall the two tests were modified respective to the needs of this study and were able to deliver satisfactory results. However, there are some issues that have to be further examined, which for the P test could be the amount of carbon taken up simultaneously with the phosphorus release in order to be sure that there is no secondary release. Moreover, the test has to be conducted with the addition of solid free fraction of disintegrated sludge in order to ensure that the phosphorus being released is coming from the substrate (RAS) and not from the added sludge. For the N test future research will investigate the performance in the presence of those bacteria responsible for denitrification. In addition, a combination of the two tests by changing the anaerobic conditions after two hours to anoxic by adding a certain amount of nitrates would indicate the performance of phosphorus release, phosphorus uptake under anoxic conditions and denitrification process.

Acknowledgements

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Chapter 6 An internal carbon source for improving biological nutrient removal

Water Research (Submitted)

6. An internal carbon source for improving biological nutrient removal

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ABSTRACT

Many methods have been examined in the past for the enhancement of biological nutrient removal process (BNR). Most of them focus on increasing the available carbon source in the wastewater. The methods used to assess the impact of an extra carbon source on BNR were always connected to the carbon to phosphorus or carbon to nitrogen ratios. This study investigates whether mechanically disintegrated surplus activated sludge can be applied as an internal source for BNR, using two laboratory tests to monitor phosphorus release and denitrification rates. According to the phosphorus release test the examined carbon source was able to improve phosphorus release process (45 -744 %), dependant on the amount of carbon added. Similarly, the denitrification process was improved with an increase in the denitrification rates (21 – 215 %).

6.1 Introduction

The enhancement of a biological nutrient removal (BNR) process is directly connected to the availability of a carbon source. Many methods have been examined in the past in order to increase the soluble carbon content and improve BNR performance. Pre-treatments such as fermentation either of the wastewater (McCue *et al.*, 2003) or primary sludge

(Charlton, 1994) have been investigated. Another method to improve BNR performance is the addition of external carbon. Organic carbon in the form of methanol (Tam *et al.*, 1992, Nyberg *et al.*, 1996), ethanol (Hasselblad & Hallin 1998), acetic acid (Naidoo *et al.*, 1998) and glucose (Tam *et al.*, 1992) have effectively been used to improve biological phosphorus removal (BPR) and/or denitrification rates. The most suitable carbon source for BPR is considered as the short-chain volatile fatty acids (Abu-ghararah and Randall, 1991).

The addition of industrial wastes was also examined by many researchers (Pavan *et al.*, 1998, Llabres *et al.*, 1999, Lee *et al.*, 1997 and Lim *et al.*, 2000), who reached to the conclusion that industrial wastewaters can be used as external carbon source for improving BNR performance and can be comparable to acetic acid in terms of phosphorus removal and denitrification rates.

Unfortunately, the above methods cannot be applied in every wastewater treatment plant (WWTP), as either the transportation of industrial wastes is not feasible or there is a high operational cost. Moreover, the pre-fermentation process requires site enlargement and extra design needs such as retention time and temperature control (Munch and Koch, 1999).

In order to investigate the suitability of a carbon source for phosphorus and nitrogen removal a number of parameters have been examined. For example, the carbon to phosphorus and carbon to nitrogen ratios. In these ratios the carbon could be BOD, COD or VFA (Johnsson *et al.*, 1996; Randall *et al.*, 1992 and Carlson *et al.*, 1996). According to these predictive parameters, when the ratio is above a specific value the wastewater is suitable for BNR treatment and when is below that value is considered unsuitable. Unfortunately, these methods have been found unreliable for indicating BNR potential, as in many cases there is no correlation between P or N removal and the respective predictive ratio (Avendano 2003; Llabres *et al.*, 1999). The methods used in this research to predict the biological phosphorus (P) and nitrogen (N) removal were the phosphorus release test (Vale *et al.*, 2005 and Park *et al.*, 2001) and the denitrification test, a modification of Nitrate Utilisation Rate (NUR) test described by Kujawa and Klapwijk (1999). The P test is based on the release of phosphorus under anaerobic conditions for a specific period of time with the higher P release to indicate a better P removal. Similarly, the N test is based on the denitrification rates with the high denitrification rate to indicate good denitrification and hence good N removal.

This paper examines the suitability of an internal carbon source for BNR enhancement using the P release and denitrification tests. The additional carbon was released from mechanically disintegrated thickened surplus activated sludge using a deflaker device (Kampas *et al.*, 2007 (Chapter 4)).

6.2. Materials & Methods

For the completion of the phosphorus release test (P test) and the denitrification test (N test) grab samples of domestic wastewater after primary sedimentation were collected from different WWTPs operating in either BNR (sites A and B) or standard activated sludge mode (site C). In addition, return activated sludge (RAS) was used for the P test collected from a successful BNR WWTP (site A). The collection of the samples took place at different times in a period of a year and according to the requirements that have been described in Kampas *et al.*, (2006) (Chapter 5) The carbon source tested in this study was thickened SAS collected from the same site as the wastewater and disintegrated with the deflaker, an equipment used in the paper industry, at different retention times (2-15 minutes) (Kampas *et al.*, 2007 (Chapter 4)). This process was able to release extra organic matter in the liquid phase. The disintegrated sludge was also compared with industrial wastewater (brewery effluent), which is being used as carbon source in a successful BNR WWTP. Table 6.1 summarizes the samples used in this study.

Table 6.1 Summary of the sample collection

	BNR sites (A & B)	**Non BNR site (C)**
Wastewater	✓	✓
RAS	✓	
SAS	✓	✓
Brewery effluent	✓	

6.2.1 Phosphorus release test

To assess the impact of the examined carbon source (disintegrated sludge) on BNR, a series of experiments investigating the phosphorus release under anaerobic conditions was completed. Four vessels made of clear plastic (2.5L) with 1L of wastewater and 1L of RAS were kept under anaerobic conditions for 2 hours. The experimental rig is demonstrated in Figure 6.1.

The P test was conducted in three different ways following a different methodology according to the objective of each experiment. The goal of the first experiment was to investigate whether the addition of disintegrated sludge would cause a phosphorus release and how is compared to other carbon sources (acetate) or no extra carbon. Based on that objective the P test took place as follows: The first vessel had no addition of external carbon, the second and third were operated with the addition of disintegrated sludge and the fourth one with the addition of sodium acetate. In every reactor the same amount of carbon was added, as all the carbon sources were matched in terms of VFA or SCOD (25 mg COD l^{-1}) (Kampas *et al.*, 2006 Chapter 5)). All vessels were sealed and a nitrogen blanket maintained over the solution, which was mixed by magnetic stirrers. Moreover, all the vessels were inside a water bath with heater and circulation pump to keep the temperature constant (20 ^{o}C). During the experiment pH and dissolved oxygen (DO) were monitored and samples were taken every 30 minutes. The samples were filtered immediately with a syringe filter (0.45 μm) and the concentration of phosphates (PO_4) was measured.

After completing this series of experiment the next step was to investigate the source of the additional phosphorus that appeared in the tests reactors and in particular if was coming from the RAS or from the biomass already present in the added disintegrated sludge. In order to meet the new objective the P test took place with the test reactors operated with the same carbon source (disintegrated sludge by the deflaker, 10 minutes retention time), adding the same amount in terms of VFA (3.5 mg l^{-1}), but with the important difference that in one reactor the biomass had been removed and the solid free fraction of sludge (Kampas *et al.*, 2007 (Chapter 4)) has been added.

Finally, we examined how different sludge disintegration in terms of retention time in the deflaker can affect the phosphorus release process. The P test was conducted without using two reactors for control and acetate dose, but all the vessels were operated with the addition of the same volume of sludge (100 ml), which has been disintegrated in the deflaker for four different retention times (2, 5, 10 and 15 minutes). According to Kampas *et al.*, (2007) (Chapter 4) the source from which the carbon comes from during disintegration is different, depending on the time of disintegration and that experiment took place to show which source can give the most suitable carbon for the phosphorus release process.

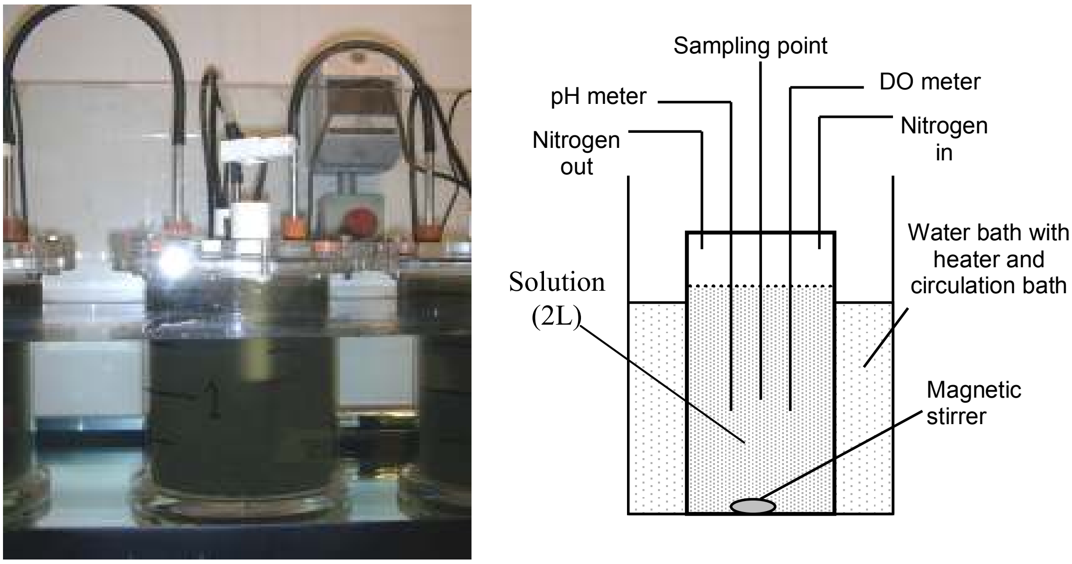


Figure 6.1 A picture and a schematic of the experimental rig

6.2.2 Denitrification test

The same experimental rig used for the P test (Figure 6.1) was also used for the denitrification test with the difference here that 2L of wastewater were used in the reaction vessels. Again, the first vessel was unamended with carbon, the second and third with the addition of the solid free fraction of disintegrated sludge and the fourth one with sodium acetate (Kampas *et al.*, 2006 (Chapter 5)). The carbon was again matched in terms of VFA or SCOD (25 mg COD l^{-1}). The same amount of nitrate (30 mg l^{-1} N-NO_3) in the form of KNO_3 was added in all vessels. Samples were taken every 30 minutes, filtered immediately with syringe filter (0.45 μm) and the concentrations of nitrate (NO_3) were measured. The volatile suspended solids (VSS) were also measured from the solution of each vessel. Similarly, to the P test the N test was also conducted without the control and the acetate reactors, but all the vessels were operated with the addition of the same volume of solid free fraction of sludge (50 ml), which has been disintegrated in the deflaker for four different retention times (2, 5, 10 and 15 minutes).

6.2.3 Analytical methods

The concentration of soluble COD, VFA, total solids (TS), VSS, and PO_4 was measured according to APHA Standard Methods (1998). Analysis of nitrates (NO_3) was carried out using an ion chromatography (IEC) system, (Dionex, DX500 series, UK).

6.3 Results- Discussion

As mentioned above the examined carbon source was disintegrated sludge produced using the deflaker at different retention times (2-15 minutes) (Kampas *et al.*, 2007 (Chapter 4)). This process was able to increase significantly the concentration of VFA and SCOD in the sludge, always dependant on the retention time or energy input (Table 6.2).

Table 6.2 VFA and SCOD concentration of thickened SAS before and after disintegration

	Raw	Deflaker
	BNR thickened SAS	
VFA (mg l^{-1})	0-19	110-530
SCOD (mg l^{-1})	110-340	1200-6180
	Non BNR thickened SAS	
VFA (mg l^{-1})	180-311	480-850
SCOD (mg l^{-1})	750-1180	3740-6530

Phosphorus release test

A comparison of phosphorus release in reactors with acetate and without acetate addition (control) shows that the release of phosphorus is always higher (71-180 % higher than the control), when acetate is added (Figure 6.2). This is in agreement with the results from the tests made by Vale *et al.*, (2005) and Park *et al.*, (2001). According to their results the addition of acetic acid was always beneficial to the phosphorus release process apart from cases, where wastewater contained sufficient carbon for the phosphorus release process and the acetic acid had no effect with the phosphorus release in control and acetate reactor to be the same. The different concentration of the released phosphorus in the control and acetate reactor (Figure 6.2) happened due to the different wastewater (different sites) and/or different bio-P sludge from different sampling times.

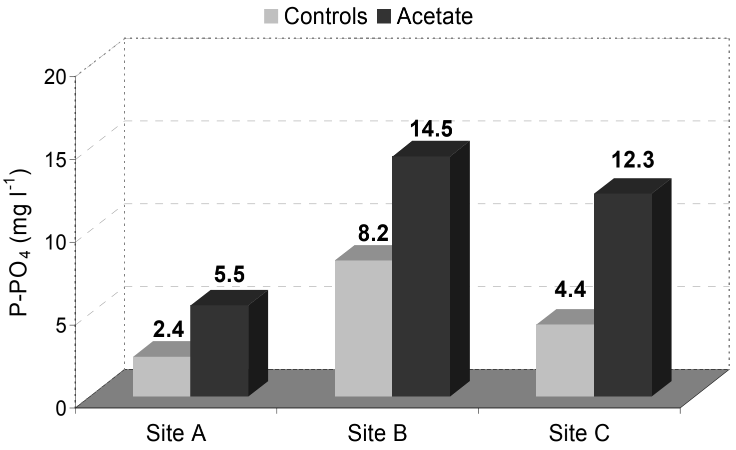


Figure 6.2 Phosphorus release during the P test for control and acetate addition reactors

The suitability of the internally produced carbon (disintegrated sludge) in biological phosphorus removal was examined with the phosphorus release test. When carbon was matched in terms of VFA (23.4 mg l^{-1}) the added SCOD was 0, 258 and 25 mg l^{-1} for the control, deflaker sludge and acetate reactor. The reactor with the disintegrated sludge performed better (341 %) giving the highest concentration of $P\text{-}PO_4$ among the three reactors (Figure 6.3). The initial concentration of $P\text{-}PO_4$ was higher at the reactor with deflaker sludge, because of the addition of disintegrated sludge with high concentration of phosphorus (Kampas *et al.*, 2007 Chapter 4)). Deflaker sludge and acetate reactor gave almost the same rate (12.9 mg l^{-1} h^{-1} and 10.1 mg l^{-1} h^{-1} for deflaker and acetate reactor, respectively) of phosphorus release in the first hour (Figure 6.3a), but at the second hour of the test the rate of release in acetate reactor was reduced. That resulted in a much higher concentration of PO_4 at the reactor with the added deflaker sludge (19.2 mg l^{-1}), despite the same amount of VFA was added. That can be explained by either the extra biomass present due to the addition of disintegrated sludge or that a part of SCOD, which is not VFA, was utilised by the bacteria in the deflaker sludge reactor. That indicates that VFA is not the only suitable carbon source for enhanced biological phosphorus removal (EBPR). However, to identify and explain the higher phosphorus release some extra tests had to be done.

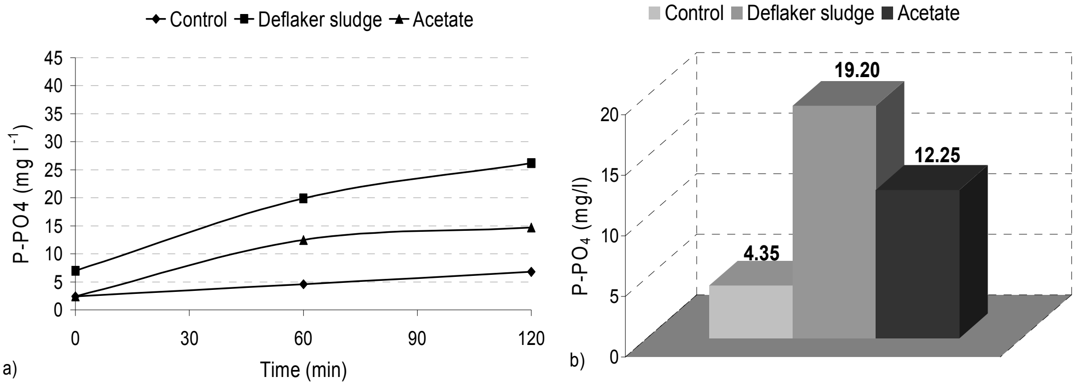


Figure 6.3 Results from P test when addition of carbon was matched in terms of VFA. a) Concentration of P-PO_4 against time and b) Phosphorus release after 2 hours

On the other hand, when the addition of carbon was matched in terms of SCOD, the concentration of the added VFA in the reactor with the deflaker sludge was 0.63 mg l^{-1}, much lower than the VFA in the acetate reactor (23.4 mg l^{-1}). That led to a higher phosphorus release in the acetate reactor (Figure 6.4). Moreover, the disintegrated sludge was also compared with brewery effluent, which already is being used as a carbon source in a BNR site. The highest phosphorus release as mentioned above appeared in acetate reactor with 14.55 mg l^{-1}, then the deflaker sludge and brewery effluent reactor with 11.85 mg l^{-1} and 10.1 mg l^{-1}, respectively and finally the control with 8.2 mg l^{-1} of released PO_4. Although, the concentration of the applied VFAs in deflaker sludge reactor was relatively low, the phosphorus release process was improved indicating again that organic matter, which is not VFA but included in SCOD is utilised by the bacteria. The results from the P test with the carbon matched in VFA or SCOD compare well to the ones produced by using hydrothermally treated sludge as carbon source for phosphorus release process (Kim *et al.*, 2006). According to these authors the excess treated sludge was adjusted to 100 mg BOD l^{-1} and the released phosphorus after 2 h under anaerobic conditions was around 6, 4.3 and 3.8 mg l^{-1} for three different hydrothermal treatments. In addition, another study using exactly the same P test compared the carbon produced from deflaker with the carbon produced from primary sludge fermentation and showed that there was higher phosphorus release (100%) in reactors with carbon from deflaker than in reactors from fermented primary sludge (Maillard, 2006). That can be a strong indication that the bacteria responsible for P removal have a preference in the carbon produced from mechanical activated sludge disintegration rather than the carbon produced from anaerobically fermented primary sludge.

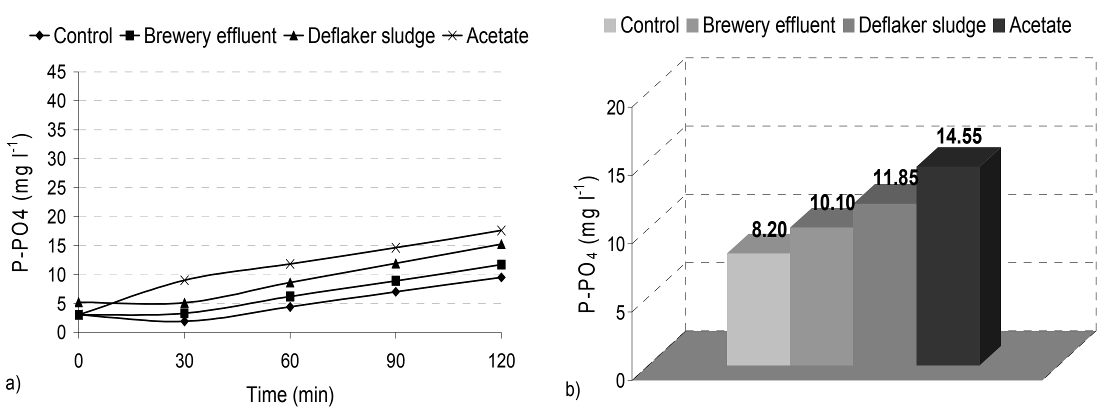


Figure 6.4 Results from P test when addition of carbon was matched in terms of SCOD. a) Concentration of P-PO_4 against time and b) Phosphorus release after 2 hours

The P test was conducted again by comparing the effect of disintegrated biomass on the release process. The same set up was used with a control and acetate reactor but the two test reactors operated differently. One with the addition of disintegrated sludge and the other with the solid free fraction of the same disintegrated sludge. In all reactors the same amount was added in terms of VFA (3.5mg l^{-1}). Both test reactors performed similarly, with higher phosphorus release than the control and also higher than the acetate reactor (744% and 220%, respectively) (Figure 6.5). This is in agreement with previous experiments which showed that when carbon is matched in terms of VFA the released phosphorus is higher in the reactor with the disintegrated sludge. The similar performance of the two test reactors indicates that is the biomass present in RAS that utilises the carbon from disintegration and not the biomass present in disintegrated sludge. That was expected as the bio-P bacteria had released a high amount of phosphorus (450 mg l^{-1}) during disintegration with plenty of carbon available (380 mg l^{-1} of VFA) to uptake. Hence the available carbon during the experiment was utilized by the bacteria included in RAS releasing the measured phosphorus. After that result we also concluded that the bacteria are capable of utilising a part of released carbon from disintegration that is not VFA but is included in the SCOD as was suspected from the previous experiments.

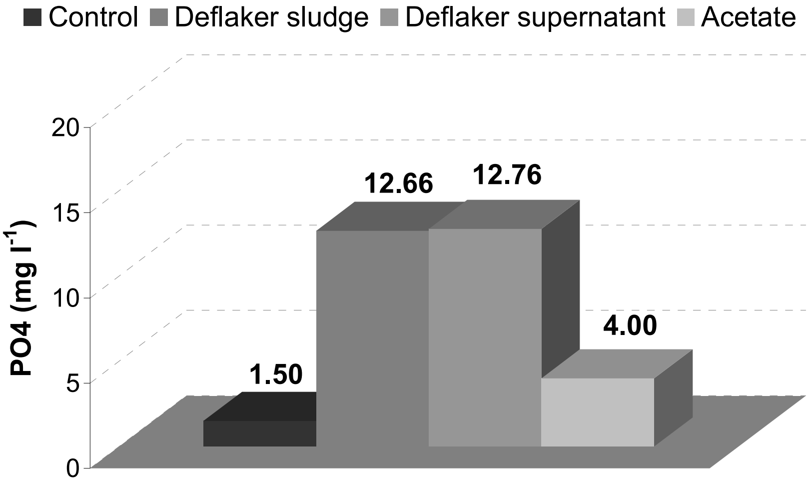


Figure 6.5 Results from P test examining the effect of biomass. Carbon matched in terms of VFA (3.5 mg l^{-1})

The P test took place with the extra carbon to be matched in terms of volume (100ml) investigating how different retention time in the deflaker or different amount of energy applied can affect the phosphorus release process. The amount of carbon added in the four reactors in terms of VFA and SCOD is presented in Table 6.3. At this test all the reactors operated with the addition of disintegrated sludge treated in the deflaker for different retention times (Figure 6.6). The concentration of the released phosphorus reached 16.2, 17.7, 20.6 and 18.8 for 2, 5, 10 and 15 minutes retention time, respectively. The difference between minimum and maximum phosphorus release was only 4.4 mg l^{-1} indicating that long disintegration time (15 minutes) and high energy input (12000-15000 kJ kg^{-1} TS) is not required for the production of suitable carbon source for phosphorus release process and during the first part of disintegration, where flocs are destroyed (Kampas *et al.*, 2007 (Chapter 4)) the most suitable type of carbon for EBPR is being released. The next part of disintegration, in which cell lysis starts taking place is able to release more carbon in the liquid phase (Kampas *et al.*, 2007 (Chapter 4)), but according to the P test the additional carbon is not as appropriate for the P release process compared to the carbon released from the first part of disintegration.

Table 6.3 The amount of VFA and SCOD added for every litre of solution in the four reactors for P test

	Deflaker retention time			
	2 minutes	**5 minutes**	**10 minutes**	**15 minutes**
VFA (mg)	5.6	13.1	14.9	24
SCOD (mg)	91	137	207	262

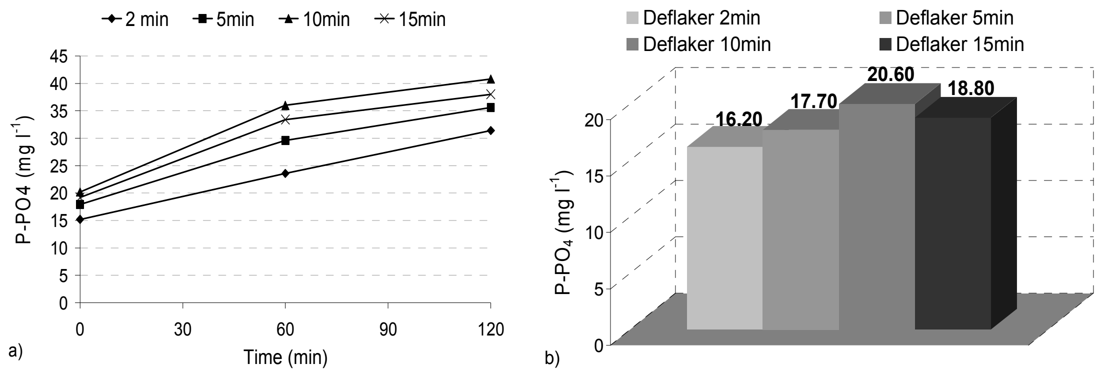


Figure 6.6 Results from P test when addition of carbon was matched in volume. a) Concentration of P-PO_4 against time and b) Phosphorus release after 2 hours

Denitrification test

The denitrification test aimed to establish rates of nitrate reduction as a result of different carbon additions (Figures 6.7 and 6.8). Similarly to the P test additional carbon was matched in either VFA or SCOD. The reactor, in which solid free fraction of disintegrated sludge was added, performed better than the control and acetate reactor resulting in the lowest concentration of nitrates. Moreover, deflaker sludge was compared with industrial wastewater (Figure 6.7b and 6.8b) and the reactor with the addition of carbon from the deflaker performed better with a higher denitrification rate than the control, industrial wastewater and acetate reactors (215, 40 and 56%,respectively), when carbon was matched in SCOD.

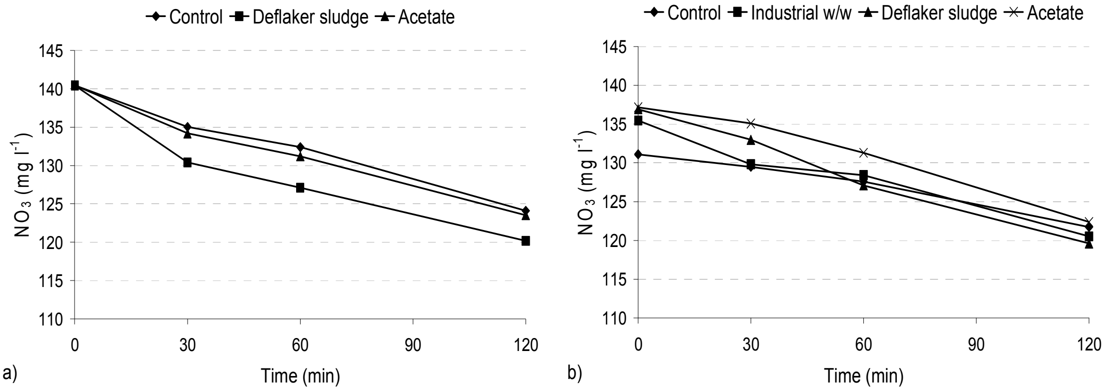
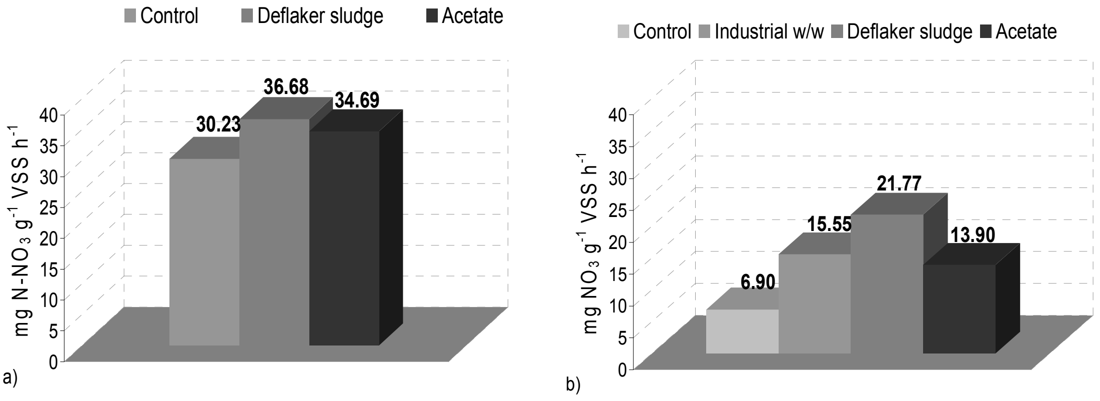


Figure 6.7 Nitrate reduction when addition of carbon was matched in a) VFA and b) SCOD for two different wastewaters

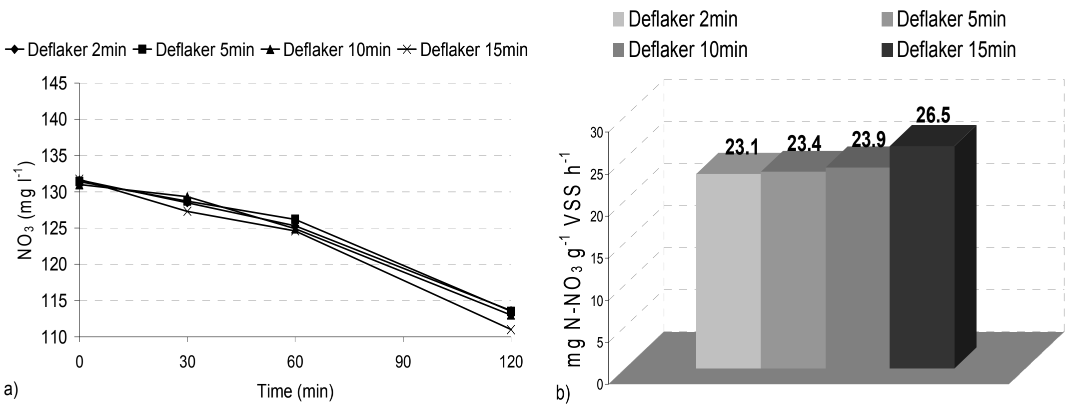


Figures 6.8 Denitrification rates when addition of extra carbon was matched in a) VFA and b) SCOD for two different wastewaters

The denitrification test was repeated adding to the four reactors the solid free fraction of disintegrated sludge produced from different retention times in order to examine how the carbon produced by different disintegration time can affect the denitrification process. According to Kampas *et al.*, (2007) (Chapter 4) short disintegration time releases the carbon found mainly outside of the cells and longer period of disintegration can release the carbon that is typically inside the cell. The added carbon was matched in volume (50 ml) and the denitrification rates were 23.1, 23.4, 23.9 and 26.5 mg N-NO_3 g^{-1} VSS h^{-1} for 2, 5, 10 and 5 minutes of disintegration in deflaker, respectively (Figure 6.9). Although the concentration of the added soluble carbon was different (Table 6.4), the denitrification rates were similar. This can be due to the fact that the carbon source, which is faster assimilated by the bacteria, is being produced after short time of disintegration. Particularly the concentration of VFA added in the reactor with the carbon from 2 minutes of disintegration was almost 3 times less that the one added in the reactor from 10 minutes of disintegration (2.8 and 7.5 mg for every litre of solution), but according to the N test the denitrification rate in the “10 minutes” reactor was slightly higher (23.9 compared to 23.1 mg N-NO_3 g^{-1} VSS h^{-1}). On the other hand if the external carbon source added is more than enough than what the available bacteria can utilize in the short period of time of two hours, the system becomes organic saturated with a limit on the denitrification rates. However, the organic saturation effect will not take place in full scale application, where the concentration of heterotrophic bacteria (~3000 mg l^{-1} of VSS) is much higher than the concentration of the bacteria used in this study (~100 mg l^{-1} VSS).

Table 6.4 The amount of VFA and SCOD added for every litre of solution in the four reactors for N test

	2 minutes	**5 minutes**	**10 minutes**	**15 minutes**
VFA (mg)	2.8	6.6	7.5	12
SCOD (mg)	46	69	104	131



Figures 6.9 Nitrate reduction and denitrification rates when addition of extra carbon was matched in volume

The denitrification rates calculated at the above experiments were higher than the ones found in literature (8.2, 5.5 and 3.6 mg $N\text{-}NO_3$ g^{-1} VSS h^{-1}) (Lee *et al.*, 2002; Bolzonella *et al.*, 2001 and Kujawa and Klapwijk, 1999). The above authors used anaerobically fermented leachate of food waste, anaerobically fermented organic fraction of municipal solid waste and acetate as carbon source for denitrification. The differences in the denitrification rates can be explained by the fact that the test in this study took place under different conditions. The major difference as mentioned above is that this study did not use any biomass with high concentrations of heterotrophs, responsible for denitrification, but only sewage with the existing bacteria. However, a recent study (Maillard, 2006) using the N test with the mixture of biomass (RAS) and sewage as the substrate, comparing the carbon produced from deflaker with the carbon produced from primary sludge fermentation, showed that the denitrification rates (0.8 – 3.5 mg $N\text{-}NO_3$ g^{-1} VSS h^{-1}) were similar to the ones mentioned above. According to the N test of this study the carbon from deflaker gave 300, 50 and 130% faster denitrification than without any additional carbon, carbon produced form primary sludge fermentation and acetate, respectively. On the other hand, according to the tests conducted by other researchers biomass was used for denitrification, resulted in quicker reduction of nitrates but lower denitrification rates per unit of biomass (VSS). However, the results of this study are comparable with the research done by Fass *et. al.*, (1994) and Bernet *et al.*, (1996), where the carbon sources they used (mixture of VFA and effluent of wine distillery, respectively), gave the maximum denitrification rates of 31.9 mg $N\text{-}NO_3$ g^{-1} SS h^{-1} and 35.2 mg $N\text{-}NO_3$ g^{-1} VSS h^{-1}.

6.4. Conclusions - Future work

This study investigated the impact of the addition of disintegrated sludge and in particular whether this carbon source is suitable for biological nutrient removal. The phosphorus release test showed that the addition of disintegrated sludge is able to improve the phosphorus release process and increase the concentration of released phosphorus, 744 % when addition of carbon was matched in terms of VFA and 45 % when was matched in terms of SCOD. The utilised carbon was not only the VFA, but also a part of the SCOD and the released phosphorus came from the bio-P bacteria in RAS and not from the disintegrated biomass. Similarly, according to the denitrification test the addition of the carbon produced by sludge disintegration is able to increase the denitrification rate, 215 % and 21.3 %, when carbon was matched in terms of VFA and SCOD, respectively. The comparison of the carbon produced by different time of disintegration showed that short disintegration time (2 – 5 minutes) is adequate for the production of useful organic matter.

In overall, disintegrated sludge from deflaker proved to be a suitable carbon source for the phosphorus release and denitrification process, according to the tests conducted in laboratory scale. Further research will examine the application of this internal carbon source in pilot scale and whether can improve biological nutrient removal process performances.

Acknowledgments

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Chapter 7 Disintegration of sludge recycles and its impact on BNR process performance

Water Research (submitted)

7. Disintegration of sludge recycles and its impact on BNR process performance

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Abstract

The need for nutrient removal and the disposal of excess sludge are two of the most significant challenges in wastewater treatment. In this study the effectiveness of partial mechanical disintegration of return activated sludge for the production of useful organic matter for enhanced biological phosphorus removal (EBPR) and sludge minimization is examined. Two parallel pilot scale biological nutrient removal (BNR) reactors (1.5 m^3 d^{-1}) were used to investigate the impact of a disintegration process on treatment performance and sludge production. The mechanical disintegration device was a deflaker, which was able to cause an increase in the concentration of volatile fatty acids (VFA) of the total flow of wastewater by 2.5-7 mg l^{-1}. At the same time sludge disintegration was giving an extra 3.5-6.5 mg l^{-1} of phosphorus. During the experiment the performance of the test reactor in terms of nitrogen, suspended solids and chemical oxygen demand was unaffected and also 44%-89% more phosphorus compared to the control reactor was removed. At the same time a 20-26% reduction in bacteria growth yield was observed.

Keywords biological nutrient removal, mechanical sludge disintegration, sludge reduction, pilot scale reactors, phosphorus fractionation, denitrification

7.1 Introduction

Biological nutrient removal (BNR) processes are now widely accepted as an effective and economical method for wastewater treatment. Enhanced biological phosphorus removal (EBPR) reduces the cost of chemicals and also reduces the amount of excess sludge produced compared to chemical phosphorus removal (Mulkerrins *et al.*, 2004). However, the disposal of sludge remains a serious environmental issue.

It is well known that denitrification and phosphorus removal efficiencies are strongly dependant on the availability of a suitable carbon source. The most suitable for the biological removal of phosphorus are short-chain volatile fatty acids (VFA) (Abu-ghararah and Randall, 1991). Many options have been investigated to enhance BNR process performances, many of which have focused on increasing the concentration of the available VFA in the influent. That can be achieved by dosing organic chemicals such as acetate or methanol or industrial wastes such the fermented food wastes (Lee *et al.*, 2002; Lim *et al.*, 2000), fermented swine wastes (Lee *et al.*, 1997) and wine distillery effluent (Bernet *et al.*, 1996).

Another option that has been assessed to satisfy the need of VFA in the EBPR process is the production of useful organic matter from internal sources such as the influent wastewater solids or primary and/or secondary sludge. The most commonly applied method is primary sludge fermentation, which has been reported to increase the VFA concentration in the total flow of wastewater by 7-49 mg l^{-1} (Munch and Koch, 1999). Hydrothermal, chemical (ozonation) and biological (hydrolysis and fermentation) treatment of secondary sludge (as well as combinations of these) have also been examined in the past, but the target of those treatments was mainly solid destruction and carbon source production (Isaacs and Henze, 1995; Shanableh, 2000; Kim *et al.*, 2006; Vollertsen *et al.*, 2006; Saktaywin *et al.*, 2006; Dytczak *et al.*, 2007). There is little information in the literature on the application of carbon source produced by mechanically disintegrated sludge to BNR processes. Muller (2000) for example, reported that carbon from mechanical sludge disintegration can be utilised during denitrification but its application to biological phosphorus removal has not been investigated.

In this research the carbon produced from mechanical disintegration of a proportion of return activate sludge (RAS) is applied directly to the anaerobic zone of a BNR pilot scale reactor in order to improve phosphorus removal. The equipment used for this purpose is the deflaker, which has been proved to be able to increase the concentration of VFA and soluble chemical oxygen demand (SCOD) in activated sludge sources (Kampas *et al.*, In Press (Chapter 4)). The impact of sludge disintegration on the BNR process performances and the bacteria growth (excess sludge production) is examined.

7.2 Materials and Methods

7.2.1 Pilot plant

The pilot scale trials took place on the pilot hall facilities of sewage treatment works of Cranfield University, UK. Although it was operated indoor there was no temperature control, therefore operating conditions reflected the seasonal temperature variation that occurs in Bedfordshire, UK. The pilot rig was consisted of two separate modified University of Cape Town (MUCT) BNR reactors and clarifiers constructed by Balmoral Group (Aberdeen, UK) (Figure 7.1). The active volume of each reactor and clarifier was 1025 l and 334 l, respectively. Each reactor basin included anaerobic, two anoxic and aerobic compartments. The clarifier was equipped with slow rotating (0.4 rpm) scrapper.

The size of the anaerobic zone was 125 l. The wastewater flowed by gravity to first anoxic zone and then moved to second anoxic and aeration zone. The anaerobic and first anoxic zones were two different and completely separate compartments, while the two anoxic and aerobic were separated by baffle walls without being sealed. That resulted to some backflow, but without any effect on the dissolved oxygen (DO) concentration. The DO was constantly kept below 0.2 mg l^{-1} in both anaerobic and anoxic zones. The size of the first and second anoxic zones was 120 l and 230 l, respectively and equipped with Lightnin® Industrial Batch Mixers (Cole-Palmer Instrument Co Ltd., London UK). Finally, the aeration basin (550 l) was supplied with air, providing agitation and a DO concentration of 2-4 mg l^{-1}.

The influent wastewater was pumped to anaerobic zones by a doubled head variable speed peristaltic pump (Watson and Marlow 500 series pump with marprene tubing, Watson-Marlow-Bredel Pumps, Corwall UK) providing an identical flow rate for the two reactors of $Q=60\ \mathrm{l\ h^{-1}}$. The same type of pumps were used for the RAS flow ($Q_R=51\ \mathrm{l\ h^{-1}}$), the aerobic recycles ($Q_1=60\ \mathrm{l\ h^{-1}}$) and the anoxic recycles ($Q_2=60\ \mathrm{l\ h^{-1}}$). At the end of the aeration basin the solution was led by gravity to the settler with the hydraulic loading rate to be $3.74\ \mathrm{m^3\ (m^2\ d)^{-1}}$. The waste sludge was removed from the system by two single head peristaltic pumps (Watson and Marlow 500 series) from the bottom of the two clarifiers. The amount of wasted sludge was dependant on the operating conditions. The total hydraulic retention time (HRT) of the anaerobic, anoxic and oxic zones was 17 h and the mean cell residence time (sludge age) was maintained between 14-18 days. The operating conditions of the pilot plant are summarised in Table 7.1.

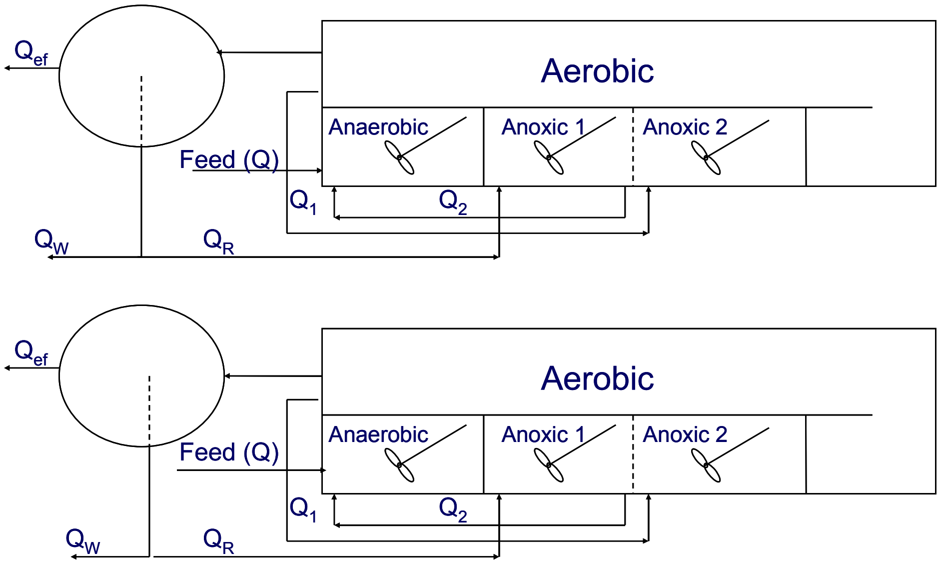

Figure 7.1 Schematic diagram of the two pilot-scale BNR reactors. Q_R: RAS, Q_1: aerobic recycle, Q_2: anoxic recycle, Q_{ef}: effluent, Q_w: waste

Table 7.1 Operating conditions

Flow ($l\ h^{-1}$)		Retention time (h)	
Influent	60	Anaerobic	2
RAS	51	Anoxic 1	2
Anoxic recycle	60	Anoxic 2	3.8
Aerobic recycle	60	Aerobic	9.2

7.2.2 Disintegration process

The equipment used for sludge disintegration was a 10” Pilao DTD Spider Deflaker with a 30 kW motor fitted with 230 mm discs with 3 active cell layers. The gap distance between stator and rotor was 0.6-0.9 mm and the rotation speed 3000-3600 rpm. The disintegration process was conducted as a batch with five litres of sludge to be treated each time at the retention time of 10 minutes (Kampas *et al.*, In Press (Chapter 4)).

The sludge was collected form the bottom of the clarifier of the test reactor using a peristaltic pump (500 series) in a sack filter (Bioclere Technology International, Surrey, UK) increasing the solid concentration from ~6.5 g l^{-1} up to 40-60 g l^{-1}. The liquors was collected in a tank (Tank 1) located underneath the sack filter. The average retention time in the sack that was required in order to achieve the desirable thickening was 24 h. The disintegrated sludge then was placed in a tank (Tank 2), where was mixed (Lightnin® Industrial Batch Mixer) with the liquors produced from the thickening process. The flow chart for the disintegration process is demonstrated in Figure 7.2.

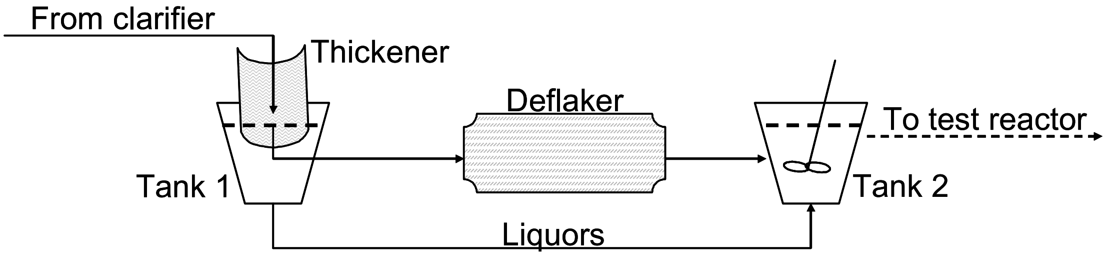

Figure 7.2 Schematic of the thickening and disintegration process

7.2.3 Wastewater characteristics and experimental procedure

The biological population used in the process was developed from a successful full scale plant operating in BNR mode. The influent wastewater was pumped from the primary tank of Cranfield sewage works to the pilot hall facilities. The characteristics of the wastewater are summarized in Table 7.2.

Table 7.2 Wastewater characteristics

Influent characteristic	Concentration (mg l^{-1})					
	Phase I			Phase II		
		Min	Max		Min	Max
TSS	(n=24) 106 ± 14	83	138	(n=24) 100 ± 13	73	128
TCOD	(n=32) 348 ± 44	250	436	(n=38) 342 ± 47	240	480
NH_4	(n=35) 31 ± 5	20	40	(n=36) 32 ± 6	20	41
TN	(n=22) 52 ± 7	36	62	(n=20) 53 ± 8	34	62
TP	(n=47) 7.42 ± 0.71	5.5	8.8	(n=47) 6.94 ± 0.95	5.4	9.9

The experimental plan has been separated in two phases. However, in both phases the pilot plant was operated with the addition of external carbon source as initial test showed that the carbon present in the influent was not sufficient for the phosphorus release and denitrification process and biological phosphorus removal could not be achieved. The external carbon was acetate and dosed in both anaerobic and anoxic zones for phosphorus release and denitrification, respectively. The amount of acetate ranged between 50 and 70 mg for every litre of wastewater. During the experiment the carbon produced from sludge disintegration was not enough to replace the acetate and hence the test reactor was operated with the addition of both acetate and disintegrated sludge. However, both reactors (control and test) were receiving the same amount of carbon in terms of VFA.

Phase I

Phase I took place in the summer and the average temperature of mixed liquors was ~23°C. During Phase I ~20 mg of acetate were dosed in the first anoxic zone and ~38 mg in the anaerobic, for every litre of wastewater. When the disintegration started 5.88% of RAS flow, was passing through the sack filter. The thickened sludge was disintegrated by deflaker producing 7 mg VFA and at the same time replacing 7 mg from the acetate dose. The sludge waste of the test reactor was stopped and it was operated in very long sludge age (40-45 days) as the only amount of solids wasted was through the losses from the thickening and disintegration processes. The control reactor was operated under the normal conditions described above.

Phase II

After Phase I a period of two sludge ages was used to allow both reactors to reach steady state and no residual effect of Phase I was present. The average temperature of mixed liquors was 17°C. During Phase II ~20 mg of acetate was dosed in the first anoxic zone and ~40 mg in the anaerobic. The amount of sludge that was disintegrated was equivalent to 5.88% of RAS flow increasing the concentration of VFA in the influent by 2.5 mg l^{-1}. Consequently, the acetate dose was reduced by 2.5 mg for every litre of wastewater. At this phase the two reactors were matched in terms of MLSS concentration and the appropriate amount of sludge was removed from the aeration basin leading to a ~16 and ~22 days of sludge age for the control and test reactor, respectively.

In both phases disintegration process gave an extra load of phosphorus in the test reactor. In Phase II in order to investigate the effect of the disintegration without that extra amount of phosphorus we also established a simple sidestream chemical phosphorus removal step. The precipitation of phosphorus as struvite ($NH_4MgPO_4{\cdot}6H_2O$) was attempted by dosing $MgCl_2$ and NH_4Cl to Tank 2 in order to achieve a molar ratio of NH_4:Mg:PO_4 of 1:2:1 and at the same time maintaining the pH at ~9.

7.2.4 Analytical methods

The concentration of total suspended solids (TSS), volatile suspended solids (VSS), total solids (TS), total COD, total P (TP), phosphates (PO_4), ammonium (NH_4), total nitrogen (TN) and nitrates (NO_3) was measured according to APHA Standard Methods (1998). The analysis of VFA, soluble COD and soluble P were carried out in the solid free fraction of sludge after centrifugation (10500 g, 7°C) and filtration (0.45 μm) and again according to the APHA Standard Methods (1998). Turbidity was measured using the HACH 2100N Turbidimeter from Camlab Ltd, (Cambridge, UK) and the sludge volume index (SVI) of the biomass was also calculated.

In order to evaluate the phosphorus removal by the test reactor in the second phase and whether the phosphorus is stored in the solids as mineral phosphorus or polyphopshates, the cold perchloric acid (PCA) procedure was followed (De Haas *et al.*, 2000). Based on that method 20 ml of mixed liquor centrifuged (4960 g, 3°C, 5 minutes) and the pellets were washed twice with deionised (DI) water. Then 20 ml of perchloric acid (0.5 M) were added to the pellets and mixed under ice-cold conditions (2-4°C) for 15 minutes. The mixture was centrifuged (4960 g, 3°C, 5 minutes), the supernatant was stored in the fridge (4°C) and the residue was resuspended and washed with DI water. Finally, 20 ml of DI water were added to the residue. The concentration of PO_4 and TP was measured in the stored supernatant and the TP was measured in the residue and in the initial mixed liquor sample. The concentration of PO_4 in the supernatant represents the mineral part of P in the biomass, while the difference between TP and PO_4 in the supernatant represents the complex part of P in the solids consisted of polyphosphates (biologically stored PO_4) and other organic P. Finally, the residue contains the non extractable P.

7.3 Results – Discussion

The results from the pilot scale trial have been separated into Phase I and Phase II and the effect of sludge disintegration on sludge production is examined separately for both phases.

7.3.1 Phase I

Disintegration

During the trials, the sludge collected from the test reactor was thickened in a sack filter, in which a degree of fermentation was taking place (Table 7.3). The average SCOD concentration increased from 38 to 425 mg l^{-1} and there was also an increase in VFA and Sol. P content (7 and 29 times, respectively). Treatment in the deflaker increased the concentration of SCOD, VFA and Sol. P by an additional 8.6, 4.1 and 4.2 times, respectively. After blending the disintegrating sludge with the thickening liquors the concentration of SCOD, VFA and Sol. P was 630, 140 and 130 mg l^{-1}, respectively, gave an actual dose of SCOD, VFA and Sol. P was 31.5, 7 and 6.5 mg for every litre of influent wastewater. During the thickening and disintegration processes a loss of solids was observed leading to a slight reduction in the total solid concentration of sludge.

Table 7.3 Sludge characteristics on different streams for Phase I

	RAS	inside the sack filter	after deflaker	after mixing with the liquors from thickening process
TS (%)	0.7	5.1	5.1	0.65
SCOD (mg l^{-1})	38	425	3650	630
VFA (mg l^{-1})	13	92	374	140
Sol. P (mg l^{-1})	2.7	78	330	130

The amount of carbon released by the deflaker, in terms of VFA, is low when we compare it to other processes such as hydrothermal treatment (~370°C, 28 MPa), which was able to release 3000 mg l^{-1} of acetic acid from activated sludge and lead to an estimated increase of VFA concentration in the total flow of wastewater by 45-50 mg l^{-1} (Shanbleh, 2000). The levels reported here are at the low end of the reported range of full scale fermenters of primary sludge (7-49 mg l^{-1}) (Munch and Koch, 1999). A comparison with the pre-fermentation of the wastewater shows that the deflaker causes lower increase in the VFA content than the increase reported by McCue *et al.*, (2003) (15 mg l^{-1}) and higher than the one reported by Urbain *et al.*, (2001) (5 mg l^{-1}).

A major drawback of the fermentation processes is the release of NH_4 and the concentration found in thermal or biological hydrolysate can be as high as ~500 mg l^{-1}, increasing the NH_4 concentration of the influent wastewater by 15-20 mg l^{-1} (Barlindhaug and Odegaard, 1996; Shanableh, 2000). In this study, the concentration of NH_4 in disintegrated sludge was between 30 and 50 mg l^{-1} increasing the overall concentration of NH_4 in the influent by only 1.5-2.5 mg l^{-1}.

Pilot plant performance

Prior to disintegration the performance of the two reactors in terms of TSS, TCOD, TN, NH_4 and NO_3 was almost identical (Table 7.4). The average performance of the two reactors after 40 days of disintegration had not changed, showing that disintegration of sludge and also the long sludge age used in this phase did not have any significant effect on the process and the only slight reduction was in the effluent concentration of NO_3 (10%).

Table 7.4 The performance of the pilot plant before and during disintegration (Phase I)

		Before disintegration			During disintegration		
		IN	OUT	Removal (%)	IN	OUT	Removal (%)
TSS (mg l^{-1})	Control	108 ± 15	12 ± 6	89 ± 6.5	102 ± 12	10 ± 3.5	90 ± 4
	Test		10 ± 4	91 ± 3.8		8 ± 3	92 ± 3.2
TCOD (mg l^{-1})	Control	338 ± 49	61 ± 14	82 ± 4.5	360 ± 39	53 ± 11	85 ± 3.7
	Test		58 ± 17	83 ± 4.8		56 ± 9	84 ± 3.5
NH_4 (mg l^{-1})	Control	30 ± 5	0.03 ± 0.01	99.9 ± 0.05	33 ± 4.5	0.03 ± 0.01	99.9 ± 0.03
	Test		0.03 ± 0.02	99.9 ± 0.06		0.03 ± 0.01	99.9 ± 0.03
TN (mg l^{-1})	Control	49 ± 7	14 ± 2.4	71 ± 8.4	55 ± 4.5	14 ± 3	74.5 ± 4.6
	Test		15 ± 4	69 ± 11.3		15 ± 3	73 ± 4.8
NO_3 (mg l^{-1})	Control		7.5 ± 2.1			8.2 ± 2.8	
	Test		8.1 ± 3			7.3 ± 2.8	

In order to better understand the impact of disintegration process on the TP removal the difference (ΔTP) in the concentration of TP in the effluent of the two reactors is considered.

$\Delta TP = TP_{control\ (effluent)} - TP_{test\ (effluent)}$

The concentration of TP in the effluent of the two reactors was similar before the disintegration period with a ΔTP of -0.4 (1.8 and 2.2 mg l^{-1} on average) (Figure 7.3A).

During the disintegration period and due to the extra P added to the system, as a result of disintegration, the test reactor was receiving on average 6.1 mg l^{-1} more P than the control. Nevertheless, the effluent TP was not very different resulting to an average ΔTP of -1.1. The lower P removal in the test reactor could be attributed to the long sludge (40-45 days), as it is well known that P removal is adversely affected by the increase of the sludge age (Rodrigo *et al.*, 1996).

The concentration of TP in the effluent of the test reactor was higher than the control, but the amount of TP removed was also higher by 5 mg l^{-1} on average (Figure 7.3B). The PO_4 mass balance in the anaerobic selectors, conducted at the last 10 days of the experiment, showed that the PO_4 release was higher in the control reactor (Figure 7.4). The P responsible bacteria of the test reactor despite their lower PO_4 release in the anaerobic zone, could take up 5 mg l^{-1} more P than they do under normal conditions (control reactor).

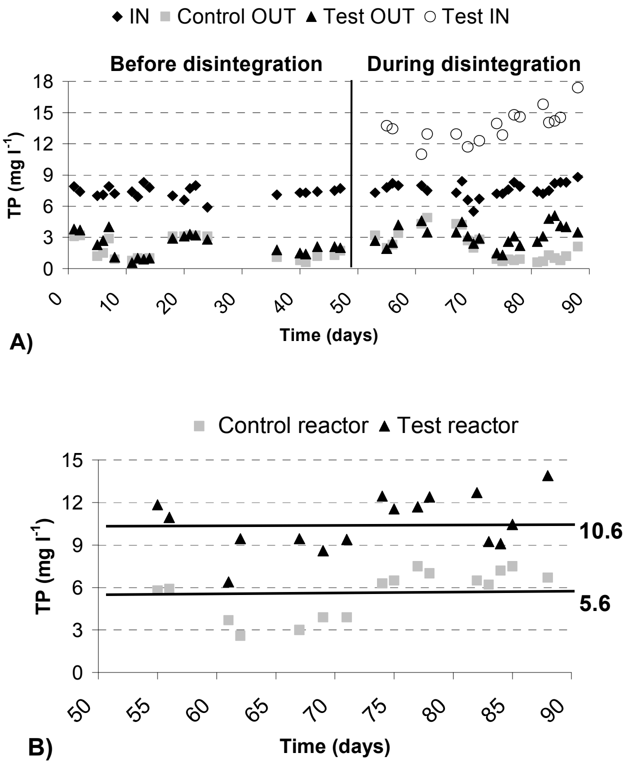

Figure 7.3 The TP concentration in Phase I. A) The performance of the two reactors before and during disintegration and B) the amount of TP removed from the two reactors during disintegration

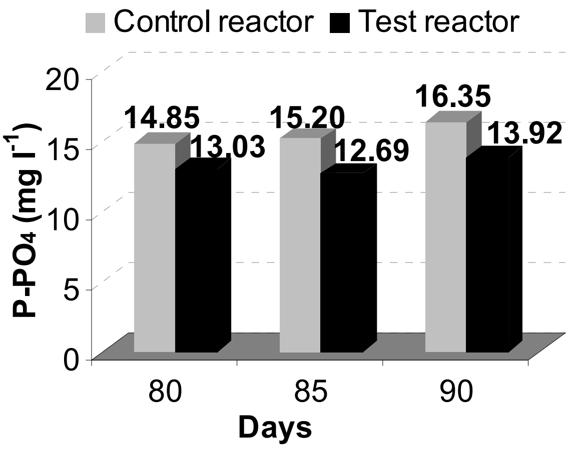

Figure 7.4 The net PO_4 release in the anaerobic selectors calculated at the end of the disintegration period of Phase I

7.3.2 Phase II

Disintegration

The procedure followed for sludge collection, thickening and disintegration was the same as in Phase I and the changes of SCOD, VFA and Sol. P are reported in Table 7.5. The effects of fermentation in the sack filter on sludge characteristics are different compared to that found in Phase I with the concentration of SCOD, VFA and Sol. P after the deflaker to be 26, 55 and 42% lower. That difference is attributed to the different weather conditions, as Phase I was during a very hot summer with the temperature reaching 30-35°C and Phase II in autumn with the temperature not exceeding 19°C. It is well known that higher temperature accelerates sludge hydrolysis and fermentation (Canziani *et al.*, 1996; Chen *et al.*, 2004; Ahn and Speece, 2006). As a consequence, the dose of SCOD and VFA being returned to the test reactor during Phase II was 16 and 2.5 mg l^{-1}, respectively and gave an extra load of 3.6 mg l^{-1} of P.

Table 7.5 Sludge characteristics on different streams for Phase II

	waste line	inside the sack filter	after deflaker	after mixing with the liquors from thickening process
TS (%)	0.71	5.4	5.4	0.69
SCOD (mg l^{-1})	42	131	2700	320
VFA (mg l^{-1})	14	44	168	50
Sol. P (mg l^{-1})	2.9	37	190	72

Pilot plant performance

In Phase II 5.88% of the RAS flow was going through the filter and deflaker giving an additional 2.5 mg l^{-1} of VFA in the influent. The test and control reactor were matched in MLSS concentration, which resulted in a sludge age between 15 and 24 days. Prior to disintegration the performances of the two reactors in terms of TSS, TCOD, NH_4, TN and NO_3 are similar. This did not change during the disintegration period (Table 7.6).

Table 7.6 The performance of the pilot plant before and during disintegration (Phase II)

		Before disintegration			During disintegration		
		IN	OUT	Removal (%)	IN	OUT	Removal (%)
TSS (mg l^{-1})	Control	92 ± 7	13 ± 4	86 ± 4.9	104 ± 13	11 ± 2.5	89 ± 3.1
	Test		10 ± 4	89 ± 4.6		10 ± 3	90 ± 2.5
TCOD (mg l^{-1})	Control	335 ± 52	69 ± 17	79 ± 4.2	347 ± 45	64 ± 14	81 ± 4.1
	Test		67 ± 13	80 ± 4.3		61 ± 13	82 ± 3.4
NH_4 (mg l^{-1})	Control	30 ± 5	0.06 ± 0.01	99.8 ± 0.05	33 ± 6	0.07 ± 0.02	99.8 ± 0.09
	Test		0.05 ± 0.01	99.8 ± 0.04		0.07 ± 0.04	99.8 ± 0.1
TN (mg l^{-1})	Control	50 ± 8	14 ± 4	72 ± 4	54 ± 7.7	17.7 ± 2.2	67 ± 3.8
	Test		14 ± 4	72 ± 6.1		17.6 ± 4	67 ± 5.3
NO_3 (mg l^{-1})	Control		8.5 ± 3.4			10.9 ± 3.2	
	Test		7.4 ± 3.9			10.9 ± 2.1	

During the disintegration period the amount of TP that had to be removed by the test reactor was higher than the control by 3.5 mg l^{-1}. This extra P led to a ΔTP of -0.27 in the effluent (Figure 7.5A), however, the test reactor was again able to remove more P than the control by 2.9 mg l^{-1} (Figure 7.5B). Chemical dosing to precipitate phosphorus in the deflaker and thickening liquors started after the 60th day of the experiment. This reduced the PO_4 concentration by ~50%, leading to an increase in the TP concentration in the influent of the test reactor by only 1.8 mg l^{-1}.

During the chemical precipitation period the amount of TP removed by the test reactor was 2 mg l^{-1} more than the control and the ΔTP was +0.21, meaning that better removal was observed in the test reactor than the control even though it was receiving higher strength influent. After 20 days the deflaker was halted and the plant then operated for a further 10 days. To investigate the impact the extra carbon had on the P removal, the control operated with 2.5 mg l^{-1} of VFA more than the test and the results showed that the ΔTP from +0.21 was decreased to -0.95 indicating that the performance of the system was not due to the acetate addition alone.

However, the statistical analysis (t-test) conducted to compare the performance of the two reactors in terms of P removal showed that the t-stat is lower than the t-critical for the experimental periods of prior to disintegration and during disintegration. This is a strong indication that the two reactors are not statistically different for those periods. On the other hand, when the disintegration was stopped there was a difference in the P removal for the two reactors as was shown by the t-test (Table 7.7).

Table 7.7 t-test analysis for the different experimental periods (p=0.05)

	Before disintegration	During disintegration		Without disintegration
		-	Chemical precipitation	
t-stat	0.08	1.38	1.18	7.3
t-critical	2.05	2.02	2.1	3.18

There are few comparative studies on sludge disintegration of RAS that we can compare our study with. Saktaywin *et al.*, (2006) reported the ozonation of 3.2% of RAS of an anaerobic/oxic (A/O) system fed with synthetic wastewater aiming to reduce sludge production and recover P by crystallization process. They reported a deterioration in the system in terms of TSS and COD removal, as well as the effluent NO_3 concentration increased by 4 mg l^{-1}. The TP concentration in the effluent increased up to 5 mg l^{-1} for a period, but on average similar to this study was unaffected.

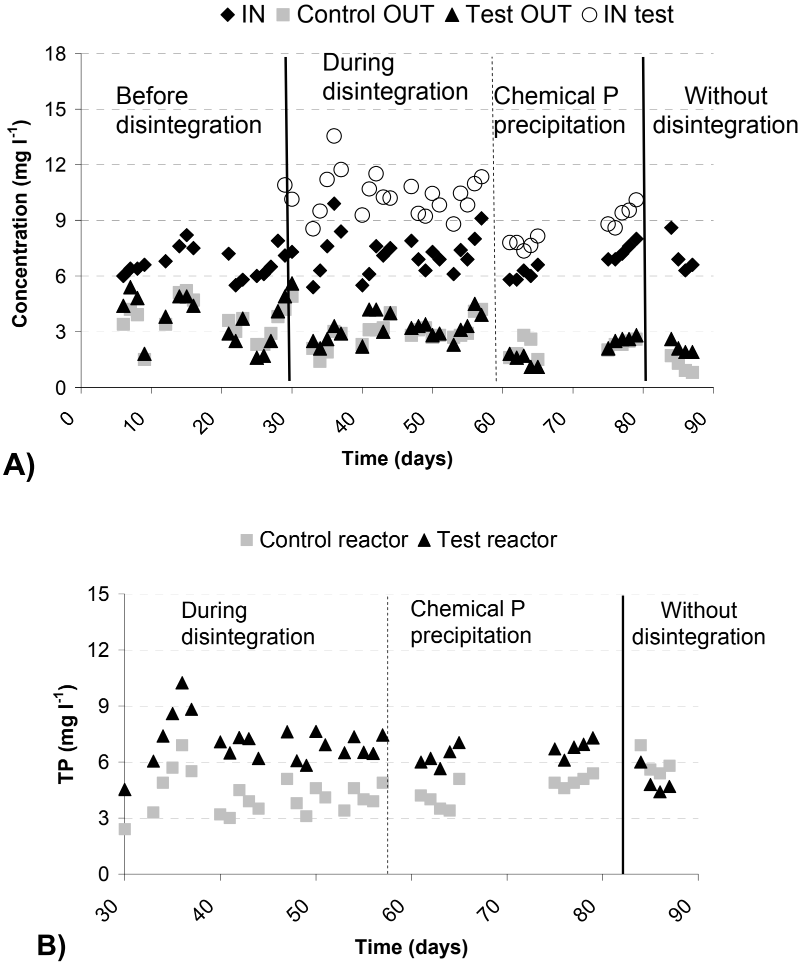

Figure 7.5 The TP concentration in Phase II. A) The performance of the two reactors before and during disintegration and B) the amount of TP removed from the two reactors during disintegration

In order to explain the higher P uptake in the test reactor in both Phase I and Phase II, we examined whether the P was being stored biologically or chemically in the solids. Fractionation of P in the sludge with the cold perchloric method showed an equal amount of P stored biologically for the two reactors before and during the disintegration period

(Figure 7.6). The amount of mineral P was increased during the disintegration by 34 % showing an increase in the inorganic compounds in sludge. However, this difference represents only the 5.3 % of the TP in sludge (2.6 of 49 mg P g^{-1} VSS), indicating that an enhancement of the chemical storage of P within the sludge is not the only reason for the higher P uptake in the test reactor.

Another option of the higher P uptake in the test reactor could be the result of increased available surface area and activity of the microorganisms as a result of particle size reduction due to disintegration. In addition, part of the P-bacteria of the test system remains into Tank 2 under anaerobic conditions and with carbon available, which can lead to the release of most of their stored P and hence then they have an increased P uptake potential. It should also be considered that when a BNR system is phosphorus limited and there is more carbon available than the required, an increase in the influent TP concentration will not effect the performance as the bacteria have the capacity to remove more P (Randall *et al.*, 1992). Testing these hypotheses will be the focus of future work.

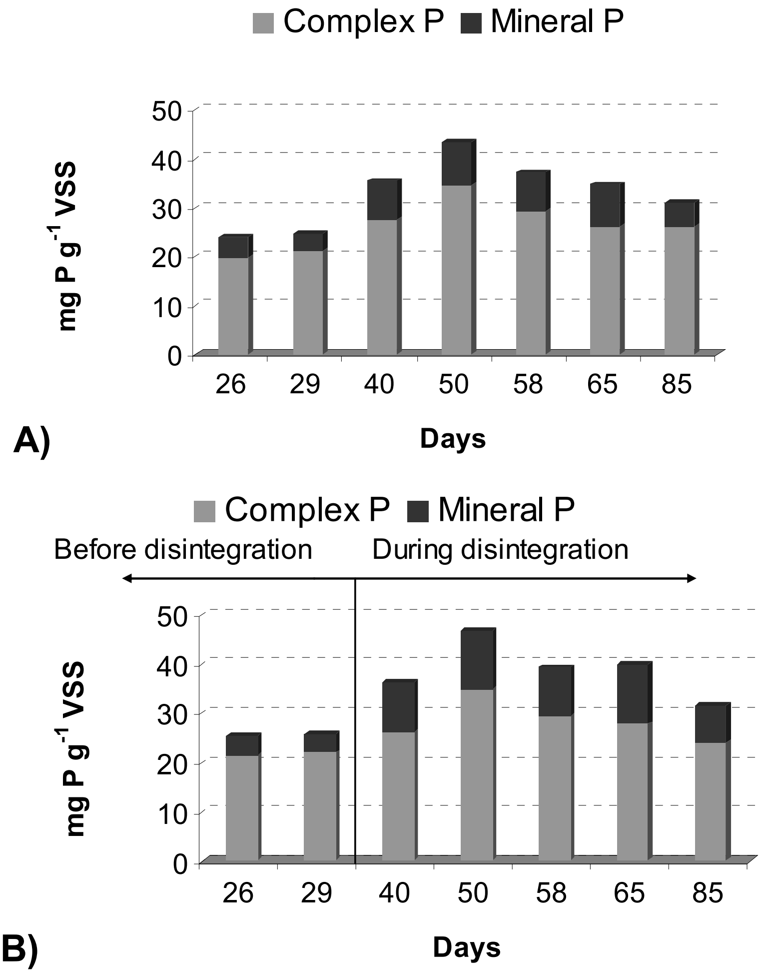

Figure 7.6 Results from the P fractionation of A) control and B) test reactor

The effect of sludge disintegration on the settleability of sludge and the turbidity of the effluent was also examined. The SVI increased in the test reactor immediately after the disintegration started and remained high until the end of the experiment (~250) (Figure 7.7A). The high SVI is due to the presence of filamentous bacteria or increased floc size (Sezgin, 1982). Although, previously it has been reported that sludge disintegration can improve settleability and reduce bulking sludge by destroying the filamentous bacteria and reducing the floc size (Kamiya and Hirotsuji, 1998; Muller, 2001; Deleris *et al.*, 2002), the opposite results were observed in this study. On the other hand the disintegration process did not have any effect on the turbidity of the effluent (Figure 7.7B).

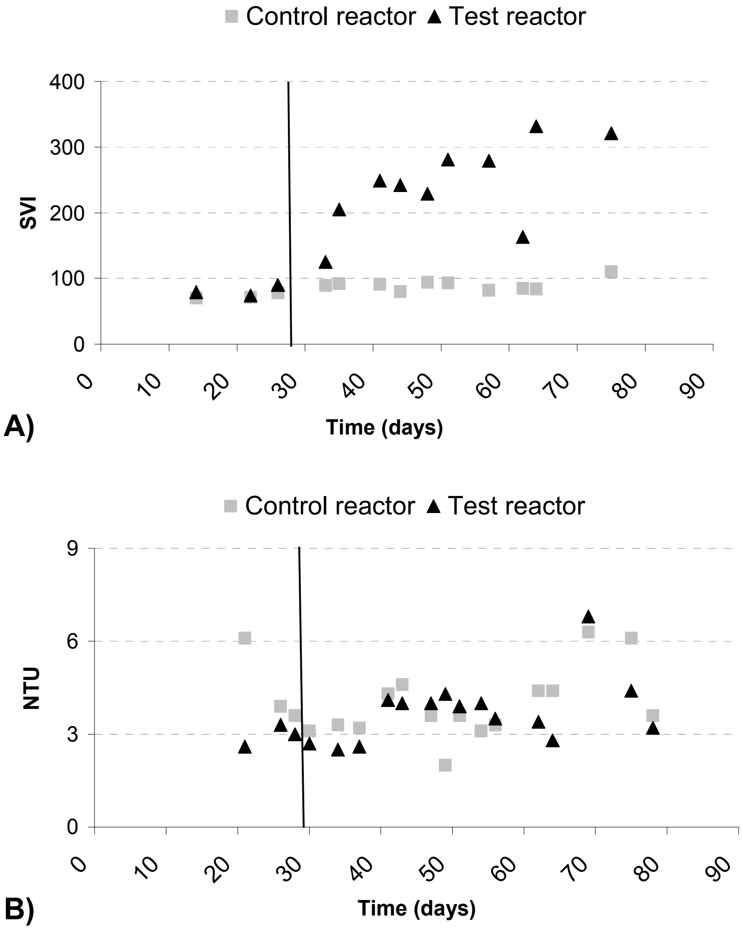

Figure 7.7 A) the SVI and B) the turbidity for the two reactors before and during the disintegration of Phase II

7.3.3 Excess sludge reduction

In both phases the amount of sludge wasted from the two reactors was constantly monitored. In Phase I, in the test reactor, solids were only removed via the effluent as well as the losses during the thickening and the disintegration processes. This led to an increase in the mixed liquor concentration (Figure 7.8A). In the end of the experiment, using the difference in the MLSS concentration we were able to estimate the additional sludge present in the test reactor and clarifier. The difference between the amount of sludge produced (wasted sludge) from the control reactor during the disintegration period of 40 days and the sludge produced from the test (losses from sack filter and deflaker plus the increase in mixed liquor), showed that 26% less sludge was produced in the test reactor than in the control. This can be attributed to the combination of the disintegration and the long sludge age (endogenous respiration).

In Phase II the two reactors were matched in terms of mixed liquor concentration (Figure 7.8B). The average growth yield (mass of biomass produced to mass of COD consumed) over each sludge age, before and during the disintegration for the two reactors is presented in Figure 7.9. Before the disintegration the growth yield in the test reactor was slightly higher than the control (0.42 and 0.44 for control and test, respectively). When disintegration was started the yield in the test reactor was reduced and remained lower than the control until the end of the experiment. The average yield during the disintegration period was lower in the test reactor by between 20-25%, with part of this reduction to be due to longer sludge age in the test reactor. The six days difference can cause a 6% reduction in the growth yield (Metcalf and Eddy, 2003). The overall reduction correlates well with the amount of sludge removed from the test system, which was on average ~22% less than the control.

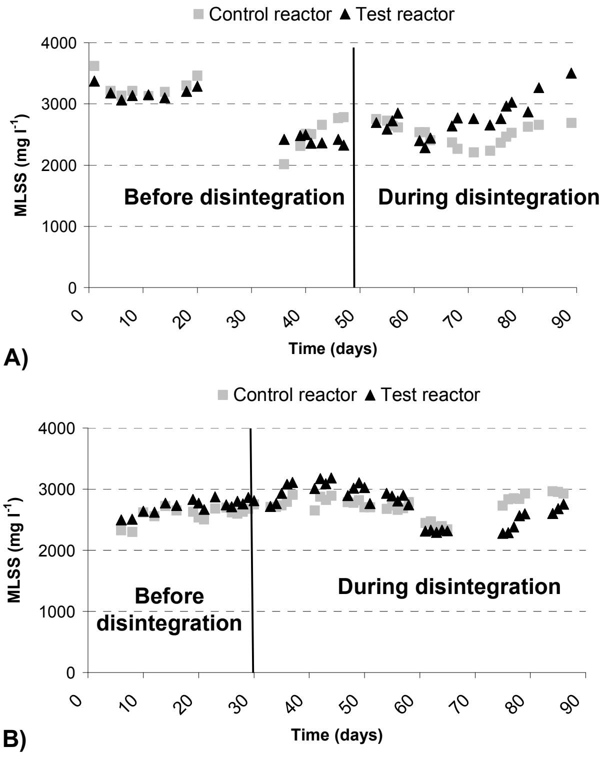

Figure 7.8 The MLSS concentration for the two reactors. A) Phase I and B) Phase II

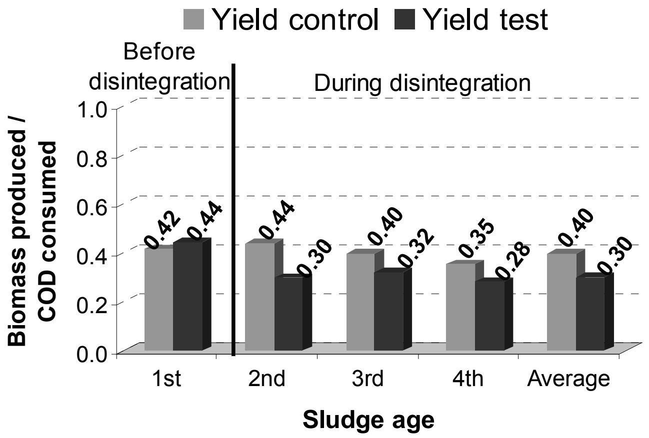

Figure 7.9 The growth yield for the control and test reactor before and during the disintegration of Phase II

The theories developed in the past to explain reduction in sludge production as a result of disintegration, are lysis-cryptic growth and enhanced maintenance metabolism (Wei *et al.*, 2003). There are many reports in the literature of sludge reduction using ozone treatment and mechanical devices. Saktaywin *et al.*, (2006) reported a 60% reduction in sludge produced sludge in a laboratory scale reactor fed with synthetic wastewater and ozonating 3.2% of RAS. Bohler and Siegrist, (2004) observed a 25-35% sludge reduction conducting batch tests on real wastewater. Finally, Dytczak *et al.*, (2007) reported a 25% sludge reduction on laboratory scale sequencing batch reactors fed with synthetic wastewater ozonating 20% of RAS. All the above studies achieved equal or greater degree of reduction in sludge production than this study.

Strunkmann *et al.*, (2006) examined the sludge reduction as a result of mechanical disintegration using ultrasound homogenizer, high pressure homogenizer and stirred media mill on a lab-scale activated sludge system fed with real wastewater. The maximum reduction was achieved with the high pressure homogenizer (72%) processing 20% of the total sludge volume of the system per day at an energy input of 30,000 kJ kg^{-1} TS. When the amount of sludge was reduced to 5% the ultrasound homogenizer instead of reduction caused an increase in the sludge produced by 8%. For comparison, here the amount of sludge processed, represented the 14% of the total sludge volume with an energy input of 10,500 kJ kg^{-1} TS.

7.4. Conclusions

In this study two parallel pilot scale BNR reactors, treating real wastewater were used to examine the effects of mechanical sludge disintegration on process performances and sludge growth. The main conclusions obtained are as follows.

- The disintegration of 5.88% of RAS increased the VFA content in the total flow of wastewater by 2.5-7 mg l^{-1} in terms of VFA, but also increased the load of P by 3.5-6.5 mg l^{-1}.
- The performance of the test reactor in terms of TSS, TCOD, NH_4 and TN was unaffected. A significant deterioration on SVI was observed, but the turbidity in the effluent was also unaffected.
- In both Phase I and II the test reactor was able to remove between 44 to 89% more P than the control, but the reasons require further investigation.
- In Phase I a 26% reduction in sludge production was due to the disintegration and the long sludge age, whilst in Phase II a 24% reduction in sludge production was observed as a result mainly of sludge disintegration with the difference in sludge age to contribute only by 6%.
- Overall, the mechanical sludge disintegration by the deflaker can successfully replace 2.5 -7 mg l^{-1} of acetate, which is considered as the best carbon source for EBPR and at the same time reduce the amount of excess sludge produced by 20-26%.

Acknowledgments

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Chapter 8 Practical implications for water utilities

8. Practical implication for water utilities

The review of the literature showed that the suitable carbon source in the influent wastewater is of major importance for the success of BNR processes. For that reason many options have been examined in order to increase the concentration of the suitable carbon in the wastewater. The idea in this project was the production of suitable carbon from internal sources by disintegrating activated sludge. This project started investigating the proposed equipment for disintegration, moved to the phase where the impact of the produced carbon source on the carbon limited BNR processes had to be evaluated and finally ended by researching the effect of disintegration on the total BNR process performance. The findings arising throughout the project are important for the research part of this study, but whether the water utilities will benefit from them has to be further examined.

The prediction of the performance of a BNR site in terms of phosphorus and nitrogen removal is a major issue for the water utilities, when a new BNR site has to be commissioned. In the past, the suitability of the influent wastewater for BNR processes was examined, based on the carbon to phosphorus and carbon to nitrogen ratio. Unfortunately, these ratios have been proved unreliable for the prediction of BNR process performance. Then laboratory scale tests were more successfully used for this purpose such as the VFA potential test (Curto, 2001), the phosphorus release test (Avendano 2003; Vale *et al.*, 2005) and the nitrate utilization rate (NUR) test (Kujawa and Klapwijk, 1999). In this project (Chapters 5 and 6) the phosphorus release and NUR tests were developed allow us to examine the impact of different carbon sources on the carbon limited processes. These tests can be a useful tool for the water utilities, since the lack of available carbon in the influent wastewater leads to the investigation of alternative carbon sources.

In previous chapter (Chapter 7) it was shown that mechanical disintegration of thickened return activated sludge is able to replace successfully the best external carbon source (acetic acid) for enhanced biological phosphorus removal (EBPR). The amount of acetic acid that can be replaced depends on the performance of the device used for disintegration. It was shown that deflaker combined with some fermentation effects can increase the concentration of VFA in the wastewater by 2.5-7 mg l^{-1}. In full scale applications the sludge fermentation prior to disintegration will not be present. However, comparing the performance of the deflaker observed in Phase I of Chapter 7 (Table 7.3) disintegrating sludge from the pilot plant, with the results in Chapter 3 (Figure 3.5) and Chapter 4 (Table 4.2) disintegrating thickened sludge from full scale wastewater treatment plants (WWTP), showed a similar increase in the concentration of SCOD and VFA. The lower increase observed in Phase II of Chapter 7 (Table 7.5), when the degree of fermentation that was taking place during the thickening process was low (due to different weather conditions), is attributed to the completely different way of sludge thickening and absence of flocculation, compared to a full scale WWTP. This unavoidably, leads to a lower degree of disintegration, since the carbon released from deflaker (10 minutes retention time) mainly comes from the floc destruction (Chapters 3 and 4) and hence absence of flocculation reduces the amount of carbon released.

Taking all these factors into account we conclude that the disintegration of properly flocculated and thickened sludge from a WWTP will cause an increase of ~7 mg l^{-1} in the concentration of VFA in the wastewater. This increase is relatively low compared to the most common method of increasing the organic matter, which is primary sludge fermentation (7-49 mg l^{-1}) (Munch and Koch, 1999). The primary sludge fermentation increases the concentration of NH_4, while mechanical disintegration of activated sludge increases the concentration of soluble phosphorus that has to be removed. In both fermented and disintegrated sludge in order to take full advantage of the processes and the produced carbon a sidestream removal of the produced nutrients (N and P) is required. A proposed method of the sidestream removal of phosphorus is the precipitation of struvite ($MgNH_4PO_4 \cdot 6H_2O$). The extra benefit of sludge disintegration compared to primary sludge fermentation, is that the former can cause a 20-25% reduction in sludge production and taking into account the major sludge disposal issues, can be the key parameter for its selection among other methods for BNR enhancement.

The results from the phosphorus release and denitrification tests (Chapter 6, Figures 6.3 and 6.8) showed that the addition of carbon produced from disintegration leads to higher phosphorus release and denitrification rates than the addition of acetic acid. That indicates that a part of the produced carbon, which is not VFA can also be utilized in these processes and hence more acetic acid than the VFA measured in the disintegrated sludge could be replaced by disintegration. Due to time limitation this has not been confirmed in the pilot scale experiments and will not be taken into account in the following cost analysis.

Whether the mechanical sludge disintegration will be used in the future by the water utilities has to be further examined. Here we have undertaken a cost analysis to evaluate the disintegration process. The basis of the cost analysis is to compare the savings produced by using the deflaker with the capital and operational cost of the deflaker for a WWTP of 250,000 P.E. A number of assumptions were made after discussion with Severn Trent water and Thames Water (Table 8.1). Based on those assumptions, the savings by using the deflaker to enhance BNR were calculated (Figure 8.1). The savings come from the replacement of acetate (7 mg l^{-1}) and the reduced amount of sludge produced (23%). In addition, the performance of the anaerobic digester played a significant role in the total savings through the final amount of sludge and biogas produced. It has been reported that mechanical sludge disintegration prior to anaerobic digestion can cause an increase in biogas production (Muller, 2000), but is still unknown whether the sludge disintegration of a proportion of RAS will have a positive or negative effect on the performance of the digester. Assuming that the performance of the anaerobic digester will not change the saving is ~£30,000 for the minimum sludge disposal cost and ~£70,000 for the maximum. A 5% difference of the volatile solids (VS) destruction can give an extra cost of ~£113,000, when there is a deterioration in the solid destruction or a ~£233,000 saving if the solid destruction is increased by 5%.

Table 8.1 Assumptions made for the cost analysis

WWTP	**50,000 m^3 d^{-1} or 250,000 P.E.**	
Parameter	Assumption	Source
Amount of primary sludge	270 kg per 1000 m^3 of influent wastewater	STW[*] & TW[**]
Volatile solids (VS)	70%	Metcalf and Eddy, (2003)
Amount of secondary sludge	200 kg per 1000 m^3 of influent wastewater	STW & TW
Volatile solids (VS)	75%	Metcalf and Eddy, (2003)
Secondary sludge reduction due to disintegration	23%	This study
Destruction of VS in anaerobic digestion	45%	STW & TW
Biogas produced	0.8 m^3 biogas per 1 kg VS destroyed	Metcalf and Eddy, (2003)
Heating value of biogas	22,400 kJ m^{-3}	Metcalf and Eddy, (2003)
Price of produced energy	£0.08 per kWh	STW & TW
Minimum sludge disposal cost	£120 per Mg of total solids	STW & TW
Maximum sludge disposal cost	£190 per Mg of total solids	STW & TW
Amount of acetate replaced	7 g m^{-3} of wastewater	This study
Cost of acetate	£0.6 per kg	Chemical Market Reporter
Deflaker capacity	10 l	Estimation
Price	£15,000	Estimation
Cost of energy	£0.043 per kWh	Department of Trade and Industry
Amount of flocculant required	1 kg per Mg of dry solid	STW & TW
Cost of flocculant	£2.5 per kg	STW & TW
Depreciation	10 years span with 5% interest	Estimation
Maintenance cost	£1000 per annum per deflaker	Estimation

[*] Severn Trent Water, [**] Thames Water

On the other hand the cost of using the sludge disintegration method was calculated based on the capital (annual depreciation) and operational cost (energy consumption and maintenance) of the deflaker and according to the assumptions presented in Table 8.1. A main parameter affecting the cost is the operational time of the deflaker. In Chapter 7 the deflaker was used with the sludge retention time to be 10 minutes and based on our assumptions, this would cost ~£1.3 million per year (Figure 8.2). The major drawback of the process that leads to the high cost is the capacity of the deflaker, with the maximum found in the market to be 10 l. The increase of the throughput of the deflaker can reduce significantly the cost. Moreover, reducing duration of disintegration the cost will be reduced as well (~£155,000 for 1 minute retention time). However, is uncertain whether different disintegration times have the same effect on the overall process. It was shown in Chapter 6 (Figure 6.6) that different retention times in the deflaker can produce carbon, which is able to cause similar phosphorus release under anaerobic conditions. However, it was proved in this study that shorter retention time in the deflaker causes lower degree of disintegration in terms of SCOD and VFA release and there will be a lower increase in the concentration of available carbon in the wastewater. Moreover, it was shown that cell lysis, which can cause sludge reduction through the lysis cryptic growth mechanism, is present only at retention time ≥10 minutes (Figure 3.7 and 4.9), therefore the operation of the deflaker at shorter retention times is unlikely to have the same effect on sludge production as the 10 minute time.

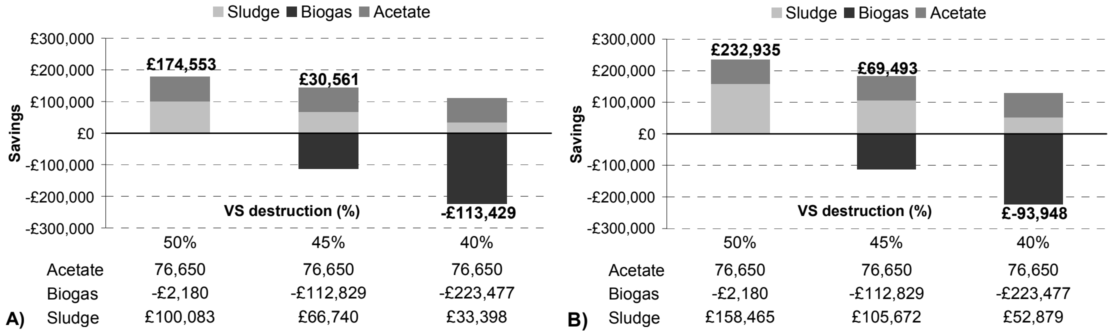

Figure 8.1 The savings that the sludge disintegration can provide for A) the minimum (£120 Mg^{-1} DS) and B) the maximum (£190 Mg^{-1} DS) sludge disposal cost for different performances of the anaerobic digester

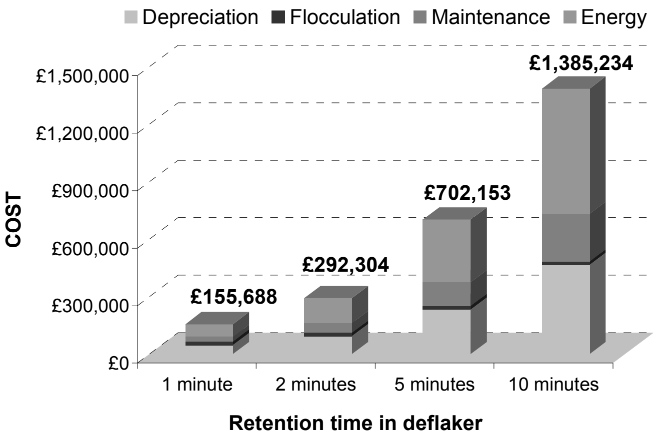

Figure 8.2 The annual cost of deflaker processing 5.8 % of RAS for different retention times

Another parameter that can be examined is the volume of sludge to be treated by the deflaker. In this study the examined volume was equal to 5.88% of RAS, but less sludge reduces the overall cost (Figure 8.3). In particular, using the deflaker with a retention time of 1 minute the operating cost of the deflaker is lower than the savings. Unfortunately, this is likely to be the only way that the deflaker can be used in an economical viable way. But as it was mentioned earlier the operation of deflaker under conditions different than the ones examined in Chapter 7 will have a different effect on the process and any comparisons will lead to mistaken conclusions.

It is obvious that the cost of the mechanical sludge disintegration by the specific deflaker (10 l capacity) outweighs the savings from the internal carbon source produced and from the reduction in the sludge produced. Other mechanical devices or ultrasound equipment with higher capacity and lower energy input would be more appropriate for BNR enhancement and sludge reduction, assuming that they will perform similarly in terms of sludge disintegration.

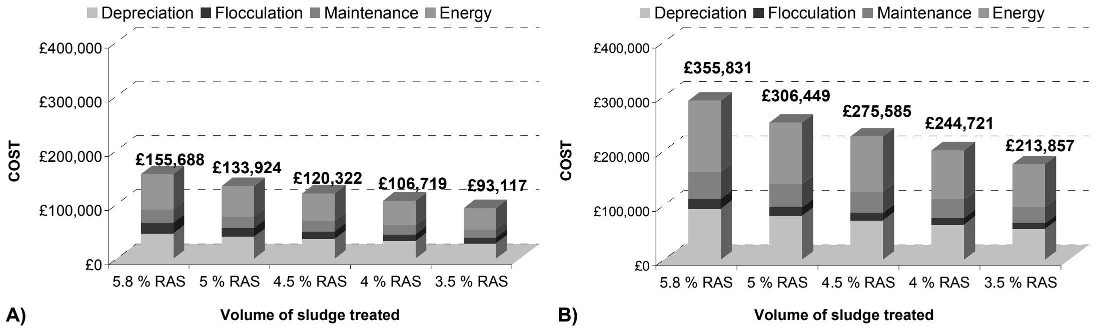

Figure 8.3 The annual cost of deflaker operated at A) 1 minute and B) 2 minutes retention time for different sludge quantities treated

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Chapter 9 Conclusions and future work

9. Conclusions and future work

9.1 Conclusions

This project has investigated the mechanical sludge disintegration for the production of useful organic matter for the carbon limited BNR processes, has identified and developed practical methods to evaluate different carbon sources and finally has explored the impact that mechanical sludge disintegration can have on the overall BNR process performance. The specific conclusions arising from this study can be summarized as follows:

- The three examined disintegration processes (radial horn, dual frequency processor and deflaker) were able to increase the SCOD concentration in thickened SAS and RAS depending on the energy input and solid concentration in sludge. The radial horn required the least energy for a specific increase in SCOD among the three equipments. The deflaker was more efficient in terms of carbon release and energy input in samples with high solid concentration (thickened SAS) and disintegration of RAS caused mainly an increase in the temperature. For all processes long disintegration times or high energy inputs led to cell lysis, while in disintegration of low energy input the carbon release was a result of floc disruption.
- For the deflaker the threshold for cell lysis in terms of energy input was ~9000 kJ kg^{-1} TS. It was also shown that during mechanical disintegration nutrients are released and specifically phosphorus, which leads to a low SCOD to phosphorus ratio in disintegrated sludge (~13).
- The phosphorus release and denitrification tests were developed in order to be used for the evaluation of external carbon sources for BNR processes. The phosphorus release test showed that the addition of the carbon produced from deflaker can increase the phosphorus released under anaerobic conditions. According to the denitrification test the carbon produced from deflaker can be utilized by the bacteria responsible for denitrification and hence improve denitrification process.
- In the phosphorus release test, when the dosed carbon was matched in terms of VFA, the addition of carbon produced from disintegration gave higher phosphorus release than the addition of acetate. The opposite results appeared when the addition of carbon was matched in terms of SCOD, indicating that there is some

useful organic matter in the disintegrated sludge that is included in SCOD and is not VFA.

- Disintegration of RAS by the deflaker caused an increase in the concentration of VFA in the influent wastewater by 2.5-7 mg l^{-1} and the phosphorus concentration by 3.5-6.5 mg l^{-1}. The operation of the BNR reactor with the disintegration process and long sludge age of 40-45 days led to a deterioration of phosphorus removal, while the concentration of TCOD, TSS, NH_4 and TN in the effluent was unaffected.
- The results from the operation of the control and test reactor under similar sludge age (15-23 days) showed that disintegration of RAS does not have any significant effect on the performance in terms of phosphorus and nitrogen removal.
- Phosphorus could be removed from the disintegration liquors by chemical precipitation. This led to an improvement in the overall phosphorus removal in the BNR plant.
- Finally, the new disintegration process used for the production of an internal carbon source affected the growth yield of the biomass causing a 20-26% reduction in sludge production.
- The cost analysis of the examined process revealed that the specific device used for mechanical sludge disintegration (deflaker), cannot be considered to be currently economically viable under the conditions explored in this study.

9.2 Future work

The research conducted in this project showed that mechanical sludge disintegration can be an alternative way to enhance BNR process performance, but as was evidenced in Chapter 8, it is not currently economically viable. Another disintegration process with higher capacity and low energy has to be identified and examined and further research that comes out of this project has to focus on the new disintegration process and should concentrate on the following parameters:

- Another mechanical disintegration process should primarily be able to increase the soluble carbon concentration in sludge. Then, and in order to be economically viable must have low energy demand and at the same time high throughput.
- For the better investigation of the new disintegration process and its effects on BNR process performance, longer experimental period than the period the deflaker was examined in this study has to take place.
- Further research has to be conducted to explain the reasons for the higher phosphorus uptake when disintegration was applied and to investigate the hypotheses made in this study (Chapter 7).
- The operation of the experiment for long period of time will also reveal any long terms effects of sludge disintegration on the BNR processes and also will certify the degree of reduction in sludge production.
- The sidestream removal of the produced by disintegration phosphorus with chemical precipitation or crystallization requires further examination in order to identify the form, in which phosphorus is precipitated. Furthermore, the economical aspect of this process has to be investigated in order to be used by the water utilities.

Appendix Mechanical sludge disintegration: providing an alternative carbon source for nutrient removal

Environmental Technology (In Press)

Appendix. Mechanical sludge disintegration: Providing an alternative carbon source for nutrient removal

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ABSTRACT

The primary driver for efficient biological nutrient removal (BNR) in activated sludge treatment is the sufficient supply of soluble carbon. Several methods have been proposed to increase available carbon sources and enhance BNR. This study examines the effect of ultrasonic equipment and mechanical disintegration technologies on surplus activated sludge (SAS), to release additional soluble chemical oxygen demand (SCOD) and volatile fatty acids (VFA), as a carbon food source for BNR. A laboratory sonicator with a maximum power of 550W, a 3KW SONIX^{TM} radial horn and a deflaker declared to be used in paper industry were investigated. All caused significant release of SCOD, up to 48 fold. The maximum concentration of VFA reached (from 0-1 mg l^{-1}), was 530 mg l^{-1}. To assess likely impact to BNR, batch (2L) anaerobic lab tests examining the use of disintegrated sludge on phosphorus and nitrogen removal were completed. Phosphorus removal was estimated by observing the phosphate release under anaerobic conditions and up to 460% more release was observed relative to controls. In addition, denitrification rates were improved over 106%. Ultrasonic and mechanical disintegration technologies have been shown to release soluble carbon for BNR, with subsequent laboratory nitrogen and phosphorus removal efficiencies observed to be comparable to acetate.

Keywords activated sludge, biological nutrient removal, denitrification, mechanical disintegration, phosphorus release, ultrasonic

Introduction

Successful biological nutrient removal (BNR) can be achieved by using a range of pre-treatments to generate a carbon source from either the wastewater or sludge in order to improve the two carbon limited processes, phosphorus release and denitrification. The most popular methods for BNR enhancement are the use of pre-fermenters treating the entire wastewater stream (McCue, *et al.*, 2003) or treating a side-stream such as the primary clarifier underflow (Kristensen et al., 1992).

The addition of an external carbon source for denitrification and phosphorus removal has also been examined. Naidoo *et al.*, (1998) reported a range of 3.2-7.3 mg N g^{-1} VSS h^{-1} for denitrification rate with acetate as the carbon source. Fass *et al.*, (1994) compared short chain fatty acids, with butyrate found to give the maximum denitrification rate. The rate when a mixture of VFA was used was 31.9 mg N-NO_3 mg g^{-1} SS h^{-1}. Another alternative external carbon source is industrial wastes, in particular those that contain readily biodegradable organic matter (Pavan *et al.*, 1998; Llabres *et al.*, 1999; Lee *et al.*, 1997). For instance, Pavan *et al.*, (1998) examined the addition of fermented organic fraction of municipal solid waste (OFMSW) to the wastewater and observed an increase of RBCOD in wastewater by approximately 580% and the denitrification rate from 0.41 to 2.5 mg N-NO_3 g^{-1} VSS h^{-1}.

Researchers investigating carbon sources with high content of organic matter, observed the release of SCOD and VFA from sludge disintegration by mechanical, thermal, chemical and biological methods. Chiu *et al.*, (1997) reported that with a combination of alkaline pre-treatment and ultrasonic vibration, a 41.5 soluble COD and 28 VFA fold, was reached. The maximum solubilization in COD has been identified by ultrasound equipment with 50 fold increase in SCOD (Wang *et al.*, 1999). Withey (2003) used a deflaker technology, declared to be used in paper industry for sludge disintegration for improving anaerobic digestion and reported a 10 fold increase in SCOD. However, there is little information about the application of the treated sludge to BNR in order to improve P and N removal performances. In this study sludge was disintegrated by mechanical devices (ultrasound and deflaker) and the suitability of this sludge as a carbon source for BNR was examined, using laboratory scale tests designed to investigate the phosphorus release and nitrate reduction under anaerobic conditions.

Methodology

Disintegration techniques

The deflaker used in this study was a 10”Pilao DTD Spider Deflaker, fitted with 230 mm discs with 3 active cell layers and the gap distance between stator and rotor to be 0.6-0.9 mm (Withey 2003). Five litres of SAS were treated as a batch for three different retention times, 5, 10 and 15 minutes. The ultrasonic sonicator was a model XL2020 from Heat Systems Inc. with the frequency of 20 kHz and maximum output power of 550 W. The two different probes that were used were immersed into a beaker with SAS with the retention time ranging from 35 to 70 minutes. Finally, the radial horn SONIX^{TM} from Purac Ltd. was also used. This titanium probe works in 20 kHz frequency and with 3 kW maximum power. Batch tests have taken place by immersing the horn and stirring the SAS. The volume of SAS used was 5L and the retention times were 75, 150 and 375 seconds which is equivalent of 1, 2 and 5 seconds for full scale application, where 3-5 horns are used in a reactor vessel.

Phosphorus release test

To assess the potential impact of recycling disintegrated sludge on BNR, a series of experiments investigating the phosphorus (P) release under anaerobic conditions were conducted. Four vessels with 1L of wastewater and 1L of activated sludge (RAS) were kept under anaerobic conditions for 2 hours. The first vessel had no addition of external carbon, second and third were operated with the addition of disintegrated sludge and the fourth one with the addition of sodium acetate. The test took also place comparing the disintegrated sludge to industrial wastewater (brewery effluent). In every reactor the same amount of carbon was added, as all the carbon sources were matched in terms of VFA or SCOD. All vessels were sealed and a nitrogen blanket was over the solution, which was mixed by magnetic stirrers. Moreover, all the vessels were inside a water bath with heater and circulation pump to keep the temperature constant (20 ^{o}C). During the experiment pH and DO were measured and samples were taken every 30 minutes. The samples were filtered immediately with a syringe filter 0.45 μm and the concentration of phosphates (PO_4) was measured.

Denitrification test

The same experimental set up was used for the denitrification test, but here 2L of wastewater were used in the reaction vessels instead of the wastewater and RAS mixture. Again, the first vessel was unamended with carbon, the second and third with the addition of solid free fraction of disintegrated sludge and the fourth one with sodium acetate. The carbon was matched in terms of either VFA or SCOD. Moreover, the same amount of nitrate (30 mg l^{-1} N-NO_3) in the form of KNO_3 was added in all vessels. Samples were taken every 30 minutes, filtered immediately with syringe filter (0.45 μm) and the concentrations of nitrate (NO_3) and nitrite (NO_2) were examined. The volatile suspended solids (VSS) were also measured from the solution of each vessel.

Analytical methods

The concentration of soluble COD, VFA, TS, VSS, soluble P and phosphates was measured according to APHA (1998). Analysis of nitrates (NO_3) and nitrites (NO_2) from the phosphorus release and denitrification tests was carried out using ion exchange chromatography (IEC) system, (Dionex, DX500 series, UK).

Results and Discussion

Disintegration

The concentration of SCOD and VFA in raw SAS was dependant on the sewage works from which it was collected. It was found that SAS collected from sites that operate in BNR mode contained very low concentration of VFA ~0mg l^{-1} and SCOD 100-200 mg l^{-1}.

SAS from non BNR sites had concentration of VFA ~200-300 mg l^{-1} and SCOD 700-1100 mg l^{-1}. Their different initial concentrations led to different degrees of disintegration. For example, Table 1 shows the disintegration results from the lab sonicator for BNR SAS, in terms of VFA and SCOD release and Tables 2 and 3 show the results for both thickened SAS from SONIX^{TM} ultrasound radial horn and deflaker, respectively.

Table 1 Disintegration results using lab sonicator

BNR SAS (n=2)		
	Before	After
VFA (mg l^{-1})	0-1	210-405
SCOD (mg l^{-1})	120-230	3225-6700

Table 2 Disintegration results using SONIX^{TM}

BNR SAS (n=2)			**non BNR SAS** (n=2)		
	Before	After		Before	After
VFA (mg l^{-1})	0-1	37-263	VFA (mg l^{-1})	186-311	388-805
SCOD (mg l^{-1})	120-230	1025-5650	SCOD (mg l^{-1})	1072-1198	1745-14320

Table 3 Disintegration results using deflaker

BNR SAS (n=6)			**non BNR SAS** (n=3)		
	Before	After		Before	After
VFA (mg l^{-1})	0-1	20-530	VFA (mg l^{-1})	186-311	286-852
SCOD (mg l^{-1})	120-230	1205-6190	SCOD (mg l^{-1})	744-1198	2685-6820

All the disintegration processes caused a significant increase in VFA and SCOD. The maximum value of VFA was reached with deflaker 530 mg l^{-1} fro BNR SAS and 852 for non BNR SAS. Disintegration with SONIX^{TM} radial horn reached the maximum value of SCOD ~14300 mg l^{-1} in non BNR SAS and the highest % release was with the lab sonicator for the BNR SAS, where there was an increase of 48 fold, similar to the one reported by Wang *et al.*, (1999)(50 fold).

Phosphorus release test

The phosphorus release test has been undertaken with disintegrated sludge the dose of which was matched in terms of VFA concentration (Figure 1). This led to different SCOD concentration being dosed into the reactors, 0, 25, 258 and 414 mg l^{-1} for the control, ultrasonic sludge, deflaker sludge and acetate dosed reactor, respectively. Phosphorus release was found to be much higher in the reactors where the disintegrated sludge was applied, indicating that the available carbon source for the bacteria is not only VFA but also a proportion of the carbon included in SCOD. When carbon was matched in terms of SCOD (Figure 1b), the maximum phosphorus release took place in the reactor with acetate. In this experiment the disintegrated sludge from the deflaker are compared with an industrial wastewater (brewery effluent). The concentration of VFA in the acetate dose reactor was 23.4 mg l^{-1}, while in the other three reactors was much lower; less than 1 mg l^{-1}. Although, the difference in VFA concentration was significant, there was a similar phosphorus release for both the deflaker and the acetate dosed reactors. Both experiments showed that soluble carbon released by the disintegration can be utilised by the phosphorus accumulating organisms (PAOs).

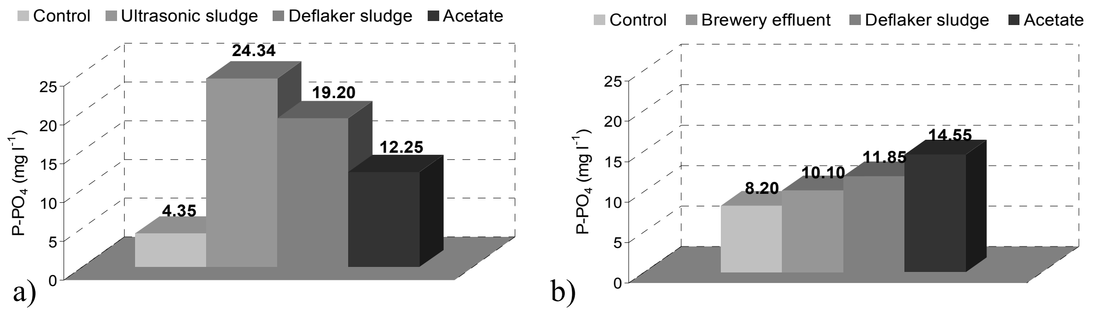

Figure 1 a) Phosphorus release when carbon source was matched in VFA=23.43 mg l^{-1}. The concentration of SCOD was: 0, 25, 258 and 414 mg l^{-1} for control, ultrasonic, deflaker and acetate, respectively. b) Phosphorus release when carbon source was matched in SCOD=25 mg l^{-1}. The concentration of VFA was 0, 0.07, 0.63 and 23.4 mg l^{-1} for control, brewery, deflaker and acetate (adapted from Kampas *et al.*, (submitted))

Denitrification test

During the denitrification test the extra carbon was again matched in terms of either SCOD or VFA. As with the P release test the reactors with the added carbon performed better than the control (Figure 2). The maximum denitrification rate was found with the addition of deflaker treated sludge (41.2 mg $N\text{-}NO_3$ g^{-1} VSS h^{-1}) or (31.2 mg $N\text{-}NO_3$ g^{-1} SS h^{-1}), which is similar to the denitrification rate when mixture of VFAs was used [4].When carbon was matched in terms of VFA the SCOD concentration was similar in all reactors. However, the reactor with ultrasonic treated sludge had the highest denitrification rate (Figure 2b).

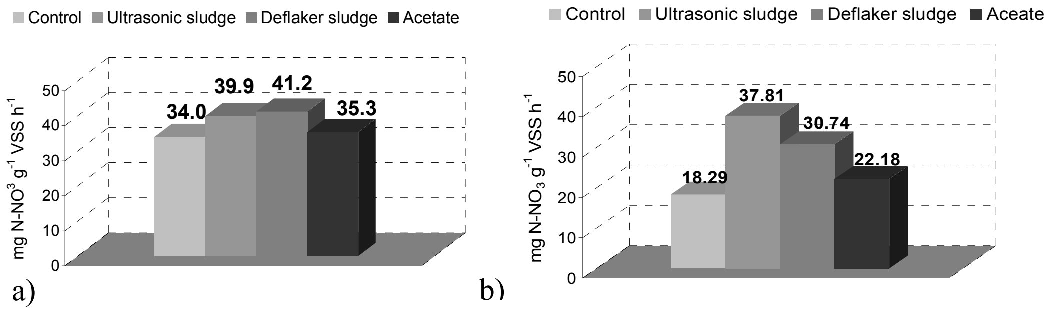

Figure 2 a) Results from denitrification test with the use of supernatant and carbon matched in SCOD=25 mg l^{-1}. The VFA concentration was 0, 2.8, 4.5 and 23.4 mg l^{-1} for control, ultrasonic, deflaker and acetate reactor. b) Results from denitrification test with carbon matched in VFA=2.8 mg l^{-1}. The concentration of SCOD was 0, 102, 105 and 2.8 mg l^{-1} for control, ultrasonic, deflaker and acetate reactor.

Conclusions

- All the disintegration processes tested on SAS during this study gave significant increases in VFA and SCOD. The highest increase in VFA concentration was found with the deflaker when it was applied to BNR SAS (0 to 530 mg l^{-1}). When a non BNR SAS was treated in deflaker the highest concentration of VFA achieved, was 852 mg l^{-1}. The maximum release in SCOD was observed with the lab sonicator (48 fold) and the maximum concentration reached with the SONIX^{TM} horn (14320 mg l^{-1}). The degree of disintegration was related to the retention time that the sludge was treated for.

- The phosphorus release test showed that the carbon produced by the disintegration of SAS can be assimilated by the microorganisms responsible for enhanced biological phosphorus removal (EBPR). The release of P observed when extra carbon was added, was constantly higher than the release in the control reactor. Moreover, when the carbon was matched in terms of VFA, the release was higher in the reactors with disintegrated sludge than with just acetate addition.

- Rapid denitrification took place when sludge was added to the reactors. In all the experiments denitrification rates were higher in the reactors with the additional carbon from disintegration. In this study was proved that phosphorus release and denitrification processes can be significantly improved by the addition of disintegrated sludge.

- Further research will examine the mechanism of disintegration including microscopy tests in order to understand how mechanical disintegration affects the bacteria and the biomass. The optimum conditions of disintegration (equipment, retention time) will be determined in terms of BNR enhancement.

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