Further Treatment of Digested Blackwater for Extraction of Valuable Components

Vom Promotionsausschuss der
Technischen Universität Hamburg-Harburg
zur Erlangung des akademischen Grades

Doktorin der Naturwissenschaften

genehmigte Dissertation

von
Öznur Alp

aus
Adana, Türkei

2010

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Tag der mündlichen Prüfung: 20.04.2010

Acknowledgement

This Ph.D. thesis would not have been possible without the support of many people.

First of all, I would like to thank my supervisor Prof. Dr. Ralf Otterpohl, who gave me the opportunity to conduct my study in his department; at the Institute of Wastewater Management and Water Protection at Hamburg University of Technology.

I am very grateful to Prof. Dr. Frank Schmidt-Döhl, who kindly accepted being the second supervisor of my Ph.D. thesis.

It is also a pleasure to mention Dr. Holger Gulyas for his valuable support and friendly help. Without his support achievement of such results would not have been possible. His extensive discussions have been very helpful for this research study.

I would also like to acknowledge the support of Dr. Martina Winker and Felix Tettenborn who shared their valuable experiences and ideas with me which have been very helpful towards the development of this project.

During this research study I have collaborated with many colleagues for whom I have great regard, and I wish to extend my warmest thanks to all those who have helped me with my work at the Institute of Institute of Wastewater Management and Water Protection. Special thanks to Susanne Eggers who gave of her assistance at every stage of my laboratory works.

Many thanks go in particular to Eva Petersen and Gisela Becker for their sympathetic help in secretarial work.

It is a pleasure to thank Burcu Yazgan, Lilia Andrea Perez Cantu and Nie Jieanwen who supported me with their valuable results.

I also wish to thank Dr. Daniel Aaron Press and Aleksandra Drewko for revising the English of my manuscript.

A very special thanks goes out to Prof. Dr. Göksel Akcin for her patient guidance, encouragement and excellent advice throughout my studies. It was an honor for me to work with her.

I would like to express my special gratitude to Burcu for her comments and suggestions for the editing of my thesis. Thanks for the science discussion, creating such a great friendship and enjoyable time we spent together as roommates.

I take this opportunity to express my profound gratitude to my beloved parents, my sister Özgür for their moral support and patience during my study in Germany.

I owe my loving thanks to Philip. Without his encouragement and understanding it would have been impossible for me to finish this thesis.

Last but certainly not least, I would like to show my gratitude to IPSWAT Program for funding my Ph.D. study.

Herausgeber / Editor
Gesellschaft zur Förderung und Entwicklung der Umwelttechnologien an der Technischen Universität Hamburg-Harburg e. V. (GFEU)

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ISBN 978-3-941492-18-9

Abstract

Application of the ecosan projects in practice are based on the separate collection and treatment of different wastewater flows to minimize the water consumption and optimize the potential for nutrient recovery and reuse. Toilet waste, known as blackwater, constitutes of only 1-2 volume % of the total domestic wastewater stream, but contains more than 95 % of the total nitrogen and about 90 % of the total phosphorus. Through blackwater collection, with a minimum quantity of flush water, the organic matter and nutrients present in the material remain concentrated.

The primary objective of this study was to assess the nutrient enrichment, removal, recovery potential in digested blackwater through evaporation, precipitation, and adsorption. Nitrogen (N) and phosphorus (P) are the target nutrients that are to be removed and recovered in this research study. However, P has a more significant role since its sources are limited on the earth.

In this study, fresh samples of blackwater were obtained from Flintenbreite-Lübeck ecological settlement. This settlement is the first residential estate that realized source separation for 350 inhabitants residing in a densely populated area. The system incorporates vacuum toilets and vacuum sewers. Blackwater was treated anaerobically in a continuously stirred tank reactor (CSTR) in the laboratory of the Institute of Wastewater Management and Water Protection at Hamburg University of Technology.

The water content of digested blackwater was reduced by evaporation, in order to decrease the volume and create a valuable concentrate from which important nutrients could be recovered. Other advantages from this volume reduction are the decrease in cost for both, transport and storage, due to smaller volumes. This also makes the handling of the blackwater easier. Evaporation showed to be an effective technique to achieve volume reduction and nutrient enrichment in digested blackwater. The average volume reduction achieved was around 91 % and all of the important parameters like PO_4^{3-}, TN and TOC increased their concentration when an appropriate low pH value around 4.5 and 4.0 was used for the substrate.

The precipitation study focused mainly on the removal and recovery of PO_4^{3-} from BW as it is recognized as a limited resource on earth. Additionally, recovery of the removed P and N in the form of an agricultural product, namely *struvite*, was aimed as a part of the project. Effects of pH and the Mg:P ratio on PO_4^{3-} removal were investigated for $MgCl_2$, MgO, $Mg(OH)_2$, and $MgSO_4$. At pH value of 9.5 and Mg:P ratio of 2, $MgCl_2$ and MgO produced the highest PO_4^{3-} removal efficiencies with 94 and 91 %, respectively. In conclusion, struvite precipitation was decided to be an attractive alternative to remove and recover PO_4^{3-} in blackwater.

For the adsorption experiments, zeolite (clinoptilolite) was the main material used as adsorbent. The objective of this study was to investigate the effectiveness of using zeolite to remove and recover nitrogen and phosphorus from blackwater. In this study, batch and column adsorption tests were performed. It has been seen that the removal of NH_4^+ was quite high, up to 90 % for higher amount of zeolites, due to the fact that the pre-treatment has increased the ion exchange capacity of the zeolite. Adsorption on zeolite was proved as an effective method as well.

Table of Contents

List of Tables

List of Figures

List of Abbreviations

AAS	Atomic absorption spectrophotometer
AC	Accumulation system
AD	Anaerobic digestion
AWW	Abwasserwirtschaft
BDEW	Der Bundesverband der Energie- und Wasserwirtschaft
BV	Bed volume
BW	Blackwater
C_e	Equilibrium concentration
Ch	Chinese zeolite
C_i	Initial NH_4^+ concentration of the solution
COD	Chemical oxygen demand
Cp	Clinoptilolite
C_p	Heat capacity
CSTR	Continuously stirred tank reactor
DBW	Digested blackwater
EBV	Empty bed volume
EUR	Euro
GTZ	Deutsche Gesellschaft für Technische Zusammenarbeit
GW	Greywater
HRT	Hydraulic retention time
ICP-OES	Inductively coupled plasma optical emission spectrometry
IUE	Institut für Umwelttechnik und Energiewirtschaft
m	Mass
MAP	Magnesium ammonium phosphate
MW	Molecular weight
RotaVap	Rotary evaporator
RT	Retention time
Q	Heat
q_e	Capacity of zeolite
T	Temperature
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
TS	Total solids
TUHH	Technische Universität Hamburg Harburg
UASB	Upflow anaerobic sludge blanket
UN	United Nations
V	Volume
VFA	Volatile fatty acids
VS	Volatile solids
WHO	World Health Organisation
YW	Yellowwater
XRD	X-ray diffraction

1. INTRODUCTION

1.1 Background

1.1 billion people globally do not have access to improved water supply sources, whereas 2.4 billion people do not have access to any type of improved sanitation facility (WHO/UNICEF, 2003). The most affected people, who live with contaminated drinking water and accompanying illnesses, are in developing countries.

The main burdens are the consequences of inadequate drinking water sources and lack of sanitation facilities, which causes undeniable health and environmental problems especially water pollution.

A sanitation system that provides Ecological Sanitation (ecosan) is a cycle—a sustainable, closed-loop system, which closes the gap between sanitation and agriculture. Ecosan is recognized as a modern alternative to the traditional sanitation concepts. The whole idea is based on the maximum recovery, reuse, and recycling of the waste and wastewater. Perceiving human excreta not as a waste but as a valuable resource, turning the available nutrients into the useful agricultural products, and minimizing the water consumption by developing ways to treat and reuse it with a most probable closed-loop system are the sine qua nons for the ecosan system. In that sense, ecosan can be regarded as a driving force towards sustainable development, which suggests ways to use resources efficiently and conserve them for the next generations as much as possible.

The four main flows of wastewater involved in ecosan concept are: Blackwater, greywater, yellowwater and brownwater.

Toilet waste, known as blackwater (BW), constitutes of only 1-2 volume % of the total domestic wastewater stream, but contains more than 95 % of the total nitrogen and about 90 % of the total phosphorus (Kujawa-Roeleveld and Zeeman, 2006). The elements N and P, known as nutrients, are essential to the growth of microorganisms, plants, and animals. Trace quantities of other elements, such as iron, are also needed for biological growth, but N and P are, in most cases, the major nutrients of importance.

On the other hand, nitrogen (N) and phosphorus (P) can be a threat to the surface water quality. Eutrophication is recognized as a pollution problem in aqueous environments sourced by the increase of nutrients N and P in water bodies (Ueno and Fuji, 2001). These problematic substances of the aquatic environments can be also transformed into valuable agricultural products (Esrey et al., 2001) and can substitute artificial fertilizers (Vinnerås et al., 2003) produced mostly by limited fossil resources (Palmquist and Jönnson, 2004).

1.2 Objectives

The general scope of this research was to assess the nutrient removal and recovery potential in digested BW through evaporation, precipitation and adsorption. The experiments were conducted to prove the technical feasibility of below mentioned processes:

Anaerobic digestion (AD) of BW is a favorable alternative within the context of ecosan, as it promises resource conservation and reuse potential for the digested effluents (STOWA, 2005). In order to recover nutrients with further treatment methods (evaporation, precipitation, and adsorption) in this study, the substrate was treated anaerobically (Chapter 4).

Evaporation

BW contains a high amount of nutrients and also trace elements that are important for the growth of plants. For an application in agriculture a concentrated or a solid product would be more useful (Ergünsel, 2006). However, in some countries, reuse of nutrients contained in BW by spreading onto fields is not allowed. Additionally, for peri-urban areas where agricultural areas can only be found in remote distances, amount of BW to be transported would be very large, therefore economical storage on-site and later transport to agricultural fields is questionable (Tettenborn et al., 2006). Thus, it would be beneficial to concentrate the nutrients for transportation and storage purposes (Maurer et al., 2006). Hence, new approaches have to be found to reduce volumes of BW and extract contained nutrients on-site. Therefore, in this research, the evaporation process as an alternative solution to reduce the volume of anaerobically digested BW and its effect towards hygienisation were investigated (Chapter 5).

Precipitation

Nitrogen and phosphorus were the target nutrients that are to be removed and recovered. Additionally, recovery of the removed N and P in the form of an agricultural product was aimed as a part of the study. Experimental investigations formed the basis of the whole study, while similar researches in the literature were referred frequently to interpret and compare the results of the experiments (Chapter 6).

Adsorption

In order to remove ammonium (NH_4^+), ion exchange has been demonstrated to be competitive with other methods in terms of performance and costs (Mercer et al., 1970; Culp et al., 1978). However it might be very expensive if commercial resins are used (López-Vigil et al., 2006). In order to cope with this problem natural zeolites have been successfully applied over the past two decades (López-Vigil et al., 2006).

The effectiveness of using zeolite (clinoptilolite) to remove and recover ammonium and phosphorus from BW was investigated as well. Therefore, batch and column adsorption tests were performed (Chapter 7).

Finally, a case study was conducted which contains a detailed economical analysis concerning two different settlements having anaerobic digestion and evaporation, precipitation or adsorption in process. This case study looks intensively at each treatment process and stresses their economical feasibilities (Chapter 8).

2. SUSTAINABLE SANITATION

20 % of the world's population do not have access to safe or affordable drinking water and 50 % to safe or sufficient sanitation (WHO/UNICEF, 2000). The majority of people, who live with contaminated drinking water and accompanying illnesses, are in Asia and Africa (UN, 2003; Gordon et al., 2004).

Conventional sanitation concepts are based on flush toilets which are wasteful of water and are not an ecological solution for both industrialized and developing countries. The most commonly used solutions to sanitation problems are describes as either "drop and store" or "flush and forget" (Winblad, 1997; Esrey et al., 2001; GTZ, 2003). Alternative wastewater systems, focusing on source control, were initially developed with emphasis on sanitation without water (Winblad and Kilama, 1985). This idea was further developed with the aspects of reuse gaining importance and is now widely known as ecosan (ecological sanitation) or susan (sustainable sanitation) (Otterpohl et al., 1997; Otterpohl et al., 2003; Winker, 2009).

Ecosan projects are based on the separate collection and treatment of different wastewater flows to minimize the water consumption and optimize the potential for nutrient recovery and reuse (Esrey et al., 1998; Wilderer, 2001; GTZ, 2003). The four main flows of wastewater involved in ecosan concept are:

- Blackwater (BW): Wastewater generated from a toilet and a mixture of urine and faeces with toilet paper.
- Greywater (GW): Domestic wastewater without BW respectively from kitchen, bathroom and laundry.
- Yellowwater (YW): Separately collected urine.
- Brownwater or Faecal Matter: Separately collected faeces, with or without flush water respectively.

The objective of this research was to investigate methods for removal and recovery of nitrogen and phosphorus from BW. Since BW is the major wastewater flow focused on in this study, the following section gives specific information on the BW concept as a part of ecosan.

2.1 Blackwater (BW)

Blackwater (BW) is a wastewater stream originated from toilets and thus comprises urine, faeces, and flushing water. Blackwater contains more than 95 % of the total nitrogen and about 90 % of the total phosphorus. Moreover, it contains half of the COD present in domestic wastewater (Kujawa-Roeleveld and Zeeman, 2006) and the major part of the pathogens, drug residuals and hormones (Otterpohl, 2002).

When BW is collected, either with or without a minimum quantity of flush water; the organic matter and nutrients present in the material remain concentrated and can be used for energy recovery through anaerobic digestion and for reuse as agricultural fertilizer (STOWA, 2005). In addition, potentially hazardous components, such as pathogenic organisms and drug residuals, can be isolated and degraded. The remaining greywater is then relatively simple to treat.

2.2 Vacuum Collection of Blackwater

Some toilets based on vacuum and gravity that uses only 0.5 – 1.5 L per flush, are commercially available. These toilets produce 5 – 7 L of BW per person per day, whereas conventional toilets produce 6 – 15 times more.

The idea of separate collection of BW by vacuum is not new. A pneumatic system for separate collection was invented by Charles Liernur (1828 – 1893) and developed in the Netherlands in the 1870s.

Vacuum toilets have been used widely in aircraft and maritime applications, now their use in commercial buildings and public restrooms is increasing. In these systems the waste is evacuated from the toilet bowl using a vacuum that is generated by a vacuum pump. The waste is then macerated and is either directly discharged to a sewer or transported to a holding tank or treatment system. A major advantage of vacuum systems is that all the nutrients originating from the faeces and urine are collected with a very low dilution rate. A major disadvantage of these systems is that they are highly mechanized and therefore need considerable maintenance (Vinnerås, 2001).

Example: Flintenbreite, Lübeck, Germany

Residential source separation was first realized for 350 inhabitants in Lübeck-Flintenbreite, Germany (Otterpohl et al., 1997; Wendland and Oldenburg, 2003). The construction of the technical equipment and the buildings started in February 1999 and by 2002, 28 houses for 95 inhabitants had been completed. The project demonstrates the feasibility of the source control system combined with water saving technology with additional fertilizer and energy production. The installed system comprises a strict separation of blackwater, greywater and stormwater.

The vacuum toilet system has been running for 8 years with only minor technical problems. The flushing system needs approximately 0.7 L per flush. The average water consumption is 77 L/p.d (liters per person per day), which is significantly lower than the German average of 129 L/p.d (Langengraber and Muellegger, 2005). After an adjustment period, vacuum toilets are well accepted by residents and are seen as more hygienic than conventional flushing toilets. The installation produces an average of 5 L/p.d of BW.

It was planned, but up to now not implemented, that BW together with organic waste should be treated anaerobically to produce biogas for energy and heat production. Despite the highly technical approach the operating costs have been found to be much lower than for a conventional sanitation system. The monthly operating costs, including the costs for electricity and solid waste disposal, are 1.44 EUR/m^2 compared to 2.22 EUR/m^2 in the neighboring houses with conventional systems (Langengraber and Muellegger, 2005).

Example: Sneek, The Netherlands

In Sneek in the Netherlands, a housing estate of 32 houses has been fitted with a collection, transport and treatment system for BW. Each house is equipped with two vacuum toilets; a central vacuum station, comprising vacuum pump, receiver tank and transfer pump situated in an outside cellar. BW is conveyed to the vacuum station receiver tank from where it is pumped in batches to the treatment system (Zeeman et al., 2007). Two 6 m^3 UASB-septic tanks were installed for anaerobic treatment and production of biogas. The effluent is then subjected to a post-treatment where residual COD is removed and nitrogen, as NH_4^+ and phosphorus, as PO_4^{3-} recovered. First results indicated a water consumption of about 70 L/p.d, which is very low compared to the Dutch average of 134 L/p.d (STOWA, 2005).

3. MATERIALS AND METHODS

In order to measure certain parameters, different methods were used in this study. This chapter contains the explanation of the working principles behind them.

3.1 Materials

3.1.1 Blackwater

In this study, fresh samples of BW were obtained from Flintenbreite, Lübeck. Samples were taken directly from the pipe. During the sampling, first flush coming from the pipe was always allowed to flow. This avoids the collection of sludge that may previously accumulate within the pipes. Samples were collected in various sizes of drums, transported to the Hamburg University of Technology (TUHH), Institute of Wastewater Management and Water Protection (AWW), and stored at 4 °C in the refrigerator.

3.1.2 Digested Blackwater

Digested BW was obtained from the anaerobic digesters (CSTR). The reactors were run at mesophilic temperature (37.5 °C). More information is given in chapter 4.7.

3.2 Methods

3.2.1 pH Measurement

The pH values of the wastewater samples were measured with a microprocessor pH meter. Every time, prior to the experiments, the pH meter was calibrated using buffer solutions of pH 7.0 and pH 10.0.

3.2.2 Chemical Oxygen Demand (COD)

The COD test is used to measure the oxygen equivalent of the organic material in wastewater that can be oxidized chemically (Metcalf and Eddy, 2003). The determination of COD was carried out with Dr. Lange test kits, LCK114 (150-1000 mg/L) (Hach Lange, Germany). Samples in the cuvettes were oxidized at 148 °C for 120 min and then analysed photometrically.

3.2.3 Total Organic Carbon (TOC)

The TOC test is used to determine the total organic carbon in an aqueous sample. The TOC of wastewater can be used as a measure of its pollution characteristics (Metcalf and Eddy, 2003).

The determination of TOC was performed with the TOC/TN Analyzer multi N/C 3000 (Analytik Jena, Germany).

Since the TOC test is faster, cheaper and environmentally friendlier than COD measurement, in this study TOC tests were chosen as the process control parameter.

3.2.4 Volatile Fatty Acids (VFA)

Volatile fatty acids are created as intermediate products during anaerobic digestion. Levels of up to 6000 mg/L have been shown not to inhibit the reactions, however if the pH of the reactor moves away from the optimum levels, inhibition of the methanogenic bacteria can occur at lower concentrations (Seereeram, 2004). It is known, for instance, that concentration of volatile fatty acids (VFA) in excess of 2000 mg/L inhibits methane formation in anaerobic digester (McCarty and McKinney, 1961; Kroeker et al., 1979; Chen et al., 1980).

For determination of VFA, 3 mL of H_3PO_4 was added to the sample and the solution was distilled with water steam (Büchi 321, Switzerland). After 10 minutes boiling in the Büchi gadget, the solution was cooled down, 5 drops of phenolphthalein was added and titrated with NaOH solution (0.1 mol/L) until pink colour appeared. The concentration of organic acids was calculated in terms of equivalents (mg/L HA).

3.2.5 Total Solids (TS) and Volatile Solids (VS)

The term "total solids" refers to matter suspended or dissolved in water or wastewater, and is related to both specific conductance and turbidity. TS is the residue remaining after a wastewater sample has been evaporated and dried at a specified temperature (103 to 105 °C). For the determination of the TS, crucibles were dried overnight at 105 °C, cooled in a dessicator and then weighted (empty weight). After measuring the sample volume, it was added to the crucible and weighted again (A). Then the crucible was placed overnight at 105 °C, cooled in a dessicator, and then weighted again (B). The difference in between A and B represents the TS.

Volatile solids are those solids in water or other liquids that are lost on ignition of the dry solids at 550 °C. For the determination of the VS, the crucible with the sample was placed in an oven and ignited around 2 hours at 550 °C, cooled in a dessicator and weighted (C). The difference between B and C represents the VS.

3.2.6 Total Nitrogen (TN)

TN in water is comprised of dissolved inorganic (NO_2^-, NO_3^- and NH_3) and organic N. TN was analysed with the TOC/TN Analyzer multi N/C 3000 as well as TOC.

3.2.7 Ammonium (NH_4^+)

The ammonium cation is a positively charged polyatomic cation of the chemical formula NH_4^+. NH_4^+ content of the BW samples was determined using the Büchi 321 Distillation Apparatus. This method was developed by the *Central Laboratory of TUHH*. This method has three steps: distillation, absorption in an acid solution (0.1N H_2SO_4), and titration with a base (0.1N NaOH). This method is capable of extracting pure NH_4^+ from the complex BW solution.

A sample of 50 mL was used during the measurement. After conversion to ammonia through the alkalinization with NaOH, the sample is distilled into H_2SO_4 solution. For each measurement, a blank sample consisting of deionised water was distilled to be included into the calculations. BW samples were subjected to 1:5 dilution due to their high NH_4^+ content. Distilled NH_4^+ was collected simultaneously in the acid solution consisting of 20 mL 0.1N H_2SO_4 and 100 µL of "mixed indicator 5" (a mixture of bromocresol green and methyl red, Merck) indicator solution. This acid solution was then titrated with 0.1 N NaOH until the color turned from purple into green. The volume of NaOH consumed during the titration was used in the calculations.

Calculation of NH_4^+ concentration with the consideration of blank is given as:

$$\text{g N/L} = \frac{((A\text{x}N_1) - (B\text{x}N_2)) - ((A_{BV}\text{x}N_1) - (B_{BV}\text{x}N_2))}{E} \text{ x } 14 \qquad \text{[Eq. 3.1]}$$

A	: Volume of H_2SO_4, mL
N_1	: Normality of H_2SO_4
B	: Volume of NaOH consumed during titration, mL
N_2	: Normality of NaOH
A_{BV}	: Volume of H_2SO_4 for the blank, mL
B_{BV}	: Volume of NaOH for the blank, mL
E	: Exact volume of sample used (disregarding dilution), mL

3.2.8 Phosphate (PO_4^{3-})

Determination of orthophosphate concentration of BW samples was carried out with the stannous chloride method (APHA, 1999). The principle of this method is the formation of molybdophosphoric acid. By stannous chloride ($SnCl_2$), molybdophosphoric acid is reduced to intensely colored molybdenum blue.

Since the above mentioned PO_4^{3-} measurement method was available only for the substrates with low concentration of PO_4^{3-}, a new method for the highly concentrated substrates have been developed. The new optimized method was carried out by standard addition.

Initially BW was diluted with the appropriate dilution ratio that ensures the range valid for the spectrophotometric measurement. To have a dilution ratio of 1:50, a sample of 2 mL was drawn from the drum containing BW and was diluted to 100 mL with distilled water. 60 mL of this dilution was divided into three bottles of sub samples each amounting to 20 mL. The initial PO_4^{3-} concentration was kept in the first bottle as it was, whilst 25 and 50 µL of standard phosphate solution were added into the second and the third bottles. Subsequently, 1 drop of phenolphthalein solution was added into each bottle. If a pink color was observed at any of the bottles, 1 drop of strong H_2SO_4 solution was added to dispel the color. Finally, 800 µL of ammonium molybdate solution and 2 drops of stannous chloride solution were added into the bottles. In this case, three different tones of blue were obtained changing from light to dark blue with the increase in PO_4^{3-} concentration. The sample having the highest PO_4^{3-} concentration gave the darkest blue.

Figure 3.1 Samples that are to be analyzed at the spectrophotometer

Approximately 10-12 minutes after the addition of $SnCl_2$, three samples were analyzed with a spectrophotometer at a specific wavelength of 690 nm. Afterwards they were plotted against the added PO_4^{3-} concentrations in mg/L and the standard addition graph was obtained (Figure 3.2). This graph was used to extrapolate the unknown PO_4^{3-} concentration of the BW sample by making use of the two samples of known PO_4^{3-} concentrations.

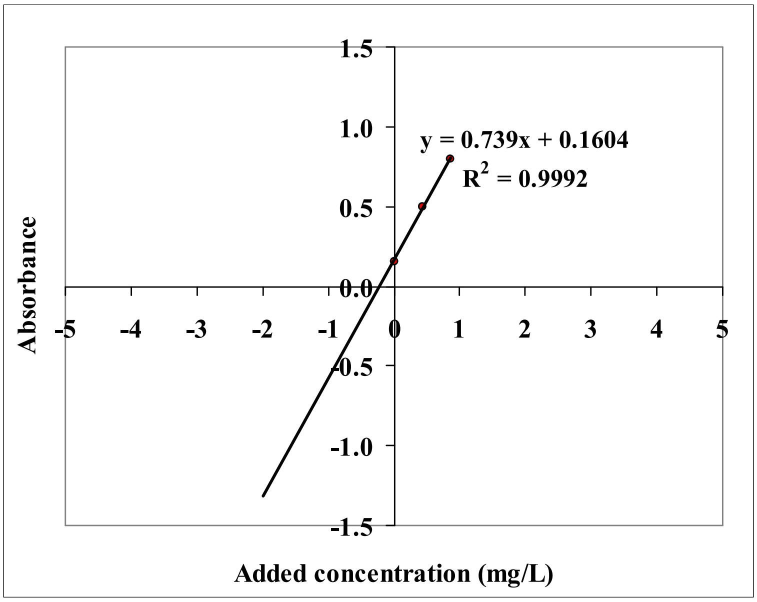


Figure 3.2 Standard addition graph

4. ANAEROBIC DIGESTION OF BLACKWATER

Anaerobic digestion (AD) of BW is a favorable alternative within the context of ecosan, as it promises resource conservation and reuse potential for the digested effluents (STOWA, 2005). In order to recover nutrients with further treatment methods (evaporation, precipitation, and adsorption) in this study, the substrate was obtained from the anaerobic digester.

Wendland (2008) focused on to find out the performance of AD in a CSTR with BW from vacuum toilets (and together with kitchen refuse). She conducted her experimental work with the same substrate (BW from Flintenbreite), in the same CSTR as well as under the same experimental conditions as explained in chapter 4.7. Since the biodegradability of BW and the performance of the CSTR were known from her study, this study was more focused on the behaviour of the nutrients during the AD process.

4.1 History of Anaerobic Digestion

Anecdotal evidence indicates that biogas was used for heating bath water in Assyria 3,000 years ago. The first digestion plant is said to be built at a leper colony in Bombay, India in 1859. AD reached England in 1895, when biogas was recovered from a sewage treatment facility to fuel street lamps in Exeter, Devon.

In 1907, in Germany, a patent was issued for the Imhoff tank (Haandel and Lettinga, 1994), an early form of digester and than in 1951 half the biogas from sewage sludge was being converted for use as fuel in cars. AD has also been used to treat agricultural waste for several years and it now treats segregated municipal solid waste. Putrescibles and paper in household waste are ideally suited to AD, as are certain types of garden waste.

After the energy crisis in 1973, the interest of AD has been increased again. Many researches were carried out on the AD of different wastes during the last four decades (Buhr and Andrews, 1977; Ahring, 1994; Battistoni et al., 1997).

4.2 A General Overview

AD is a well established technology to convert organic material from a wide range of wastewaters, solid waste and biomass. It is a technologically simple process that requires little energy. One of the end products – biogas consisting principally of methane (55-75 % volume) and carbon dioxide (25-45 % volume) is a useful, renewable energy source. Digested medium is rich in organics and nutrients and it can be considered for reuse in agriculture (STOWA, 2005). The principle advantages and disadvantages of anaerobic treatment are given below:

Advantages

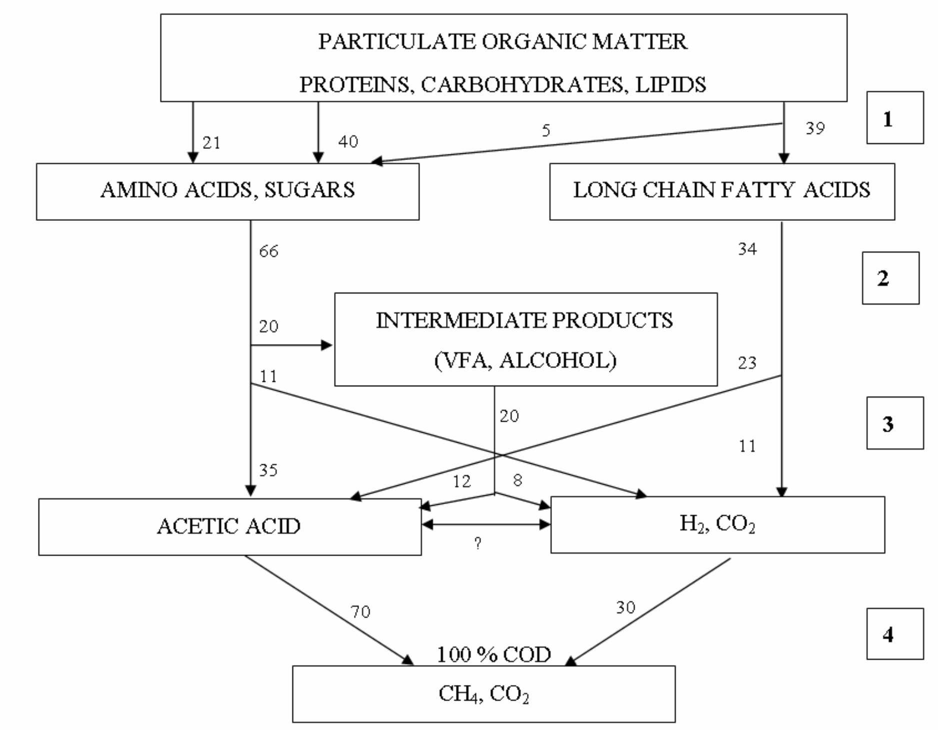
- Low energy requirements
- Low biological sludge production
- Fewer nutrients required
- Methane production, a potential energy source
- Small reactor volume requirements
- Elimination of off-gas air pollution
- Rapid response to substrate addition after long periods without feeding

Disadvantages

- Longer start-up time to develop necessary biomass inventory
- May require alkalinity addition
- May require further treatment with an aerobic treatment process to meet discharge requirements
- Biological nitrogen and phosphorus removal is not possible
- Much more sensitive to the adverse effect of lower temperatures on reaction rates
- May be more susceptible to upsets due to toxic substances

4.3 The Anaerobic Digestion Process

Transformation of complex macromolecules, present in sewage into biogas, requires mediation of several groups of microorganisms. Figure 4.1, which is suggested by Gujer and Zehnder (1983), shows a schematic presentation. Different steps are necessary for the AD of proteins, carbohydrates and lipids. Four different phases can be distinguished in the overall conversion process:



1. Hydrolysis
2. Acidogenesis
3. Acetogenesis
4. Methanogenesis

Figure 4.1 Reaction sequence for the anaerobic digestion of complex macromolecules (Gujer and Zehnder, 1983)

* Numbers refer to percentages, expressed as COD

1. Hydrolysis

In this process, complex particulate matter is converted into dissolved compounds having lower molecular weight. Proteins are degraded via (poly)peptides to amino acids, carbohydrates are transformed into soluble sugars (mono- and disaccharides) and lipids are converted to long chain fatty acids and glycerine. In practice, the hydrolysis rate can be limiting for the overall rate of AD (Van Velsen, 1981; Zeeman, 1981).

2. Acidogenesis

During this process sugars, amino acids, and fatty acids are converted to C3 and C4 volatile fatty acids (76 %), H_2 (4 %), and acetic acid (20 %).

3. Acetogenesis

The products of acidogenesis are converted into the final products for methane production: acetate, hydrogen, and carbon dioxide. A fraction of approximately 70 % of COD originally present in the influent is converted into acetic acid and the remainder of the electron donor capacity is concentrated in the formed hydrogen.

4. Methanogenesis

Methane is produced from acetate or from the reduction of carbon dioxide by hydrogen using acetotrophic and hydrogenotrophic bacteria respectively (Haandel and Lettinga, 1994).

4.4 Affect of Temperature on the Anaerobic Digestion Process

Important environmental factors affecting AD are pH, temperature, presence of essential nutrients and excessive concentrations of toxic compounds in the influent.

AD, like other biological processes, strongly depends on temperature (El-Mashad, 2003). It is an important factor affecting the performance of AD. According to Grady and Lim (1980), the exact effect of temperature on the performance of a system depends on the characteristics of waste and can only be determined experimentally. Three ranges of temperature classify three types of 'controlled' digestion: psychrophilic (10-20 °C), mesophilic (20-40 °C) and thermophilic (50-60 °C). Due to a lower bacterial growth rate under lower temperatures, longer retention of wastewater is required resulting in larger volumes.

Most of the AD systems are mesophilic, while psychrophilic operation has been considered difficult due to the slower degradation rates and long hydraulic retention times (Lettinga, 2001).

Thermophilic temperatures of 50 to 55 °C are commonly applied throughout Europe for treatment of manure from several farms in large scale biogas plants for the treatment of municipal solid waste (Ahring, 1995). The main reason of applying thermophilic temperatures is the better sanitizing effect of the higher process temperature in comparison to mesophilic temperatures and need for lower retention times (Buhr and Andrews, 1977; Ahring et al., 2002).

4.5 Anaerobic Digestion Systems for Treating Concentrated Domestic Wastewater

As explained in chapter 2, one of the objectives of ecosan is the implementation of a simple, effective and robust treatment system. Considering AD of concentrated domestic wastewater, there are three relatively simple technical configurations: accumulation system (AC), high rate system (UASB), continuously stirred tank reactor (CSTR) (STOWA, 2005; Wendland, 2008).

The AC is continuously fed, by which its effective (digestion) volume increases in time and it has been used for the digestion of liquid animal manure (Wellinger and Kaufmann, 1982; Zeeman, 1991; El-Mashad, 2003) as well as for the concentrated wastewater and solid wastes (Zeeman, 1991; Gaillard, 2002).

High rate anaerobic treatment systems refer to bioreactors in which the sludge retention time (time for sludge biomass solids to pass through system) is separated from the hydraulic retention time (time for liquid to pass through system). The UASB reactor is the most applied high rate anaerobic system for the treatment of industrial and domestic sewage (Zeeman and Lettinga, 1999; Lettinga, 2001).

Continuously Stirred Tank Reactor (CSTR)

The most common form of an anaerobic digester is the CSTR. The content of a CSTR consists of a mixture of bacteria and treated medium. It is a continuously fed system. Both bacteria and wastewater have same retention times, so hydraulic retention time (HRT) equals solid retention time (SRT). CSTR systems are often applied for digestion of sludge and slurry (Van Velsen, 1981; Zeeman, 1991; Angelidaki and Ahring, 1994). The CSTR system operates usually well between 15 and 20 days (Zeeman and Lettinga, 1999).

The term "steady state" can be applied to CSTR under the condition that the system is "well" adapted and loading is constant. Steady state conditions will ensure stable gas production and effluent quality.

In general, it can be stated that the mesophilic CSTR systems are applicable when the influent is highly concentrated that it will at least provide enough biogas to produce the energy for heating the system. The higher the concentration, the more surplus energy is produced for other applications. Moreover, concentration of the medium to be treated (e.g. vacuum collection of blackwater) will result in a smaller reactor volume to be installed, providing that the same SRT can be applied for a diluted and a concentrated influent (considering that no inhibiting compounds are present). The digested effluent can be applied easier in agriculture (if possible), as the transport cost will be limited when small volumes are produced.

4.6 Benefits of Anaerobic Digestion

Energy

Opportunity of biogas production from wastewater for using as a fuel energy resource qualifies AD as a sustainable technology for renewable energy generation. For every 1 kg of COD in wastewater that is converted by AD, 0.35 m^3 of CH_4 is produced. For solid wastes, concentrated BW and high-strength wastewaters, amount of biogas produced is significantly higher than the amount of energy required by the process (STOWA, 2005).

Environmental Quality

Application of AD should be considered for the environmental benefits of the process, in addition to its potential for energy production from wastewater. There are many potential environmental benefits that can be realized as a result of the application of AD, such as low excess sludge production (Wilkie, 2005), odour, green gas and pathogen reduction (Olsen and Larsen, 1987; Dumontet et al., 1999) and nutrient recovery (STOWA, 2005).

4.7 Experimental Set-up

A pilot plant was installed in the laboratory of the AWW at TUHH. This unit consisted of two parallel CSTRs each having 10 L volume and made of PVC. The reactors were run at mesophilic temperature (37.5±1 °C) in a heated water tube (Figure 4.2). Temperatures of both reactors were controlled with a thermostat. Water loss through evaporation was reduced by means of spherical plastic bubbles covering the water surface.

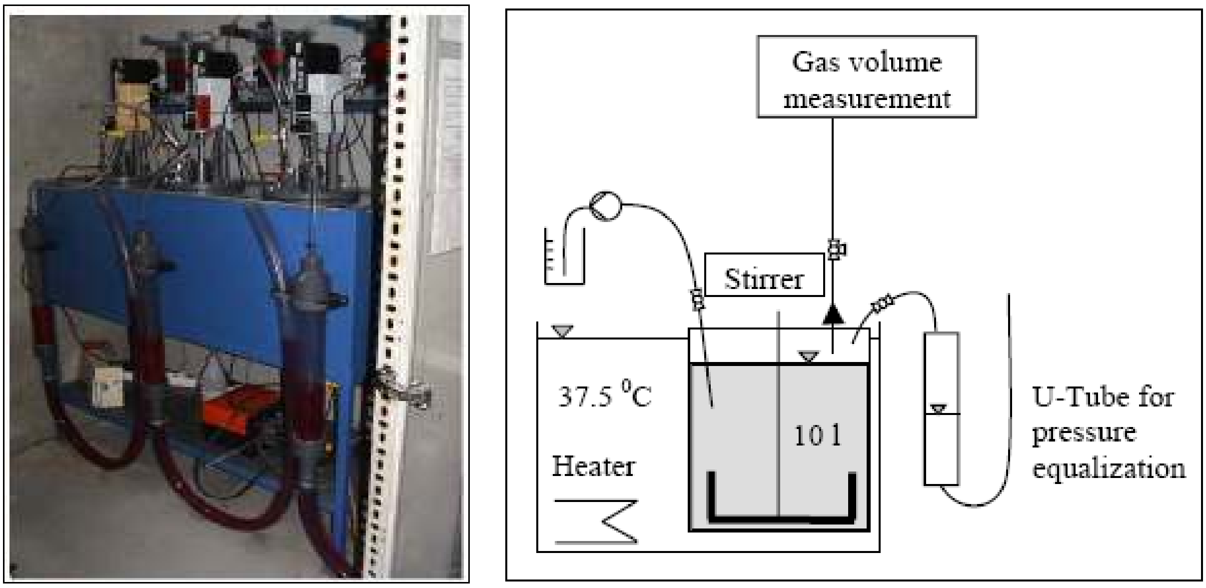


Figure 4.2 Scheme of the CSTR (Wendland et al., 2007)

In order to reduce the time required for start-up, reactors were initiated with the use of adapted sludge obtained from a mesophilic sludge digester with a 1:3 feed/seed ratio. Both reactors were fed discontinuously with raw BW obtained from Lübeck, Flintenbreite three times a week, each time with a volume of 1 L. Hydraulic retention time (HRT) of each reactor was 20 days.

Each reactor was equipped with a flexible U-tube for pressure equilibration during the feeding. The gas volumes, produced in the reactors as a result of anaerobic processes, were determined by the replacement method. The headspaces of both digesters were purged with nitrogen gas (N_2).

In order to characterize BW and understand the behaviour of nutrients in AD, parameters such as pH, COD, TOC, VFA, TS, VS, TN, NH_4^+ and PO_4^{3-} were analyzed as explained in chapter 3. In addition to them, calcium (Ca), magnesium (Mg) and potassium (K) concentrations of the samples were measured by the *Central Laboratory* with the inductively coupled plasma - optical emission spectrometer (ICP-OES).

4.8 Results and Discussion

4.8.1 Characteristics of BW from Vacuum Toilet

The concentrations of BW are much higher than typical German wastewater due to the low flush water demand for flushing the vacuum toilets. In Germany, daily mean drinking water consumption is 124 L/p.d and 27 % (ca. 35 L) of it in private households is for flushing toilet (BDEW, 2008).

As it can be clearly seen from the results of Wendland (2008) as well, concentrations are significantly varying, especially for the organic parameters like COD, VS and TS. The high standard deviations result from the high fraction of solids and the sample taking practices.

Table 4.1 Characteristics of raw BW from Flintenbreite

Parameter	**Blackwater**	
	Wendland, 2008	**This study**
Total P, mg/L	175	229
PO_4^{3-}, mg/L	-	59.6 ± 20
Total N, mg/L	1495 ± 244	1382 ± 435
NH_4-N, mg/L	1111 ± 137	1002 ± 59
Ca, mg/L	-	148 ± 20
Mg, mg/L	-	111 ± 39
K, mg/L	-	429 ± 57
Total COD, mg/L	8060 ± 2950	5461 ± 1634
TOC, mg/L	-	2253 ± 780
TS, mg/L	6530 ± 2110	4800 ± 366
VS, mg/L	4090 ± 1830	2685 ± 375
pH	7.7	7.1 ± 0.3

4.8.2 Performance of the CSTR

According to Wendland (2008), AD is a very stable process for the BW treatment. The anaerobic biodegradability of BW was determined as total COD removal of 72 %.

The value and stability of the pH in an anaerobic reactor is extremely important because methanogenesis proceeds only at a high rate when the pH is maintained in the neutral range. At pH values lower than 6.3 or higher than 7.8 the rate of methanogenesis decreases (Haandel and Lettinga, 1994). The pH value in the reactor was ranged between 7.4 and 7.8. VFA concentrations were always lower than 120 mg/L HA. Low VFA concentrations and pH values proved that the digestion process was stable (Seereeram, 2004). These results meet Wendland's outcomes.

Table 4.2 Characteristics of digested BW

Parameter	**Mean value ± Standard deviation**
pH	7.8 ± 0.2
PO_4^{3-}, mg/L	159 ± 38
NH_4^+, mg/L	1101 ± 96
TS, mg/L	3271 ± 1621
VS, mg/L	2050 ± 800
TOC, mg/L	1371 ± 268
Total COD, mg/L	4771 ± 1123

In order to recover nutrients from digested BW, it was important to know the quality of the effluent. Table 4.2 shows that nutrients in BW mostly remained in the effluent of the anaerobic digester as expected. The average concentration of NH_4^+ in the effluent was slightly higher than influent due to hydrolysis and ammonification of the organically bound nitrogen. The same tendency was observed by Kujawa-Roeleveld et al. (2005) as well.

PO_4^{3-} concentrations in the digested BW are quite higher than in the raw BW. The increased PO_4^{3-} concentration supported the idea that AD increased phosphorus availability (Wrigley et al., 1992; Battistoni et al., 1997; Beal et al., 1999; Adnan et al., 2003). This high PO_4^{3-} concentration may lead to scaling and pipe blockage, which increase operating and maintenance costs (Neethling and Benisch, 2004). On the other hand, controlled precipitation allows PO_4^{3-} recovery. Further details on PO_4^{3-} recovery will be explained in chapter 6.

4.9 Conclusions

Since AD removes mainly carbon, nutrients contained in organic matter are conserved and mineralized to more soluble forms. This provides an opportunity of recovering nutrients from BW.

AD of BW is a favorable alternative within the context of ecosan, as it promises resource conservation and reuse potential for the digested effluents. BW is one of the most concentrated wastewater fractions and regarded as a useful substrate for AD.

The fact that the nutrients are present mainly in a soluble form makes the reuse of digester effluent in agriculture an attractive option, when distance for transportation is limited. When distances to agricultural fields are too long, further processes are necessary to form products which can be handled easily.

5. VOLUME REDUCTION AND CONCENTRATION OF NUTRIENTS IN BLACKWATER BY EVAPORATION

As explained in chapter 2, BW contains a high amount of nutrients and also trace elements that are important for the growth of plants. For an application in agriculture a concentrated or a solid product would be more useful (Ergünsel, 2006). However, in some countries, reuse of nutrients contained in BW by spreading onto fields is not allowed. Additionally, for peri-urban areas where agricultural areas can only be found in remote distances, amount of BW to be transported would be very large, therefore economical storage on-site and later transport to agricultural fields is questionable (Tettenborn et al., 2006). Thus, it would be beneficial to concentrate the nutrients for transportation and storage purposes (Maurer et al., 2006). Hence, new approaches have to be found to reduce volumes of BW and extract contained nutrients on-site.

The main objective of this part of study was to investigate the evaporation process as an alternative solution to reduce the volume of anaerobically digested BW and its effect towards hygienisation.

5.1 Wastewater Treatment by Evaporation

Evaporation is the process, by which water is converted from its liquid form to its vapor form. It is being considered as an alternative process in an increasing number of wastewater treatment applications. It can be effective for concentrating or removing salts, heavy metals and a variety of hazardous materials from solution. Also, it may be used to recover useful by-products from a solution, or to concentrate liquid wastes prior to additional treatment and final disposal.

Water evaporation was first used by the Phoenicians, Romans and Chinese to obtain salt from seawater. Large flats were filled with seawater and natural evaporation from sun evaporated the water and left dry salt behind (Fink, 2002).

In practice, there are several processes that are already in use for volume reduction and nutrient enrichment in wastewater or urine. Many attempts have been made to concentrate or extract nutrients from these streams (Ek et al., 2006). Membrane filtration has been discussed (Ek et al., 2006), as well as evaporation or drying (Duarte and Neto, 1996; McKeough and Fagernäs, 1999; Lind et al., 2001) but there has not been any study concerning the evaporation of BW but urine.

According to Maurer et al. (2006), evaporation is the most straightforward technology for removing water from urine. Following is an overview of the reported technologies for the evaporation of urine in literature (Maurer et al., 2006):

- Vapor compression distillation (VCD): These processes have been proved to recover around 96 % of the original water content. Depending on the operating conditions, the energy requirement for a small-scale unit has been estimated to be 277 – 396 MJ/m^3. This unit was supposed to be installed in the space station by NASA in 2005.
- Thermoelectric integrated membrane evaporation systems (TIMES): The urine is pre-treated with ozone (or ideally UV) and H_2SO_4. It is then heated, pumped through hollow fiber membranes and exposed to reduce pressure so that it evaporates.

- Air evaporation systems (AES): Pre-treated urine is pumped through a particulate filter to a wick package. Heated air is used to evaporate water from the wick, leaving the solids.
- Lyophilization: Frozen urine sublimates under vacuum and is recovered at -90 °C to produce ice with a total TS content of 51 mg/L.

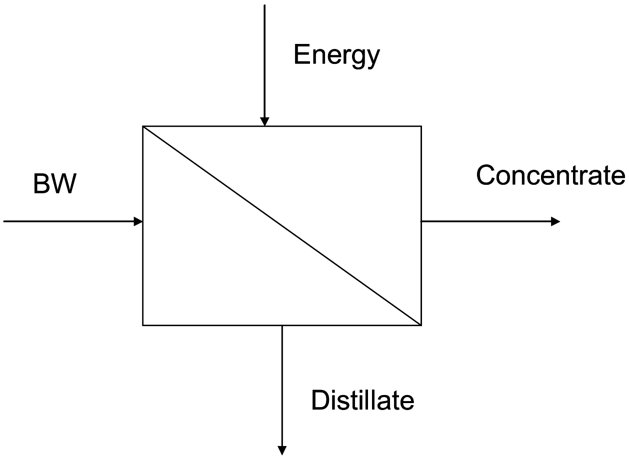


Figure 5.1 Evaporation process scheme (modified after Maurer et al., 2006)

5.2 Materials and Methods

5.2.1 Blackwater

Laboratory experiments were performed using digested BW samples.

5.2.2 Rotary Evaporator (RotaVap)

In this research, vacuum evaporation was run with a rotary evaporator (Figure 5.2). With vacuum evaporation, under reduced air pressure, the boiling point of water can be brought down to temperatures well below 100 °C. However, this type of evaporator is normally just used at laboratory scale. Vacuum evaporators at industry scale may be classified as submerged or rising (climbing) film (Wang et al., 2006).

5.2.3 Experimental Procedure

For volume reduction, a rotating glass bulb of RotaVap was heated in an oil bath. The system was run at a vacuum of -300 mbar with the help of a water-jet pump. The initial pH values of the digested BW samples were measured and recorded.

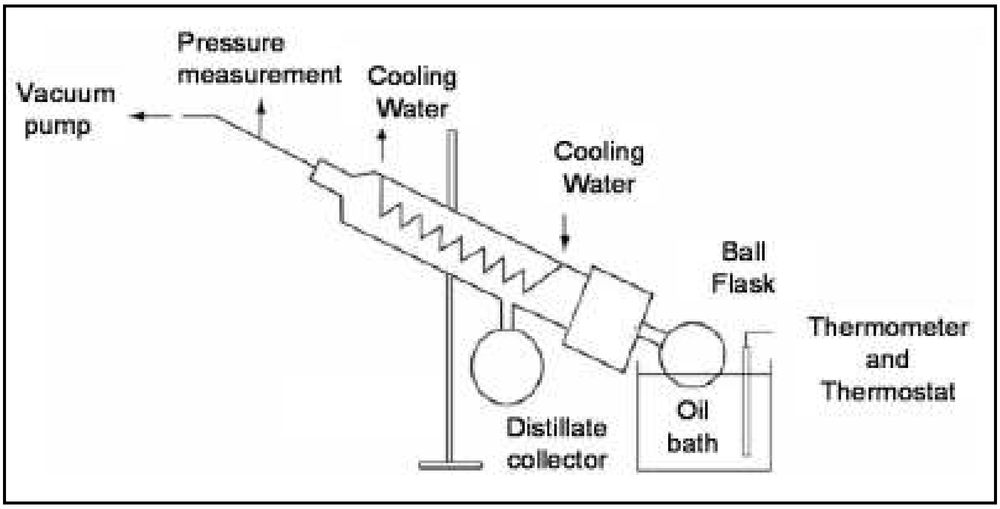


Figure 5.2 Rotary evaporator and its components

According to Maurer et al. (2006), evaporation of urine presents two major challenges: (i) loss of ammonia and (ii) energy consumption. Ammonia loss can be avoided by using non-hydrolyzed urine or by acidification. In order to avoid the loss of N as NH_3, samples were acidified with the addition of H_2SO_4 (98 %w). With acidification, pH values of substrates were lowered to 6.0, 5.0, 4.5 and 4.0.

Temperature was an important parameter to handle. Preliminary experiments showed that temperatures below 120 °C gave extremely long boiling times, around 1.0 to 1.5 hours per cycle. This time was prohibiting for the experiment itself, thus the temperature was increased above 120 °C (122 – 128 °C).

Once the temperature reached to the desired value, an initial sample of around 50 mL from the acidified sample was added in a 250 mL ball flask and connected to the evaporator. In order to obtain a larger volume of the concentrate, the glass bulb was refilled manually when the liquid level dropped below 25 mL. This process was repeated 7 times (called as “cycle”) for each experiment. Distillate samples were taken after each cycle, before refilling the bulb with the new substrate. Each taken sample of the distillate was analyzed separately. Concentrate samples were taken only at the end of the process. For all samples, pH value, PO_4^{3-}, TN, TS, VS and TOC were measured.

Following parameters were the key factors for evaluating the performance of evaporation process:

- Volume reduction (V_r)

  This parameter refers to the decrease in volume from the original BW sample achieved with the removal of water through evaporation. It is important to notice that volume reduction should facilitate transport and increase the concentration of nutrients. It can be calculated as follows:

$$V_r = 1 - \frac{V_c}{V_s} \qquad \text{[Eq. 5.1]}$$

V_r : Volume reduction factor, %
V_c : Volume of the concentrate after the n^{th} cycle, mL
V_s : Volume of substrate (BW), mL

- Evaporation velocity (EV)

  It is defined as the amount of substrate evaporated (treated) per hour. It can be calculated from the amount of distillate collected in a specified (and measured) period.

$$EV = \frac{V_d}{t} \qquad \text{[Eq. 5.2]}$$

EV : Evaporation velocity, mL/min
V_d : Volume of distillate in the corresponding cycle, mL
t : Duration (cycle time), min

- Distribution of the nutrients

  The primary aim of evaporation is to concentrate nutrients in order to make it easier to recover them in a step forward in the overall process. The distribution is then interesting to evaluate the possible separation procedures. This division can be calculated once the concentrations of each of the elements of interest (P, N or TOC) have been analyzed with the corresponding method.

$$\text{Distribution rate} = \frac{\text{Concentrate x } V_c}{\text{Substrate x } V_s} \qquad \text{[Eq. 5.3]}$$

Concentrate : Concentration of the nutrient in the concentrate, mg/mL
Substrate : Concentration of the nutrient in the substrate, mg/mL
V_c : Volume of the concentrate after the n^{th} cycle, mL
V_s : Volume of substrate (BW), mL

5.2.4 Analyses of Escherichia coli (E.coli) and Streptococcus

E. coli and Streptococcus are faecal coliform bacteria commonly found in the intestines of animals and humans. The presence of E. Coli and Streptococcus in water is a strong indication of recent sewage or animal waste contamination.

E.coli was analyzed by spreading the sample material on the surface of Chromocult® coliform agar plates and incubating at 35 °C for 24 hours (Merck).

Analyses of substrate for Streptococcus were performed by pour plate method. KF Streptococcus agar base was used as agar and incubated at 35 °C for 48 hours (Merck).

5.3 Results

5.3.1 Volume Reduction

As described before, volume reduction relates the volume left as concentrate after all evaporation cycles. Figure 5.3 shows the achieved volume reduction. The average temperature through the whole process is shown in the extra axis.

As it can be seen clearly, a fairly equal volume reduction was achieved throughout the cycles, without any effect of pH. An average of 89 % volume reduction was achieved. This could be related to the evaporation time and the temperature used. However, throughout the processes, temperatures were kept as constant as possible and their variation were around ±6 °C. This means that the differences could sourced by different solids concentration of the original substrates, which would produce a change in boiling point and thus, a direct impact on the efficiency of evaporation. According to literature, an increase of 0.7 °C and 2 °C was observed in the boiling point of urine for TS contents of 4.3 % and 14.7 % respectively (Mayer, 2002). This also affects in the course of the evaporation, since the concentration of the solids increased with time.

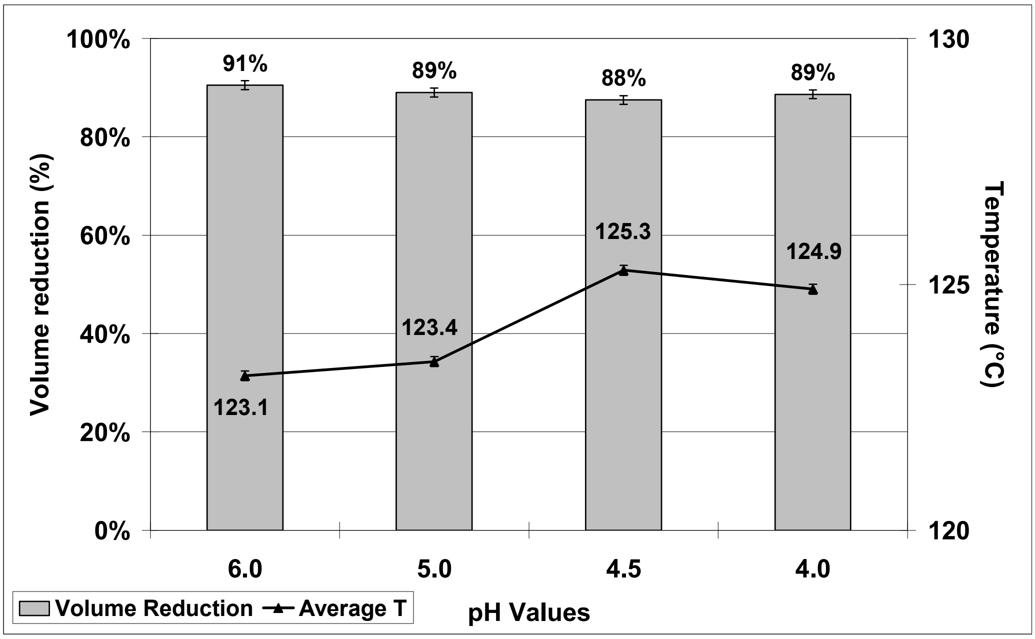


Figure 5.3 Volume reduction and average temperature values for the evaporation cycles

5.3.2 Distillation Velocity, pH and Acid Consumption

Distillation velocity refers to the amount of liquid evaporated in unit time, in this case, liters per hour (L/h). Since pH has no effect on the evaporation velocity and the temperature was kept constant, all tests gave similar results.

The average distillation velocity was close to 0.09 L/h, which is quite larger than the velocity of approximately 0.06 L/h achieved in a research done by Nie (2007), although temperatures were kept mostly the same. This could be a consequence of lower TS contents in the substrate used for the experiments conducted lately, which would decrease the boiling point of the solution and thus, increase the amount of distillate collected. Tettenborn et al. (2006) reported an evaporation rate of 1.6 L/h for their experiments with urine.

Table 5.1 Distillation velocity, average pH values and acid consumption at different pH values

Test	**Velocity**		**pH**			**Acid Consumption**
	mL/min	L/h	**Substrate**	**Distillate**	**Concentrate**	mL/L BW
pH 6.0	1.3	0.08	8.0	9.4	5.3	1.5
pH 5.0	1.3	0.08	7.9	8.5	4.5	2.5
pH 4.5	1.5	0.09	8.0	7.4	3.7	2.7
pH 4.0	1.4	0.09	8.0	6.2	3.7	2.6

Another important parameter was the pH value of the substrate (BW, prior to acidification), distillate, and concentrate. The tests with higher pH values showed a higher pH in the distillate, which indicated an increased loss of nitrogen as ammonia. Ammonia presence is the main problem for wastewater evaporation and has to be prevented (Ek et al., 2006; Maurer et al., 2006). The pH value is also important for the reuse of effluents: distillate and concentrate.

Finally, for acidification of the BW, 98 %w H_2SO_4 was used and since it is an economic factor, the amount used in each case was quantified and reported as mL/L of BW. As it was expected, lower pH values needed higher amounts of acid. On the other hand, the buffer behavior of the BW was also noticed, which acted up to around the value of pH 4.5 after which any extra addition of concentrated acid would lower the pH below 3.0. This behavior has already been observed in literature (Wendland, 2008), where the buffer ability of wastewater was explained as the consequence of the diversity of organic and inorganic compounds, which can compensate up to a certain point the addition of acidic or basic substances. Due to the decomposition of urea, ammonia and carbonate are present in high concentrations in BW and therefore BW has a high buffer capacity. The buffer capacity of BW was reported as 79.7 mmol/L by Nie (2007).

Due to the high buffer capacity of BW, diluted H_2SO_4 solutions were used to adjust the pH from 4.5 to 4.0.

5.3.3 Content of Total Solids and Volatile Solids

As explained before, the TS content of the substrate can influence its boiling point, and for further use of the concentrate, it was important to monitor this value.

Both TS and VS are limited parameters in wastewater discharge and are to be monitored for the further use and treatment of the effluents of the evaporation process. TS values for discharge are becoming stricter every time (Metcalf and Eddy, 2003). Distillate was found to be free of TS and VS.

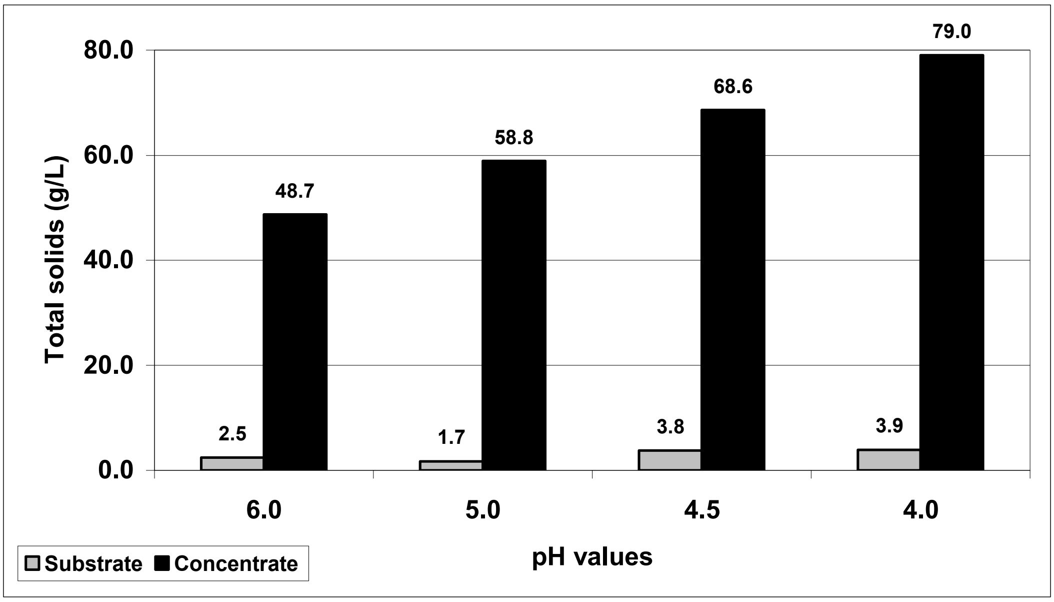


Figure 5.4 Total solids content of the substrate and the concentrate at different pH values

Figure 5.4 shows the TS concentration in the substrate and the concentrate. Here, a clear relationship between pH of the substrate and the achieved concentration of TS can be seen. The TS increase was expected and corroborated by these experiments, because most solids are not evaporated at such low temperatures. However, another part of the increase of the TS concentration could be explained by the precipitation of compounds due to probable saturation of the solution, which could occur when the evaporation concentrates the substances that are present in the substrate. For example, some crystal precipitates were observed in one of the ball flasks after the process, having a form similar to a snowflake. The amount was too little to be analyzed but it could indicate the precipitation of MAP (or struvite), which is a valuable agricultural product that could be used as a slow-release fertilizer (Scherer and Werner, 2003).

Figure 5.5 shows the VS content (as g/L) of the substrate and the concentrate. The initial VS concentration of the substrate was almost constant, however the highest content in the concentrate could be observed at a pH of 4.0.

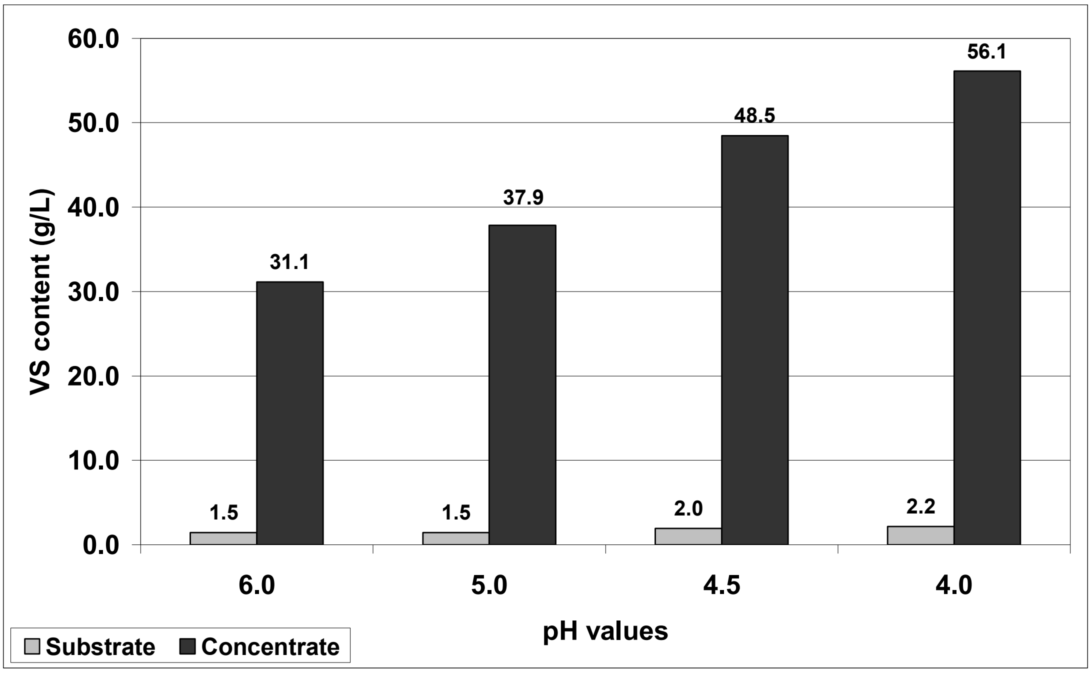


Figure 5.5 Volatile solids content of the substrate and the concentrate at different pH values

5.3.4 Overall Mass Balance and Final Distribution of PO_4^{3-}, TN, and TOC

One of the main interests of evaporation was the concentration of substances, which could then be either regained in another form or it could be applied directly onto a field. Therefore, the analysis of the distribution of the components in the substrate, the distillate and the concentrate is very important.

Recovery of material film from the ball flasks

After evaporation, a material film remained on the ball flasks. In the same way, a precipitate was found in the bottom of the flasks, but unfortunately it could not be determined if any of the compound of interest was formed (MAP, K-MAP, other phosphates).

However, some research was done in order to determine under which conditions the film could be removed, to regain any nutrient or compound of interest that could have been retained there. The solutions used for the recovery were: distilled water, 1M H_2SO_4, 10 %w H_2SO_4, 30 %w H_2SO_4. Figure 5.6 shows the film formation in the ball flasks. The flasks shown are the ones used for recovery trials with H_2SO_4.

For all of the solutions, 200 mL of solution was added to flasks. Afterwards, samples were taken and then analyzed for PO_4^{3-}, TN, and TOC. For distilled water, 1M and 10 % H_2SO_4, there was no PO_4^{3-} detected for a 1:5 dilution. This means that the content of the sample should be lower than 0.5 mg in 200 mL of the solution added. It was also negative for TN and TOC.

However, for a 30 % H_2SO_4, concentration of PO_4^{3-} was around 1.94 mg/L. This value represents a 1.7 % of the initial substrate content and it could be described as "*recyclable*" PO_4^{3-}. Recyclable means that it could be regained from the film on the ball flasks. For the other ball flasks, it was not possible to calculate an amount of recyclable PO_4^{3-}; this percentage was taken as an overall value and used in the other cases as well.

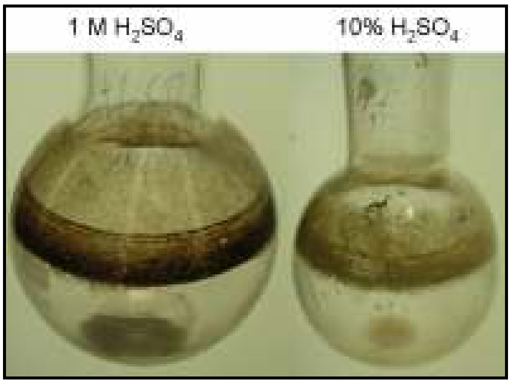


Figure 5.6 Film formation on the walls of the ball flasks after evaporation

Calculation of loss as NH_3

Based on the equilibrium reaction between NH_3 and NH_4^+, the speciation of NH_3 will depend on the pH value, the equilibrium being displaced to left in alkaline water (Figure 5.7).

$$NH_4^+ \leftrightarrow NH_{3(aq)} + H^+$$

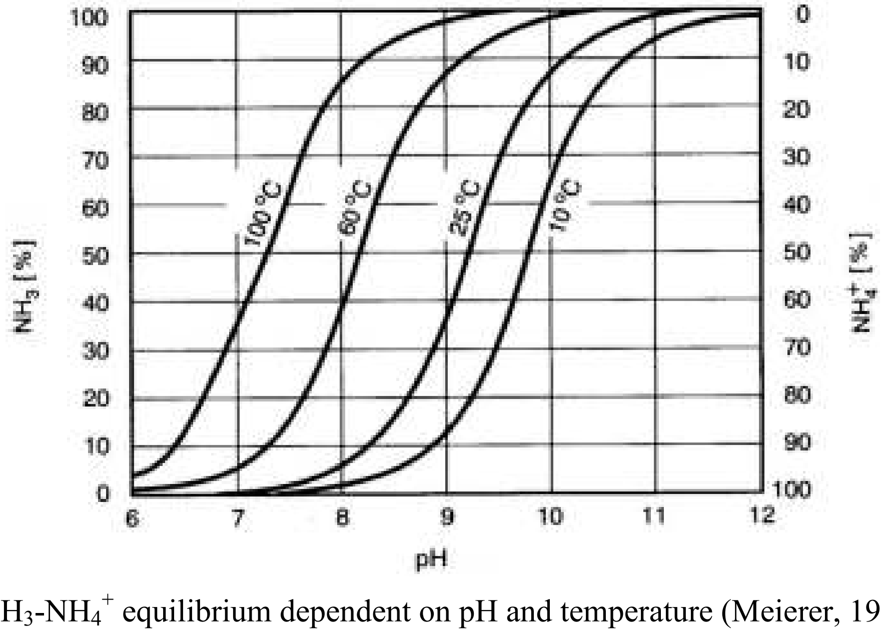


Figure 5.7 NH_3-NH_4^+ equilibrium dependent on pH and temperature (Meierer, 1995)

Table 5.2 Total nitrogen and free ammonia (NH_3) of the substrate for each pH test

Test	**TN**	**Free NH_3**		
	mg/L	mg/L	mg	%
pH 6.0	1465.5	0.833	0.167	0.057
pH 5.0	1372.0	0.078	0.016	0.006
pH 4.5	1299.0	0.031	0.006	0.002
pH 4.0	1731.5	0.009	0.002	0.001

The losses of N as free NH_3 represent a very little part of the total loss and can be easily neglected from the overall mass balance.

Fractions of PO_4^{3-}, TN and TOC mass

Once the amounts of PO_4^{3-} and TN that could be regained from the film in the flask have been calculated, as well as the amount of N lost as NH_3, a more detailed mass balance could be done.

$$(m_N)_{Substrate} = (m_N)_{Distillate} + (m_N)_{Concentrate} + (m_N)_{Lost} \quad \text{[Eq. 5.4]}$$

$$(m_N)_{Lost} = (m_N)_{NH_3} + (m_N)_{Recyclable} + (m_N)_{Nonrecyclable} \quad \text{[Eq. 5.5]}$$

$(m_N)_{NH_3}$: Mass of N lost as NH_3, mg
$(m_N)_{Recyclable}$: Mass of N (or PO_4^{3-}) recovered from the ball flask's film, mg
$(m_N)_{Nonrecyclable}$: Mass of N (or PO_4^{3-}) that cannot be recovered, mg

For a better comprehension of the distribution of PO_4^{3-}, TN, and TOC into different components of the evaporation process, Figure 5.8, 5.9 and 5.10 are shown. The values for the losses as free ammonia were not included, since its values being too low to be recorded.

In the case of PO_4^{3-} (Figure 5.8), a decrease in the pH value of the solution leads to the increase of concentration of this compound in the concentrate. This means, that the PO_4^{3-} amount available for reuse in the concentrate increases due to the decrease in the pH value of the solution. The highest value recorded, 85 % of the original content in the substrate, was obtained with the lowest acidified solution, at a pH value of 4.0. The same result was obtained by Nie (2007), where the concentrate retained around 60 to 85 % of the PO_4^{3-} originally in the substrate. In case of TN, at a lower pH value, the concentration of TN was higher in the concentrate. Because N loss in form of ammonia could be prevented through acidification and N could be more retained in the concentrate.

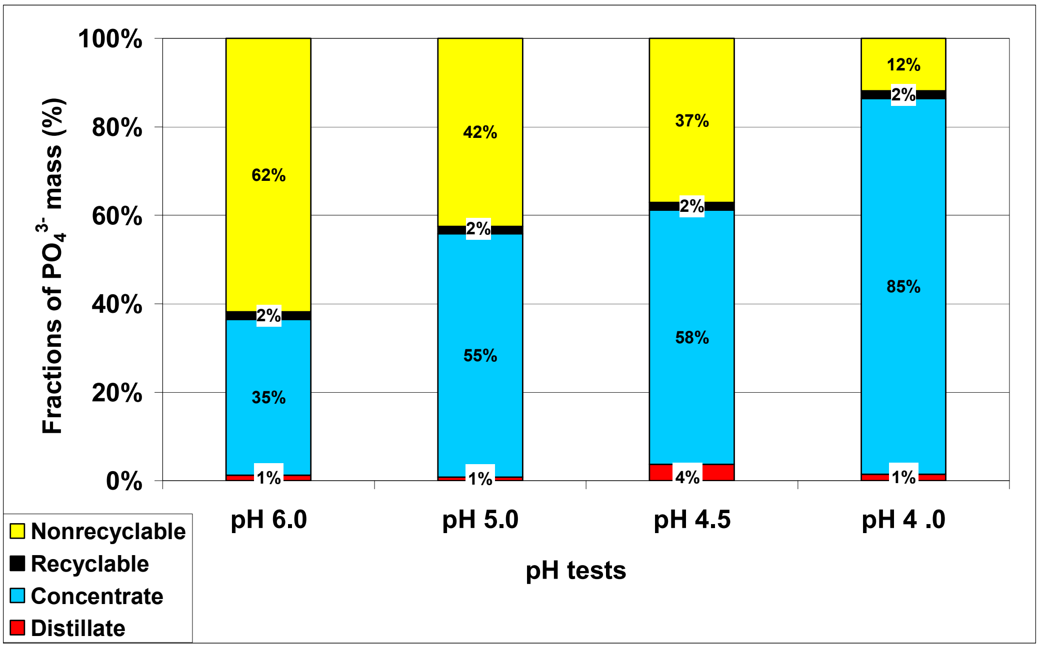


Figure 5.8 PO_4^{3-} mass balance and its distribution at different pH values

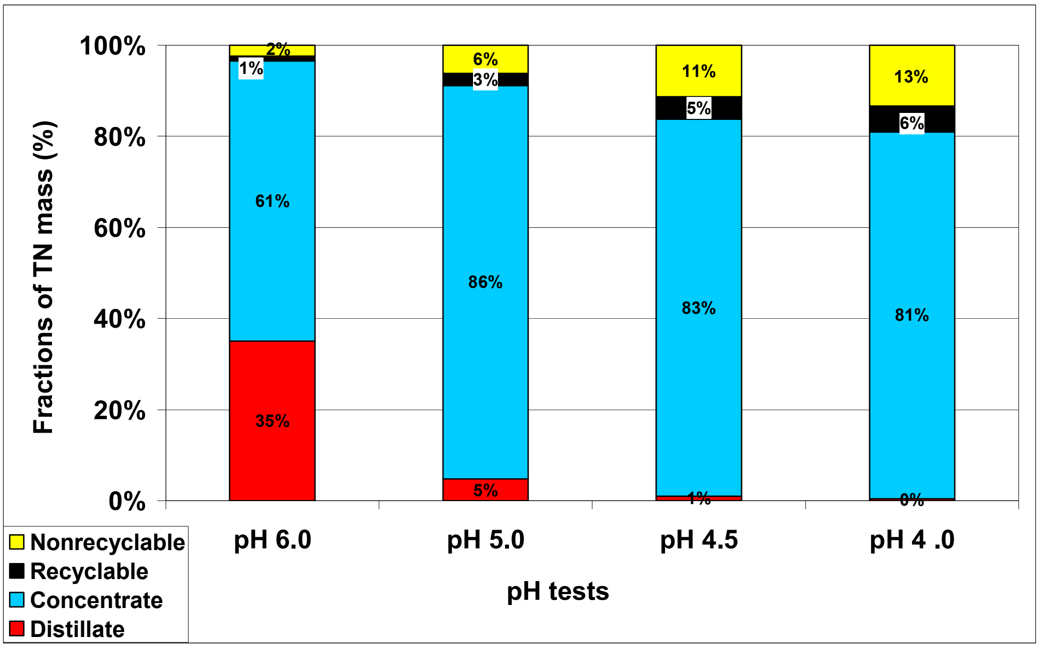


Figure 5.9 Total TN mass balance and its distribution at different pH values

The content of the concentrate was around 80 to 85 % of the originally found in the substrate. This agrees with the literature, where Ek et al. (2006) reported that 89 % of TN for pH 5.5 and 95 % of TN for pH 4.5 was obtained in the concentrate. On the other hand, lower pH values led an increase in the losses as nonrecyclable material as well. This behavior could be mainly due to the differences in the original substrate and the complex matrix of BW.

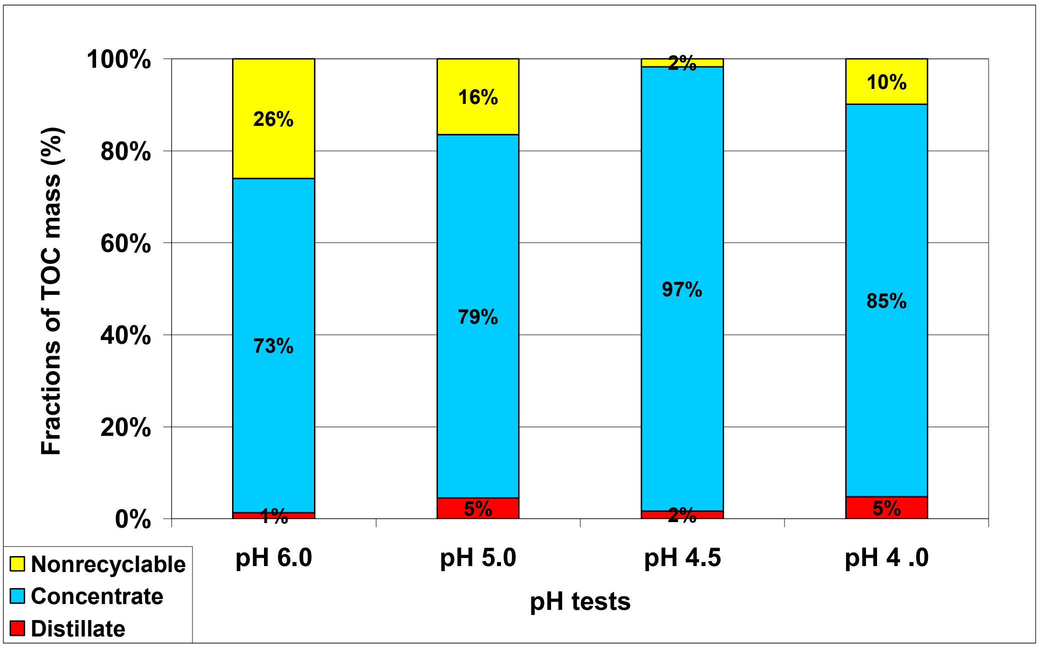


Figure 5.10 TOC mass balance and its distribution at different pH values

Figure 5.10 shows that decreasing the pH value of the substrate is inversely related to the amount of TOC in the concentrate. This trend is in agreement with the literature as well (Ek et al., 2006; Nie, 2007). However, the best results were found at a pH of 4.5 with 97 % of TOC remaining in the concentrate.

5.3.5 Physical Observations

One of the main observations was the formation of foam during the acidification process, especially at lower pH values of 4.0 and 4.5. This formation might be explained by the CO_2 production due to the significant hydrogen carbonate concentration in blackwater. This phenomenon couldn’t be observed during the evaporation itself.

Figure 5.11 shows samples of substrate (BW), distillate, and concentrate respectively. The distillate presented itself as a colorless liquid, whose smell was penetrating although not too unpleasant. The concentrate was highly turbid, almost black and had a tolerable smell.

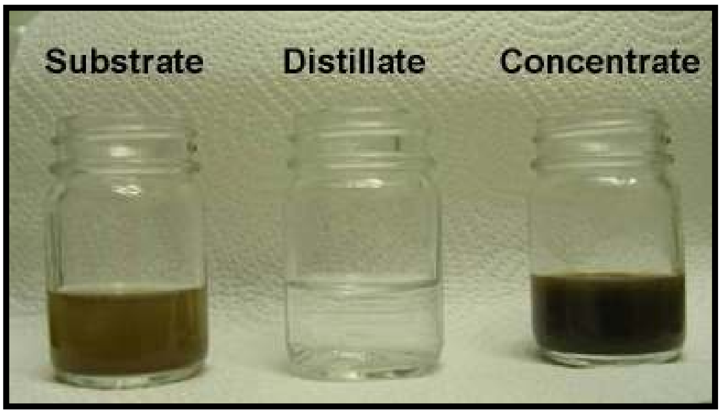


Figure 5.11 Appearance of the substrate (digested BW), distillate and concentrate from evaporation process

5.3.6 Sterilization Affect of Evaporation

Due to the fact that high temperatures (around 120 °C) and the long times of boiling (more than 90 minutes) were run, it was expected that both, distillate and concentrate, to be free of dangerous pathological microorganisms, e.g. to be sterilized. In literature, there are different ways to sterilize a solution theoretically, but it also indicates that not much research has been made in the area of wastewater (Maurer et al, 2006).

Laboratory experiments have proved that evaporation removed coliform bacteria significantly. Concentrate and distillate were completely free of E.coli and Streptococcus (Figure 5.12 and 5.13). These two organisms are indicative for fecal contamination and important parameter for water quality.

Digested BW Concentrate Distillate

Figure 5.12 E.coli results of the substrate, concentrate and distillate

Digested BW Concentrate Distillate

Figure 5.13 Streptococcus results of the substrate, concentrate and distillate

5.4 Conclusions

The water content of digested BW was reduced by evaporation, in order to reduce the volume and create a valuable concentrate from which important nutrients can be recovered. Other advantages of this volume reduction are the decreases in transport and storage costs due to smaller volumes. This also makes the handling of the BW easier.

Evaporation can be regarded as an effective technique to achieve volume reduction and nutrient enrichment in BW. The average volume reduction was around 91 % and the concentration of all the important parameters like PO_4^{3-}, TN and TOC increased when favorable low pH values 4.0 and 4.5 were used for the substrate.

However, use of the final effluents from evaporation processes and the energy consumption typical to thermal processes is among the main drawbacks of evaporation.

Further research could be done to find proper utilization options for the concentrate and distillate. The distillate, for example, which is free of suspended solids and sterilized, could be useful as flush water for the toilette or as cooling water for industrial systems. Because of its neutral pH value, it may be also used for watering the plants and landscaping purposes in parks and fountains.

The concentrate can be more complicated, as it may have a complex composition and this composition may vary according to the BW input. The pH of the concentrate is highly acidic, which could make its direct application on crops and farms difficult. However, with the proper pH adjustment, the concentrate could be used for struvite production through precipitation, its levels of PO_4^{3-} being more than adequate for it. The costs of this adjustment could be the limiting factor, as the change in pH might be from 4.0 to 9.5.

Finally, more experimental tests could be done for the recovery of the film from the ball flasks, not only for the value of the contents on the film, but also because in a large-scale operation, cleaning methods for the vessels used for evaporation are to be found.

6. EXPERIMENTAL INVESTIGATION OF THE REMOVAL AND RECOVERY OF NUTRIENTS THROUGH PRECIPITATION

The concept of sustainable development requires a holistic approach towards the fate of phosphorus. Technologies for phosphorus removal should include recovery alternatives that enable recycling of phosphorus into the environment. A promising process that has been used in several industries for phosphorus removal and recovery is the precipitation of the phosphate ion, PO_4^{3-}, as the Mg^{2+} and NH_4^+ containing mineral *struvite,* otherwise known as magnesium ammonium phosphate (MAP); a valuable and marketable product in the agriculture industry (Salutsky et al., 1970; Buchanan, 1993; Li et al., 1999; Gaterell et al., 2001). Among several methods available for nutrient removal from wastewater, struvite precipitation is a unique alternative for simultaneous removal of PO_4^{3-} and NH_4^+ (Zeng and Li, 2006); it is very robust, cost-effective, easy to operate and requires only a small footprint area (Münch and Barr, 2001). Consequently, the whole process aims to minimize the depletion of P and N resources by recycling the nutrients from the environment.

The sections below focus mainly on phosphorus, its removal and recovery, while giving relevant information on nitrogen when required. Precipitation of PO_4^{3-} as calcium phosphates was also investigated.

6.1 Theoretical Background

6.1.1 Nutrients

One of the main benefits of ecosan is its contribution to the sustainable ecosystems concept by creating recovery and reuse potential for the nutrients in urine and faeces, thereby helping the preservation of limited resources. The considerable amounts of nitrogen (N), phosphorus (P) and potassium (K) present in urine and the high organic content of faeces means they can be used to produce valuable products. Vinnerås et al. (2003) suggested that urine and faeces derived products could be used in agriculture as an alternative to the artificial fertilizers. In Jönnson (2001), recycling of all N, P and K present in urine and faeces, with a small loss of N in the form of NH_3, was proposed and it was suggested that this would increase of energy conservation in agriculture.

Nitrogen (N)

Nitrogen can be considered as an infinitely abundant element; it is present in the atmosphere at 78.1 % (by volume) and there are 75.10^6 kg of N above each hectare of the earth (Wilsenach, 2006). Biological N fixation accounts for the conversion of 90 – 130.10^6 ton N into ammonium annually (Galloway, 1998). Most of this N is also denitrified and returned to the atmosphere as N_2. In addition to this biological activity, a relatively large amount of N is deposited to soil and surface water directly from the atmosphere via dust or rain. Based on the results of Otterpohl (2001), and a world population of 6 billion, around 29.10^6 ton per year N are present within BW. In urine, N is mainly present as urea (80 %), ammonia (7 %), and creatine (6 %) and further small concentrations of free amino acids or shorter peptides (Johnston and McMillan 1952; Kirchmann and Petterson 1995; STOWA, 2005). Around 50 % of faecal N is water soluble, 20 % of it is NH_4^+, biochemically formed urea, peptides and amino-acids.

Phosphorus (P)

Phosphorus is a scarce natural resource for which there is intense competition between life forms, both on land and in aquatic environment. In nature it always occurs combined with other elements, forming phosphates. Unlike N, which in soil or water can be replenished from atmospheric sources, the only natural source of P is from the weathering of phosphate containing rocks (Van Wazer, 1961). The main commercial deposits are located in Morocco, the USA, the Former Soviet Union, China and South Africa (Driver et al., 1999).

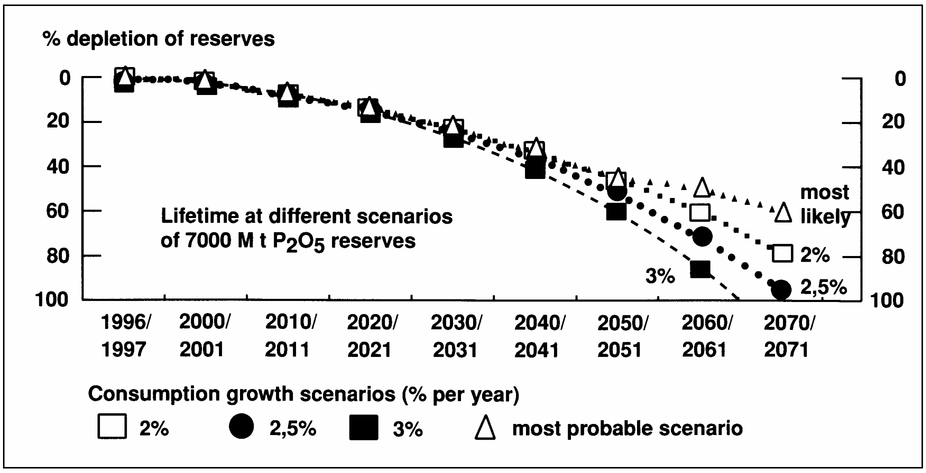


Figure 6.1 Lifetime of phosphate reserves (Steen, 1998)

Around 38 million tons of PO_4^{3-} (expressed as P_2O_5) is extracted each year (Driver et al., 1999). The known reserves of PO_4^{3-} rock are also limited. It is clear, that the resource base which could be commercially exploited by methods currently regarded as economic will last, at best, little more than one hundred years and could be depleted in as little as fifty years (Figure 6.1). Additionally, it is known that there is bast PO_4^{3-} resources present in the earth crust which, with today's technology, are not yet commercially exploitable (Driver et al., 1999). The phosphate industry is now seeking a sustainable source of high purity raw material. As a result of agriculture and human food consumption, two major sources of PO_4^{3-} are available: human sludge and animal manures. This leads to the consideration of alternative technologies where PO_4^{3-} may be derived from pre-existing materials such as sewage waste or BW.

P occurs in wastewaters almost solely as PO_4^{3-} which are classified as orthophosphates, condensed PO_4^{3-} (pyro-, meta-, and other polyphosphates), and organically bound PO_4^{3-} (APHA, 1999). The dissolved inorganic PO_4^{3-} found in wastewaters is called orthophosphate. In the pH range of wastewaters (around 7.0), the dominant forms of orthophosphates are $H_2PO_4^-$, and HPO_4^{2-}. As the pH increases the equilibrium moves towards the formation of PO_4^{3-} (Ganrot et al., 2007).

6.1.2 Phosphorus Removal and Recovery through Struvite Precipitation

One approach to remove phosphorus from BW prior to land application is the forced precipitation of magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4.6H_2O$), commonly called struvite. The wider number of applications and the successful results in the removal and recovery of P by struvite precipitation makes this a favorable alternative to the post-treatment of digested effluents (Zeng and Li, 2006).

Precipitation of struvite in waste streams is not a new idea. As early as 1939, deposition of struvite inside pipes and pumps transporting wastes was recognized (Rawn et al., 1939; Booram et al., 1975; Westerman et al., 1985; Buchanan, 1993). Therefore, a large portion of struvite research has been directed towards removal and prevention of struvite formation rather than towards forced precipitation from solution. However, struvite has been found to be a good plant nutrient source for nitrogen and phosphorus since it releases them slowly and has a non-burning feature because of its low solubility in water (Salutsky et al., 1970).

6.1.2.1 Chemistry of Struvite Formation

Struvite crystallization became a research topic because of the operational problems caused by crystalline struvite deposits that may build up at various points in wastewater treatment plants (Rawn et al., 1939). It is believed that a better understanding of the precipitation chemistry of struvite is required to optimize the performance of the crystallization process and to improve the quality of the final product; this should lead to a more favorable material for agriculture.

Struvite is composed of equimolar proportions of Mg^{2+}, NH_4^+, and PO_4^{3-} and occurs when a solution is supersaturated with the constituent ions Mg^{2+}, NH_4^+, and PO_4^{3-} (Beal et al., 1999).

$$Mg^{2+} + NH_4^+ + HPO_4^{2-} + 6\,H_2O \rightarrow \underset{\textbf{Struvite}}{MgNH_4PO_4.6H_2O} + H^+ \qquad \text{[Eq. 6.1]}$$

The crystallization process has three steps: supersaturation, nucleation and crystal growth. Initial supersaturation of the solution with the constituent ions is followed by a nucleation step which determines the initial formation of crystals, whilst the subsequent step, crystal growth, determines the size of the crystals. Sufficient crystal growth is required for the precipitation to proceed (Kabdasli et al., not published).

The potential of struvite formation can be calculated by comparing the solubility product of struvite with the ionic product of struvite. Jaffer et al. (2002), reported that the struvite precipitation occurs when the ionic product given as $[Mg^{2+}][PO_4^{3-}][NH_4^+]$ is greater than the solubility product; dissolution occurs when the ionic product is less than the solubility product. The resulting negative logarithmic value of minimum struvite solubility product; pK_{so}, documented by Ohlinger (2000) was 13.26±0.04, whereas Snoeyink and Jenkins reported (1980) 12.6.

6.1.2.2 Major Parameters Affecting the Struvite Formation

Several major parameters affecting the struvite precipitation are: pH, Mg:P ratio, Mg^{2+} sources, presence of Ca^{2+} ions, and reaction time (Zeng and Li, 2006; Yazgan, 2008).

Effect of pH

pH is a very important factor in struvite precipitation as the solubility of struvite and the availability of the constituent ions are pH dependent. Struvite is soluble in acidic pH conditions and highly insoluble at alkaline pH (Münch and Barr, 2001). Schulze-Rettmer (1991) gave the lowest values for the solubility of struvite in wastewater in the pH range of 8.0 to 10.0. Booker et al. (1999) found that struvite is soluble in water when the pH is less than 5.0. They also proved that the solubility of struvite begins to increase as pH continues to rise above 9.0, since the NH_4^+ ion concentration will decrease (Figure 6.2). Various other researchers have also investigated the effect of pH on P removal (Buchanan et al., 1994; Ohlinger, 1999; Battistoni et al., 2001; Burns et al., 2001; Celen and Turker, 2001; Dastur, 2001; Stratful et al., 2001). Results of those studies have shown that there is an increase in P removal rates as pH increases.

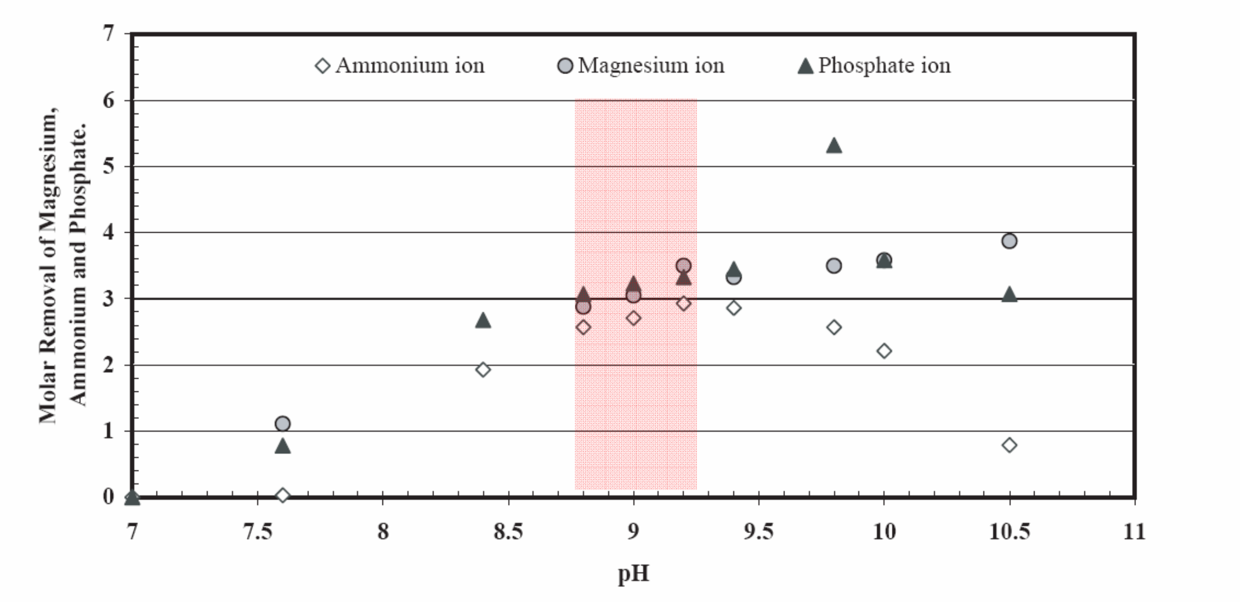


Figure 6.2 The effect of pH on molar removal of magnesium, ammonium and phosphate (Booker et al., 1999)

Effect of Mg:P molar ratio

Supplementation of Mg^{2+} by an external source is often necessary for struvite crystallization. The theoretical Mg:N:P ratio required for struvite formation is 1:1:1. Therefore, Mg^{2+} ion supplementation should at least meet the stoichiometric requirement to ensure that Mg^{2+} ions do not become a limiting factor. Nevertheless, struvite crystallization can also proceed at molar ratios other than unity. Formation of hard scales of struvite at various treatment plants is an example of such unintentional struvite formation where Mg:N:P ratio is not 1:1:1. However, in the case of intentional struvite crystallization, when the Mg:P falls below unity, where N is always in excess, Mg^{2+} concentration becomes the limiting factor and P removal efficiencies decrease. This trend is attributable to the fact that any increase in the Mg:P ratio enhances struvite formation, which in turn increases the P removal efficiency (Adnan, 2003). Westerman et al. (1985) determined the critical nutrient limit for struvite formation to be ≥ 30 mg/L for P and ≥ 15 mg/L for Mg^{2+}.

Effect of Mg^{2+} sources

Sources of Mg^{2+} are typically MgO, $MgCl_2$, and $Mg(OH)_2$; each have different advantages and disadvantages (Burns and Moody, 2002). MgO and $MgCl_2$ are the most popular Mg^{2+} sources used in the previous struvite crystallization studies. MgO can increase both Mg^{2+} concentration and pH, but has a relatively low solubility. $MgCl_2$ has quite a high solubility compared to MgO, however its acidifying effect is a disadvantage (Jenmaire, 2001; Burns and Moody, 2002).

Effect of TSS concentration

Total suspended solids (TSS) concentration has an effect on struvite precipitation. Ohlinger et al. (1998) suggested that in digested manure effluents the inhibition of struvite precipitation could possibly due to the extremely complicated matrix and the high TSS content of the substrate. Schuiling and Andrade (1999) demonstrated an interference with the struvite precipitation at a TSS concentration above 1000 mg/L. This inhibition was also observed by Beal et al. (1999) and Gaterell et al. (2000).

Effect of the presence of Ca^{2+} ions

Struvite formation is also effected by the concentration of the Ca^{2+} ions. Depending on the concentration, struvite formation can be inhibited and the formation of calcium phosphates can occur. This effect may be overcome by increasing Mg:Ca ratio (Momber and Oellermann, 1992; Wild et al., 1996; Battistoni et al., 2000; Le Corre, 2006).

6.1.2.3 Nitrogen Removal as a Side Benefit

Being a constituent element, N has the potential to be removed via struvite crystallization in the form of NH_4^+. However, most wastewaters have significantly higher concentrations of N compared to P and Mg^{2+}. Therefore, if NH_4^+ is the target element to be removed, external Mg^{2+} and PO_4^{3-} supplementation is essential. As a result, removal of NH_4^+ depends on the degree of P removal and is a side benefit instead of being the primary objective. During struvite precipitation, a proportion of the initial NH_4^+ is always removed and with PO_4^{3-} and Mg^{2+} supplementation and additional engineering of the process, removed and recovered of NH_4^+ has the potential to be increased (Dempsey 1997; Celen and Turker, 2001; Adnan 2003).

6.1.3 Phosphorus Removal and Recovery through Calcium Phosphate Precipitation

Ca^{2+} salts are also used to precipitate dissolved PO_4^{3-} in wastewaters. Ca^{2+} may be added in the form of $Ca(OH)_2$, CaO, or $CaCl_2$ to recover PO_4^{3-} as calcium phosphates in crystallization processes (Kujawa-Roeleveld and Zeeman, 2006).

Ca^{2+} may form various forms of phosphate compounds: $Ca_3(PO_4)_2$, $Ca_5(OH)(PO_4)_3$, $CaHPO_4$, $Ca_5(OH)(PO_4)_3$, $CaCO_3$, etc. Compounds consisting of Ca^{2+}, OH^-, and PO_4^{3-} are called apatites. Even though apatite is highly insoluble, a high pH is required for its formation. Ca^{2+} forms $CaCO_3$ near at pH 9.5. Therefore, a pH higher than 10 is required for a significant apatite formation. Since Ca^{2+} reacts with natural alkalinity to form $CaCO_3$, depending on the alkalinity of the specific wastewater very high doses of Ca^{2+} may be required. This effect makes the process costly compared to other metal agents (Droste, 1997).

$$10Ca^{2+} + 6PO_4^{-3} + 2OH^- \leftrightarrow \underset{\textbf{Hydroxylapatite}}{Ca_{10}(PO_4)_6(OH)_2} \qquad \text{[Eq. 6.2]}$$

The quantity of Ca^{2+} required is generally independent of the initial PO_4^{3-} concentration, but depends on the alkalinity of the wastewater. The quantity of Ca^{2+} required in form of $Ca(OH)_2$ is typically 1.4 to 1.5 times the total alkalinity expressed as $CaCO_3$ (Metcalf and Eddy, 2003). Due to the high pH requirements of this process, the effluent usually needs final neutralization prior to disposal. High sludge generation and operational problems makes the use of Ca^{2+} somewhat limited for PO_4^{3-} removal from wastewaters (Metcalf and Eddy, 2003). Furthermore, precipitated products cannot be used directly as a fertilizer since the calcium phosphates are mainly in the form of hydroxylapatite (HAP), which is insoluble in water (Suschka and Poplawski, 1999), and therefore not plant available.

6.2 Materials and Methods

6.2.1 Blackwater

Laboratory experiments were performed using raw and digested BW samples (Chapter 3.1).

6.2.2 Mg^{2+} and Ca^{2+} Salts

Four different Mg^{2+} sources were examined within the context of this research to assess their effects on nutrients removal and recovery from BW: magnesium oxide (MgO), magnesium chloride ($MgCl_2.6H_2O$), magnesium hydroxide ($Mg(OH)_2$), and magnesium sulfate ($MgSO_4.7H_2O$).

Table 6.1 Characteristics of the Mg^{2+} sources (Zeng and Li, 2006)

Mg^{2+} Source	Effect on pH	Solubility in BW
MgO	Basic	Low
$MgCl_2.6H_2O$	Acidic	High
$Mg(OH)_2$	Basic	Low
$MgSO_4.7H_2O$	Acidic	High

Even though Mg^{2+} salts were decided to be efficient precipitants for P removal from BW, effects of Ca^{2+} salts were also tested within this research. Three different Ca^{2+} sources were tested: calcium oxide (CaO), calcium hydroxide ($Ca(OH)_2$), and calcium chloride ($CaCl_2$).

Table 6.2 Characteristics of the Ca^{2+} sources

Ca^{2+} Source	Effect on pH	Solubility in BW
CaO	Basic	Low
$Ca(OH)_2$	Basic	High
$CaCl_2$	Acidic	High

$$\text{Mass of Mg compound (mg)} = \frac{(PO_4 - P) \text{ x } MW_{MgX} \text{ x } (Mg : P) \text{ x } V_{sample}}{MW_P} \qquad \text{[Eq. 6.3]}$$

$$\text{Mass of Ca compound (mg)} = \frac{(PO_4 - P) \text{ x } MW_{CaX} \text{ x } (Ca : P) \text{ x } V_{sample}}{MW_P} \qquad \text{[Eq. 6.4]}$$

MW : Molecular weight, g/mol
V : Volume, L
MgX : Mg^{2+} source
CaX : Ca^{2+} source

Table 6.3 Molecular weights (MW) of the relevant chemicals

	P	MgO	$MgCl_2.6H_2O$	$Mg(OH)_2$	$MgSO_4.7H_2O$	CaO	$Ca(OH)_2$	$CaCl_2$
MW (g/mol)	31.0	40.3	202.3	58.3	246.5	56.1	74.1	111.0

The original pH of the BW samples lie between 6.5 and 8.0 and was not sufficient for high PO_4^{3-} removal rates through struvite precipitation. This requires adding 1N NaOH to raise the pH value to the desired value.

6.2.3 Experimental Set-up

Precipitation experiments were performed using a jar test apparatus (Figure 6.3). It has five stirrers that can be employed simultaneously. Mixing speed of the stirrers can be adjusted manually within a range of 0 to 1600 rpm. The maximum speed applied in this study was 400 rpm for rapid mixing and the lowest speed was 50 rpm for slow mixing.

Figure 6.3 Jar test apparatus

The jar test apparatus was run two times in a row allowing 5 samples to be tested at each run. The success of struvite formation was assessed after the characterization of the precipitate formed at the bottom of the beakers with XRD measurements. Experimental procedure given in the following section was followed.

6.2.4 Procedure of the General Precipitation Experiments

1. For PO_4^{3-} concentration, 500 µL BW sample was pipetted from the storage bottle and diluted 1:200 with distilled water in a flask.
2. Initial pH and PO_4^{3-} concentration of the BW were determined.
3. The amount of Mg^{2+} or Ca^{2+} salts required was calculated according to the measured PO_4^{3-} concentration.
4. Mg^{2+} or Ca^{2+} salts were placed into the 500 mL beakers.
5. The required volumes of BW were measured and poured into the beakers.
6. After the initial mixing, any changes in pH after the dissolution of the Mg^{2+} or Ca^{2+} salts were recorded.
7. The pH was adjusted to the desired value in each beaker by the addition of 1N NaOH.
8. The substrate was stirred for 15 minutes and additionally 30 and 45 minutes during the preliminary experiments
9. Upon completion of mixing, beakers were taken out of the jar test apparatus and left for 30 minutes to allow for sedimentation. During the sedimentation period, any changes in pH were recorded.
10. After 5, 15 and 30 minutes of sedimentation (optimized conditions; additionally samples taken at 45 and 60 minutes in the preliminary experiments), 20 mL of sample was taken from the supernatant in each beaker into small bottles.
11. The collected samples were analyzed for PO_4^{3-} using the standard addition method.
12. Relative to the initial PO_4^{3-} concentration of the BW, removal efficiencies of PO_4^{3-} in each beaker were assessed.

13. Same samples were investigated for the Ca^{2+} and Mg^{2+} concentrations to determine their consumption rates during PO_4^{3-} removal.
14. Precipitates formed at the bottom of the beakers were collected diligently. After drying them at 105 °C, the residues were scraped off, pounded with the aid of a mortar and analysed by XRD.

6.2.4.1 Ca^{2+} and Mg^{2+} Determination by Atomic Absorption Spectroscopy (AAS)

Ca^{2+} and Mg^{2+} are both bivalent cations competing for the PO_4^{3-} anion. For this reason, in addition to the PO_4^{3-} determination, Ca^{2+} and Mg^{2+} concentrations were also monitored. To measure the Ca^{2+} and Mg^{2+} concentrations of the samples, the AAS (Perkin Elmer SIMAA AAS) apparatus of the *Environmental Technology and Energy Economics* department (IUE) was employed.

In analytical chemistry, atomic absorption spectroscopy is a technique for determining the concentration of a particular metal element in a sample. AAS uses the absorption of light to measure the concentration of gas-phase atoms. Since samples are usually liquids or solids, the analyte atoms or ions must be vaporized in a flame or graphite furnace. The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The instrument measures the absorption of light at specific wavelengths by elements in the free state, such as calcium and magnesium.

Measurements of different metal ion concentrations with AAS require lamps specific to those metals. For each measurement individual calibration curves were performed using stock standard solutions of Ca^{2+} or Mg^{2+}. Due to the sensitivity of the AAS, prior to the measurements, samples were filtered through 0.45µm-pore-diameter membrane filters to remove suspended materials. The results from AAS give the concentrations of Ca^{2+} and Mg^{2+} in mg/L (APHA, 1999).

6.2.4.2 Precipitate Characterization by X-Ray Diffraction Technique

Characterization of the precipitates was carried out using X-Ray diffraction (XRD). The XRD device of the IUE was used for this purpose.

XRD is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials.

The XRD technique takes a sample of the material and places a powdered sample in a holder, then the sample is illuminated with x-rays of a fixed wave-length and the intensity of the reflected radiation is recorded using a goniometer.

XRD analysis yields reliable results for samples having particular characteristics.

In order to be measured by XRD, samples should possess a crystalline structure and be out of moisture. Therefore, prior to the analysis, samples were dried in the oven at 105 °C and then the residues were powdered using a laboratory mortar. The powdered end products were put into small tubes prior to the final analysis that will be done by the XRD device. The XRD device can identify different struvites by their distinctive orthorhombic structure. The XRD generates a spectrum whose peaks' intensities and positions were matched to a database of known crystal structure XRD spectra to identify which struvites where present in the samples.

6.3 Results and Discussions

6.3.1 Determination of Optimum Mixing and Sedimentation Time

Precipitation experiments followed a sequence of mixing, sedimentation and analysis steps. Preliminary experiments were performed to determine and optimize the mixing and sedimentation times. Initial experiments were run to test three different mixing times: 15, 30, and 45 minutes, followed by a 60 minute sedimentation time. The initial one third of the mixing time was performed with the rapid mixing setting and the remaining with the slow mixing setting. Mixing the samples provided not only homogenization of the solutions but also prevented the settling of the solids prior to the sedimentation phase (Beal et al., 1999).

Results obtained from the experiments performed by using MgO as a Mg^{2+} source with 15, 30, and 45 minutes of mixing at pH values of 9, 10 and 11 are given in Figures 6.4, 6.5, and 6.6; these are the optimum pH values given in the literature.

In these graphs, relative PO_4^{3-}-P concentrations (C/C_o) were plotted against sedimentation times. The lowest PO_4^{3-} removal rates were obtained for the 45 minutes mixing times. This can be attributed to the fact that excessive mixing can disturb and break the formed flocs, which has a negative effect on the efficiency of the precipitation (Rahaman et al., 2007). The PO_4^{3-} removal rates for the 15 and 30 minutes experiments are comparable except at pH 9.0. At this pH, a markedly higher removal rate was obtained in the 15 minute experiments. Considering these results, 15 minutes was selected as the optimum mixing time because it yielded the highest PO_4^{3-} removal rate over all different pH values, in addition the shortness of the reaction period resulted in a time and energy saving. These results were in agreement with Beal et al. (1999) and Burns et al. (2002).

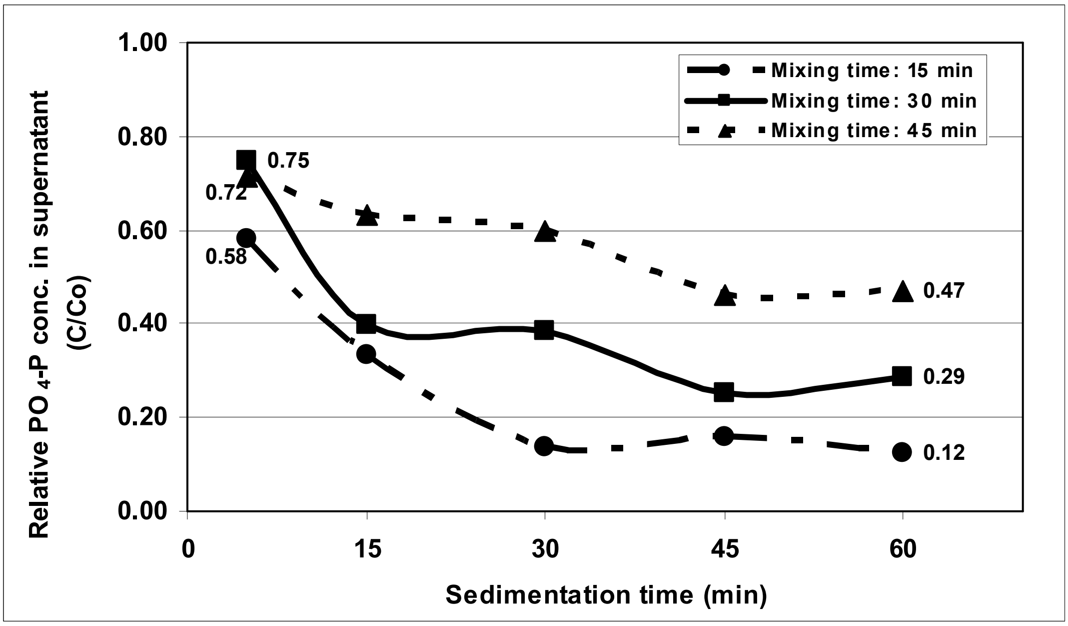


Figure 6.4 Optimum mixing time experiments with MgO at pH 9 by (Mg:P ratio: 1.0)

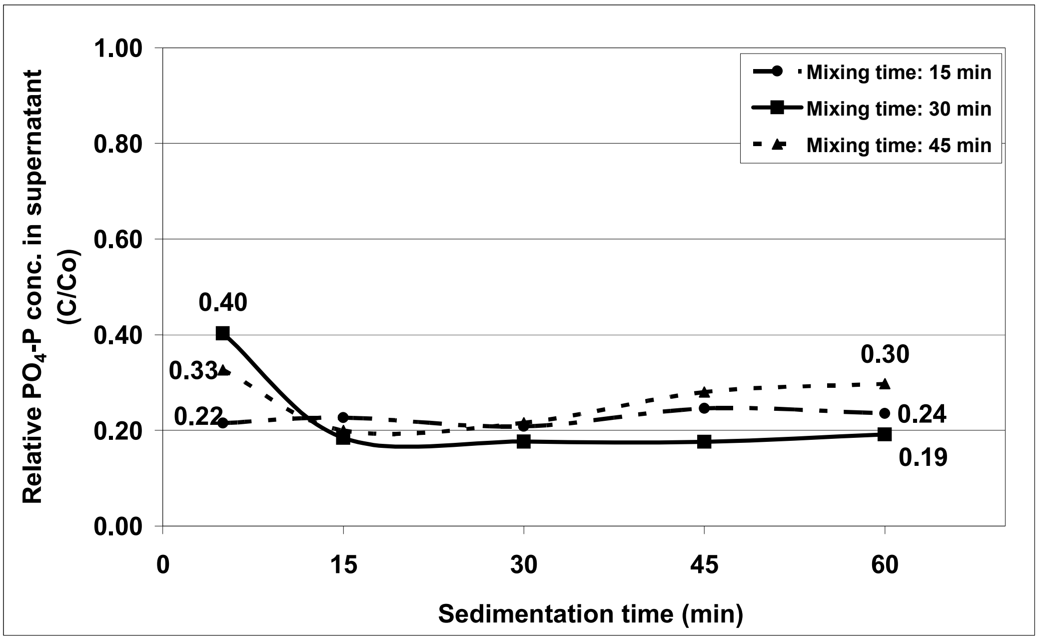


Figure 6.5 Optimum mixing time experiments with MgO at pH 10 (Mg:P ratio: 1.0)

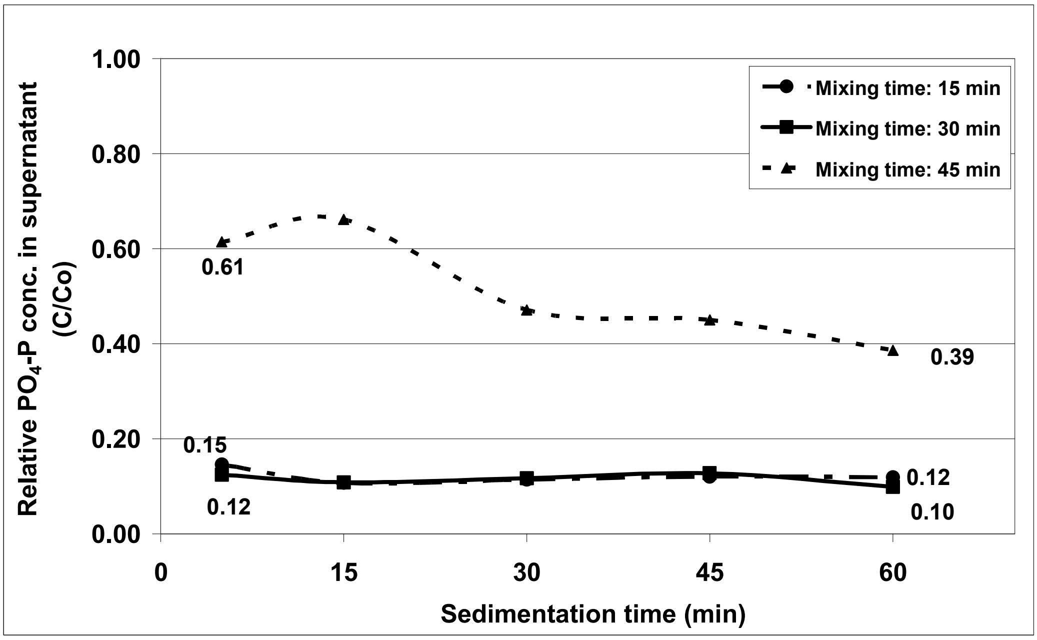


Figure 6.6 Optimum mixing time experiments with MgO at pH 11 (Mg:P ratio: 1.0)

Figure 6.4, 6.5, and 6.6 present that after 30 minutes of sedimentation, further increases in PO_4^{3-} removal are minor. Since a distinct sedimentation time that assures highest PO_4^{3-} removal could not be observed in these experiments, determination of the optimum sedimentation time was left to the subsequent experiments. Those experiments performed later to assess the optimum Mg:P ratio supported the conclusion that no profound increase in PO_4^{3-} removal could be achieved with more than 30 minutes of sedimentation, whilst principally 15 minutes of sedimentation was sufficient to achieve almost 90 % of PO_4^{3-} removal (Figure 6.7 and 6.8).

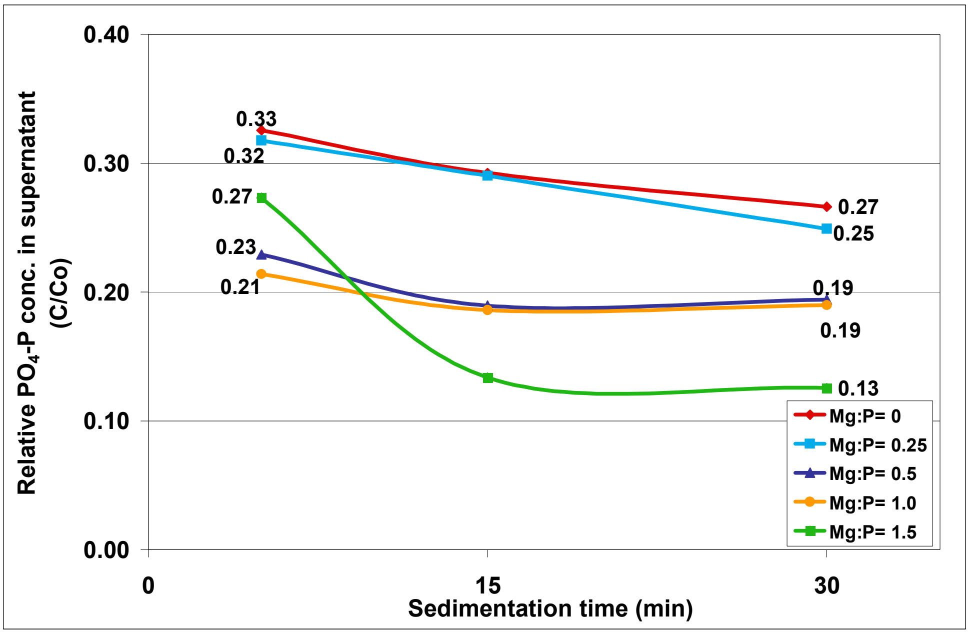


Figure 6.7 Optimum sedimentation time experiments with $MgCl_2$ at pH 9.0 for Mg:P ratio of 0-1.5

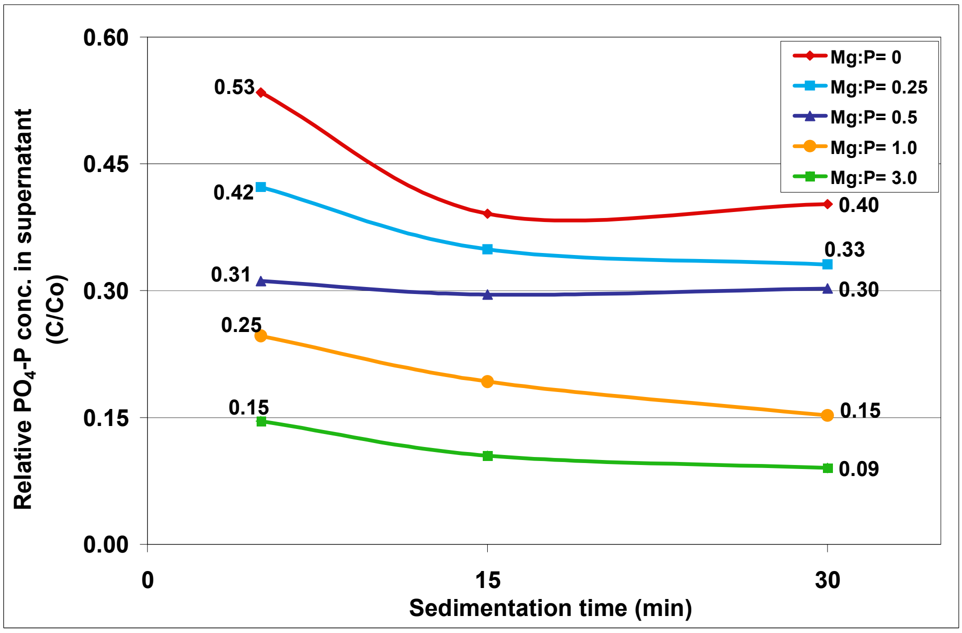


Figure 6.8 Optimum sedimentation time experiments with $MgCl_2$ at pH 9.5 for Mg:P ratio of 0-3

Figure 6.9 Samples during flocculation and subsequent sedimentation

These experiments also showed that, to a large extent, PO_4^{3-} precipitation was completed in the first 5 minutes, while perpetuating the sedimentation phase provided further increases in PO_4^{3-} removal. Celen and Turker (2001) reported that the struvite precipitation proceeds very fast and is completed within minutes. Similarly, Shin and Lee (1997) observed in struvite precipitation experiments, the residual NH_4^+, PO_4^{3-} and Mg^{2+} concentrations were all decreased rapidly in the first few minutes and that a reaction time of 10 minutes was suggested for achieving high nutrient removal efficiencies. Burns et al. (2001) experienced only a 1.3 % increase in PO_4^{3-} removal as the total reaction time increased from 10 to 40 minutes. Considering the results of these experiments and the results obtained from the previous studies, a sedimentation time of 15 minutes was found to be sufficient for PO_4^{3-} removal through precipitation. Nevertheless to be on the safe side 30 minutes was selected as the optimum sedimentation time that ensures maximum PO_4^{3-} removal efficiencies. As a result, a total reaction time of 45 minutes, comprising precipitation and sedimentation, was found reasonable to justify the energy input and time required for the reaction.

6.3.2 Effect of pH on PO_4^{3-} Removal

The pH of a solution is an important parameter affecting a variety of precipitation processes in wastewater treatment (Metcalf and Eddy, 2003). PO_4^{3-} removal from BW through precipitation is similarly pH dependent. Therefore, the effect of pH on PO_4^{3-} removal was investigated comprehensively. An initial study was undertaken to determine an optimum range of values pH for which struvite precipitation could be further investigated with digested BW. The PO_4^{3-} removal efficiencies from raw BW samples were investigated at pH 9.0, 9.5 and 10.0 using MgO. pH 9.5 was found to be the optimum pH that yielded nearly 91 % PO_4^{3-} removal, the removal efficiency achieved at pH 9.0 was marginally less at 88.5 % (Figure 6.10). It should also be noted that the removal efficiency decreased as the pH was increased to10.0.

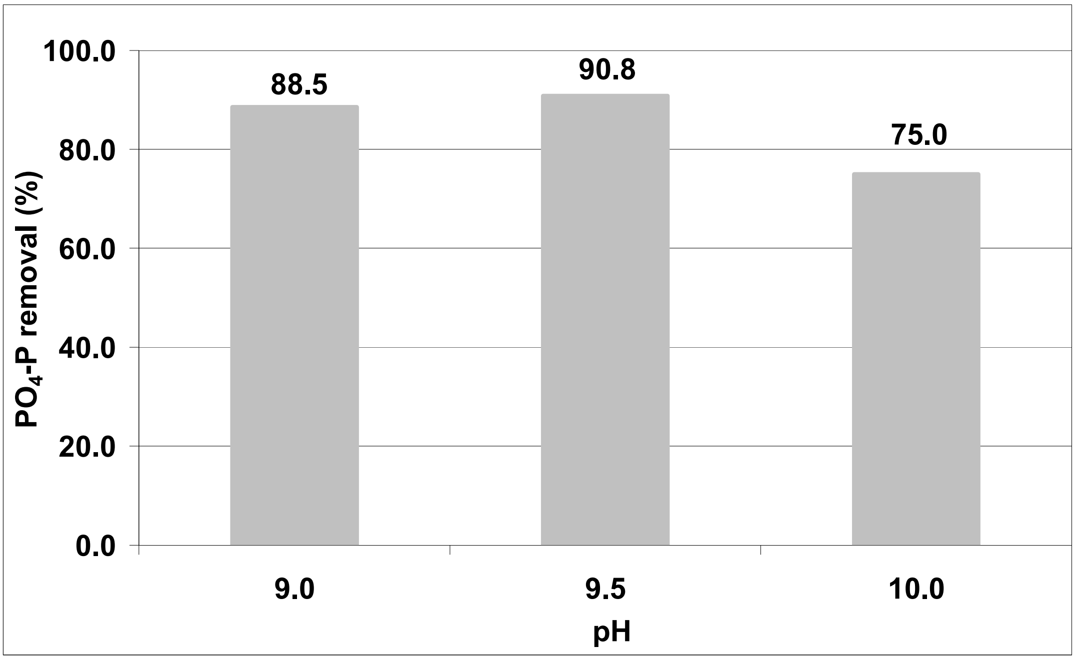


Figure 6.10 Preliminary optimum pH experiments with MgO at pH 9.0, 9.5 and 10.0

Use of Mg^{2+} salts

The effect of pH on PO_4^{3-} removal was assessed by testing seven different pH values with two different Mg^{2+} sources (MgO and $MgCl_2$) and for two different Mg:P ratios (1 and 2); pH values were adjusted to 8.5, 9.0, 9.5, 10.0, 11.0, and 12.0 using 1N NaOH. The seventh experimental condition was without pH adjustment (pH 7.8).

The highest PO_4^{3-} removals were achieved with pH of 9.5 (Figure 6.11 and 6.12). The initial pH of the BW samples was around 7.8. Between 7.8 and 9.5, PO_4^{3-} removal efficiency increased gradually with the increase in pH. After pH 9.5, removal efficiency started to decrease as the pH was increased to 12.0. This result can be explained by the reduction in availability of the necessary ions for the struvite formation at pH values above 10.0 (Figure 6.2).

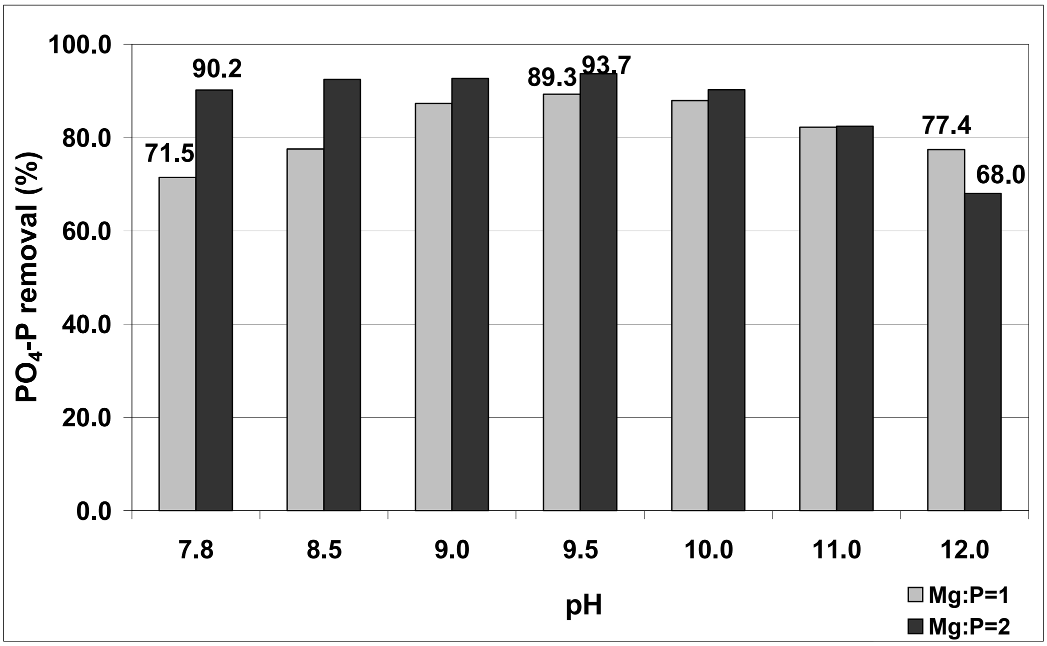


Figure 6.11 Effect of pH on PO_4^{3-} removal with MgO for Mg:P ratio of 1 and 2

At pH 7.8 (without any pH adjustment) and a Mg:P ratio of 1, between 60-70 % of the PO_4^{3-} was removed, and at a Mg:P ratio of 2 approximately 90 % was removed with both MgO and $MgCl_2$ (Figure 6.11 und 6.12). As the pH was raised towards 12, the PO_4^{3-} removal efficiencies decreased even below the efficiencies achieved at the initial pH values. In other words, as the Mg:P ratio increased, requirement for pH elevation to achieve higher removal rates decreased resulting in a lower NaOH addition requirements. Burns and Moody (2002) obtained similar results in the experiments they performed without pH adjustments. The results of the pH optimization experiments and the data in the literature are in agreement that the optimum pH for PO_4^{3-} removal through precipitation is between 9.0 and 9.5.

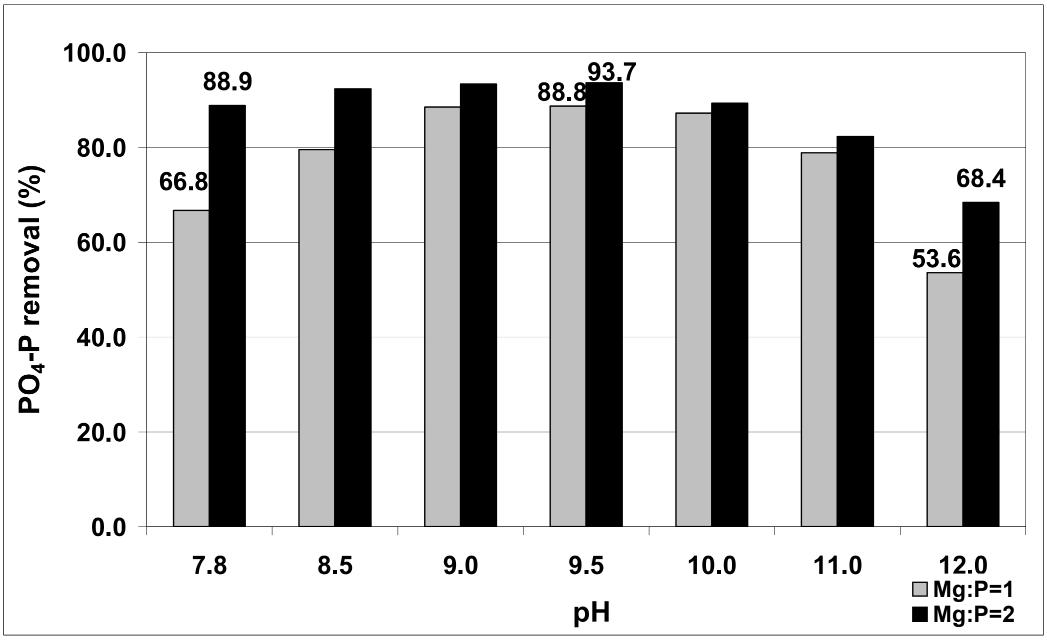


Figure 6.12 Effect of pH on PO_4^{3-} removal with $MgCl_2$ for Mg:P ratio of 1 and 2

Theoretically struvite crystallization occurs when the Mg:P:N ratio is 1:1:1 (Rahaman et al., 2007). At Mg:P ratios greater than 1, $MgCl_2$ produced higher PO_4^{3-} removal rates at pH 9.5 compared to 9.0 (Figure 6.13). MgO, $Mg(OH)_2$ and $Mg(SO)_4$ showed higher or slightly lower removal efficiencies at pH 9.5 compared to pH 9.0 (Figure 6.14, 6.15 and 6.16).

Consequently, results of these experiments carried out with different Mg^{2+} sources are in agreement with the results the pH optimization experiments. A pH value of 9.5 yields the highest PO_4^{3-} removal through precipitation in the presence of a Mg^{2+} source from BW.

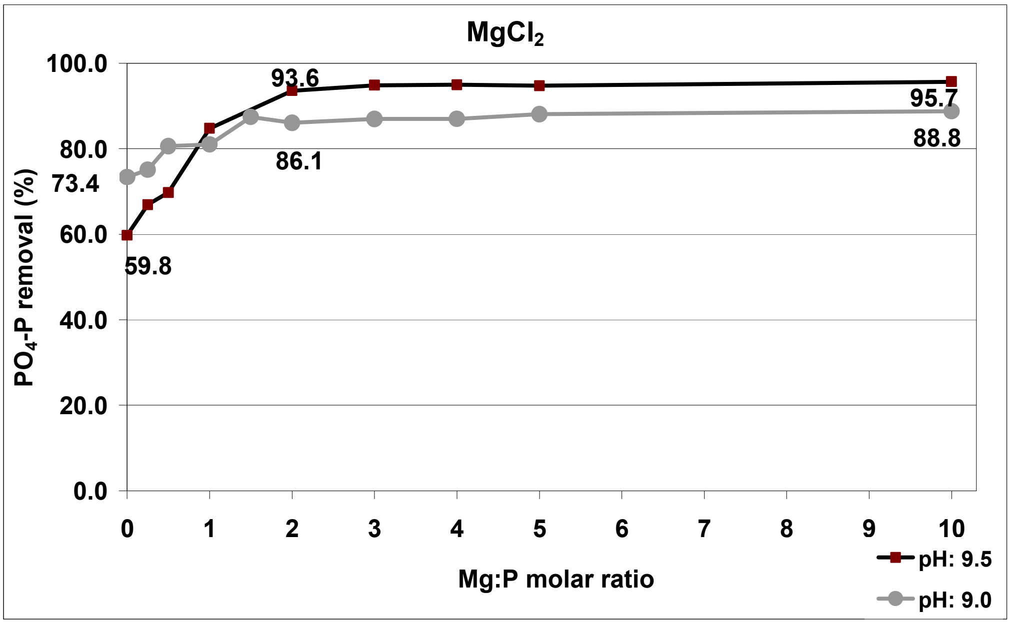


Figure 6.13 Effect of pH on PO_4^{3-} removal with $MgCl_2$ at pH 9.0 and 9.5

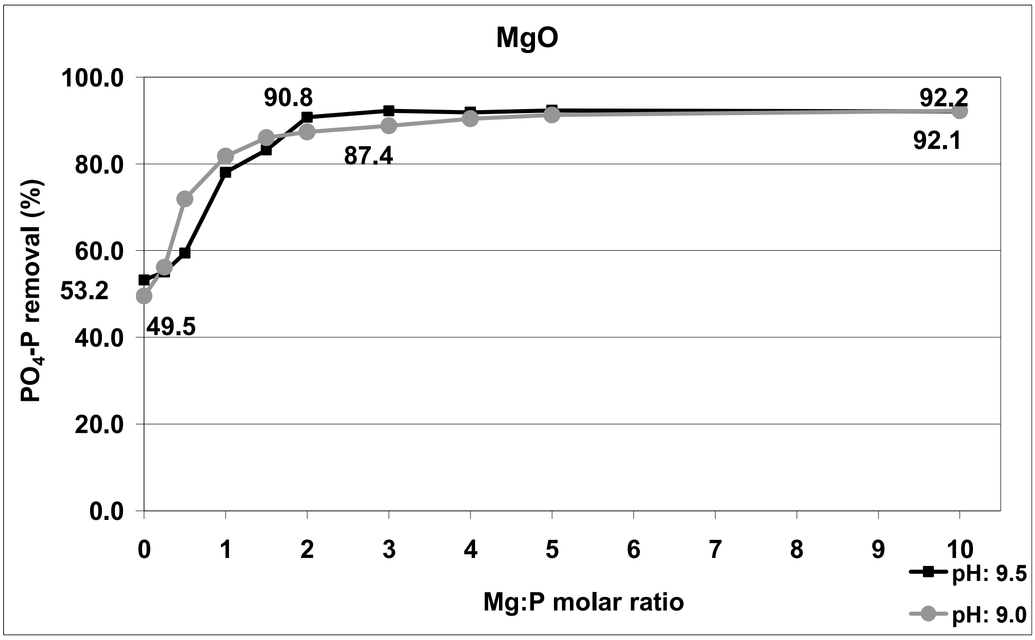


Figure 6.14 Effect of pH on PO_4^{3-} removal with MgO at pH 9.0 and 9.5

As the Mg:P molar ratios increased from 2 to 10, pH 9.5 gave consistently higher PO_4^{3-} removal rates than were observed for the pH 9.0 experiments. The same trend was also observed with $Mg(OH)_2$ and $MgSO_4$.

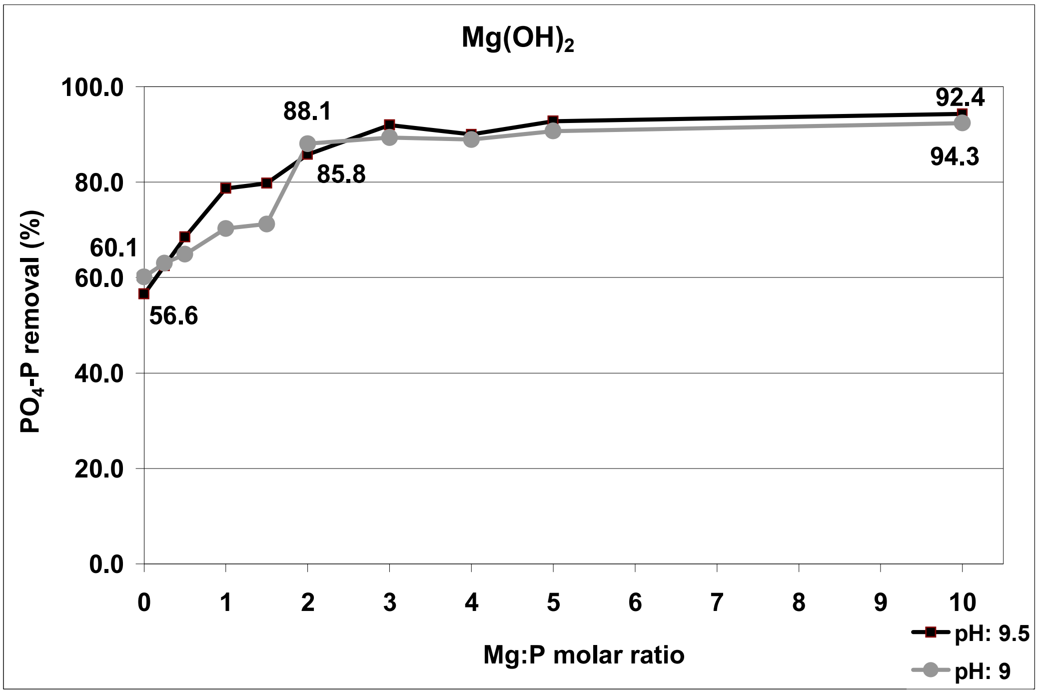


Figure 6.15 Effect of pH on PO_4^{3-} removal with $Mg(OH)_2$ at pH 9.0 and 9.5

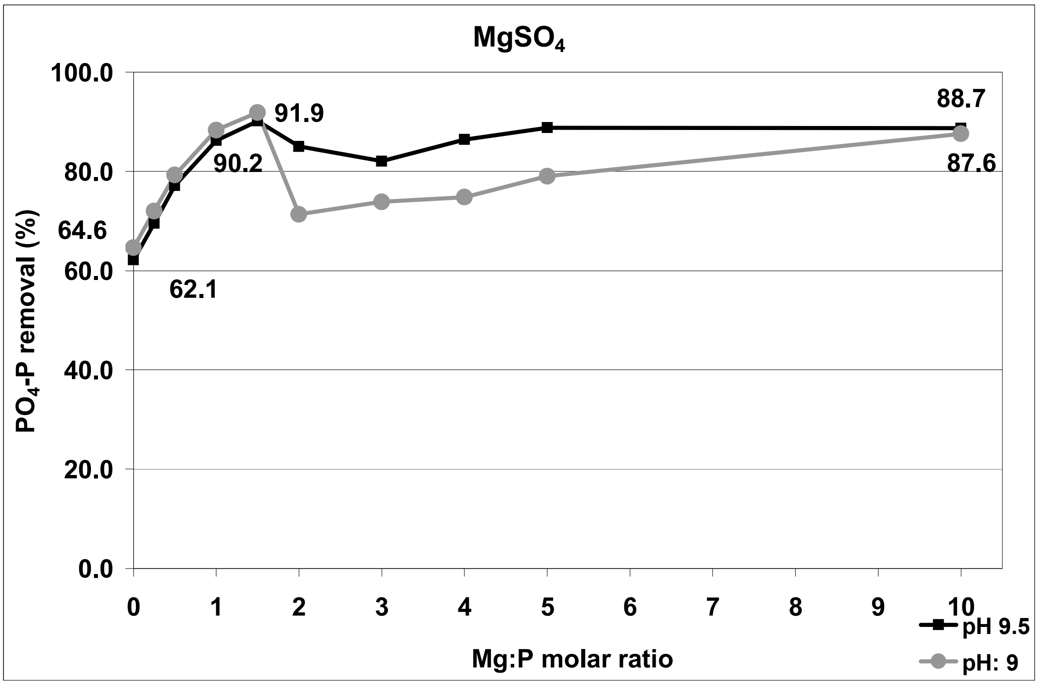


Figure 6.16 Effect of pH on PO_4^{3-} removal with $MgSO_4$ at pH 9.0 and 9.5

Use of Ca^{2+} salts

In addition, Ca^{2+} salts were also tested to remove PO_4^{3-} from BW. However, since the primary aim of this study was to remove and recover PO_4^{3-} in the form of struvite, the extent of the tests with Ca^{2+} salts were kept limited.

First, the optimum pH for PO_4^{3-} precipitation was determined with a similar procedure applied for Mg^{2+} sources. From the experience with Mg^{2+} salts and literature data, it was expected that $CaCl_2$ would have a high solubility in BW. This test was not repeated for other Ca^{2+} sources such as CaO and $Ca(OH)_2$, because with Mg^{2+} the optimum pH for PO_4^{3-} removal was the same for all different Mg^{2+} sources. Therefore, pH optimization tests were carried out with $CaCl_2$ only, with a Ca:P ratio of 2 and at 5 different pH values: pH unadjusted (7.9), 9.0, 10.0, 11.0 and 12.0.

The removal efficiency of PO_4^{3-} through forced precipitation by $CaCl_2$ increased as the pH was increased to 10. At pH 11, the highest removal rate of 87 % was observed. An additional increase of pH to 12 resulted in a sudden decrease in the PO_4^{3-} removal efficiency. These result shows a similarly trend with the experiments done with Mg^{2+} sources. The optimum pH for PO_4^{3-} removal through precipitation with Ca^{2+} salts was between 10 and 11.

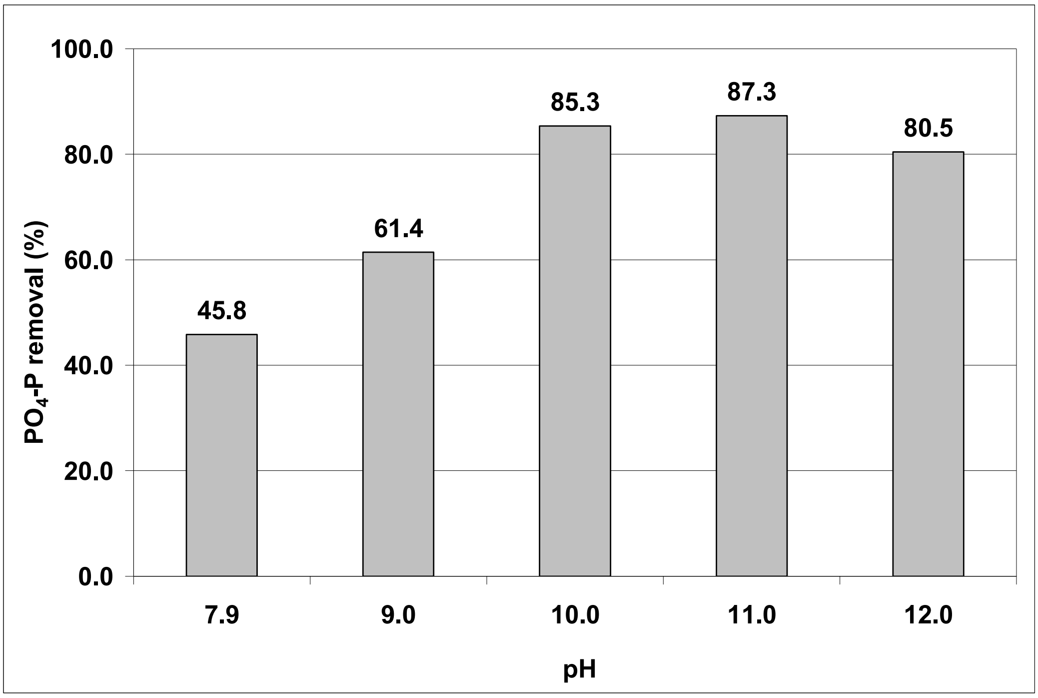


Figure 6.17 Effect of pH on PO_4^{3-} removal with $CaCl_2$ for Ca:P = 2

6.3.3 Effect of the Mg:P Molar Ratio on PO_4^{3-} Removal

Initial experiments were done with a blank BW sample (no additional Mg^{2+} added) and subsequently with Mg:P molar ratios of 0.25, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, and 10.0, and at pH 9 and 9.5. During the experiments, 15 minutes of mixing time was followed by a 30 minutes of sedimentation period.

Use of $MgCl_2$

Results of the experiments with $MgCl_2$ showed very similar trends for both pH values. Figure 6.18 shows that PO_4^{3-} removal increases with increasing stoichiometric amounts of $MgCl_2$. For both pH values, between molar ratios of 0 and 2, there occurs a considerable increase in the PO_4^{3-} removal efficiencies. Further increases in the Mg:P molar ratios result in only minor improvements in the PO_4^{3-} removal efficiencies. For the pH 9.5 experiments, there is a sharp increase of nearly 10 % in the removal efficiency as Mg:P ratio increases from 1.0 to 2.0. Between Mg:P ratios 2 and 10, despite a fivefold increase in Mg:P ratio there is only a 2 % increase in the removal efficiency.

It appears that in the pH 9 experiments the highest removal was achieved at Mg:P ratio 1.5 and there was a small decrease in the removal efficiency as the Mg:P ratio was increased to 2. This could be due to the fact that a Mg:P ratio 1.5 gives the optimum coagulant dose and that further addition of $MgCl_2$ yields a decrease in efficiency of the coagulation flocculation process. This result could also be due to non-identical experimental conditions or human error during the analysis of samples. As mentioned before, at most 5 experiments can be conducted simultaneously, therefore, experiments at pH 9 were carried out over two different days, this may have resulted in differences in BW composition, pH, etc. Considering these factors, such minute fluctuations might be expected regardless of any chemical explanation.

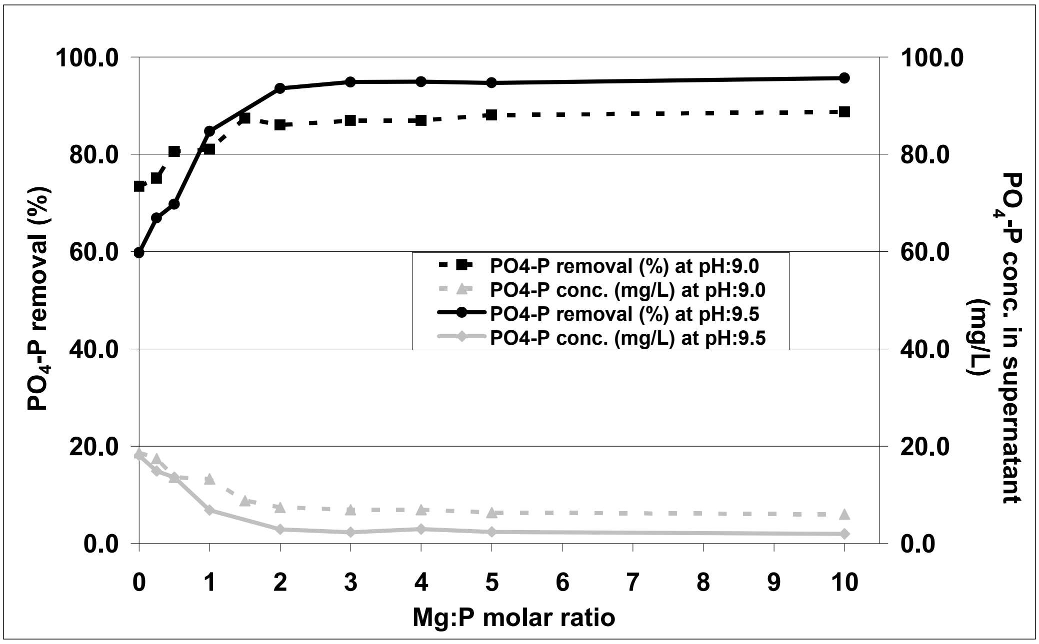


Figure 6.18 Effect of Mg:P molar ratio on PO_4^{3-} removal for $MgCl_2$ at pH 9.0 and 9.5

At pH 9.5, there occurred a more significant increase in PO_4^{3-} removal efficiency between Mg:P ratios 0 and 1 compared to pH 9 experiments. However, the removal efficiency of nearly 85 % achieved at Mg:P ratio 1 was still relatively low and was further improved to 94 % by increasing the Mg:P to 2. Despite the fivefold increase in Mg:P ratio between 2 and 10 the PO_4^{3-} removal efficiency only increased by 2 %. It can be concluded that a stoichiometric ratio of 1 between Mg^{2+} and PO_4^{3-} is insufficient and a minimum Mg:P molar ratio of 2 was reasonable to achieve a sufficient levels of PO_4^{3-} removal.

Experiments performed with no Mg^{2+} addition gave 60 % and 70 % PO_4^{3-} removal at pH 9.5 and 9.0 respectively; this is in agreement with previous researchers such as Zeng and Li (2006). They attributed this finding to the fact that a certain amount of Mg^{2+} and Ca^{2+} ions were originally present in the digested BW (Table 6.4), which resulted in the precipitation of struvite and calcium phosphates at an elevated pH (Figure 6.35).

Table 6.4 Initial Ca^{2+} and Mg^{2+} concentrations of the digested BW

Parameter	Mean value ± Standard deviation
Ca^{2+}, mg/L	42.4 ± 40.8
Mg^{2+}, mg/L	33.0 ± 54.5

Use of MgO

At pH 9.0, when the Mg:P ratio was increased from 1 to 2, the PO_4^{3-} removal efficiency was enhanced by 7 %. A further fivefold increase in Mg:P ratio from 2 to 10 resulted in a rise of 5 % in PO_4^{3-} removal efficiency (Figure 6.19). However, in the pH 9.5 experiments, when the Mg:P ratio was increased from 1 to 2, the PO_4^{3-} removal efficiency was enhanced by 16 %. A further fivefold increase in Mg:P ratio from 2 to 10, only increased the PO_4^{3-} removal efficiency by 1 %. A large excess of Mg^{2+} did not result in a considerable increase in PO_4^{3-} removal efficiencies and a maximum of Mg:P ratio 2 seems reasonable to achieve efficient PO_4^{3-} removal from BW.

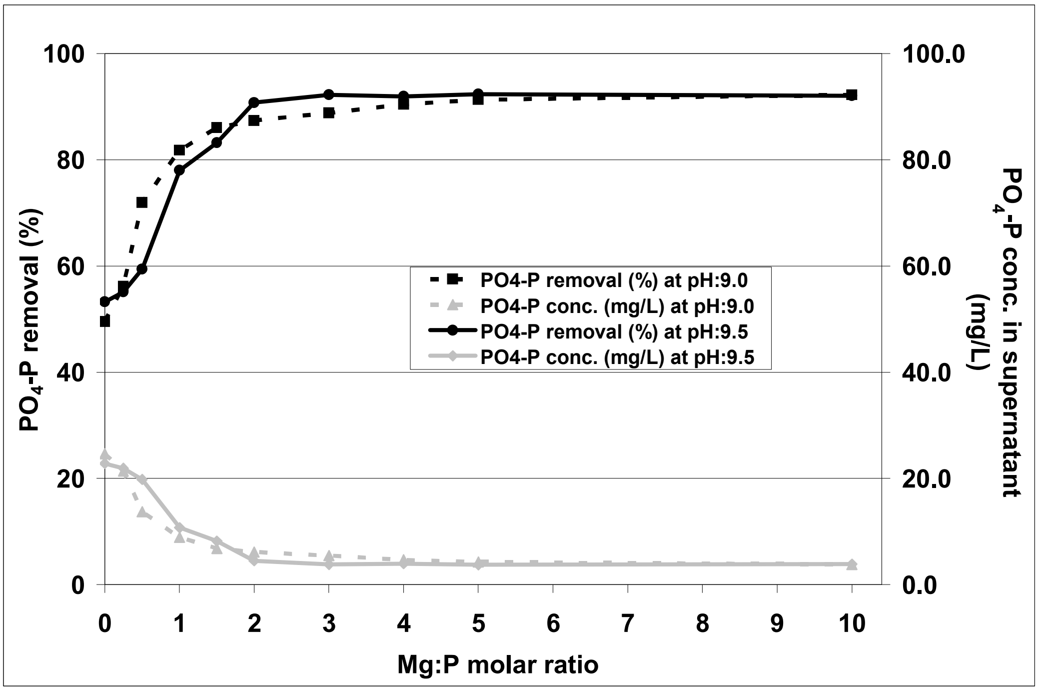


Figure 6.19 Effect of Mg:P molar ratio on PO_4^{3-} removal for MgO at pH 9.0 and 9.5

Use of Mg(OH)₂

At pH 9.0, there was a large increase in PO_4^{3-} removal efficiency when the Mg:P ratio was changed from 1.5 to 2.0. At a Mg:P ratio of 10, the PO_4^{3-} removal efficiency was only 5 % higher that it was at a Mg:P ratio of 2.0.

In the pH 9.5 experiments, in order to achieve the 90 % PO_4^{3-} removal efficiency found in the $MgCl_2$ and MgO experiments, at a Mg:P ratio of 2, a Mg:P ratio of 3 had to be used. The increase in PO_4^{3-} removal efficiency when this Mg:P ratio was increased to 10 was only 2 %.

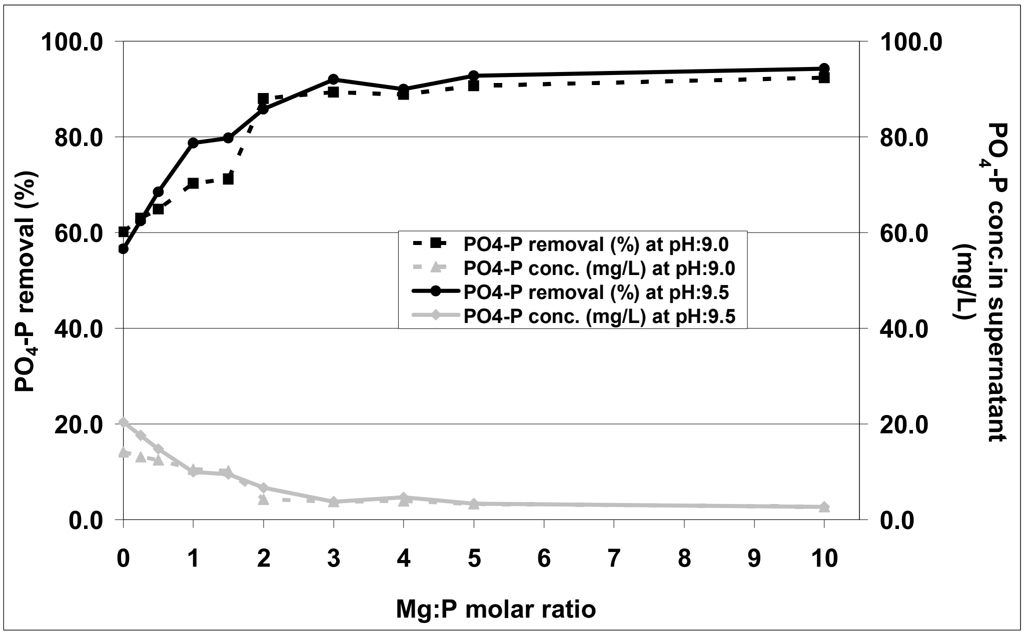


Figure 6.20 Effect of Mg:P molar ratio on PO_4^{3-} removal for $Mg(OH)_2$ at pH 9.0 and 9.5

Use of $MgSO_4$

The results obtained with $MgSO_4$ showed a different trend than those for the other Mg^{2+} sources. For both pH conditions, the highest PO_4^{3-} removal efficiency was achieved at a Mg:P ratio of 1.5. There was an abrupt decrease in PO_4^{3-} removal efficiency as the Mg:P ratio was increased above 1.5. This could be due to exceeding the Mg^{2+} dose that can be effectively applied to the BW samples without interfering with precipitation process. $MgSO_4$ has a rather high molecular weight (Table 6.3) and according to the formula [Eg. 6.3], this marked difference in molecular weight necessitates the addition of higher amounts of $MgSO_4$. As a result, regardless of pH, increasing the Mg:P ratio over 1.5, cannot bring any benefit in terms of PO_4^{3-} removal efficiency, but in fact worsen the achieved removal efficiency.

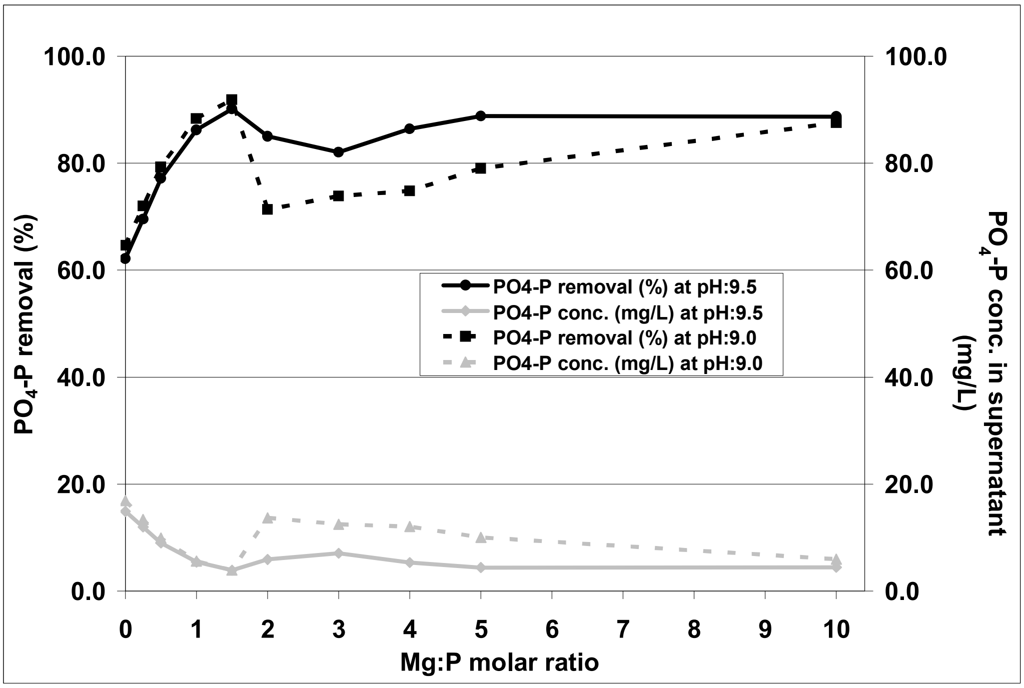


Figure 6.21 Effect of Mg:P molar ratio on PO_4^{3-} removal for $MgSO_4$ at pH 9.0 and 9.5

6.3.4 Effect of the Ca:P Molar Ratio on PO_4^{3-}-P Removal

The effect of Ca:P ratio on the efficiency of PO_4^{3-} removal was studied with a similar protocol as was used to study the effect of Mg:P ratio. Based on earlier pH optimization experiments, a pH of 10.5 was selected to test ratios ranging from 1.6 to 5. A ratio of 1.6 represents the stoichiometric ratio between Ca^{2+} and PO_4^{3-} for the formation of hydroxylapatite [Eq. 6.2]. The trends obtained were similar to those observed for Mg^{2+} sources; when the Ca:P ratio was increased the PO_4^{3-} removal efficiency also increased. The efficiency obtained at the stoichiometric ratio was only 72.4 % but increased to 86.2 % as the Ca:P ratio was increased to 5. The removal efficiencies over 90 % achieved with Mg^{2+} sources, at relatively lower molar ratios, could not be achieved with $CaCl_2$, even at the higher pH of 10.5 (Figure 6.22).

Therefore in terms of PO_4^{3-} removal efficiencies, Mg^{2+} sources having the highest solubility, show a marked superiority over the Ca^{2+} sources. It is possible that further increases in Ca:P ratio beyond 5 may result in improved PO_4^{3-} removal rates and this could be investigated further.

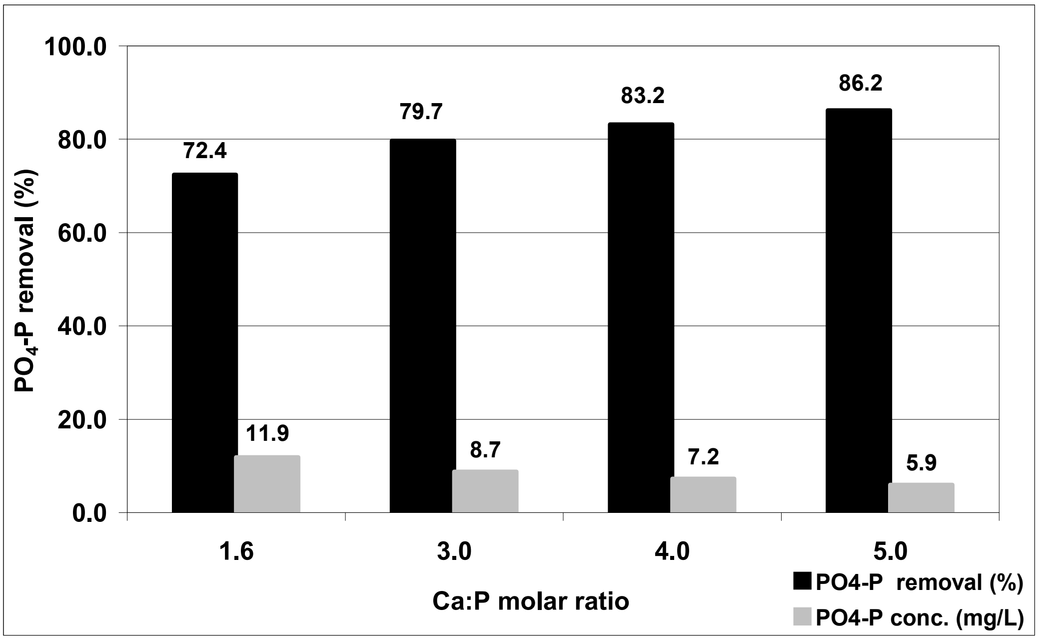


Figure 6.22 Effect of Ca:P molar ratio on PO_4^{3-} removal for $CaCl_2$ at pH 10.5

6.3.5 pH Adjustment

Using NaOH

To determining the effect of pH on PO_4^{3-} removal efficiency, the pH of the BW samples had to be raised using NaOH. The required amount of 1N NaOH to elevate the pH of BW to a desired value is very important in terms of estimating the costs of chemicals. During the tests, a 500 mL BW sample, having an initial pH of 7.9, required 25-30 mL 1N NaOH to raise the pH to 9.5, the optimum pH for the struvite precipitation (Figure 6.23).

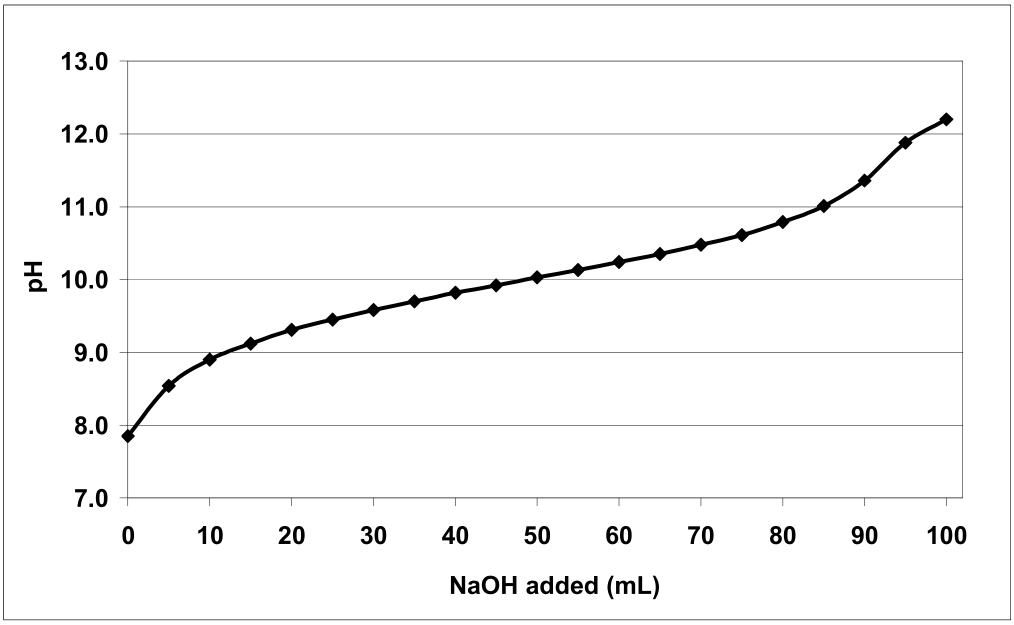


Figure 6.23 Change in pH with NaOH addition

Using MgO

A 500 mL digested BW sample, having an initial pH value of nearly 7.8, had its pH raised by the addition of MgO in 5 mg increments. A pH of 9.0 was easily achieved by addition of MgO but after pH 9.0 the rate of increase of pH with MgO addition slowed. A pH of 9.5 could only be achieved upon the addition of extremely large amounts of MgO and very long reaction times. This phenomenon might be due to the fact that MgO has a low solubility which decelerates the reaction and requires vigorous and extended agitation. As more MgO was added, several minutes of waiting were needed to completely dissolve the MgO which was less efficient in changing the pH. Beal et al. (1999) observed the same trend in their experiments.

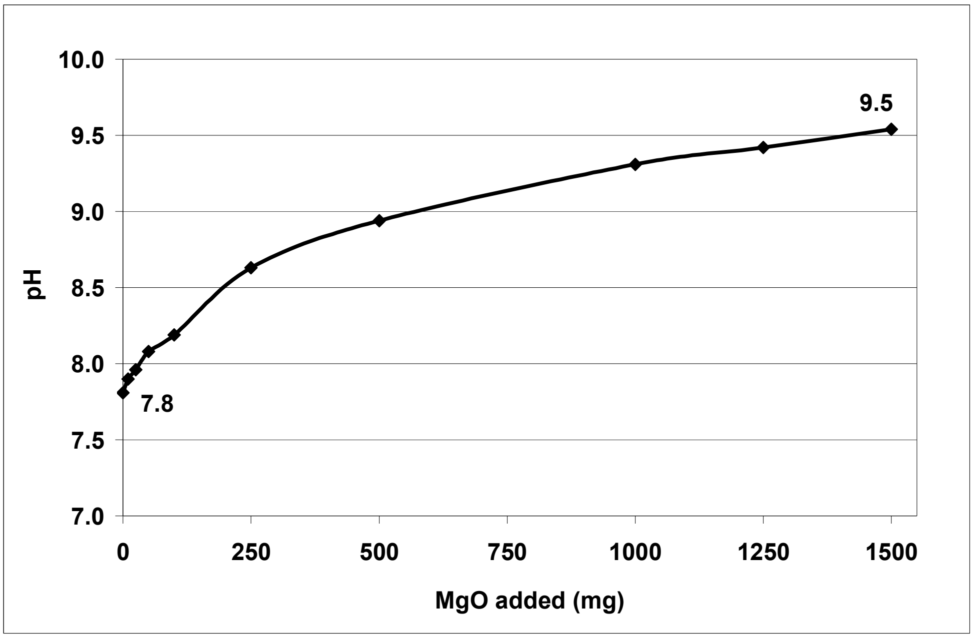


Figure 6.24 Change in pH with MgO addition

The amount of MgO that was required to raise the pH of a 500 mL digested BW sample from an initial pH of 7.8 to 9.5, without any NaOH addition, was nearly 1500 mg. The initial PO_4^{3-} concentration was 78.3 mg/L; the numbers of moles of PO_4^{3-} and Mg^{2+} in the solution were 1.26 mmol and 37.2 mmol, respectively. As a result, when MgO was used to raise the pH, the amount of MgO added yielded a Mg:P molar ratio of nearly 30:1, dominating the solution profoundly with Mg^{2+}.

6.3.6 Comparison of the PO_4^{3-} Removal Efficiencies of Different Mg^{2+} Sources

From the results conducted with different Mg^{2+} sources, two different conclusions may be drawn. Firstly as the Mg:P ratio increases from 1 and 2 there is always a significant increase in the PO_4^{3-} removal efficiency. Secondly for ratios between 2 to 10 the systems form equilibriums. In the pH 9 experiments, the efficiency of different Mg^{2+} salts for PO_4^{3-} removal follows the order $MgO = Mg(OH)_2 > MgCl_2 > MgSO_4$. Between Mg:P ratio of 1.0 and 1.5, the order was $MgSO_4 > MgCl_2 = MgO > Mg(OH)_2$ (Figure 6.25).

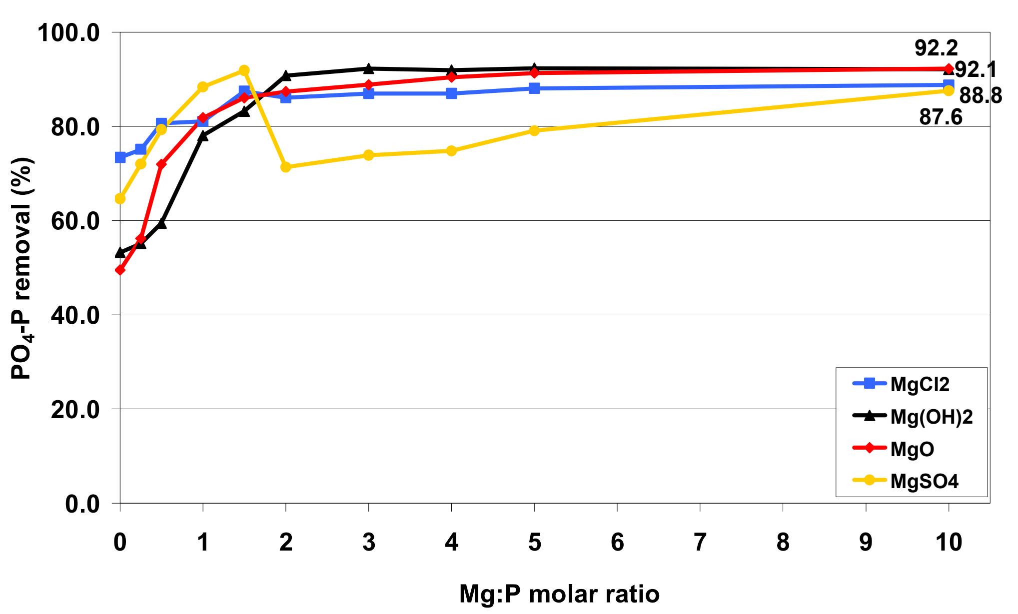


Figure 6.25 Comparison of PO_4^{3-} removal efficiencies of different Mg^{2+} sources at pH 9.0

In the pH 9.5 experiments, a clear superiority of $MgCl_2$ over both MgO and $Mg(OH)_2$, at all Mg:P ratios between 0 and 10, is observed. At a Mg:P ratio of 2 the order of efficiency of PO_4^{3-} removal was $MgCl_2 > MgO > MgSO_4 \approx Mg(OH)_2$ (Figure 6.26).

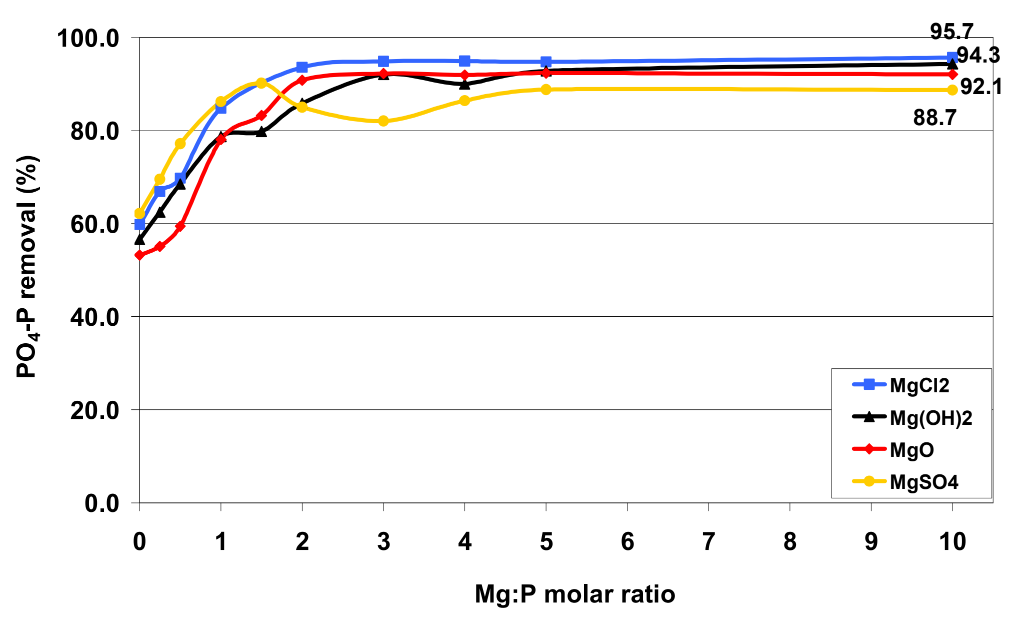


Figure 6.26 Comparison of PO_4^{3-} removal efficiencies of different Mg^{2+} sources at pH 9.5

In practice high Mg:P ratios are avoided due to cost concerns. However, stoichiometric ratios between Mg^{2+} and PO_4^{3-} did not prove to be sufficient for removal of PO_4^{3-} through struvite precipitation. At both pH values tested, as the Mg:P ratio increased towards 2 from 1, the highest PO_4^{3-} removal efficiency was produced by $MgCl_2$, likely due to its high solubility. At pH 9.5, $MgCl_2$ showed a distinct superiority over the entire Mg:P ratio range. An interesting result was that the removal efficiency of $MgSO_4$ was similar to, or even higher than, that of

$MgCl_2$, however at a Mg:P ratio 2 the efficiency drops sharply. The reason of this decrease is unknown**.** Depending on the exact Mg:P ratio, MgO could sometimes reach the efficiencies seen with $MgCl_2$, while $Mg(OH)_2$ always produced the lowest PO_4^{3-} removal efficiency, most likely due to its low solubility (Miles and Ellis, 2001). In all cases, the theoretical stoichiometric ratio of 1 between Mg^{2+} and PO_4^{3-} was not sufficient to achieve high removal efficiencies and we propose that the ratios should be raised to a minimum of 2 to give high PO_4^{3-} removal efficiencies.

Another aspect that needs consideration when comparing different Mg^{2+} sources is their effects on pH. MgO and $Mg(OH)_2$ have a basicifying effect and elevated the pH values; MgO proved to be a more effective pH raising agent than $Mg(OH)_2$. During experiments, two BW samples of 250 mL each, having similar initial pH values, were subjected to MgO and $Mg(OH)_2$ additions at Mg:P ratios ranging from 0 to 10, MgO raised the pH of the sample from 7.9 to 8.3, whereas $Mg(OH)_2$ yielded an increase from 7.9 to only 8.0. Conversely, $MgCl_2$ and $MgSO_4$ have acidifying effects on the pH.

In conclusion, $MgCl_2$ and MgO might be considered as the most favorable Mg sources for enhancing PO_4^{3-} removal. In most of the experiments $MgCl_2$ produced higher (94.4 %) PO_4^{3-} removal efficiencies than MgO (91.6 %) at the optimum pH and a Mg:P ratio at least 2. This is in agreement with Burns et al. (2001) and Burns and Moody (2002), who also preferred $MgCl_2$ as the precipitating reagent.

6.3.7 Comparison of the PO_4^{3-} Removal Efficiencies of Different Ca^{2+} Sources

Calcium phosphates are formed when the pH conditions are higher than 10.0. The results of the pH tests confirmed this, as well by yielding an optimum pH lying between 10.0 and 11.0. Therefore, the experiments performed to compare different Ca^{2+} sources were conducted at two pH conditions: 9.5, to prove the insufficient PO_4^{3-} removal rates and 10.5 to observe the PO_4^{3-} removal efficiencies under optimum pH condition.

All Ca^{2+} sources produced very low PO_4^{3-} removal efficiencies at pH 9.5 for all three of the Ca:P ratios: 1.0, 1.5 and 2.0 (Figure 6.27). This result proves that at pH values lower than 10.0, increasing the Ca:P ratio does not result in an improvement of PO_4^{3-} removal efficiency, since calcium phosphates do not form. Small differences were observed in the PO_4^{3-} removal efficiencies for different Ca^{2+} sources; $CaCl_2$ produced a slightly higher removal rate probably due to its high solubility. This trend can be more clearly seen in the pH 10.5 experiments.

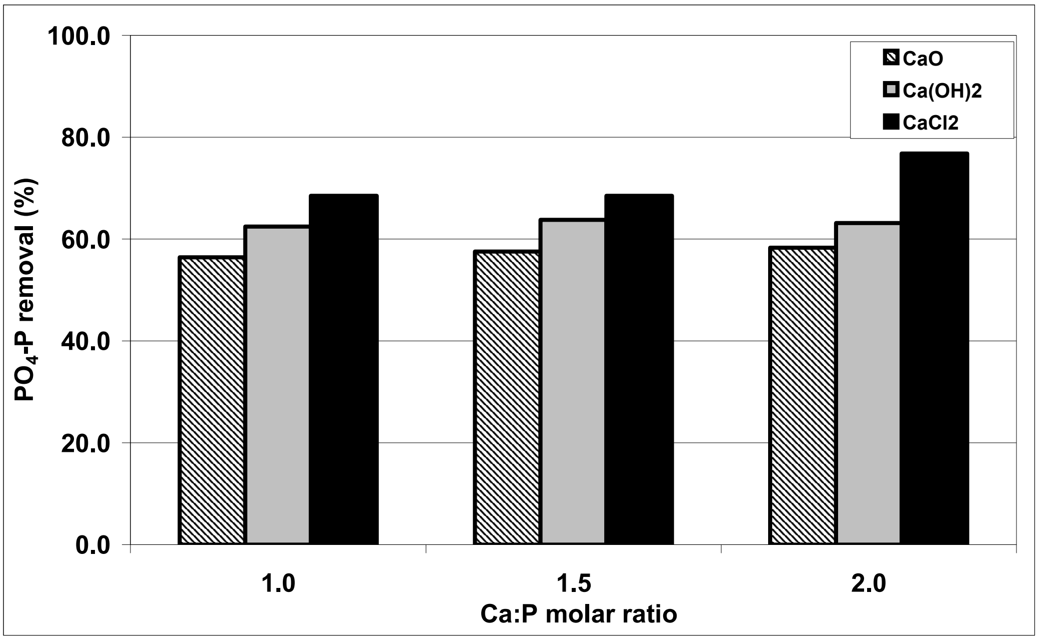


Figure 6.27 Comparison of PO_4^{3-} removal efficiencies of different Ca^{2+} sources at pH 9.5

In the experiments with a Ca:P ratio of 3, the efficiencies of the three Ca^{2+} sources for PO_4^{3-} removal were in the order $CaCl_2$ > $Ca(OH)_2$ > CaO (Figure 6.28). Nevertheless, the highest PO_4^{3-} removal value was less than 75 %, significantly lower than in the previous Ca^{2+} experiments; this could be due to dissolution problems of the Ca^{2+} sources. It was seen in previous experiments that when the Ca:P ratio was increased to 5, the achieved PO_4^{3-} removal efficiency reached nearly 86 % (Figure 6.22). It can be concluded from these result that the Ca:P ratio has a more significant role in the PO_4^{3-} removal efficiencies for Ca^{2+} salts than pH. Having to increasing the amount of Ca^{2+} added to achieve high levels of removal, the costs of the process would increase.

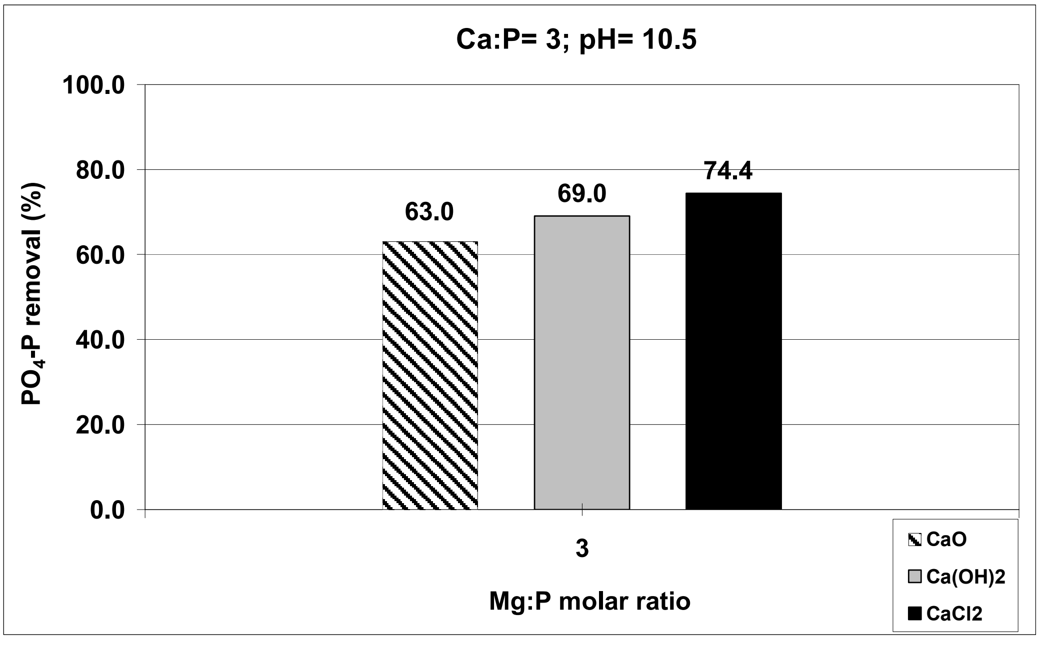


Figure 6.28 Comparison of PO_4^{3-} removal efficiencies of different Ca^{2+} sources at pH 10.5

6.3.8 Precipitate Characterization with X-Ray Diffraction Method

One of the primary aims of this study was to investigate the recovery of PO_4^{3-}. Therefore the characteristics of the precipitates are particular important; for this purpose the XRD technique was used. The results of the XRD analysis were presented in graphs having particular peaks corresponding to particular minerals. The analysis and interpretation of the results were performed by authorized persons at the IUE. According to the results of these graphs (See below and appendice), various minerals were obtained as a result of the struvite precipitation experiments: $MgPO_4NH_4.6H_2O^*$, $Mg_2P_2O_7$, $MgAl(PO_3)_6$, $KCaP_3O_9$ (unsure), $CaCO_3$, NaCl, and KCl (See appendice).

The characteristics of the BW samples (i.e., initial PO_4^{3-} concentrations, initial Mg^{2+} and Ca^{2+} concentrations, etc.), experimental pH, and the Mg:P molar ratio had a direct impact on the mineralogical composition of the precipitate.

Table 6.5 List of the minerals found in the precipitate by XRD analysis

Precipitant	pH	Mg:P	Mineral found	Sample #
MgO	9	5	$MgPO_4NH_4.6H_2O$, NaCl	1
	9.5	1.1	$CaCO_3$, NaCl	2
		1.3	$Mg_2P_2O_7$, KCl, NaCl, $CaCO_3$, $MgAl(PO_3)_6$	3
		1.5	$Mg_2P_2O_7$ and/or $KCaP_3O_9$, NaCl, $CaCO_3$	4
		3	$MgPO_4NH_4.6H_2O$, NaCl	5
		4	$MgPO_4NH_4.6H_2O$, NaCl	6
		10	$MgPO_4NH_4.6H_2O$, NaCl	7
	10	1	$CaCO_3$,$Mg_2P_2O_7$,NaCl	8
$MgCl_2$	9	0.5	$CaCO_3$, NaCl	9
		1	$CaCO_3$, NaCl	10
	9.5	1	NaCl, KCl	11
		2	n.a.	12
		3	NaCl, KCl	13
		4	NaCl	14
		10	NaCl	15
$Mg(OH)_2$	9	2	NaCl	16
	9.5	2	NaCl	17
$MgSO_4$	9.5	1.5	$MgPO_4NH_4.6H_2O$, NaCl	18

$MgPO_4NH_4.6H_2O$: Struvite*
$Mg_2P_2O_7$: Magnesium pyrophosphate
$MgAl(PO_3)_6$: Magnesium aluminium phosphate
$KCaP_3O_9$: unknown

$CaCO_3$: Calcite
NaCl : Halite
KCl : Sylvite

A Mg:P ratio of 2 was found to be sufficient if the aim was solely the removal of PO_4^{3-} from BW. However, the results of XRD showed that, struvite was formed only when the applied Mg:P ratios were 3 or more except for $MgSO_4$ (Table 6.5). These results are in agreement with Zeng and Li (2006), who found that to achieve PO_4^{3-} removal through struvite precipitation, the required Mg:P molar ratio had to be 5 times higher than the stoichiometric value when no PO_4^{3-} was added. Droste (1997) linked the phenomenon with the strength of wastewater in terms of PO_4^{3-} concentration and observed that the amount of metal needed to remove PO_4^{3-} exceeded the stoichiometric amount needed for wastewaters having low levels of PO_4^{3-}.

A pH 9.5 was found to be favorable for struvite formation. The results indicated struvite formation occurred most often when MgO was used as the precipitating agent, however, such generalization may be misleading because those samples analyzed with XRD were a random selection. There might be several samples with significant struvite precipitations, which could not be analyzed by XRD.

The results proved that removal and recovery of PO_4^{3-} from BW through precipitation is possible. PO_4^{3-} was recovered as four different products: struvite ($MgPO_4NH_4.6H_2O$), magnesium pyrophosphate ($Mg_2P_2O_7$), magnesium aluminium phosphate ($MgAl(PO_3)_6$), and an unknown mineral ($KCaP_3O_9$) (unsure) (Figure 6.30).

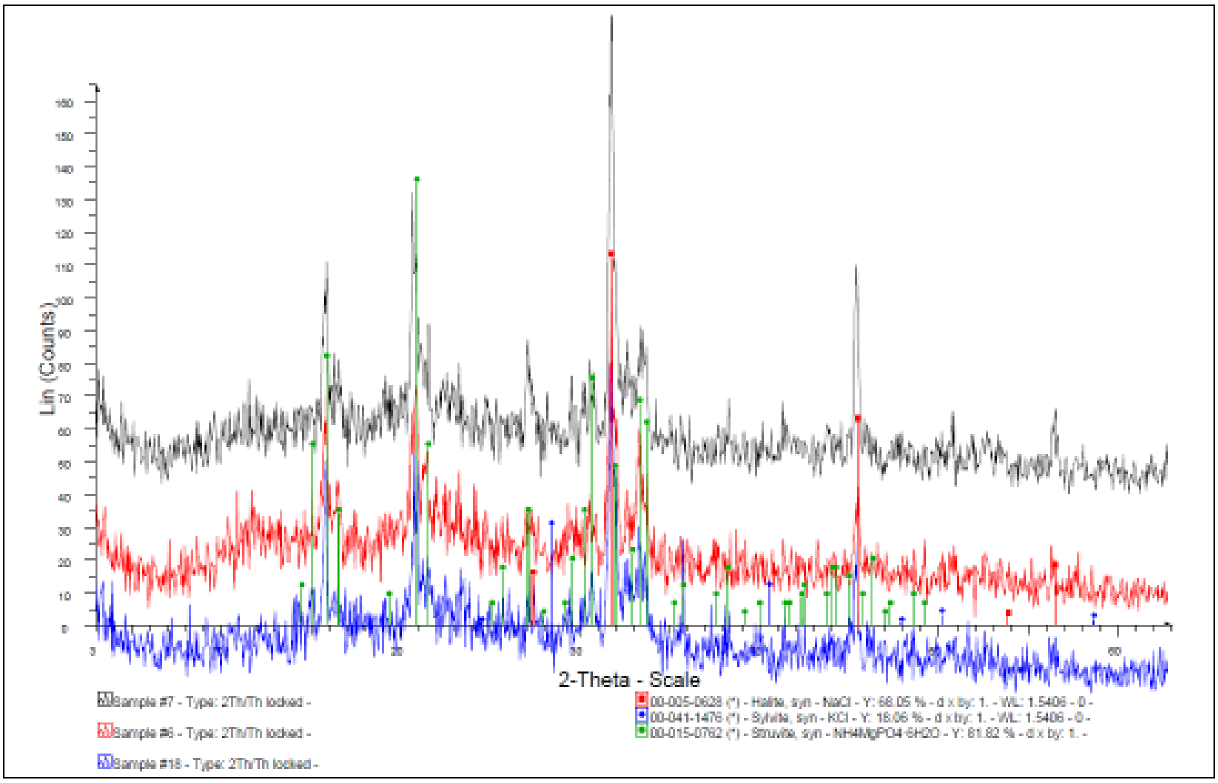


Figure 6.29 XRD diagram presenting obtained minerals NaCl, KCl (not in 18) and struvite in the samples 6, 7 and 18

During the experiment conducted with MgO at pH 9.5 for a Mg:P ratio of 1.3 (sample 3) and 1.5 (sample 4); struvite formation could not be achieved according to the results of the XRD analysis (Figure 6.30).

The supplied Mg^{2+} precipitated PO_4^{3-} in the form of $Mg_2P_2O_7$, $MgAl(PO_3)_6$, and $KCaP_3O_9$ (unsure). These magnesium phosphate products lack the NH_4^+ that are present in struvite minerals. This might be explained by insufficient NH_4^+ being present, due to NH_4^+ - NH_3

equilibrium formed at those pH values. Zeng and Li (2006) designated those magnesium phosphates as the most likely compounds that may be formed during struvite crystallization or dissolution.

The second mineral detected, $MgAl(PO_3)_6$ (Figure 6.30), was a product occurred mainly because of the aluminium concentration, which is excreted in the faces. This formation can be explained by the higher affinity of phosphate groups towards aluminium All people have small amounts of metals such as aluminium (ATSDR, 2010), cadmium, copper, iron, zinc etc. (Nie, 2007) in their bodies. The average aluminium concentration in BW reported by Palmquist and Hanæus (2005) is 0.54 mg/L.

The third mineral $KCaP_3O_9$ (unsure), was an interesting product, showing similarity with struvite but with Ca^{2+} replaced Mg^{2+}, and K^+ replaced $NH_4^+$and the presence of a different phosphate ion ($P_3O_9^{3-}$). Nevertheless, the aim of this research was to remove and recover of PO_4^{3-} which was fulfilled with the formation of these products. Upon optimization of the experimental conditions and parameters, struvite formation was observed in 5 of the experiments (samples 1, 5, 6, 7, 18).

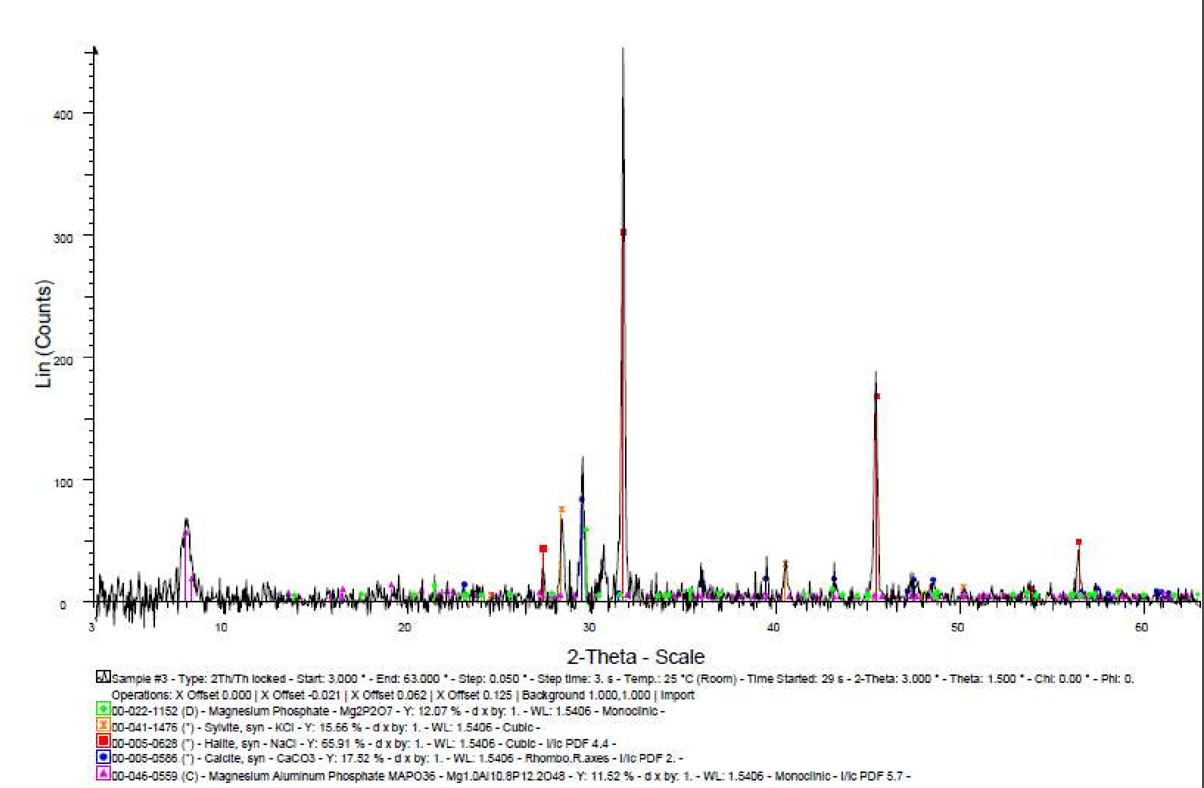


Figure 6.30 XRD diagram presenting obtained minerals $Mg_2P_2O_7$, NaCl, KCl, $CaCO_3$ and $MgAl(PO_3)_6$ in the sample 3

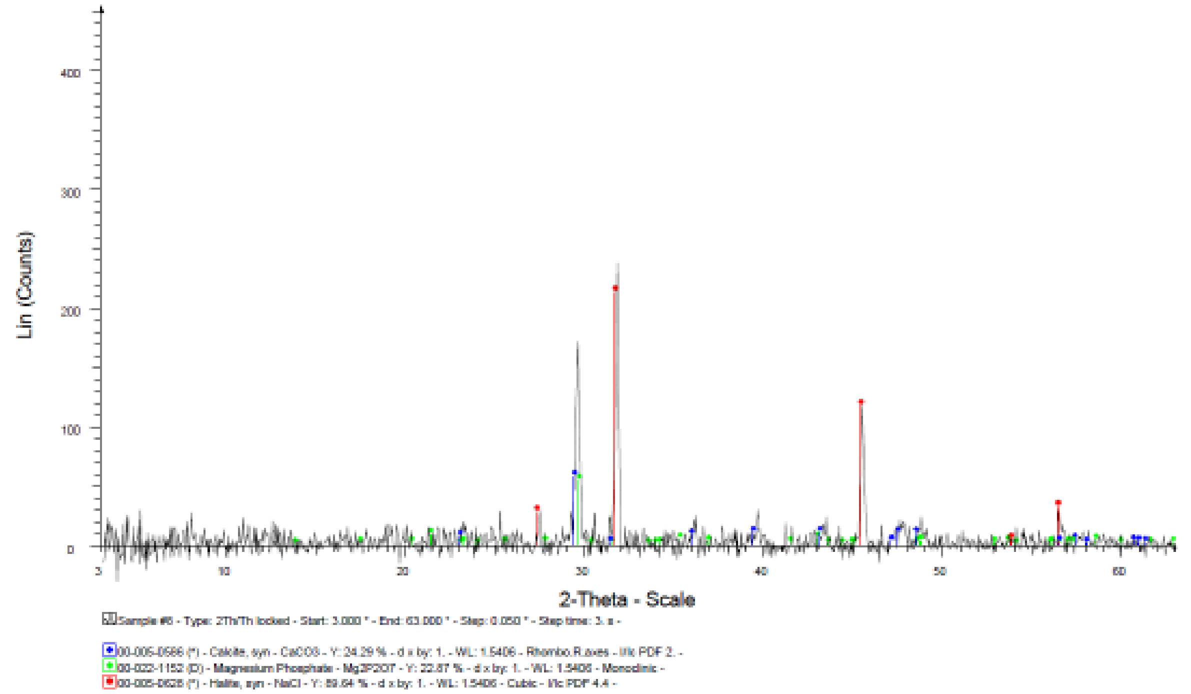


Figure 6.31 XRD diagram presenting obtained minerals $CaCO_3$, $Mg_2P_2O_7$ and NaCI in the sample 8

Some unexpected minerals obtained from the precipitation experiments were NaCl and KCl (Figure 6.32). Formation of these products can be attributed to the original characteristics of the BW; Kujawa-Roeleveld and Zeeman (2006) mentioned high Na^+ and Cl^- content of BW coming mainly from urine. High Na^+, K^+ and Cl^- content in BW enables the formation of NaCl and KCl. Additionally of considerable amounts of NaOH used for pH adjustment could be a major source of Na^+ in the system. In addition, the formation of KCl heralds the possibility of forced potassium struvite formation; potassium struvite is another valuable product for agriculture. NaCl levels of the precipitated products were not measured in this research; however levels will need to be measured for agricultural application.

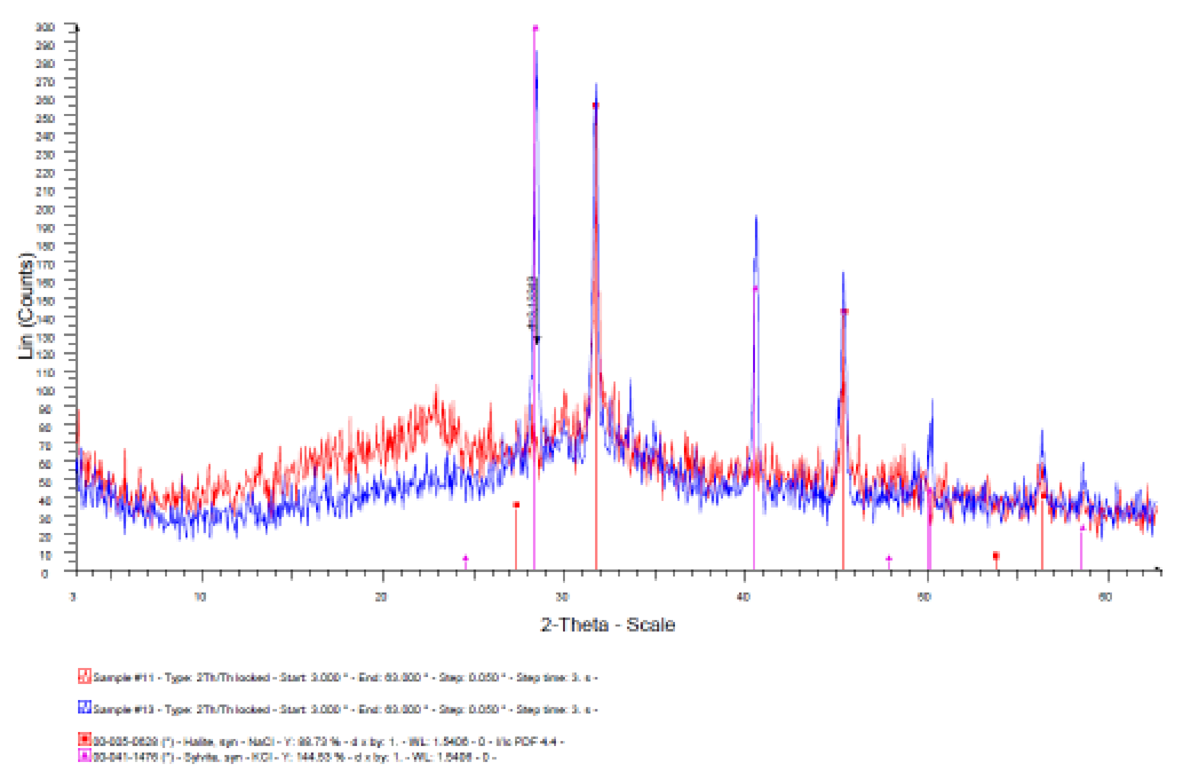


Figure 6.32 XRD diagram presenting obtained minerals NaCl and KCl in the samples 11 and 13

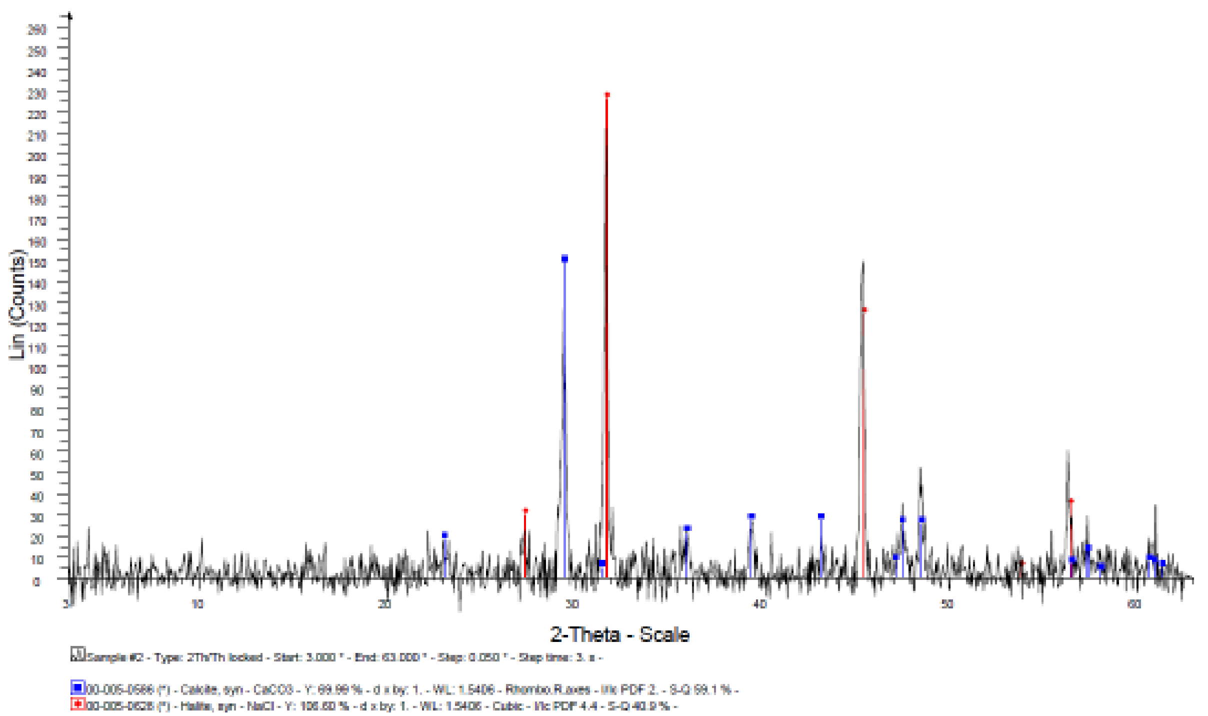


Figure 6.33 XRD diagram presenting obtained minerals $CaCO_3$ and NaCl in the sample 2

Formation of $CaCO_3$ (Figure 6.34 and 6.34) was an expected result as Ca^{2+} forms $CaCO_3$ near pH 9.5, which is the optimum pH used during the experiments (Droste, 1997). However, $CaCO_3$ formation was observed only in the earlier experiments where raw BW having a rather high initial Ca^{2+} concentration was used. Ca^{2+} concentrations of the digested BW were markedly lower than the raw BW. Therefore, no $CaCO_3$ formation was observed in the later experiments. Other researchers also obtained different calcium phosphates instead or in addition to struvite (Beal et al., 1999).

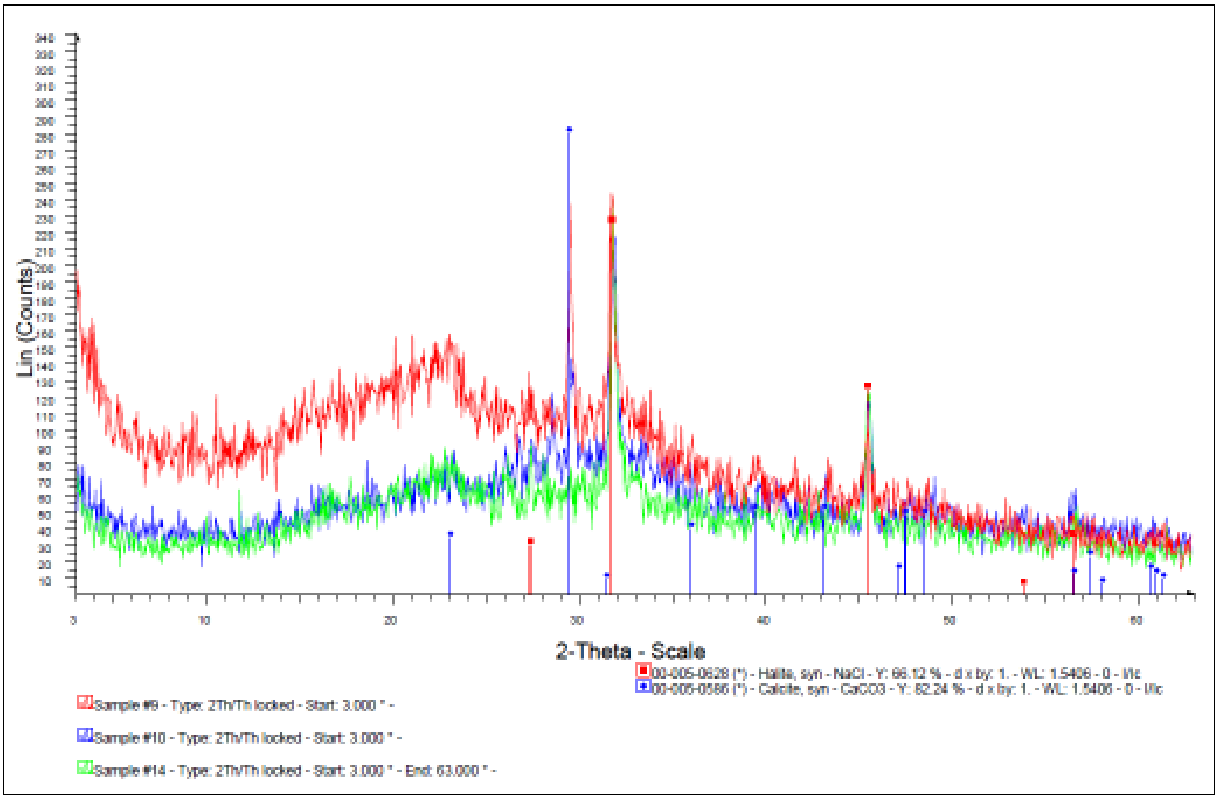


Figure 6.34 XRD diagram presenting obtained minerals $CaCO_3$ (not in 14) and NaCl in the samples 9, 10 and 14

In some of the samples, struvite formation was not observed, even though it was expected to occur. For example, the sample for the $MgCl_2$ experiment at a Mg:P ratio 10 had the potential for struvite formation with an optimum experimental pH of 9.5 and a dominant Mg^{2+} concentration, however, the mineral NaCl was the only product identified by XRD. Assuming that the XRD measurements are correct, this result could be due to the characteristics of the BW sample. It is thought that high ionic strengths in the solution might affect struvite precipitation potential, because the electrostatic interactions of ions in solution reduce their activity or effective concentrations, thereby reducing struvite precipitation potential (Ohlinger et al., 1998). The minerals identified in our measurements indicate that there were high Na^+ and Cl^- levels in the BW, probably caused by its origin. These ions may be indicators of high ionic strength in wastewater samples. A more detailed assessment of the inhibition of struvite formation under optimum conditions could be undertaken after determining the ionic strengths of wastewater samples.

Another possible explanation of the inhibition of struvite formation, when the pH and Mg:P are at optimum conditions, could be due to the interference of organic materials with struvite formation, as has been previously mentioned. Some strong organic materials can preferentially bind soluble PO_4^{3-}. Other researchers mention binding problems between PO_4^{3-} and Mg^{2+} in the presence of some organic materials (Schuiling and Andrade 1999; Burns et al., 2001; Mitani et al., 2001); they have also showed that additional amounts of Mg^{2+} are required to overcome the effects of complexing agents, such as organic materials, that can bind to Mg^{2+}. The organic material content of BW is not known yet. The complex matrix of

BW may contain such organic materials, however a single explanation of this observation is difficult to make.

Dependence on other departments caused limitations on the XRD analysis of the precipitates. These narrow circumstances necessitated the selection of definite precipitates to be analyzed. Several precipitates obtained upon precipitation had to be wasted before characterization. Therefore, it is possible that, valuable products as struvite were formed during other experiments that could not be identified by XRD.

6.3.9 Magnesium Measurements with AAS

Consumption of Mg^{2+} can be regarded as one of the indicators of struvite formation. Therefore, together with PO_4^{3-}, Mg^{2+} was also monitored during the experiments.

The results of the AAS measurements showed that the Mg^{2+} concentrations in the samples decreased considerably especially for high Mg:P ratios (Figure 6.35). The initial Mg^{2+} concentrations, consisting of the sum of the original Mg^{2+} concentration of the BW and the amounts added, were in all cases markedly higher than the final Mg^{2+} concentrations that were found in the supernatants. As a result, consumption of Mg^{2+} during the experiments indicates a possible production struvite, as the PO_4^{3-} concentrations are decreasing as well.

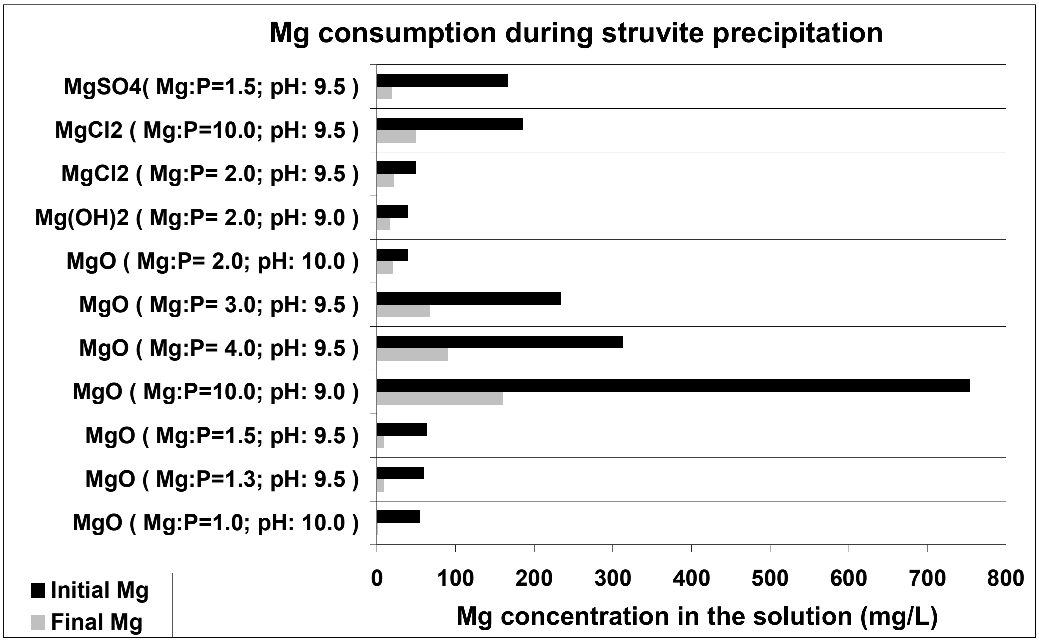


Figure 6.35 Mg^{2+}consumption during struvite precipitation

6.3.10 Ammonium (NH_4^+) Removal During Precipitation

NH_4^+ measurements were performed to monitor the decrease in NH_4^+ concentrations in the samples during PO_4^{3-} removal through precipitation.

The results show that in all the experiments NH_4^+ removal was achieved to some extent. However, without the exact data on the initial total nitrogen concentration, it is impossible to calculate what proportion of this removal is due to the conversion of NH_4^+ to NH_3 as a function of pH and what is due to precipitation as struvite. It is known from Figure 5.7 that at a pH of 9.5, 40 % of the total nitrogen is present in the form of NH_4^+.

Table 6.6 Results of NH_4^+ measurements in comparison to PO_4^{3-} removal

Sample #	Precipitant	pH	Mg:P (Ca:P)	Average NH_4^+ Removal (%)	Average PO_4^{3-} Removal (%)
1	MgO	9.5	2	13.7	89.8
2			30	30.7	93.8
3	$MgCl_2$	9.5	2	13.8	93.4
4			3	10.9	95.3
5			4	13.9	93.1
6			5	12.9	93.6
7	$Ca(OH)_2$	10.5	3	26.1	69.0
8	$CaCl_2$	10.5	3	19.5	77.1
9			4	23.7	83.2
10			5	22.0	86.2

The NH_4^+ removal was between 11 % and 31 % for all the Mg^{2+} sources. The highest removal was achieved in the experiment carried out with MgO to raise the pH instead of NaOH (sample 2). This exceptionally high removal is most likely due to the formation of struvite in addition to the proportion being removed as a result of the NH_3-NH_4^+ equilibrium. Almost the same removal efficiencies were obtained from the experiments conducted with $MgCl_2$ at pH 9.5. As the Mg:P ratio increases, more struvite may be formed, resulting in a lower NH_4^+ level. Likewise, the NH_4^+ removal in samples 8, 9, and 10 did not differ considerably between different Ca:P ratios, since the precipitated products (calcium phosphates) do not contain any NH_4^+.

The markedly higher NH_4^+ removal achieved in the experiments performed with the addition of Ca^{2+} sources (samples 7-10) are most probably due to the high pH of 10.5. At this pH 80 % of the total nitrogen is present in the form of NH_3.

In conclusion, NH_4^+ can be removed through struvite precipitation even in the experiments for which most of the change in NH_4^+ concentration was due to the high pH. This may be attributed to the low PO_4^{3-} concentrations of BW samples. As PO_4^{3-} and Mg^{2+} concentrations increase, it should be possible to achieve higher NH_4^+ removal rates due to struvite formation.

Miles and Ellis (2001) observed NH_4^+ removal through struvite precipitation from anaerobic sequencing batch reactor (ASBR) effluent with a molar ratio for N:Mg:P of 1:1.25:1 and an optimum pH of 9.5. They achieved NH_4^+ removal from an initial concentration of 1500 mg/L to less than 10 mg/L by supplying magnesium oxide and potassium phosphate to their substrate. Zeng and Li (2006) stated that NH_4^+ removal increases with the increase of PO_4^{3-} addition. Without PO_4^{3-} supplementation, they could achieve only 56 % NH_4^+ removal at a Mg:P:NH_4^+ ratio of 1.5:1.25:1. Booker et al. (1999) also mentioned the NH_4^+ removal potential of the struvite crystallization process. They observed that if only the available PO_4^{3-} in the substrate is used to produce struvite, then only about 20 % of the NH_4^+ would be removed by this process. In this case, they considered recirculation of the remaining NH_4^+ back in to the sewage treatment plant.

6.4 Conclusions

Struvite precipitation was decided to be an attractive alternative for remove and recover PO_4^{3-} in BW. Use of $MgCl_2$ at a pH of 9.5 produced the most efficient results in terms of removal efficiency.

If the aim is to recover struvite in addition to the removal of PO_4^{3-}, a Mg:P ratio of a minimum of 3 should be used. Otherwise, struvite formation may be inhibited. This means that, the theoretical Mg:P:N ratio of 1 that is required for struvite formation is not sufficient to recover PO_4^{3-} in the form of struvite from a complex matrices such as BW. On the other hand, the suggested Mg:P ratio of 3 increases the cost of the process considerably. Nevertheless, these estimated costs might be lowered further by optimizing some of the parameters affecting the process.

Struvite production may be a profitable treatment process as struvite is recognized as a marketable product. For this process to have a meaningful contribution to sustainable development it must be economically feasible.

This study was only a lab-scale investigation of the nutrients removal potential in BW through struvite precipitation. It was seen that, the removal and recovery of nutrient in the form of struvite is possible. As this study validated this potential for struvite formation, further work should be done to improve the process. Additionally, the purity of the struvite based product should be identified, and the recovered material should be analyzed for the fertilizer value.

First of all, the optimized process conditions did not suffice the formation of struvite at every experiment. The common effect such as pH and Mg:P ratio were already studied in this research. Inhibition of struvite formation may be explained with the insufficient pH conditions and Mg:P ratios. However, other parameters such as ionic strength of blackwater, or presence of organic materials that may act like complexing agents, etc. were not investigated within the context of this study. Therefore, factors affecting, particularly, hindering the struvite formation should be understood well to achieve efficient struvite production.

Furthermore, investigating the thermodynamic aspects of struvite precipitation in digested blackwater, such as calculation of solubility product and the activity coefficients, might be very helpful to understand the influence of possible equilibrium and complex-formation reactions. Due to time constraints, these parameters were not investigated.

7. EXPERIMENTAL INVESTIGATION OF THE REMOVAL AND RECOVERY OF NUTRIENTS THROUGH ZEOLITE ADSORPTION

Air stripping, ion exchange, breakpoint chlorination and biological nitrification-denitrification belong to the most widely used methods of ammonium (NH_4^+) removal (Metcalf and Eddy, 2003). Ion exchange has been demonstrated to be competitive with other methods in terms of performance and costs (Mercer et al., 1970; Culp et al., 1978). However it might be very expensive if commercial resins are used (López-Vigil et al., 2006). In order to cope with this problem natural zeolites have been successfully applied over the past two decades (López-Vigil et al., 2006).

The objective of this study was to investigate the effectiveness of using zeolite (clinoptilolite) to remove and recover ammonium and phosphorus from BW. In this study, batch and column adsorption tests were performed.

7.1 History of Zeolite

The history of zeolite began in 1756 when the Swedish mineralogist Cronstedt discovered the first zeolite mineral, stilbite (Van Bekkum et al., 2001). He recognized zeolites as a new class of minerals consisting hydrated aluminosilicates of the alkali metals and alkaline earth metals. The ion exchanging properties of zeolites were first reported in the middle of the 19th century by Way and Thompson (1850), and Eichhorn (1858). By the mid-1930's the literature described the ion exchange, adsorption, molecular sieving and structural properties of zeolite minerals (Van Bekkum et al., 2001).

7.2 Properties of Zeolites

Zeolites are described as crystalline, hydrated aluminosilicates with a framework structure. Their three-dimensional, polyanionic networks are composed of SiO_4 and AlO_4 tetrahedrally linked through oxygen atoms (Eckehart and Kleinschmit, 2000). They have a porous structure, in which water and ions that counterbalance the negative charge of the network can be found. These cations are mobile and can be exchanged. They are mainly alkali metals. This mobility gives zeolites their exchange capability.

Most of the chemical and physical properties of zeolites, and hence their areas of use, are essentially determined by the aluminium content of their frameworks. The ion exchange capacity of zeolite decreases with increasing SiO_2/AlO_4 ratio (Eckehart and Kleinschmit, 2000).

Zeolites have overall stable and solid frameworks. In particular, they are stable with regard to: high temperatures, oxidizing/reducing agents, ionizing radiation, physical attack by swelling and high pH levels (Dorfner, 1991).

More than 50 different species of zeolites have been identified (Tsitsishvili et al., 1992). Different kinds of zeolites are clinoptilolite (Kithome et al., 1998), ferrierite and mordenite (Townsend and Loizidou, 1984), erionite (Mondale et al., 1995), and chabazite (Green et al., 1996).

Clinoptilolite is one of the most abundant natural zeolites, which is highly selective for NH_4^+ (Beler-Baykal et al., 2004). Its chemical formula is $(Na_4K_4)(Al_8Si_4O)O_{96}.24H_2O$ (Vaughan, 1978). Clinoptilolite is economically efficient and effective, therefore it has been widely used for environmental protection (López-Vigil et al., 2006). Not only does the clinoptilolite have an ion sieving capability, it also has a cation exchange capacity (CEC) that is caused when silica (Si^{4+}) is substituted by aluminium (Al^{3+}), thereby raising a negative charge of the mineral lattice. This negative charge is balanced by cations such as sodium, calcium, and potassium, which are exchangeable with other cations (Curkovic et al., 1997). Other zeolites that adsorb NH_4^+ do not exactly have the same structure as clinoptilolite (Hedström, 2001).

7.3 Selectivity and Capacity of Zeolite

Natural zeolites are aluminium silicate minerals with high cation exchange capacities and high NH_4^+ selective properties (Kithome et al., 1998).

According to Dorfner (1991), for any given series of ions their selectivity can be arranged in a relative order and selectivity sequences can be established. For a general-purpose cation exchanger and aqueous solutions, usually the following selectivity sequences are valid for the most common cations:

$Ti^+ > Ag^+ >> Cs^+ > Rb^+ > K^+ > NH_4^+ > Na^+ > H^+ > Li^+ > Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mg^{2+} > UO_2^{2+}$

Ames (1960, 1967) conducted experiments to rank cations according to their affinity to clinoptilolite and developed the following order:

$Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} > Li^+$

7.4 Regeneration

The exchange or adsorption processes are done in service and regeneration cycles. There are cases where the adsorbent or the ion exchanger are used only once and then discarded or disposed of, but it is highly desirable that the material can be reused for longer time (Metcalf and Eddy, 2003). Chemical regeneration aims at desorbing ions, thus making the exchange sites of the exchanger available for new cations (Hedström, 2001). A good adsorbent, in addition to its high adsorption capacity, must also exhibit good regeneration for multiple uses. The zeolite is fully regenerable (Booker et al., 1996). Many studies confirmed that the regeneration did not significantly influence the removal of NH_4^+ by zeolite (Turan and Celik, 2003; López-Vigil et al., 2006).

Many authors have used NaCl as the regeneration brine (Table 7.1). The time needed for satisfactory regeneration of the exchanger depends on the concentration and pH of the brine (Hedström, 2001).

Table 7.1 Regeneration solutions used in the literature

Source	Type of Regeneration
EPA, 1971	12 g/L NaCl + $Ca(OH)_2$
McLaren et al., 1973	$Ca(OH)_2$
Semmens et al., 1977	25.5 g/L $NaNO_3$
Liberti et al., 1986	25 – 34 g/L $NaNO_3$
Witte et al., 1992	30 g/L NaCl
Cooney et al., 1999	NaCl pH 11
Oldenburg, 1999	4 %w NaCl

7.5 Factors Having Impact on Adsorption on Zeolites

Contact Time

Adsorption of NH_4^+ onto zeolite occurs in fact rapidly (Booker et al., 1996) but lower contact times were shown to be unsatisfactory (Beler-Baykal and Cinar-Engin, 2007). Demir et al. (2002) reported that during the first 5 to 10 min the adsorption rate of NH_4^+ was very fast and then gradually decreased with the increase in contact time.

Particle Size

The grain size distribution of the zeolite has an impact on the operating NH_4^+ ion exchange capacity (Hedström, 2001). Hlavay (1982), Rastas (2002) and Wen et al. (2006) reported that finer grain size adsorbed more NH_4^+ than the coarser ones. When using smaller grain sizes, the higher NH_4^+ exchange capacity is probably caused by a higher mass transfer into the zeolite (Hedström, 2001).

Pre-treatment

Chemical pre-treatment of the zeolite to transform it to a homoionic form and increase its NH_4^+ exchange capacity has been discussed by many authors (Carland and Aplan, 1995; Vaca Mier et al., 2001; Turan and Celik, 2003; López-Vigil et al., 2006). Pre-treatment with Na^+ ions has been shown to improve the selectivity and NH_4^+ exchange capacity of the zeolite more than pre-treatment with Mg^{2+} and Ca^{2+} (Jørgensen et al., 1979; Booker et al., 1996).

Initial Concentration of Ammonium

Ion exchange equilibrium dictates that the surface concentrations on the ion exchanger will be lower for lower solution concentrations, meaning that the surface capacity of the ion exchanger will decrease with low concentrations of NH_4^+ (Demir et al., 2002; Beler-Baykal and Cinar-Engin, 2007).

7.6 Materials and Methods

The following section shows the experimental methods for the analysis of the performance of zeolite for the adsorption of NH_4^+ from an anaerobically digested BW sample. The methods employed pursued the intention of explaining the performance and behaviour of zeolite mainly in three different areas:

- BW test with zeolite

  The purpose of this study was to obtain the optimum conditions for the design of a process, for example in a shaker or a mixing tank.

- Capacity determination experiments

  These were conducted with BW and with NH_4Cl solution as a source for NH_4^+, in order to understand the interaction of the zeolite purely with the ion and to compare this performance with the usage of BW.

- Phosphate precipitation followed by adsorption with zeolite

  In this section, the performance of zeolite with BW was tested. BW had been previously depleted from phosphorous through struvite precipitation.

7.6.1 Blackwater Tests

A summary of the processes is shown in Figure 7.1.

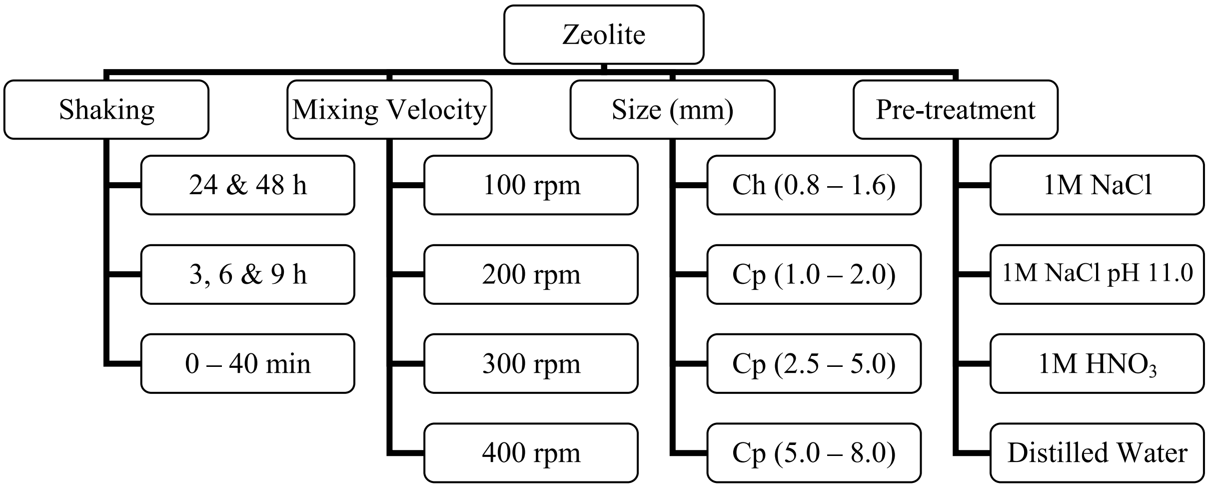


Figure 7.1 Summary of experimental procedures for optimum parameter determination (Ch = Chinese Zeolite, Cp = Clinoptilolite)

Table 7.2 Physical properties of the zeolites used in this study

	Chinese Zeolite		**Clinoptilolite**	
Particle size, mm	0.8 – 1.6		1.0 – 2.0 2.5 – 5.0 5.0 – 8.0	
Chemical composition, %	SiO_2	68 – 72	SiO_2	65 – 71.3
	Al_2O_3	10 – 13	Al_2O_3	11.5 – 13.1
	K_2O	2.7	K_2O	2.2 – 3.4
	CaO	2.7	CaO	2.7 – 5.2
	Na_2O	0.5	Na_2O	0.2 – 1.3
	FeO	0.05	Fe_2O_3	0.7 – 1.9
	Fe_2O_3	1.1	TiO_2	0.1 – 0.3
	MnO	0.03		
	MgO	1.5		
	TiO_2	0.2		
	P_2O_5	-		
	H_2O	10		
Density, kg/m^3	0.87		1.5	
Porosity	0.43		0.24 – 0.32	
Content, %	85 – 90		85 – 90	

7.6.1.1 Effect of Contact Time

The experiments were performed in order to understand the influence of the amount of zeolite and the contact time between zeolite and the solution. During this experiment, samples were mixed for several intervals. The conditions of each of the experiments are listed in Table 7.3.

Table 7.3 Experimental conditions for the effect of contact time

Parameter	Value
DBW, mL	300
Zeolite, g	2.5 / 5 / 10 / 20 / 50 / 100 / 150 / 200 / 250
Contact time, min hours	 10 3, 6, 9, 24 and 48

7.6.1.2 Effect of Mixing Velocity

In order to observe the influence of the velocity of the mixer/shaker on NH_4^+ removal, a jar test was performed. 150 g of zeolite was mixed with 300 mL digested BW. The velocities tested were 100, 200, 300, and 400 rpm. The mixing time was set to 30 minutes.

7.6.1.3 Effect of Particle Size

In order to assess the effect of particle size on the performance of NH_4^+ removal, clinoptilolite and Chinese zeolite with different particle sizes were analyzed. The range of particle sizes, were 1.0-2.0, 2.5-5.0, and 5.0-8.0 mm. The initial Chinese zeolite with particle size 08.-1.6 mm was also used in the trial.

Table 7.4 Experimental conditions for particle sizes

Parameter	Value	
DBW, mL	300	
Zeolite, g	0 / 5 / 15 / 30 / 50 / 75 / 100 / 150 / 175 / 200	
Grain size, mm	Chinese Zeolite	0.8 – 1.6
	Clinoptilolite	1.0 - 2.0
		2.5 – 5.0
		5.0– 8.0
Shaking time, min	30	
Shaker velocity, rpm	200	

7.6.1.4 Effect of Pre-treatment

For the pre-treatment, three different cation-containing solutions were used: 20 g/L NaCl, 20 g/L NaCl at pH 11 and 1N HNO_3.

Initially the zeolite was washed with distilled water. After drying it at 70 °C overnight, it was mixed with the pre-treatment solutions. The mixture was shaken for 24 hrs at 200 rpm, afterwards washed again with distilled water three times. Finally, the zeolite was dried again at 70 °C overnight.

Once the zeolite was pre-treated, the experiment with digested BW was conducted. Digested BW samples of 150 mL were placed in glass bottles. 75 g of the pre-treated zeolites were added to each sample. A sample of washed zeolite (blank) was also tested for comparison. The bottles were shaken for 30 minutes at 200 rpm and 20 °C. Afterwards, samples were taken from each bottle to analyze both PO_4^{3-} and NH_4^+.

7.6.1.5 Influence of the Initial Concentration of Ammonium

In order to observe the influence of the initial concentration of the feed solution on the ion exchange efficiency, various flasks with fixed amounts of zeolite (35 g) were contacted with NH_4Cl solutions with different initial concentrations. They were all placed on a shaker at 20 °C and 200 rpm for 30 minutes of contact time. 20 mL samples were taken in the 5 th, 10 th, 15 th, 20 th and 30th minutes of shaking. The same procedure was done with the clinoptilolite, but samples were taken only after 30 minutes of shaking.

Table 7.5 Experimental conditions for the determination of the influence of NH_4^+ initial concentrations on adsorption capacity of zeolite

Parameter	Value
NH_4Cl solutions, mg/L	673.5 / 505.2 / 336.8 / 168.4
Volume, mL	400
Zeolite, g	35
Shaking velocity, rpm	200
Contact time, min	30
Sampling time, min	5/10/15/20 and 30

7.6.2 Capacity Determination Experiments

Adsorption capacity is defined as "the value of the amount of adsorbed substance (for strongly adsorbed solutes of limited solubility) reached in a saturated solution for a specific solute. Its value depends also, in general, on the nature and, in the case of more than two components, on the relative composition of the bulk liquid" (IUPAC, 1972).

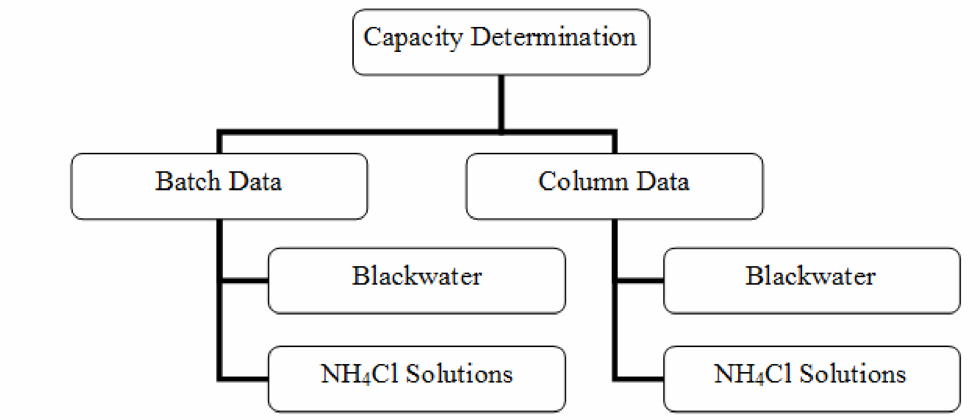


Figure 7.2 Experimental approaches for the NH_4^+ adsorption capacity determination

Two different approaches were used in the determination of the capacity, with both BW and NH_4Cl solutions: batch and column experiments.

7.6.2.1 Batch Experiment

In order to understand the interaction between the zeolite and NH_4^+, several experiments were conducted. Before experiments, the zeolite was washed with distilled water previously, dried overnight at 70 °C and placed in a dessicator, then weighted and added to flasks.

Reaching Equilibrium

The zeolite was prepared as explained above. The NH_4Cl solution was then added and the flasks placed in a shaker at 200 rpm for the period mentioned in Table 7.6.

Table 7.6 Experimental conditions for batch equilibrium tests for the capacity determination

Parameter	Value
Volume, mL	400
Zeolite amounts, g	0 / 5 / 10 / 25 / 50 / 100 / 150
Initial [NH_4^+], mg/L	1665
Time intervals,	
min	30, 90 and 180
hours	24, 48, and 72
Shaking velocity, rpm	200

The same experiment was performed with BW but the samples were taken only after 72 hours and analyzed as explained in chapter 3.2.7.

In addition to NH_4^+ adsorption, zeolite has the potential to remove PO_4^{3-} as well (Ganrot et al., 2007). That is why, all zeolite tests were also analyzed for PO_4^{3-} content.

Zeolite Capacity and Equilibrium Models

Once the equilibrium was ensured, several typical equilibrium models were used for both BW and the NH_4Cl solution. The models tried were Langmuir and Freundlich, which are common fitting models for zeolite adsorption processes (Turan and Celik, 2003; Beler-Baykal and Cinar-Engin, 2007). With this, it is also possible to obtain an approximate value for the capacity of the zeolite for both, the NH_4Cl solution and BW.

7.6.2.2 Column Data

Generally, ion exchange equipment is designed to be used in columns, due to the easier handling of the process. It is also possible to determine the capacity of the zeolite with this experimental procedure (Demir et al., 2002; Turan and Celik, 2003; Beler-Baykal and Cinar-Engin, 2007).

A glass burette with 15 mm diameter and a height of 122 mm was used for this experiment. The column experiment was conducted for both, NH_4Cl solution and BW with zeolite in Na^+ form (Na^+-Zeolite). The conditions are shown below:

Table 7.7 Experimental conditions for column tests with Na^+-Zeolite

Parameter	With NH_4Cl	With BW
Zeolite weight, g	97.5	102.5
NH_4^+ concentration, mg/L	1200	1269.6
Empty bed volume (EBV), mL	237	248
Column flow, BV/h	5.8	4.9
Reaction time, min	250	66

7.6.3 Regeneration

Distilled water, 20 g/L NaCl, 1M NaCl, 1M NaCl (pH 11), 1N HNO_3 were used as regenerants. The process for regeneration was the same for all cases. After the adsorption process, the rest of the BW was carefully decanted and 400 mL of the regeneration solution was added. The bottles were placed for 24 h in a shaker at 200 rpm. After this, a 50 mL sample was taken and tested for NH_4^+.

7.6.4 Precipitation as a Previous Step for Zeolite Adsorption

Several struvite precipitation experiments were preformed in order to combine the technique with zeolite adsorption, by using the supernatant as feed for the zeolite process. Precipitation tests were conducted with $MgCl_2$ and MgO at pH 9.5. The procedure was performed as explained in chapter 6.2.3.

Two different sets were made for the magnesium salts. The solids/solution ratio was kept constant at 50 %. The samples were taken after 30 minutes and 24 hours of continuous shaking at 200 rpm. The supernatant from the precipitation tests, after being analyzed, was used for further batch experiments with zeolite, both in natural and sodium forms. The effluent was analyzed for PO_4^{3-} and NH_4^+ content.

7.7 Results and Discussion

7.7.1 Blackwater Tests

The purpose of this study was to obtain the optimum conditions for the design of a process, for example in a shaker or a mixing tank.

7.7.1.1 Effect of Contact Time

Results indicated that there was no need to shake samples more than 24 hours, since the NH_4^+ concentration already reached the equilibrium. As Figure 7.3 confirms, there is not a substantial difference between the 24-hour and the 48-hour lines, which continues to indicate that the optimum shaking time is less than 24 hours.

The graph proves that the shaking time, the contact time needed for the ion exchange, is fast. The same tendency was observed for the shaking time of 3, 6 and 9 hours. The results showed that at 3 hours, maximum NH_4^+ removal was achieved.

As it can be seen in Figure 7.3, the NH_4^+ concentration decreased already at the beginning of the experiment, although there wasn’t any zeolite in digested BW samples. This might be explained by the conversion of NH_4^+ to NH_3 due to the characteristics of digested BW.

Increasing the zeolite weight in contact with the BW sample increases the amount of NH_4^+ removed. The ideal amount for this graph is around 150 grams for 300 mL of BW.

It was also observed that the mechanical stress on the larger amounts of zeolite that were continuously shaken was too large. This stress caused the zeolite to grind into a creamy, thick mixture that smelled like concrete, or similar to wet sand or stone. This indicates that the grain was damaged, which obviously changes its exchange capabilities. It can also be that the paste that is formed interferes in a particular way with the analyzing method, giving altered results. That might be the explanation for the concentration increment of 200 and 250 g of zeolite (Figure 7.3).

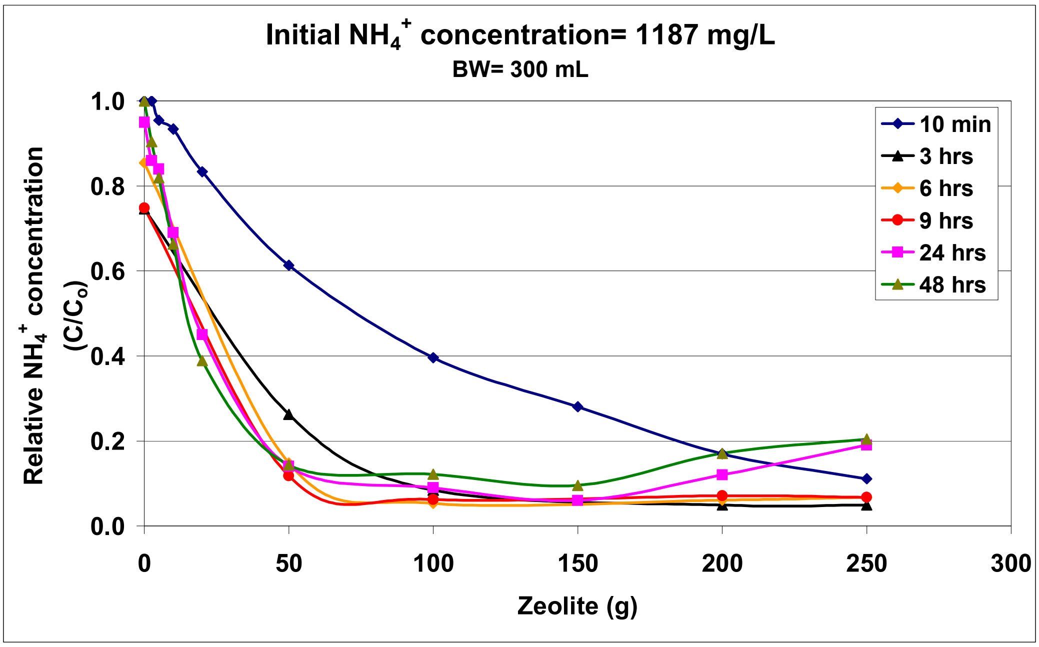


Figure 7.3 Effect of zeolite amount and contacting time on NH_4^+ uptake

During this experiment, a color change was observed. This change can be related to the adsorption capacity of the zeolite, which did not only adsorb NH_4^+, but other ions and compounds as well. It may be that some of the substances responsible for the color in BW were being removed by the zeolite in a similar way that activated carbon does it when used as a filter for drinking water. The use of zeolite for color removal were already researched and used in other fields (Singh et al., 2003; Armagan et al., 2004; Baki Engin et al., 2008). It represents an interesting side effect that could be positively used, as color is an important esthetical parameter for wastewater reuse.

In order to narrow the contact time down, another experiment was conducted between 5 to 40 minutes of shaking. An asymptotic behaviour started to develop, which indicated the approach to the equilibrium state, in almost 40 minutes of continuous shaking (Figure 7.4). According to the diagram, an optimum contact time of 30 minutes can be used, with a removal efficiency of 82 %. This shaking time was also run by Demir et al. (2002) and López-Virgil et al. (2006).

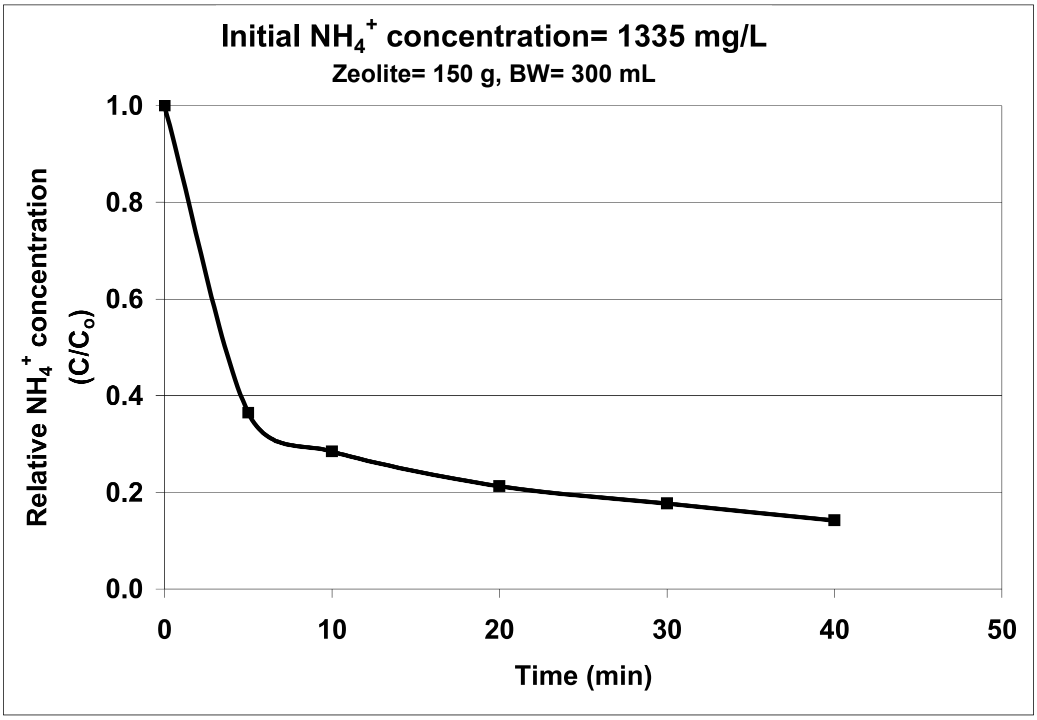


Figure 7.4 Effect of contacting time (5-40 min) on NH_4^+ uptake

As expected, the more the contact time is, the higher the removal can be achieved. This continues until an asymptotic behaviour can be observed, when the limit adsorption capacity of the zeolite is achieved.

Figure 7.5 Test flasks for BW experiments with shaking periods of 5 to 40 minutes

Figure 7.5 shows the test bottles after being shaken. One interesting observation was the formation of a precipitate film on top of the layer of zeolite. Since digested BW contains high amounts of TS (Table 4.2), this film could be in part composed of suspended solids that managed to settle down within the time the sampling was performed. It could also be that new compounds could precipitate because of the new interaction in the BW matrix when the NH_4^+ ion was removed. The removal of the ion could shift the equilibrium in many unknown reactions that could be taking place in such a complex solution.

7.7.1.2 Effect of Mixing Velocity

Figure 7.6 presents the influence of the velocity of mixing on the NH_4^+ removal. It can be seen that larger velocities offer larger efficiencies, however a four-fold increase of the speed enhances the overall effectiveness of the process by only 10 %.

It can be affirmed that the use of higher velocities for the mechanical shuttling of the zeolite was not justified and it can be said that the 200-rpm area was sufficient for the exchange process. This agrees with the literature (Cooney et al., 1999; Wen et al., 2005; Karadag et al., 2006).

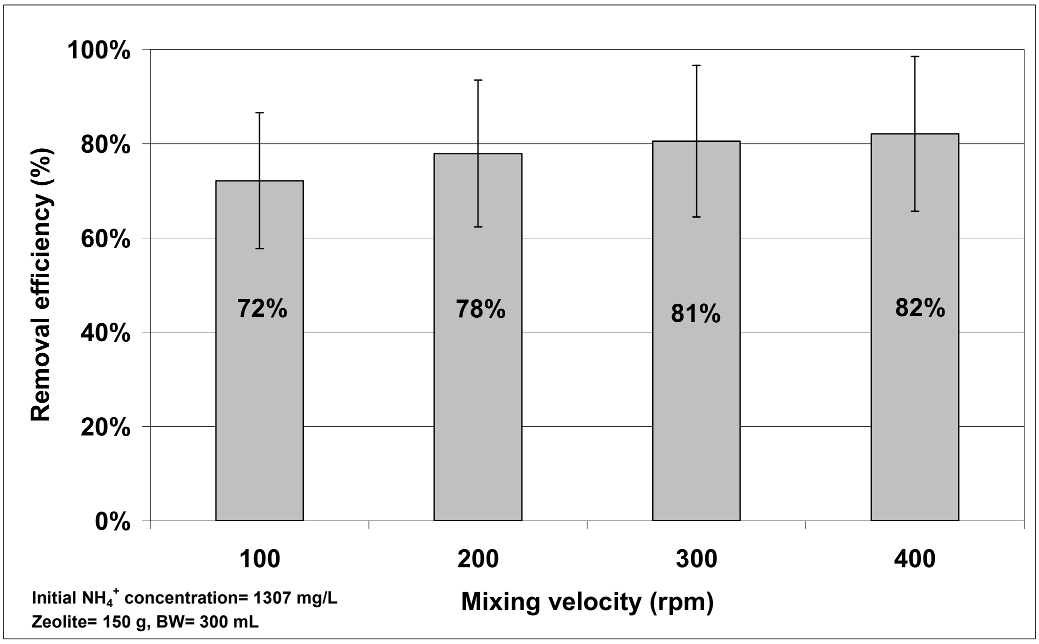


Figure 7.6 Effect of mixing velocity on the NH_4^+ removal efficiency

7.7.1.3 Effect of Particle Size

Two different types of zeolites were tested: Chinese zeolite and Clinoptilolite, in order to verify the performance of each of them. Additionally, different particle sizes of clinoptilolite were also tested.

The size of the zeolite has a clear effect on the amount of NH_4^+ removed (Figure 7.7). Smaller particles have larger surface areas, which are available for the adsorption. The finer the particle size of a zeolite, the better the access to the surface area and the faster the rate of adsorption kinetics.

In literature, a majority of researches have found a direct relationship between grain size of the material and its performance with NH_4^+ uptake (Booker et al., 1996; Rastas, 2002; Turan et al., 2003; Wen et al., 2005).

Between the Chinese zeolite and the smallest clinoptilolite (1–2 mm), there is still a perceivable difference in dimension, which could account for the better performance.

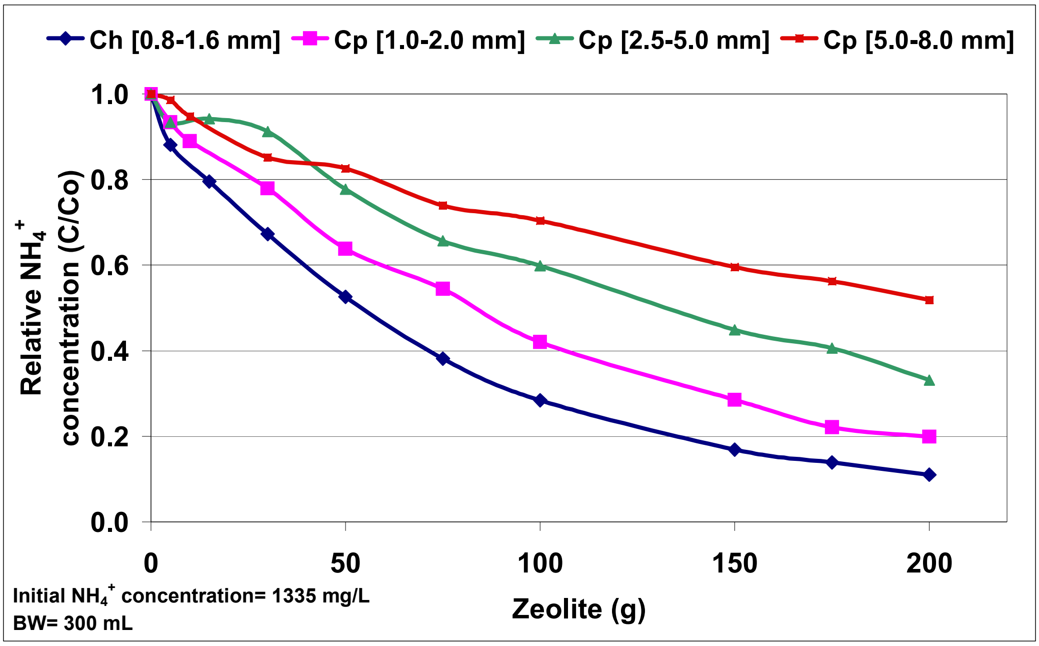


Figure 7.7 Effect of different particle sizes of zeolite on NH_4^+ uptake

7.7.1.4 Effect of Pre-treatment

For the pre-treatment, different solutions were used, mainly having Na^+ and H^+ as loading cations. In almost all cases, pre-treatment increased the ion exchange capacity of the mineral, except for the case of Chinese zeolite treated with HNO_3, although the difference between these values were not too high (Figure 7.8). The best results were obtained for Clinoptilolite with the solution of 20 g/L solution of NaCl without any pH adjustment and for Chinese zeolite, the same solution concentration of NaCl but with pH 11. However, for Chinese zeolite the removal increase was around 1 %, which may lie in the error range of the measuring method. The results proved that the homogenization of zeolite surface by pre-treatment is an effective method to increase the removal efficiency of NH_4^+.

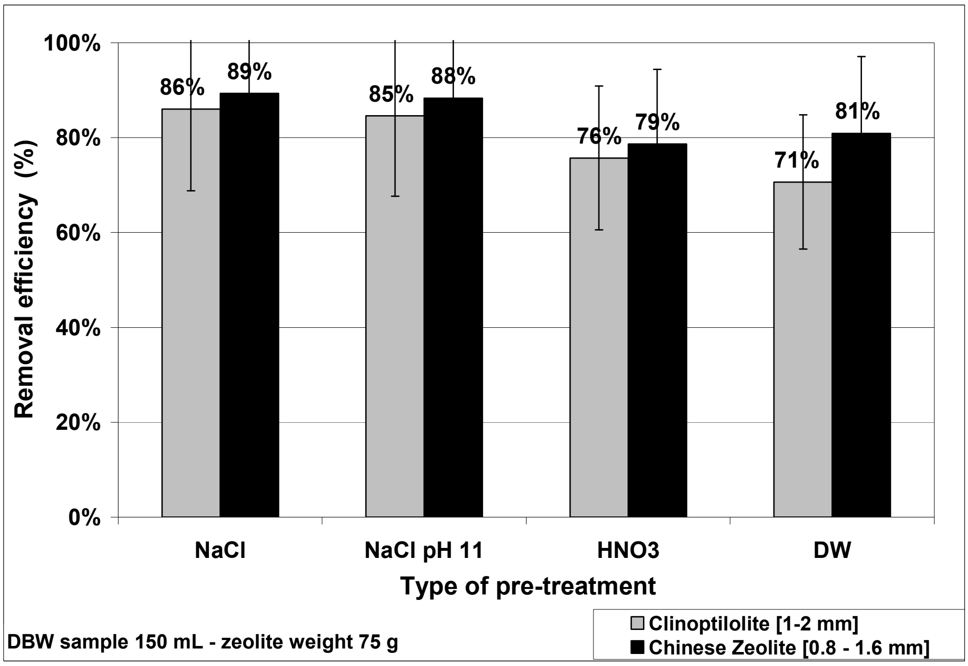


Figure 7.8 Effect of pre-treatment of zeolite with different solutions on the NH_4^+ removal

These results are similar to other findings, where pre-treatment with NaCl solutions were enough to create Na^+ form material with a superior adsorption capacity (López-Virgil, 2006) and with NaCl at pH 11, with the aid of NaOH (Cooney et al., 1999).

7.7.1.5 Influence of the Initial Ammonium Concentration of the Solution

As expected from the previous researches (Oldenburg, 1999; Demir et al., 2002; Karadag et al., 2006), a higher initial concentration increased the ion exchange capacity of zeolite.

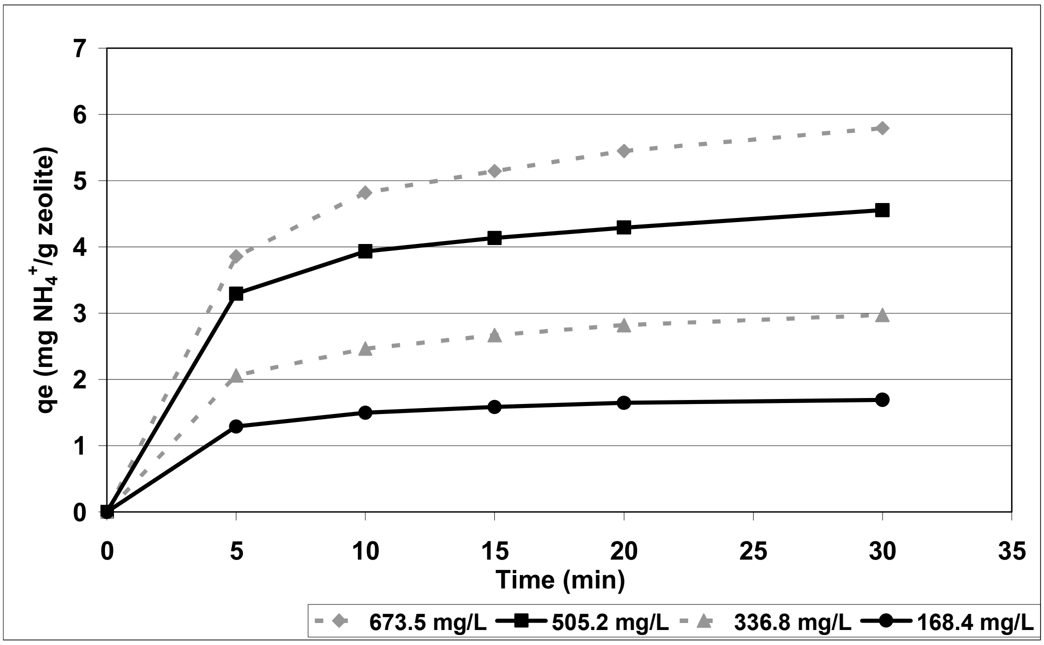


Figure 7.9 Influence of initial NH_4^+ concentration on zeolite loading

For all cases, the velocity of this process was quite fast. Already in the first 5 minutes between 90 and 95 % of the total exchange was achieved. This relates to the fact that initially a big availability of adsorption places was found and once the majority of these were occupied, the velocity went down. Ion competition can also become an important factor for this phenomenon.

7.7.2 Capacity Determination Experiments

In this section, the zeolite capacity for NH_4^+ removal was determined experimentally with two different procedures: batch experiment and column test.

7.7.2.1 Batch Experiments

This section records the results for the experimental tests done in bottles or flasks, where zeolite was mixed and the NH_4^+ removal was calculated by the analysis of the supernatant.

Reaching Equilibrium

Figure 7.10 presents the time needed for achieving equilibrium in the system. As it can be seen clearly, the system reacts quite fast. In the fist 20 hours, more than 75 % of the exchange has taken place. This fast reaction time has been reported by other authors as well (Karadag et al., 2006). Other researchers recommend more contacting times, from 60 minutes (Turan et al., 2003) up to 7 days (Cooney et al., 1999). In these experiments, however, the optimum time for equilibrium is between 20 and 40 hours.

It was observed that from the line of 24 hours, there is an overlapping of the lines, which indicates that no further major exchange took place and thus, which indicates the equilibrium. From Figure 7.10, the optimum time for the achievement of equilibrium can be estimated at 48 hours. The fluctuations seen here can be attributed to the measuring method errors.

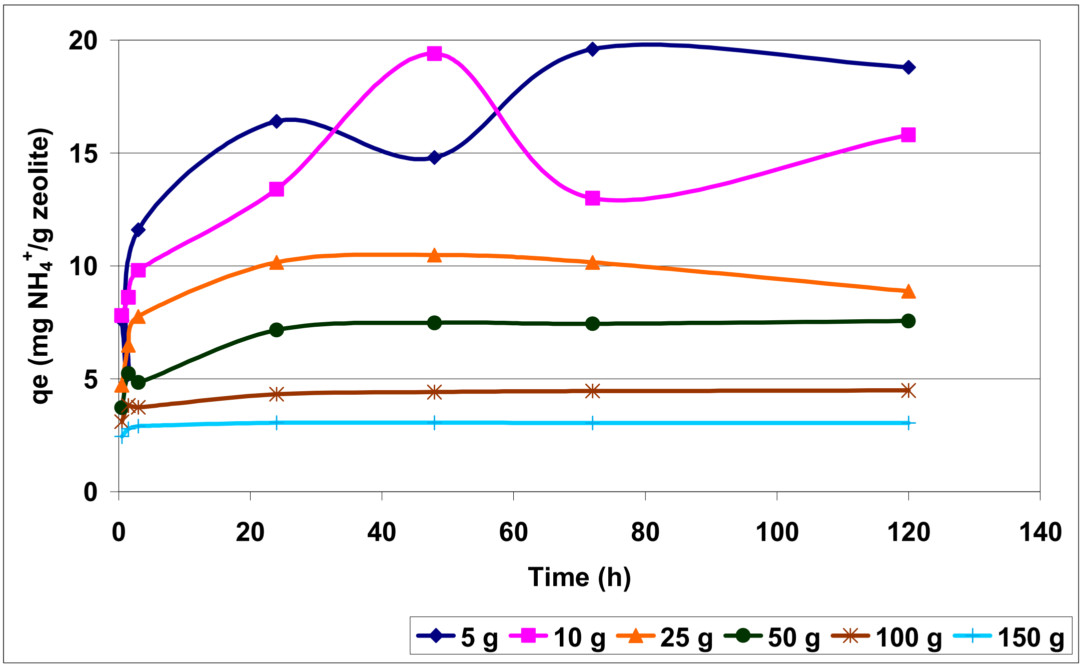


Figure 7.10 Equilibrium isotherm for the zeolite in pure NH_4Cl solution

Zeolite Capacity and Equilibrium Models

To explain or model the ion exchange of NH_4^+ between the zeolite and BW, experiments were conducted with NH_4Cl solution. The mathematical models used to describe this exchange are commonly the Freundlich and Langmuir adsorption isotherm models.

The Langmuir Model can be represented in several mathematical models as mentioned by Perry's Chemical Engineers' Handbook (2007). The one chosen here was plotting the load of zeolite (qe, mg/g) against the equilibrium concentration (Ce, mg/L).

Figure 7.11 and Figure 7.12 show the Langmuir adsorption isotherm model for NH_4Cl solution and for BW respectively. As it can be seen, the behaviour is quite similar, although as expected, a higher adsorption value can be obtained with the NH_4Cl solution, since there has not been any competing ions.

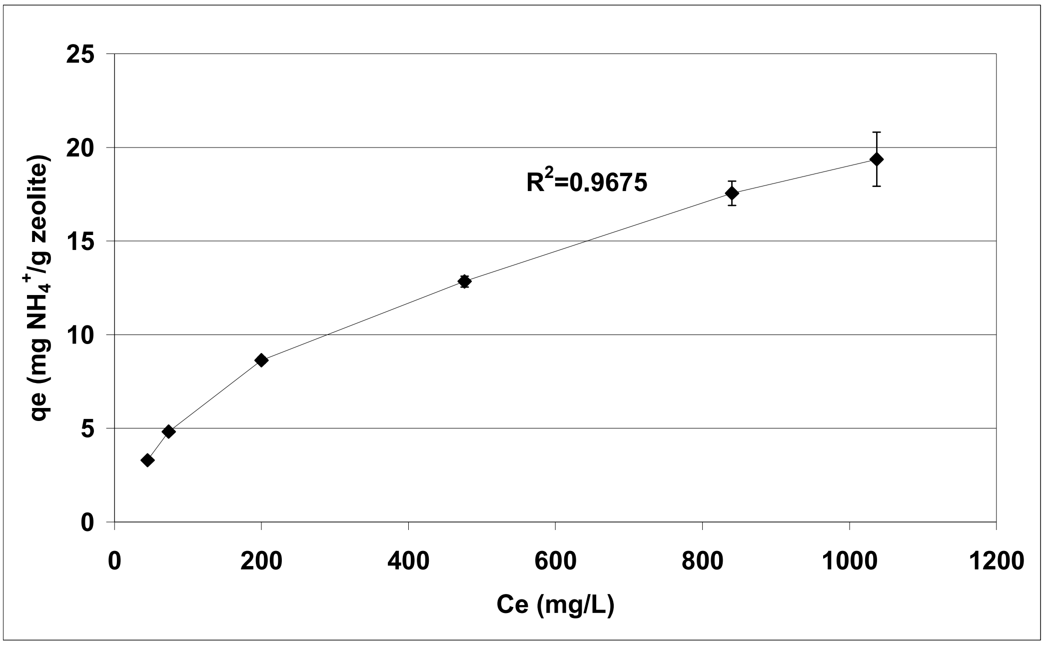


Figure 7.11 Langmuir adsorption isotherm model for NH_4Cl solution

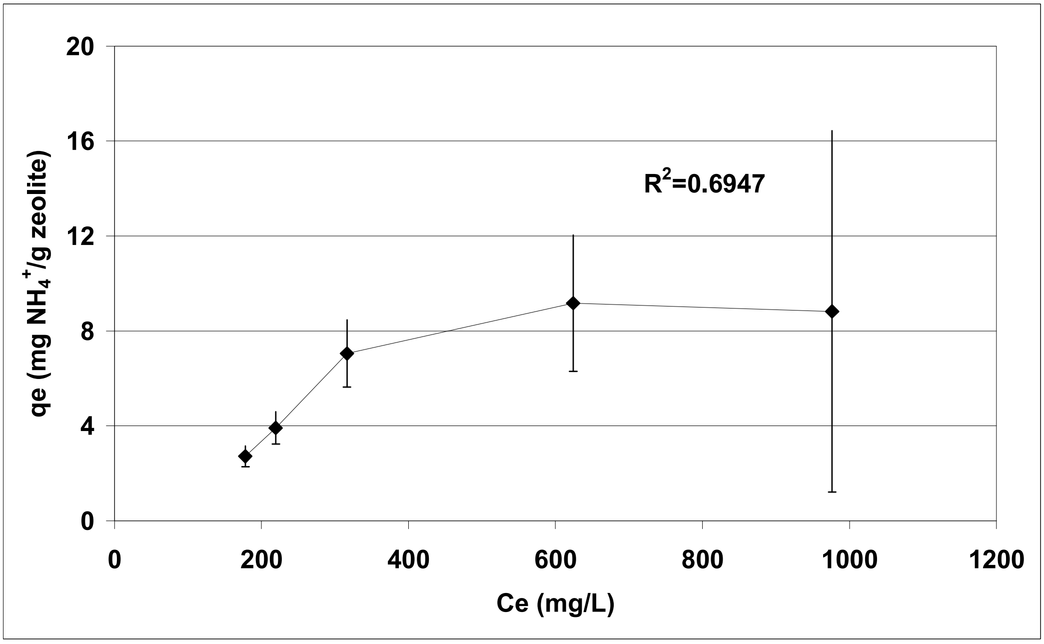


Figure 7.12 Langmuir adsorption isotherm model for digested BW

As it can be seen, the value for the maximum NH_4^+ adsorption is around 19 mg of NH_4^+/g of zeolite for the Chinese zeolite with NH_4Cl solution (Figure 7.11). It is around 9 mg of NH_4^+/g of zeolite for the same zeolite with digested BW samples (Figure 7.12). This seems to be within the range of other researches (Table 7.8). It is important to notice that no research was found that worked with such high NH_4^+ solution concentrations as contained in the anaerobically treated BW used in this study. This clearly influences the loading capacity achieved by the zeolite and can in part, explain the differences seen in the Table 7.8.

Table 7.8 Literature overview for the zeolite adsorption capacity

Author	**Adsorption capacity mg/g**	**Initial concentration mg/L NH_4^+**	**Type of solution**
This Research (Batch Data)	19	1200	NH_4Cl
	9	1197	BW
Booker, 1996	21	30	NH_4Cl
	4.6	29.4	Wastewater effluent
Cooney, 1999	14	645	NH_4Cl
Oldenburg, 1999	2.6	29.4	Waste treatment plant effluent
Turan, 2003	7.4	10	Tap water
Beler-Baykal, 2004	15	110	Urine

However, another important parameter is the type of solution used for the tests. The presence of other ions clearly interferes with the NH_4^+ uptake of zeolite, behaving as a competitor and taking adsorption capacity (Dorfner, 1991). It is known that the presence of Na^+ ion can decrease the capacity of the zeolite by up to 50 % while Mg^{2+} and K^+ up to a 25 % (Cooney et al., 1999).

For the Freundlich Model, the results for NH_4Cl solution and digested BW samples with Chinese zeolite can be seen in Figure 7.13 and Figure 7.14. As far as the R^2 values are concerned, which were highly significant in digested BW and NH_4Cl, suggesting that data are mainly fitted to the Freundlich adsorption isotherm equation better.

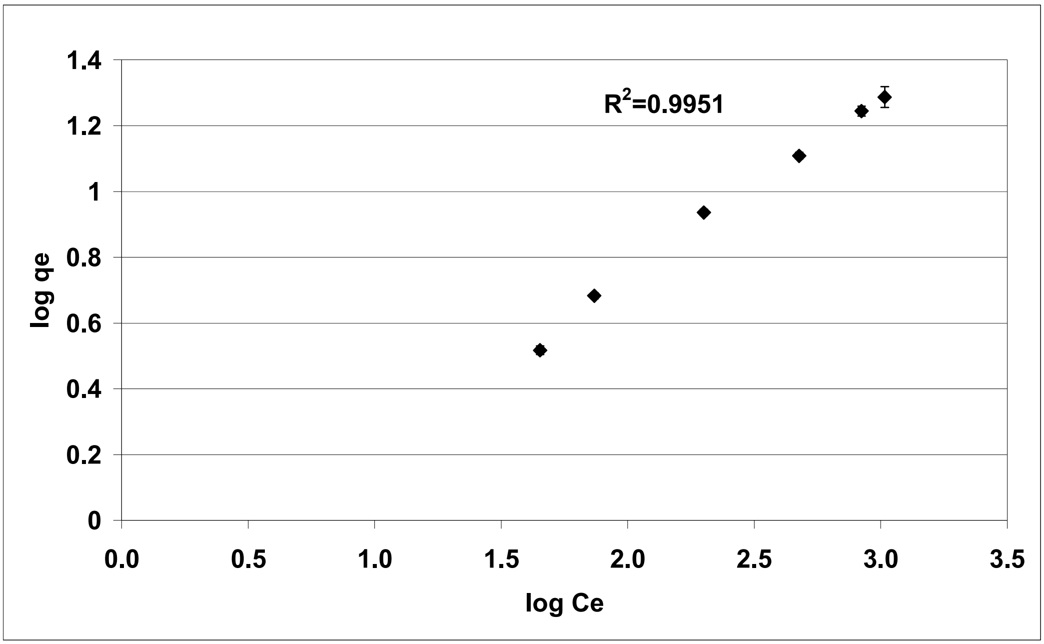


Figure 7.13 Freundlich adsorption isotherm model for NH_4Cl solution

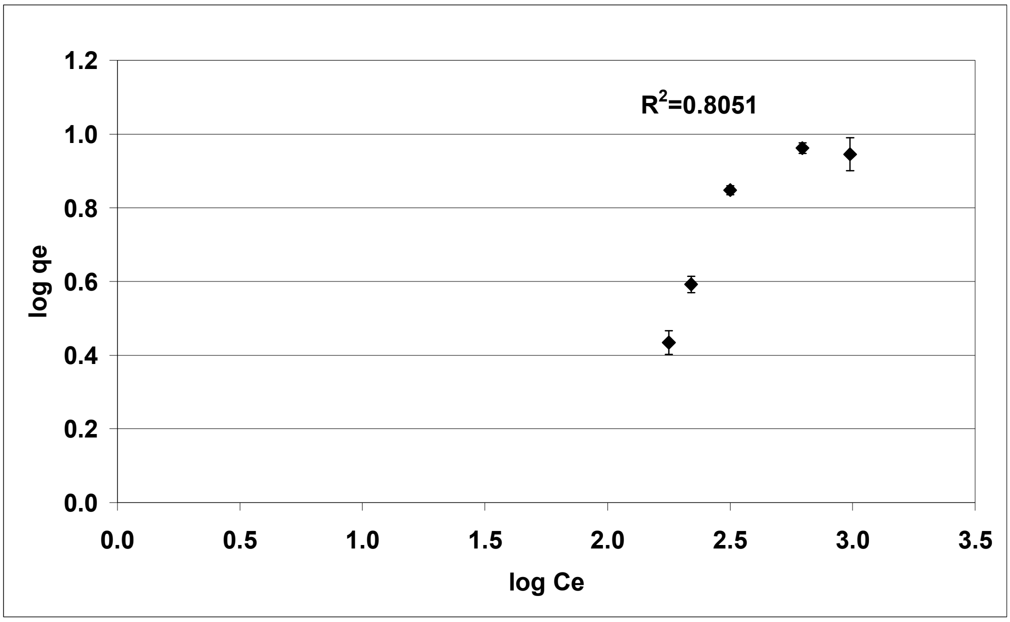


Figure 7.14 Freundlich adsorption isotherm model for digested BW

Between the Langmuir and Freundlich model, there is a better description of the process with the Freundlich isotherm, for both the BW and the NH_4Cl tests. This was described by Cooney et al. (1999) as well. On the other hand, Demir et al. (2002) and Karadag et al. (2006) reported a better fitting with the Langmuir isotherm. Differences in the best fitting of models can be related to the parameters such as solution concentration and the specific combination of adsorbate and adsorbent.

7.7.2.2 Column Data

Figure 7.15 and Figure 7.16 show the column experiments results with NH_4Cl solutions and digested BW respectively. For both cases, it can be seen that the concentration at the effluent did not completely approach the original concentration in solution. This may be attributed to a bad timing of sampling (Rastas, 2002).

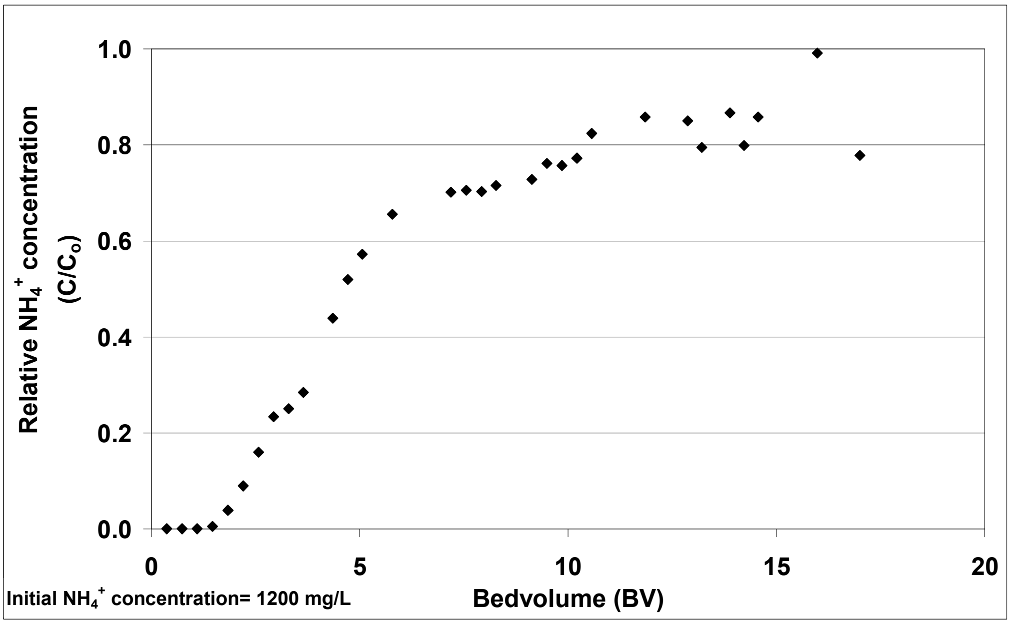


Figure 7.15 Column data: Breakthrough curve of NH_4Cl solution

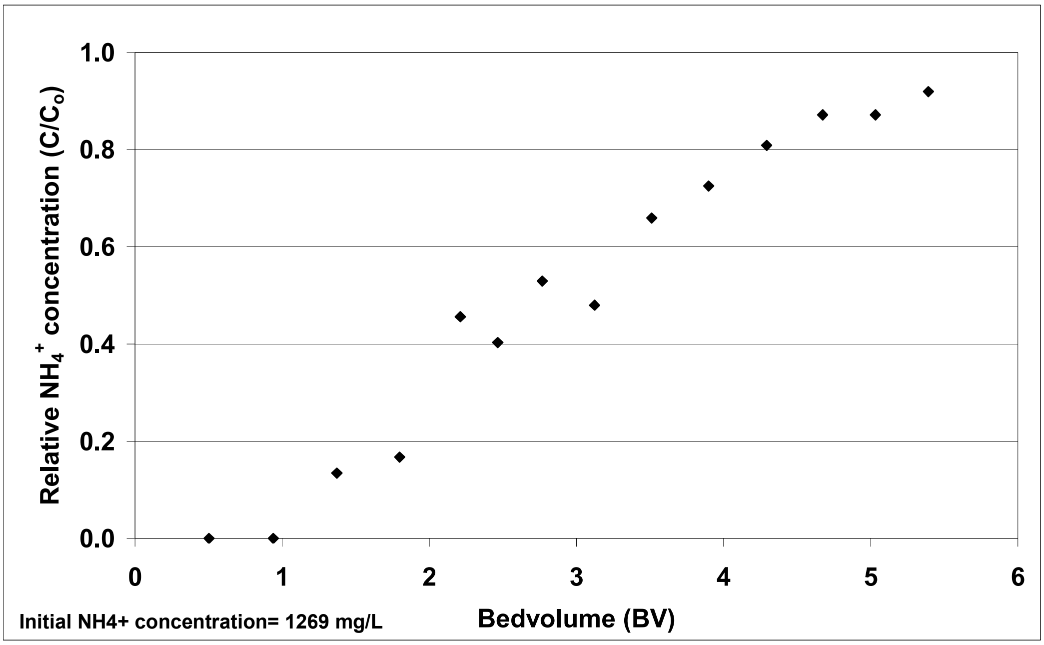


Figure 7.16 Column data: Breakthrough curve of digested BW

With these breakthrough curves, the capacity of the zeolite can be calculated for both types of solutions. In order to calculate the capacity, both “breakthroughs” were taken when the effluent concentration achieved the 80 – 85 % of the initial solution concentration. In this way, the bed volumes that were treated by the specific amount of zeolite in the column can determine the amount of ammonium removed by the ion exchanger (Dorfner, 1991).

$$\text{Capacity (mg/g)} = \frac{\text{(Volume passed, L) x (Solution concentration, mg/L)}}{\text{(Zeolite weight, g)}} \qquad \text{[Eq. 7.1]}$$

Table 7.9 NH_4^+ adsorption capacity of zeolite obtained from the column experiments

Parameter	**NH_4Cl**	**BW**
Initial concentration of NH_4^+, mg/L	1200	1269
Volume passed, L	2.8	1.3
Zeolite weight, g	97.5	102.6
Capacity, mg/g	34.6	16.5

Table 7.10 Literature overview of the zeolite adsorption capacity

Author	Adsorption capacity mg/g	Initial concentration mg/L NH_4^+	Type of Solution
This Research (Column Data)	34.6	1200	NH_4Cl
	16.5	1269	BW
Booker, 1996	4.5	150	Wastewater effluent
Oldenburg, 1999	2.6	29.4	Wastewater effluent
Kalyuzhnyi, 2000	3.6	296	Manure streams
Rastas, 2002	2.6	20	Wastewater effluent

7.7.3 Regeneration

In order to regenerate the zeolite and close the cycle as well as reuse of NH_4^+, different solutions of diverse compounds in various concentrations were employed.

Some preliminary experiments were already conducted with the loaded zeolite when the BW experiments were done, mainly with distilled water and NaCl 20 g/L. For distilled water, the average recovery efficiency was of 3.4 % with the zeolites probes of more than 100 g. For lower zeolite content there was no recovery of NH_4^+. For NaCl, results showed an average recovery efficiency of 4.3 %.

Mostly used regeneration cation in literature was Na^+. This makes sense because even though the zeolite has a preference for NH_4^+, with the zeolite completely saturated, the equilibrium shifts towards the Na^+ (Dorfner, 1991).

A Na^+-rich solution would help to deadsorb the NH_4^+ and load the zeolite with Na^+, preparing it for a new cycle for the NH_4^+ removal.

However, if the material costs are not of interest and a market can be found with the appropriate price conditions, the loaded zeolite could be used directly in agriculture, as a soil conditioner and fertilizer. This application has already been subject of studies and since the zeolite also adsorbs PO_4^{3-}, it could be used as a slow-release fertilizer. The US Geological Survey (USGS) has already done some trials with positive results; however more research needs to be done. Some of the negative results of these tests were for example, the toxicity of the zeolites that have Na^+ as the main exchange ion or that zeolites poor in NH_4^+, Ca^{2+} and K^+ can limit the growth of the plants, by adsorbing these ions from the soil (USGS, 2007).

7.7.4 Phosphate Removal as a Side Effect

For all the tests for NH_4^+ removal with zeolite, PO_4^{3-} content was measured as well. It was observed that zeolite also managed to remove some of the PO_4^{3-} present in BW. Figure 7.17 shows the removal efficiency results of NH_4^+ and PO_4^{3-} for experiments with shaking time between 5 to 40 minutes at 300 rpm in a jar test.

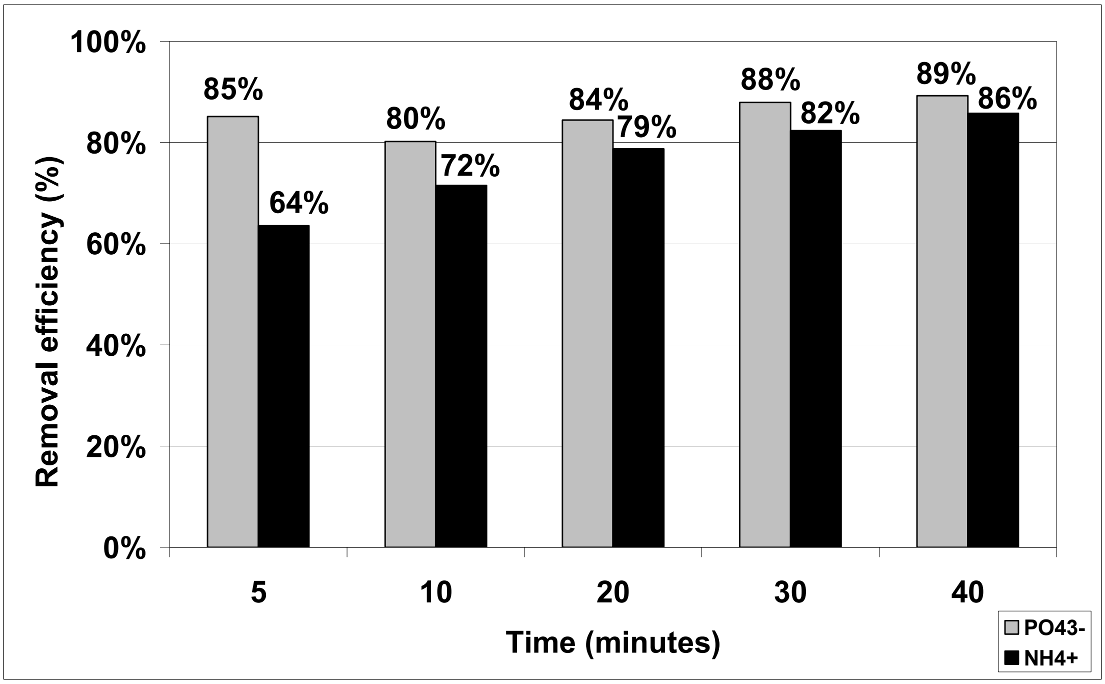


Figure 7.17 Removal efficiencies of NH_4^+ and PO_4^{3-} by zeolite

As mentioned by Ganrot et al. (2007), zeolites can also adsorb considerable amounts of phosphates to their hydrous oxides on Al^{3+} structural sites. Contacting time increases the elimination of PO_4^{3-}, this could be a consequence of the sedimentation of TS, which can contain large amounts of PO_4^{3-} compounds.

Shaken samples had difficulties with higher amounts of zeolites because with increasing shaking times, the erosion of the zeolite was bigger, increasing turbidity and pulverizing the zeolite, which could interfere with the analysis for PO_4^{3-} and NH_4^+.

Another interesting aspect was to observe how the particle size would affect the PO_4^{3-} uptake as well. The results were expected to be similar to the ones with the NH_4^+, as explained before. However, the results indicated that the best size was between 2.5 – 5.0 mm with 97 % of PO_4^{3-} removal. Another important observation was that clinoptilolite had a better efficiency against the Chinese zeolite, which seems to be in accordance with literature (Sakadevan and Bavor, 1998).

In conclusion, zeolite has a high capacity for PO_4^{3-} removal as well. This side effect, however, is irreversible, since the ions are strongly taken by the Al^{3+} centres of zeolite.

7.7.5 Precipitation as a Previous Step for Zeolite Adsorption

The compounds used for precipitation were $MgCl_2$ and MgO, which would help to remove PO_4^{3-} from digested BW and obtain it as struvite.

As it can be seen clearly from the Figure 7.18 and Figure 7.19, $MgCl_2$ achieved higher removal efficiency than MgO and there was not any significant difference between the results obtained from the zeolite in natural form and the ones homogenized with Na^+ ions.

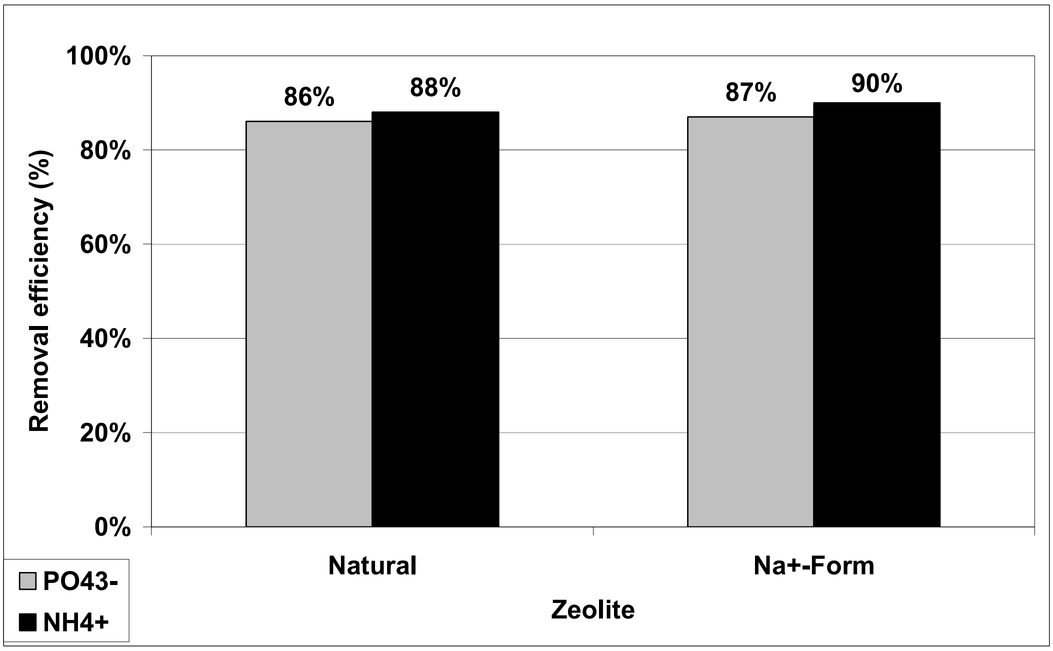


Figure 7.18 Removal efficiencies of PO_4^{3-} and NH_4^+ after precipitation with $MgCl_2$ followed by adsorption

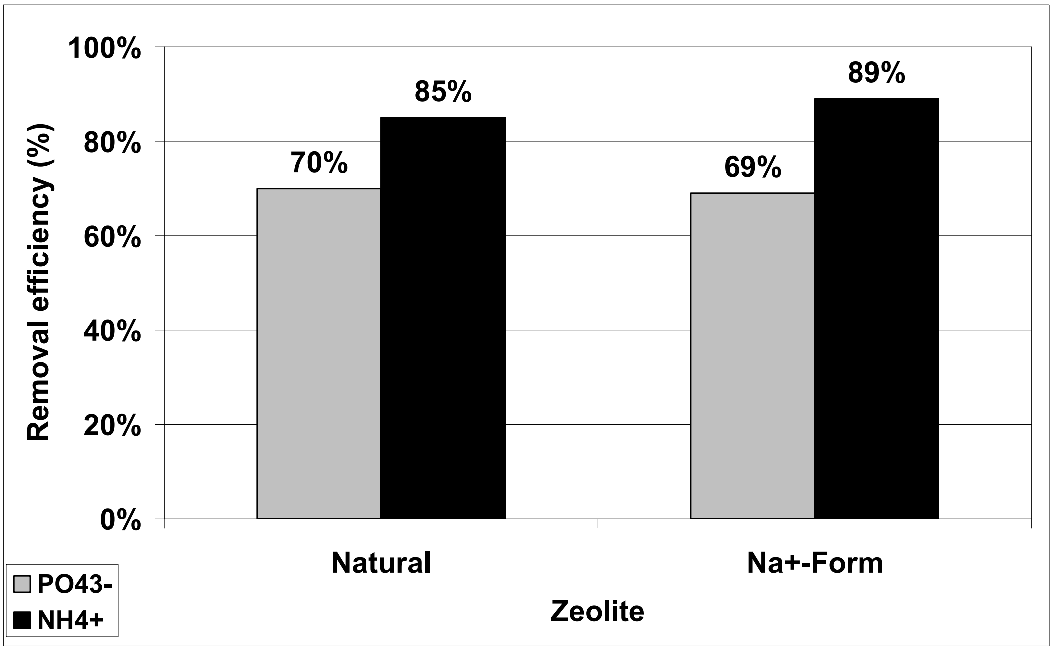


Figure 7.19 Removal efficiencies of PO_4^{3-} and NH_4^+ after precipitation with MgO followed by adsorption

The combination of precipitation and adsorption proved to be efficient for removing PO_4^{3-} and NH_4^+ from the substrates. Overall removal efficiencies were above 80 %.

7.8 Conclusions

The removal of NH_4^+ was quite high, in average up to 90 % was obtained for higher amount of zeolites, due to the fact that the pre-treatment has increased the ion exchange capacity of the zeolite.

According to the results, NH_4^+ adsorption capacity of the zeolite was dependent on its cationic form of pre-treatment conditioning as well as the initial NH_4^+ concentration of the solution.

Also the particle size had an effect on ion exchange capacity of the zeolite, since larger sizes had less surface area and proved less efficiency; shaking velocity was also studied and higher speeds resulted in limited higher removal efficiencies.

Batch experiments and breakthrough experiments showed that the amount of NH_4^+ which was adsorbed on zeolite is strongly affected by the presence of competing ions.

Results proved that zeolite has a high adsorption capacity for PO_4^{3-} removal as well. In average 85 % of PO_4^{3-} could be removed efficiently.

Regeneration solutions were also tried, but more research has to be done in this segment to obtain the optimum conditions for it. The results obtained in this experimental procedure are not enough to ensure the reuse of the zeolite and a good regain of NH_4^+ for further use.

8. CASE STUDY

A full assessment of a treatment concept includes an economical and ecological analysis. The challenge of a treatment concept is to scale up the results obtained in those tests to the actual size needed for a treatment process.

As a part of this research, a case study was conducted which contains a detailed economical analysis concerning two different settlements having anaerobic digestion and evaporation, precipitation or adsorption in process:

Case 1: 350 inhabitants (for the ecological settlement Flintenbreite)
Case 2: 2000 inhabitants

This case study looks intensively at each treatment process and stresses their economical feasibilities.

8.1 General Data

The input data for the design of the processes is given in Table 8.1.

Table 8.1 Input data of BW

Parameter	Value
Urine and faeces production, L/person.year	550
Flushing water consumption, L/flush	0.7
Number of flushes, times/day [a)]	5
BW production, L/person.day [b)]	~ 5
Average pH	7.8
Density of BW, kg/L (Metcalf and Eddy, 2003)	1.05
Temperature, °C	20

[a)] It was assumed that an ordinary person uses toilet flushing 5 times a day.

[b)] BW production = Urine + faeces + flushing water; comparable with the estimation of Vinnerås (2001).

8.2 Anaerobic Digestion

8.2.1 Digester

The capital cost of an anaerobic digester lies between 191 and 575 €/m^3 (FNR, 2005). In this study, it was assumed that the capital cost of a digester is 400 €/m^3, which presents the average market price.

Table 8.2 Dimensioning of an anaerobic digester for case 1 and case 2

Data	Case 1	Case 2
Volume of BW, m^3/d	1.75	10
HRT, d	21	21
Digester volume, m^3	36.8	210

In order to allow some extra volume for the equipment and instrumentation, it was decided to implement two digesters with volumes of 40 and 230 m^3 for case 1 and case 2 respectively.

8.2.2 Heat Demand of Anaerobic Digestion

The heat demands for an anaerobic digester (at 37 °C) for case 1 and case 2 are 30800 and 176000 kWh/year respectively (Wendland, 2008).

Some AD systems are designed exclusively to combust biogas for heat. Biogas has the potential to be used directly for various energy purposes. After purification, biogas can even reach the quality standard of natural gas and thus replace it. Several authors calculated energy data for anaerobic treatment concepts based on AD with energy production of e.g. 55 kWh/cap.year (Wendland, 2008).

8.3 Evaporation

In design, the main disadvantage of the evaporation process is the high energy consumption needed for vaporization. Therefore, it is important to understand the process mechanism and to calculate the needed variables for the determination of these energy requirements.

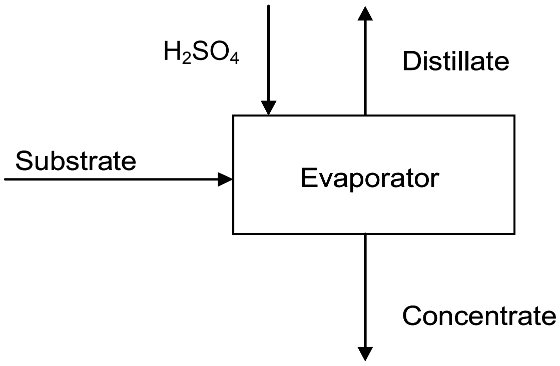


Figure 8.1 Evaporator block diagram

Table 8.3 Characteristics of BW used for evaporation

BW Input Data	Case 1	Case 2
BW volume flow, L/h	72.9	416.7
BW mass flow, kg/h	76.6	437.5
Temperature, °C	125	
Pressure, bar	-0.3	
Density BW, kg/L	1.05	
Viscosity BW, Pa.s	$4x10^{-1}$	
Density distillate, kg/L	1.05	
Density concentrate, kg/L	1.19	

8.3.1 Mass Balance

The evaporation efficiency at pH 4.5 was 82 % (Chapter 5). This efficiency was calculated as shown below:

$$RE = \frac{V_D \times \rho_D}{V_S \times \rho_S} \qquad [Eq.\ 8.1]$$

RE : Removal efficiency, %
V_D : Volume of distillate, L
V_S : Volume of substrate, L
ρ_D : Density of distillate, kg/L
ρ_S : Density of substrate, kg/L

Table 8.4 Overall mass balance during evaporation

Mass Flow	Case 1	Case 2
Substrate, kg/h	76.6	437.5
Distillate, kg/h	62.6	357.9
Concentrate, kg/h	13.9	79.6

8.3.2 Heat of Evaporation

The enthalpy of vaporization, ΔH_v, also known as the heat of vaporization or heat of evaporation, is the energy required to transform a given quantity of a substance into a gas (Treybal, 1981). It is often measured at the normal boiling point of a substance. The heat of vaporization is temperature dependent and diminishes with increasing temperature. It vanishes completely at the critical temperature because above the temperature, the liquid and vapour phases do not coexist anymore.

In this case, the enthalpy of vaporization for the BW was calculated with the amount of energy used by the oil bath in order to evaporate the obtained amount of distillate. Table 8.5 presents the data available for the oil bath.

Table 8.5 Silicone oil bath data

Silicone Oil Bath	Value
Volume, L	2
Temperature change, K	105
Heat capacity, kJ/kg.K	1800
Density, kg/L	0.92

The energy used for the oil bath, Q = 347.76 kJ, was calculated by the heat equation (Eq. 8.2):

$$Q = m \times C_p \times \Delta T \qquad [Eq.\ 8.2]$$

Q : Heat transfer, kJ
m : Mass of the substrate, kg
C_p : Heat capacity, kJ/kg.K
ΔT : Temperature change, K

The distillate mass that was evaporated with this heat was 163.6 mL (0.172 kg), and the ΔH_v can be calculated as:

$$\Delta H_v = \frac{347.76\,\text{kJ}}{0.172\,\text{kg}} = 2021.86\frac{\text{kJ}}{\text{kg}}$$

8.3.3 Overall Heat Requirement

In order to obtain 62.6 kg of distillate per hour in the Flintenbreite plant, the required heat is 126.7 MJ/h (Eq. 8.3).

$$Q_{vap} = m \times \Delta H_v \qquad \text{[Eq. 8.3]}$$

Another energy requirement is the amount of heat required to increase the temperature of BW from 20 °C to 125 °C. It was assumed that the heat capacity of BW is same as water (4.18 kJ/kg.K) and stays constant through the whole temperature interval. In order to increase the temperature, the required energy for case 1 is 33.7 MJ/h.

Table 8.6 Overall heat requirement of the evaporation process

Heat Requirement MJ/h	**Case 1**	**Case 2**
Evaporation	126.7	723.6
Temperature change	33.7	192.1
Total	160.4	915.7

8.3.4 Apparatus

For the design of the vessel, pressure, temperature and pH value have to be taken into account for the material to be chosen and the thickness of the walls.

Vacuum evaporators for volumes of up to 70 L/h and 400 L/h cost around 750 €/L and 300 €/L respectively (H_2O GmbH, 2009, personal communication).

8.3.5 Chemical Consumption

During the evaporation process, the main chemical consumed was 98 % H_2SO_4 for the pH adjustment. It was recorded that for achieving a pH of 4.5 from an average pH of 7.8, 2.7 mL of H_2SO_4 were needed for each liter of BW. The required H_2SO_4 amounts for the case 1 and 2 are 196 mL/h and 1125 mL/h respectively.

8.4 Precipitation

8.4.1 General Data

For the design of the precipitation process, the process block diagram and the input data are given below:

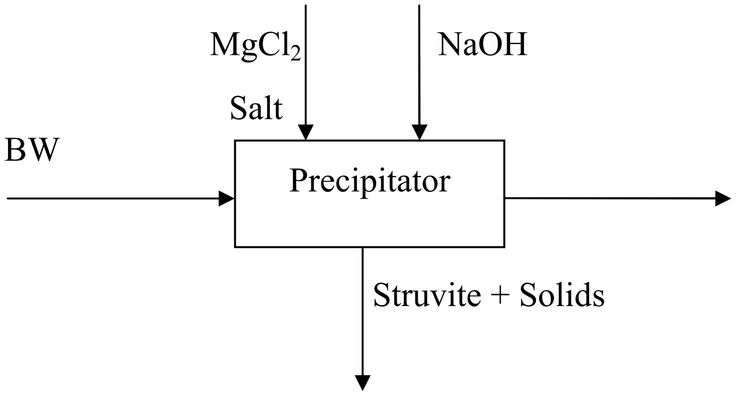


Figure 8.2 Precipitation process block diagram

Table 8.7 Data required for the calculation of PO_4^{3-} removal

Data	**Case 1**	**Case 2**
Population	350	2000
Po_4^{3-} concentration, mg/L	160	
Initial pH of digested BW	7.5 – 8.0	
Desired pH	9.5	
Mg:P ratio	3.0	
$MW_{Struvite}$, g/mol	245.4	
MW_{NaOH}, g/mol	40.0	

8.4.2 Precipitator

For the design of the vessel, where precipitation and sedimentation would take place, several types of designs already in use were analyzed. Phosphorous can be removed as different compounds (calcium phosphates, iron phosphates, potassium-struvite, struvite, etc.). There are different processes in operation with almost each possibility. The one used here is an adaptation of the design used by Wilsenach (2006). The design was based in a continuously stirred tank reactor (CSTR), where the struvite formation takes place.

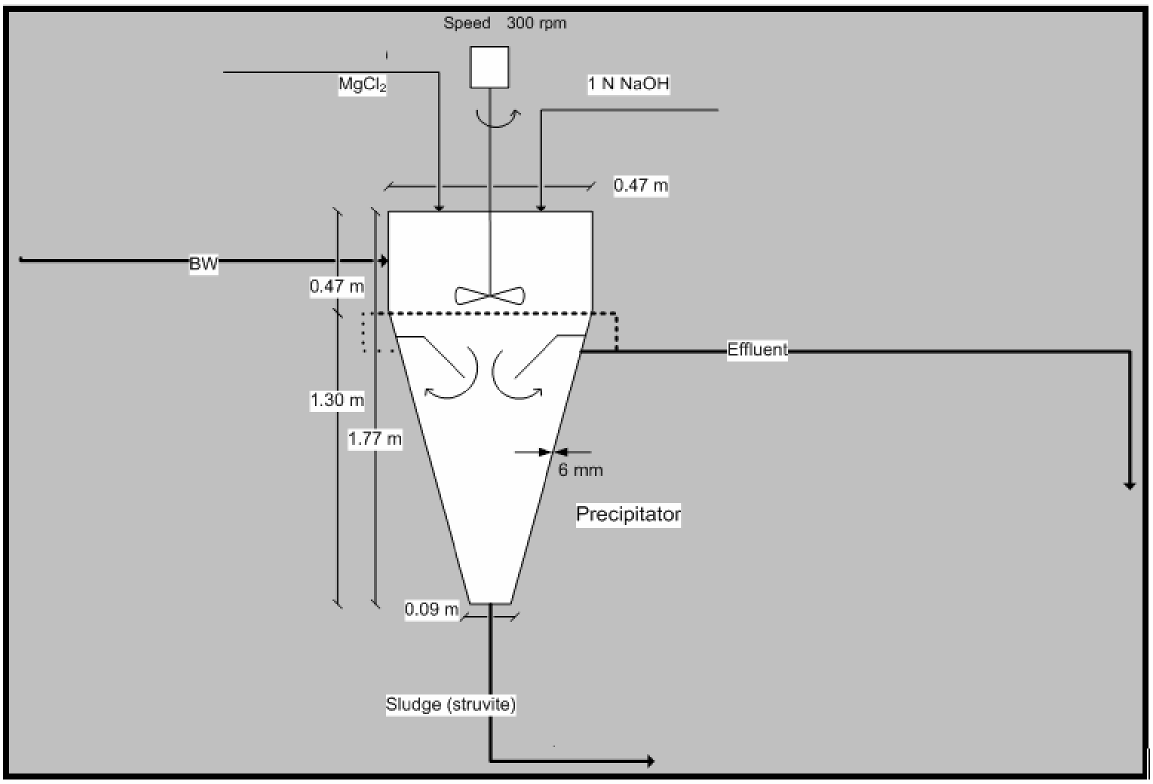


Figure 8.3 Precipitator (Pérez-Cantú, 2009)

First, the volume of the reactor needed to be defined. From the experimental tests, 15 minutes were found to be sufficient for mixing of the BW with the Mg salts in order to form the struvite. However, the volume flow for the actual precipitator is much larger than the one in the experimental procedure. The residence time (RT) was then approximated to one hour.

73 L and 417 L should be the minimum volumes to achieve a RT of one hour in the mixing section of the reactor for case 1 and 2 respectively. As a recommendation, it is desirable to allow some extra volume for security reasons, as the piping and instrumentation of the tank could affect the final level of the tank. This was defined as 10 % of the total volume. The volumes of the mixing tanks were accepted as 80 L (case 1) and 460 L (case 2).

8.4.3 Chemical Consumption

For the precipitation process, the main chemicals consumed were $MgCl_2$ and NaOH solution for the pH adjustment.

Table 8.8 Data on the used Mg^{2+} source and PO_4^{3-} removal through struvite production

Mg^{2+} Salt	**MW (g/mol)**	**Removal Efficiency (%)**	**Removed PO_4^{3-} (mg/L)**	**Mg:P Ratio**
$MgCl_2.6H_2O$	202.3	94	150.4	3

Chemical consumption during struvite precipitation was calculated based on the data available in Table 8.8.

Table 8.9 Chemical consumption values during precipitation process

Data	**Case 1**	**Case 2**
Monthly BW production, L/person	150	150
Total BW production, L/month	52500	300000
PO_4^{3-} production, kg/month	8.4	48
$MgCl_2$ consumption, kg/month	50.5	287.5
NaOH consumption, kg/month	105	600

8.4.4 Struvite Production

$$Mg^{2+} + NH_4^+ + HPO_4^{2-} + 6\,H_2O \rightarrow \underbrace{MgNH_4PO_4.6H_2O}_{\textbf{Struvite}} + H^+ \qquad \text{[Eq. 8.4]}$$

During the struvite formation through precipitation, each mol of PO_4^{3-} removed yields 1 mol of struvite production. If it is assumed that *all* of the PO_4^{3-} removed during the precipitation forms struvite, then the amount of struvite formed (in moles) will be equal to the amount of PO_4^{3-} removed (in moles).

Table 8.10 Monthly estimated struvite production

Monthly struvite production	**mol**		**kg**	
	Case 1	**Case 2**	**Case 1**	**Case 2**
By using $MgCl_2$	83	475	20.4	116.15

Struvite precipitation is a rather costly process, especially due to the requirement of adding $MgCl_2$ and NaOH (Liberti et al., 1981). Some researches stated that the struvite recovery process is economically feasible only when the recovered product can be sold at or above the price range of industrial fertilizer (Booker et al., 1999; Münch and Barr, 2001).

Table 8.11 Cost of producing and selling struvite (Doyle and Parsons, 2002)

	UK	**Japan**	**Australia**
Cost of struvite production, EUR/tonne produced	-	303	92
Recommended market value for struvite sale, EUR/tonne purchased	187	173	578

8.5 Adsorption

8.5.1 Zeolite Adsorption Capacity

The equilibrium concentration at the effluent was 110.9 mg of NH_4^+/g of zeolite. At this concentration, the bed volume (BV) that passed through the zeolite was 1.5. One BV was equal to 248 mL (Table 7.9).

The calculation is as follows:

$$(1.5\,\text{BV})\times(0.248\,\text{L})\times\left(1269\,\frac{\text{mg}}{\text{L}}\right)=472\,\text{mg of NH}_4^+\ \text{was removed}$$

Since there was 102.5 g of zeolite in the column, the capacity of zeolite was calculated as 4.6 mg NH_4^+/g zeolite.

Table 8.12 Adsorption with zeolite: Input data

Input Data	Case 1	Case 2
BW inlet flow, L/h	72.9	416.7
BW mass flow, kg/h	76.6	437.5
Temperature, °C	20	
Initial NH_4^+ concentration of the solution, mg/L	1269	
Zeolite capacity, mg NH_4^+/g	4.60	
Zeolite density, kg/m^3	890	
Operation time, day	2	
Removal efficiency, %	88	

8.5.2 Column

Mostly, adsorption processes take place in columns, which are fed either from the top or bottom and with the adsorbate fixed in the middle of the tower (Perry, 2007). For column design, several guidelines were obtained from literature (McCabe et al., 2001). However, the important parameter to be determined in the first place is the amount of zeolite needed for a defined operation time, in order to calculate the volume of the column. The amount of zeolite needed is simply the amount of NH_4^+ to be exchanged in the operation period determined divided by the capacity of the zeolite. It is calculated as shown below:

$$m=\frac{(C_i)\times(V_{flow})\times(RT)\times(RE)}{q_e} \qquad \text{[Eq. 8.5]}$$

m : Amount of zeolite needed, kg
C_i : Initial NH_4^+ concentration of the solution, mg/L
V_{flow} : Daily BW flow, L/day
RT : Retention time, day
RE : Removal efficiency, %
q_e : Capacity of zeolite, mg/L

The required amounts of zeolite are 849 kg (case 1) and 4855 kg (case 2). With this calculation and the design guidelines (Perry, 2007), for case 1 and case 2, two columns with volumes of 1 m^3 and 5.5 m^3 are needed respectively.

8.5.3 Chemical Consumption

For zeolite adsorption, the regeneration solution is the most important consumer of chemicals. For the previous research with the same Chinese zeolite a solution of 4 %w NaCl was used (Oldenburg, 1999). The common regeneration solution consumption for adsorption columns is around 5 BV. It was assumed that 15 regenerations will be performed each month.

Table 8.13 Chemical consumption values during adsorption process

Data	Case 1	Case 2
Volume of NaCl solution, m^3/ regeneration	5	27.5
Volume of NaCl solution, m^3/month	75	412.5
Mass of solution, tonne of 4 %w NaCl/month	77	423.6
NaCl mass, tonne/month	3.1	16.9

8.6 Cost Estimation

8.6.1 Capital Costs

One rough estimation can be made using the weight of the tanks to be bought. By knowing the market price of the material to be used in its construction, a base price can be obtained.

Table 8.14 Apparatus costs

Price Calculation	Costs EUR	
	Case 1	Case 2
Digester	16,000	84,000
Evaporator	54,750	124,800
Precipitator	65	200
Column	175	500

However, it can be clearly seen that the costs for the smaller vessels (precipitator and column) do not reflect a real market price for similar capacity devices. Therefore, the market prices before the manufacturing adjustment factor should be taken into consideration (Pérez-Cantú, 2009). It is important to realize that a high adjustment factor (more than 50 %) can be expected, due to the addition of engineering, labor costs and know-how from the actual manufacturing of the vessel (Peters et al., 2003). The recalculated values are shown in Table 8.15.

Table 8.15 Apparatus costs with market prices

Price Calculation **(including 50% of adjustment factor)**	**Costs EUR**	
	Case 1	**Case 2**
Digester	24,000	126,000
Evaporator	82,125	187,200
Precipitator	998	3,300
Column	5,010	14,250

8.6.2 Operation Costs

For the calculation of the operation costs, the consumption of chemicals and the heating requirements of each plant were taken into account.

The used compounds have a strong influence on the costs, because they depend on a market price that can change according to production expenses and other limitations such as disposition of residues for example.

Table 8.16 Chemical consumption and costs per month

Chemicals	**Monthly Consumption**		**Costs[a)] EUR**	
	Case 1	**Case 2**	**Case 1**	**Case 2**
Evaporation				
98 % H_2SO_4, L	141	810	535	3,078
		Total	**535**	**3,078**
Precipitation				
$MgCl_2.6H_2O$, kg	50.5	287.5	915	5,209
NaOH, kg	105	600	1,083	6,192
Discount 30 %[b)]			-	3,420
		Total	**1,998**	**7,981**
Adsorption				
NaCl, kg	3078	16929	11,735	64,541
Discount 30 %[b]			-	19,362
		Total	**11,735**	**45,178**

[a)] Market prices offered by Merck

[b)] Since the required chemical amounts for case 2 are much higher than for case 1, special prices were obtained by the supplier.

For the energy consumption, the total energy consumptions for the AD, evaporation and for the mixing in precipitation were taken into account. The adsorption section does not contribute at this point to the overall energy consumption, because the energy needed for pumping and instrumentation was not calculated.

Table 8.17 Yearly energy demand of each process

Process	**Energy Consumption kWh/month**		**Costs* EUR**	
	Case 1	**Case 2**	**Case 1**	**Case 2**
Anaerobic digestion	2,567	14,667	359	2,053
Evaporation	32,083	183,131	4,491	25,638
Precipitation (Pérez-Cantú, 2009)	565	999	80	1,480

* Price per kWh: 0.14 Euro

8.7 Results and Discussion

Anaerobic Digestion

Anaerobic digestion is a technologically simple process and requires little energy. A digester produces two outputs, biogas and digested BW. Both can be further processed or utilised. Biogas can be used for producing electricity and heat, as a natural gas substitute and also a transportation fuel. AD of highly concentrated BW produces almost enough energy for the heat requirement of the digester itself (Wendland, 2008).

Evaporation

The operation costs for evaporation are much higher than those for the precipitation process. Maurer et al. (2006) stated also that the main disadvantage of nutrient enrichment is the high costs needed for evaporation. The heat supply with steam for the evaporation can be economical than with electricity (Pérez-Cantú, 2009). However the costs for a steam generation plant should be added to the capital investment in order to be a self-sufficient steam supplier.

Since there is not any anaerobic digester in process in Flintenbreite, once in a week the BW is transported to a treatment plant, which costs monthly around 1,200 € (Oldenburg, 2009, personal communication). Through evaporation, transportation and storage costs can be reduced drastically.

Precipitation

As the struvite precipitation is a chemical treatment method, cost of the chemicals plays a significant role in process design. Considering the highest PO_4^{3-} removal rates and the reasonable prices given for $MgCl_2$, its use should be considered for the struvite precipitation process in BW. Nevertheless, it is very important to find a market to sell the recovered struvite at profitable rates.

Adsorption

For zeolite adsorption, the regeneration solution is the most important consumer of chemicals. Although the operation of the system doesn't require high energy inputs, due to high regenerant demand it might be a costly process for the NH_4^+ removal. Regenerant consumption should be optimized with further researches.

9. FINAL CONCLUSIONS and FUTURE WORK

Sustainable development in wastewater management does not only include recovery of nutrients to reduce eutrophication, but also ways to recycle the removed nutrients. About 95 % of the total nitrogen and about 90 % of the total phosphorus present in BW.

Since the BW is considered as a problematic wastewater stream, the main focus was its handling and treatment. The feasibility of anaerobic digestion for the pre-treatment of BW was investigated within this study. The results proved that the anaerobic digestion of BW can be considered as a sustainable option to recovery of energy, while nutrients are preserved for reuse. It is a technologically simple process that requires little energy. One of the end products, biogas is a useful, renewable energy source. Digested medium is rich in organics and can be considered for reuse in agriculture.

Obstacles for using BW separation technology on a larger scale are still found in the storage and transport. In order to solve this problem, the water content of digested BW was reduced by evaporation. This also makes the handling of the BW easier. Another problem with evaporation of BW was the loss of nitrogen through ammonia. This problem was reduced through acidification of the samples.

As a result, evaporation can be regarded as an effective technique to achieve volume reduction and nutrient enrichment in BW. However, use of the final effluents and the energy consumption of the process are among the main drawbacks of evaporation. Solar evaporation ponds can be an alternative to mechanical evaporators, where the meteorological and climatological conditions are available for the implementation. They are usually limited by land availability and potential odor problems, whereas mechanical evaporators are relatively compact, reliable, efficient but also expensive to operate.

Further research could be done to find proper utilization options for the concentrate and distillate.

One of the important compounds that was precipitated from BW was struvite, which is formed by reaction of magnesium with phosphate in presence of ammonium. Struvite is known as a slow-release fertiliser. Blackwater contains an excess of ammonium relative to phosphate, but it is deficient in magnesium. With the addition of different Mg^{2+} sources, it was possible to precipitate struvite in digested BW.

Struvite precipitation is a very attractive alternative to remove and recover PO_4^{3-} and NH_4^+ in BW. Its production is a profitable treatment process as struvite is recognized as a marketable product. However, the cost of the chemical used during the precipitation has to be considered. Nevertheless, it is very important to find a market, where the recovered struvite can be sold.

Since, this study was only a lab-scale investigation, it has to be optimized for a large scale design. Addition to that, after identifying the purity of the product obtained from the experiments, the recovered material should be analyzed for the fertilizer value by applying it onto fields, plants etc.

Zeolites are natural minerals and considered as cheap and effective on NH_4^+ removal. The results proved that zeolites have a significant impact on ammonium adsorption. Addition to that, a combination of struvite precipitation and adsorption is a highly effective method, in terms of removal of both target nutrients: PO_4^{3-} and NH_4^+. However, it has to be considered that when scaling up an ion exchange system, the larger system will probably not achieve the same operating exchange capacities for PO_4^{3-} and NH_4^+ as one of the smaller laboratory scale.

It was also concluded that the capacity experiments conducted with digested BW showed that the presence of other ions reduced drastically the adsorption capacity of the zeolite.

Chemical regeneration aims at desorbing ammonium ions, thus making the exchange sites of the zeolite available for new cations. For further research, determination of the most effective regeneration solution can be a valuable step. However, the main drawback of this process is the high costs of the chemicals. Therefore, optimisation of the regeneration step is necessary, in order to provide the satisfactory regeneration.

Finally, analysing the fertiliser value of the exhausted zeolite by applying it onto fields might be interesting for the further agricultural use.

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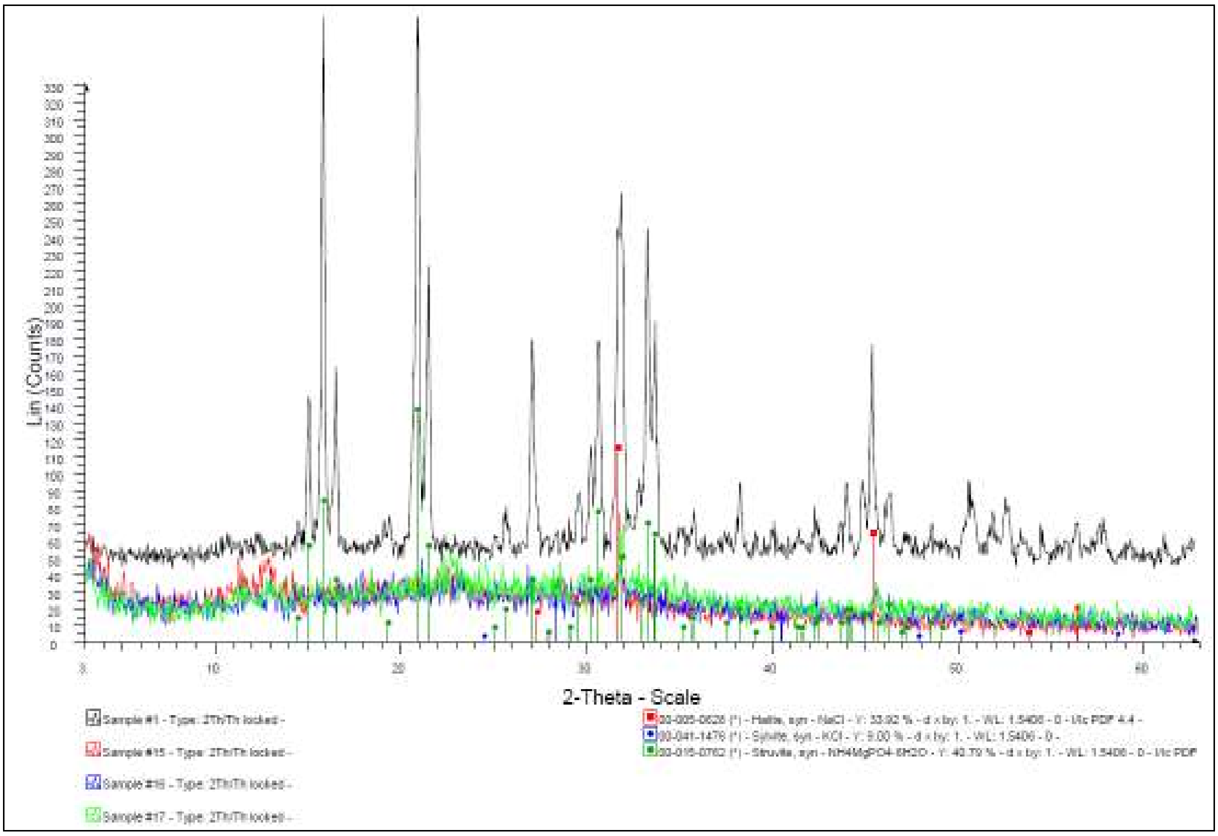
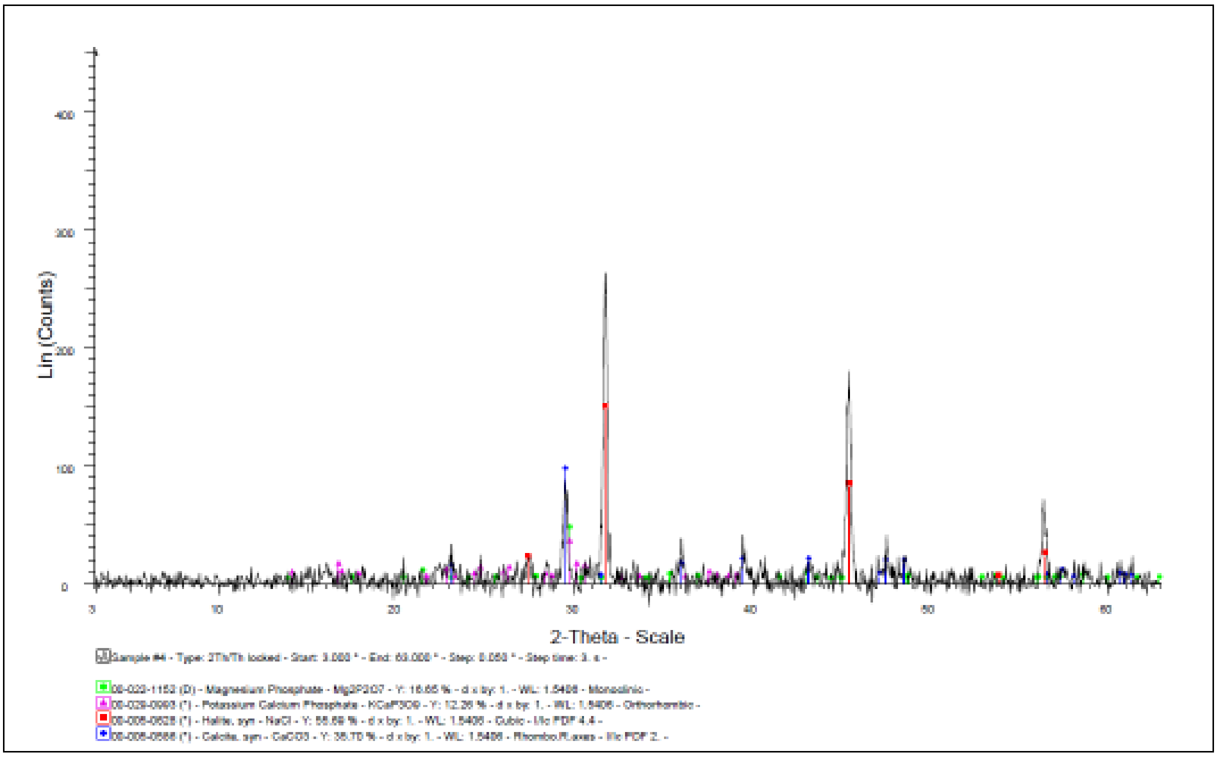
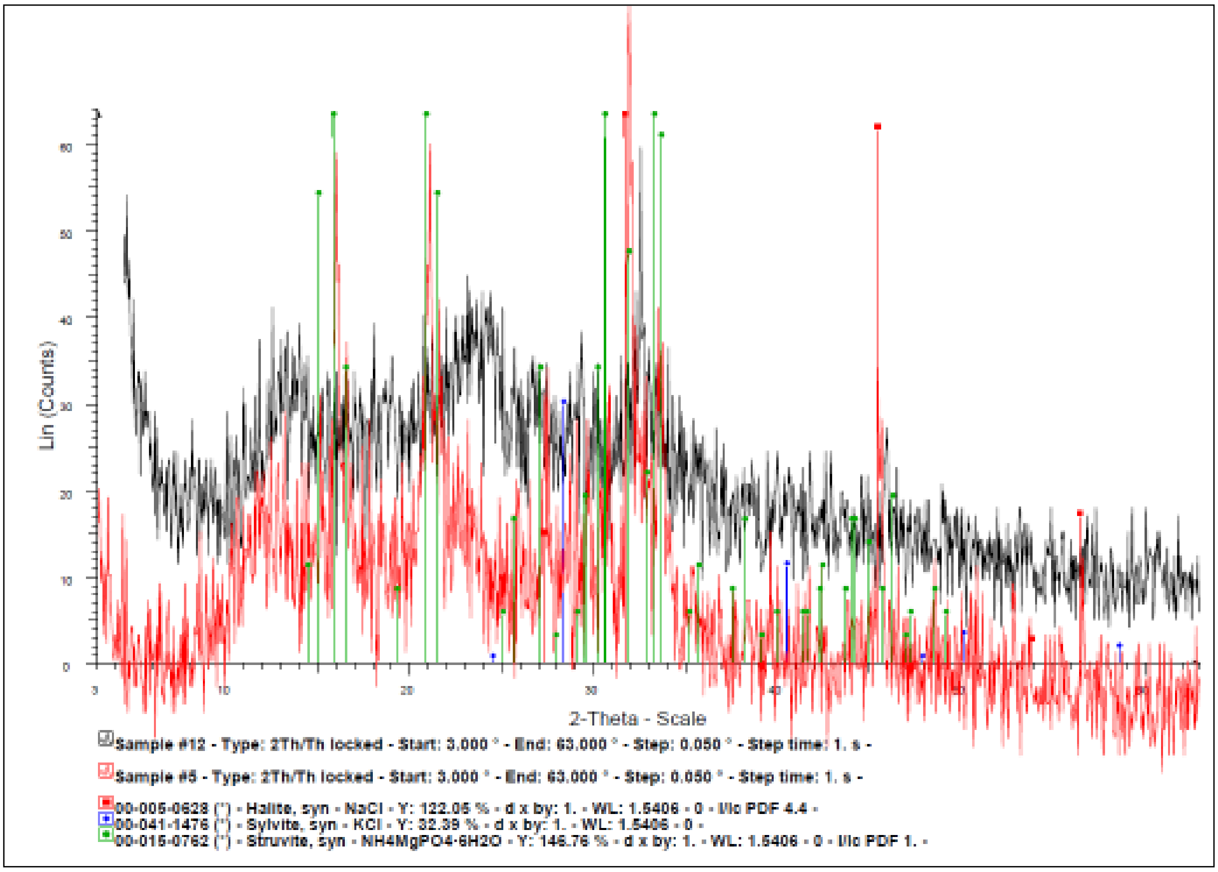
APPENDICES

1. Results of XRD analysis






Lin (Counts)
0
10
20
30
40
50
60
3
10
20
30
40
50
60
2-Theta - Scale
Sample #12 - Type: 2Th/Th locked - Start: 3.000 ° - End: 63.000 ° - Step: 0.050 ° - Step time: 1. s -
Sample #5 - Type: 2Th/Th locked - Start: 3.000 ° - End: 63.000 ° - Step: 0.050 ° - Step time: 1. s -
00-005-0628 (*) - Halite, syn - NaCl - Y: 122.05 % - d x by: 1. - WL: 1.5406 - 0 - I/Ic PDF 4.4 -
00-041-1476 (*) - Sylvite, syn - KCl - Y: 32.39 % - d x by: 1. - WL: 1.5406 - 0 -
00-015-0762 (*) - Struvite, syn - NH4MgPO4·6H2O - Y: 146.76 % - d x by: 1. - WL: 1.5406 - 0 - I/Ic PDF 1. -

Curriculum Vitae

Personal Information

Name and Surname: Öznur Alp
Date and Place of Birth: November 29, 1981
in Adana, Turkey
Nationality: Turkish
Marital Status: Single

Education

03/2006 – 02/2009	**Hamburg University of Technology (TUHH)**, Institute of Wastewater Management and Water Protection, Germany Ph.D. Student with a 3-year scholarhip from the Federal Ministry of Education and Research (BMBF) Topic: "Further Treatment of Digested Blackwater for Extraction of Valuable Components and Conversion to Dry Matter"
09/2003 – 08/2005	**Yildiz Technical University**, Istanbul, Turkey M.Sc. in Analytical Chemistry
09/1999 – 07/2003	**Yildiz Technical University**, Istanbul, Turkey B.Sc. in Chemistry
09/1995 – 06/1999	**Danisment Gazi Super Lycee**, Adana, Turkey Intensive courses: Mathematics and Natural Science

Career-Related Experiences

Since 03/2009	**JUMO GmbH & Co. KG,** Fulda, Germany Product Manager Analytical Measurement and Market Segment Manager „Water and Wastewater Technologies“
08/2004 – 04/2005	**Hamburg University of Technology (TUHH)**, Institute of Wastewater Management and Water Protection, Germany Research studies for master thesis within the international EU project EMWater
07/2002 – 09/2002	**Karlsruhe Research Center (FZK)**, Water Technology and Geotechnology Division, Karlsruhe, Germany Internship within the framework of the international project
07/2001 – 08/2001	**Quality Control Laboratory of Mustafa Nevzat Pharmaceutical Company**, Istanbul, Turkey Laboratory internship

Other Work Experiences

07/2005 – 01/2006	Miro Textile and Hosiery Company, Istanbul, Turkey - Export customer service representative

Trainings and Workshops

02/2008, Coimbatore **India**	"Resources Oriented Sanitation (EcoSan) Workshop", organized by the International Water Association (IWA) Specialist Group
09/2007, Hennef **Germany**	“Young Scientists’ and Professionals’ Programme (Meet the German Water Industry)”, organized by the German Association Wastewater and Waste (DWA)
06/2007, Bologna **Italy**	“4th Regional Training Course on Wastewater Management and Treatment” in the framework of the EMWater Project
04/2003, Bursa **Turkey**	Applications of Atomic Spectrometry, organized by the Scientific and Technological Research Council of Turkey (TÜBİTAK) Bursa Test and Analysis Laboratory

Honorary Works

09/2003	Organization committee of the “2nd Black Sea Basin Conference on Analytical Chemistry”, Istanbul, Turkey
10/2002	Organization committee of the “5th International Conference on Chemical Physics”, Istanbul, Turkey
09/2001 – 02/2002	Vice-president of the Yildiz Technical University Student Council, Istanbul, Turkey
09/2001 – 02/2002	Delegate of the Chemistry Department of the Yildiz Technical University, Istanbul, Turkey

Society Memberships

Since 09/2008	International Water Association (IWA)
Since 01/2006	German Association for Water, Wastewater and Waste (DWA)

Skills

Languages	Turkish: Mother tongue English: Fluent in speaking, writing and reading German: Fluent in speaking, writing and reading
Computer	MS-Office Applications (Word, Excel, PowerPoint, Outlook)