



**Ministry of Environment  
and Food of Denmark**  
Environmental  
Protection Agency

# **Improving phosphorus recovery by supplementing wastewater treatment with electro dialysis**

MUDP report

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Editors: Benjamin Ebbers (DTU Byg),  
Henrik R. Andersen (DTU Miljø),  
Pernille E. Jensen (DTU Byg),  
Lisbeth M. Ottosen (DTU Byg)

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Sources must be acknowledged.

# Content

<b>1.</b>	<b>Summary</b>	<b>4</b>
<b>2.</b>	<b>Introduction</b>	<b>6</b>
2.1	Motivation for the project	6
2.2	Electrodialysis during wastewater treatment	7
2.3	Combining electrodialysis with biological processes	9
2.4	Project objective	10
2.5	Project layout	11
<b>3.</b>	<b>Batch experiments</b>	<b>12</b>
3.1	Materials and methods	12
3.1.1	Sampling primary and secondary sludge	12
3.1.2	Sample preparation for influence of acetate concentration	12
3.1.3	Sample preparation for influence of volatile fatty acids created by hydrolyzed primary sludge	13
3.1.4	Sample preparation and analytical methods	14
3.2	Results and discussion	15
3.2.1	Influence of Acetate Concentration	15
3.2.2	Influence of VFA's created by hydrolyzed primary sludge	16
3.2.3	UV-254nm absorbance (DOM) versus TOC	16
3.2.4	Summary from batch experiments	17
<b>4.</b>	<b>Lab-scale electro dialytic experiments</b>	<b>19</b>
4.1	Materials and methods	19
4.1.1	Preparation of artificial solution	19
4.1.2	Laboratory scale electro dialytic cell setup	20
4.1.3	Results and discussion	20
4.1.4	Summary from lab scale ED	21
<b>5.</b>	<b>Bench-scale experiments</b>	<b>22</b>
5.1	Materials and methods	23
5.1.1	Sampling of secondary sludge and preparation of phosphorus rich solution	23
5.1.2	Bench-scale electro dialytic experiments	23
5.1.3	Sample preparation for analyses	24
5.2	Results and discussion	24
5.3	Summary from bench scale experiments	30
5.4	Recommendations	30
<b>6.</b>	<b>Conclusions</b>	<b>32</b>

# 1. Summary

The Danish government aims to recover 80% of all phosphorus from municipal sludge by 2018, either through usage of biosolids or by phosphorus recovery technologies. Current (Danish) wastewater treatment is not sufficient to meet these demands as a large part of the phosphorus that enters the wastewater treatment plant (WWTP) is removed via a combination of biological and chemical processes. The main chemical process, also known as chemical coagulation, strongly binds the phosphorus to the sludge, rendering its usage as fertilizer virtually impossible without pretreatment using strong acids.

The overall aim of this study is to investigate the usage of electrodialysis, in combination with biological wastewater treatment to obtain a phosphorus extraction method, which is energy efficient and applicable in existing wastewater treatment plants. Electrodialysis is based on applying an electric field and combined with a set of ion exchange membranes, the electric field transports and concentrates phosphorus from the wastewater, and has not previously been used for this purpose.

Initial experiments previous to the this project showed that the amount of organic matter encountered in wastewater can be detrimental for the membranes used during electrodialysis. The problem is fouling, which is clogging of the membrane. Consequently, this results in a relatively low cost-effectiveness of the technique. However, with recent developments and a new methodology tested in the present project it is hypothesized that phosphorus can be extracted from wastewater while organic matter contents are kept low. The new step added to electrodialysis is stimulating the secondary sludge under anaerobic conditions using volatile fatty acids (VFA's) to mobilize phosphorus.

The study consists of three parts:

- (I) Batch experiments were conducted to investigate optimal conditions, for example VFA addition through primary sludge or sodium acetate, which would result in the highest release of phosphorus from secondary sludge while keeping the organic matter content low,
- (II) Lab-scale electro-dialytic experiments were conducted to investigate the experimental benefit of preferential extraction of mono- or multivalent cations
- (III) Bench-scale electro-dialytic experiments were conducted where a phosphorus rich solution, obtained from anaerobically treated secondary sewage sludge, was subjected to electro-dialytic extraction.

From the batch experiments, it was concluded that the phosphorus rich solution to be used in the benchscale electro-dialytic experiments can best be created using sodium acetate. In the timespan of the experiments it was the most readily available source of VFA's, compared to hydrolyzed primary sludge, which would release the highest amount of phosphorus in the shortest time.

The regular multivalent cation exchange membranes were used in the bench-scale experiments as the preferential flow of cations over the monovalent cation exchange membrane was not significant enough to warrant the investment.

The highest phosphorus extraction over the least amount of time was observed when using a current density of  $1.0 \text{ mA}\cdot\text{cm}^2$  compared to a current density of  $0.25 \text{ mA}\cdot\text{cm}^2$ . However, the

most optimal conditions of extracting phosphorus was observed under a current density of  $0.25 \text{ mA}\cdot\text{cm}^2$  with a flow speed of  $800 \text{ ml}\cdot\text{min}^{-1}$  as opposed to a flow speed of  $400 \text{ ml}\cdot\text{min}^{-1}$ . This is likely due to the smaller size of the orthophosphate molecules as compared to the organic matter molecules, which therefore, using a higher flowrate are more easily influenced by the electric field and extracted from the solution.

Even though the concentration of phosphorus in the bench-scale experiments was relatively low, approximately  $16 \text{ mg/l}$  compared to  $55$  to  $80 \text{ mg/l}$  in the batch experiments, a concentration from  $16 \text{ mg/l}$  in the wastewater to  $35 \text{ mg/l}$  in the concentrate was obtained. This even about 70% phosphorous was attached to the thin layer of organic matter fouling the anion exchange membrane. Optimization will improve power consumption, which in the current experiments was  $12 \text{ kWh/m}^3$  at best.

## 2. Introduction

### 2.1 Motivation for the project

By 2018 the Danish Government aims to recover 80% of all phosphorus from municipal sludge, either through usage of biosolids or by phosphorus recovery technologies (Miljøministeriet, 2013). However, the current Danish wastewater treatment is insufficient to meet those demands.

With current technology a large part of the phosphorus that enters the wastewater treatment plant (WWTP) is removed via a combination of biological and chemical processes. The main biological process is the uptake of phosphorus through microorganisms. During biological treatment the wastewater is subsequently exposed to anaerobic (without air/oxygen) and aerobic (with air/oxygen) in cycles in order to stimulate the uptake of phosphate by the microorganisms. Biological uptake alone however, is generally not enough to bring the phosphorus concentrations in the effluent below legislative values. For this reason, manually induced chemical precipitation is used. The most common method for chemical precipitation is based upon chemical coagulation with iron- or aluminum. When iron and aluminum salts are dissolved in the wastewater, the released iron and aluminum ions precipitate together with the soluble phosphorus (ortho-phosphate or  $H_xPO_4^{x-3}$ ) as insoluble iron- or aluminum coagulates ( $FePO_4/AlPO_4$ ) in the sludge.

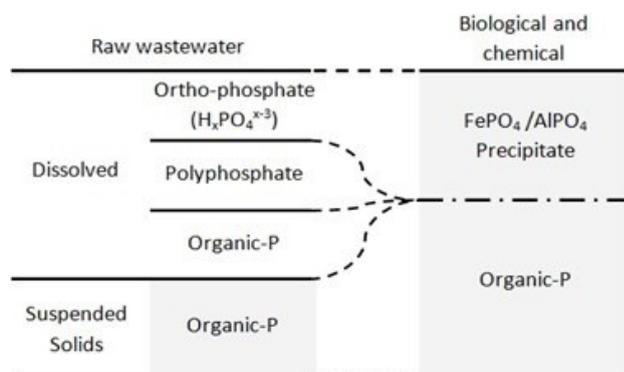


Figure 1: THE CHEMICAL STATE OF PHOSPHORUS AS IT ARRIVES IN THE WASTEWATER TREATMENT PLANT (RAW WASTEWATER) TO THE CHEMICAL STATE WITH WHICH PHOSPHORUS LEAVES THE WASTEWATER TREATMENT PLANT AFTER BIOLOGICAL AND CHEMICAL TREATMENT.

Although some studies reason that poor recovery of phosphorus from this sludge is simply due to the lack of understanding of the chemical processes occurring during wastewater treatment (Wilfert, et al., 2015), it remains a fact that the addition of iron- or aluminum salts during wastewater treatment results in a lower phosphorus fertilization value, meaning availability of phosphorus to plants. This goes for both the sludge (Samie & Römer, 2001) (Krogstad, et al., 2005) and, upon incineration, the sewage sludge ash (SSA) (Schipper, et al., 2001) (Franz, 2008). In order to mobilize phosphorus from this type of sludge (ash), exposure to strongly acidic or alkaline conditions is necessary (Cheung, 1988) (Hong, et al., 2005) (Biswas, et al., 2009) (Oliver & Carey, 1976) (Levlin, et al., 2003) (Xu, et al., 2012) (Stark, et al., 2006) (Ottosen, et al., 2013) (Cohen, 2009) (Donatello, et al., 2010) (Takahashi, et al., 2001).

Furthermore, in particular when using only biological processes to bind phosphorus, unwanted phosphorus deposits occur in the wastewater treatment plant, as for example the precipitation of struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ). Struvite will precipitate under the right conditions, with high enough phosphorus, ammonium, magnesium concentrations and in the presence of hydroxides (Metcalf & Eddy, Inc., 2002). These conditions are generally met after anaerobic digestion and results in the undesired precipitation of struvite in pumps and pipes, causing severe damage to the technical installations.

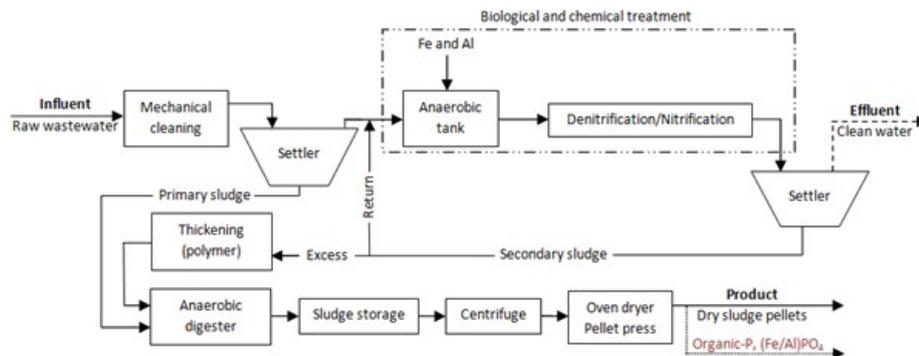


FIGURE 2. A SCHEMATIC DRAWING OF THE DANISH BJERGHOLM WWTP SYSTEM LAYOUT OPERATED BY ROSKILDE FORSYNING A/S. BOTH BIOLOGICAL AND CHEMICAL TREATMENT METHODS ARE USED TO TREAT WASTEWATER. EXCESS, SECONDARY, SLUDGE IS THICKENED BY THE USE OF POLYMERS BEFORE ANAEROBICALLY DIGESTED, CENTRIFUGED AND DRIED. MOST PHOSPHORUS IS REMOVED WITH THE SLUDGE PRODUCT IN THE FORM OF ORGANIC PHOSPHORUS (ORGANIC P) AND IRON/ALUMINUM-PRECIPITATES  $(\text{Fe/Al})\text{PO}_4$ .

In summary, biological processes alone are not sufficient to achieve complete removal of phosphorus from wastewater and additional chemical coagulation processes render phosphorus virtually unusable as fertilizer. The solution to this problem suggested in the present investigation is to supplement biological uptake of phosphorus with electro-dialytic removal during wastewater treatment.

## 2.2 Electrodialysis during wastewater treatment

Electrodialysis utilizes an electrical DC current in combination with ion-exchange membranes to extract and concentrate ions and charged molecules from a medium, in this case wastewater. Under the influence of the applied electric field and depending on their respective charge, ions and charged molecules will migrate to the anode (positive electrode) and cathode (negative electrode) as shown in Figure 3, exemplified with Cu and Cl. The anode and cathode compartments are separated from the central compartment with treated wastewater by anion- and cation-exchange membranes. After extraction, ions are concentrated in the electrolyte solutions at the electrodes. Phosphorous will concentrate in the anolyte, where to it is transported in the electric field as negatively charged phosphate.

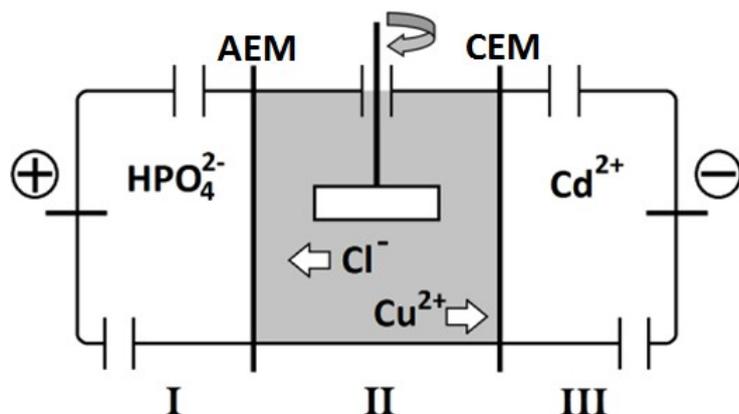


FIGURE 3. SCHEMATIC DRAWING OF A LABORATORY SCALE 3 COMPARTMENT ELECTRODIAL SETUP USED IN PHOSPHORUS EXTRACTION EXPERIMENTS. THE STIRRED WASTEWATER (CO II) IS SEPARATED FROM THE ANODE (COMPARTMENT I) AND CATHODE (COMPARTMENT III) BY EXCHANGE MEMBRANE (AEM) AND CATION-EXCHANGE MEMBRANE (CEM) RESPECTIVELY.

Electrodialysis is a well developed treatment method previously used in the remediation of heavy metal polluted media such as industrial waste streams, soils, sediments and sewage sludge ashes (SSA) (Jakobsen, et al., 2004) (Ottosen, et al., 2009). More recently, with the treatment of SSA, the focus of the technique has also broadened to the direct recovery of phosphorus and simultaneous separation of heavy metals.

Electrodialysis has previously been applied to extract phosphorus from wastewater (Fukumoto & Haga, 2014) (Pronk, et al., 2006) (Keeley, et al., 2012). However, phosphorus concentrations in the wastewater were often too low for the method to be cost-efficient (Rulkens, 2008) (Rulkens, 2009) (Keeley, et al., 2012). Whenever phosphorus concentrations were high enough for efficient extraction by ED, for example after anaerobic digestion (Figure 2), the amount of organic matter (OM) in the wastewater becomes problematic. Due to dissociation of organic acids, OM generally has a negative surface charge, meaning that it will be influenced by the electric field created during ED and transported by the mechanism named electrophoresis. The electric field and negative surface charge of OM will cause OM particles to be transported towards the anode. However, OM particles are too large to pass through the anion-exchange membrane and will inherently clog the membrane pores (membrane fouling) (Figure 4), increasing the (electrical) resistance which translates into a rise in energy usage and cost (Jakobsen, et al., 2004).



FIGURE 4. FOULING AND SUBSEQUENT BURNING OF AN ANION-EXCHANGE MEMBRANE BY TRANSPORT OF ORGANIC MATTER ONTO THE SURFACE AND INTO THE PORES.

### 2.3 Combining electrodialysis with biological processes

For electrodialysis to be effective for phosphorous recovery, it is of key importance to have considerable phosphorus concentrations in the wastewater while keeping organic matter content low in order to reduce or prevent membrane fouling (Cornel & Schaum, 2009). A relatively high phosphorus concentration combined with relative low organic matter content can be achieved by stimulating release of phosphorus from secondary sludge using volatile fatty acids (VFA's) under anaerobic conditions. Extracting phosphorus from the resulting liquid phase of the sludge will result in less fouling of the membranes as was seen in preliminary experiments previously to this project (Figure 5), and subsequently higher efficiency of phosphorus extraction

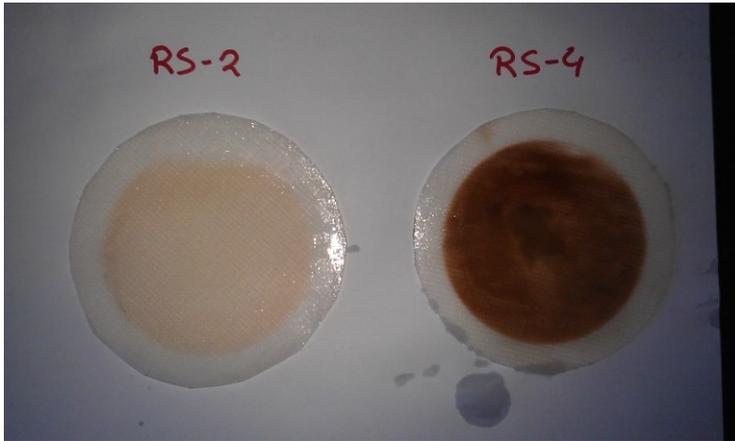


FIGURE 5. THE CATION EXCHANGE MEMBRANE (CEM) AFTER A LABSCALE EXPERIMENT EXTRACTING FROM THE LIQUID PHASE OF TREATED SECONDARY SLUDGE (RS-2) AND THE LIQUID PHASE OF ANAEROBIC DIGESTIVE (RS-4) WHICH HAS A HIGH PHOSPHORUS CONCENTRATION (> 100 mg/l) BUT ALSO A HIGH ORGANIC MATTER CONTENT IN THE LIQUID PHASE.

During biological treatment, under *aerobic conditions* (in the presence of electron acceptors such as oxygen or nitrate), microorganisms produce energy through oxidation of carbon sources (Metcalf & Eddy, Inc., 2002) (Henze, et al., 2002). This can occur through the metabolism of easily accessible carbon sources, such as previously stored polyhydroxybutyrate (PHB). PHB is a product from the assimilation by microorganisms of VFA's such as acetate or propionic acid. These VFA's are products from the fermentation of soluble organic matter under anaerobic conditions. Part of the energy released by the metabolism of PHB and most of the carbon, is used for cell growth in the microorganisms. The other part of the energy is stored in the microorganism as energy reserve through the formation of polyphosphate. This is achieved by accumulation of soluble orthophosphate ( $\text{PO}_4^{3-}$ ) from wastewater. This uptake is in particular significant in so-called phosphorus accumulating organisms.

Under *anaerobic conditions*, VFA's (e.g. acetic and propionic acid), produced from the fermentation of dissolved degradable organic material, are assimilated by phosphorus accumulating organisms through the energy available from polyphosphates stored during aerobic conditions. This assimilation of VFA's produces intracellular PHB storage products. During the assimilation, the polyphosphates are released as orthophosphate ( $\text{H}_x\text{PO}_4^{x-3}$ ) into the liquid phase in concentrations up to 100 mg/l together with magnesium, potassium and calcium (Metcalf & Eddy, Inc., 2002).

The orthophosphate released under anaerobic conditions can then in turn be extracted from the liquid fraction of the wastewater using electrodialysis. A benefit of the removal of phosphorus from wastewater through a combination of biological processes and electrodialysis, instead

of a combination of biological and chemical processes, is that a concentrated phosphorus stream can be obtained while maintaining phosphorus availability in the resulting sludge (figure 6) maintaining the fertilizer value. A suggestion for building in such treatment in a WWT plant is exemplified in figure 7 with Bjermarken WWT plant in Roskilde.

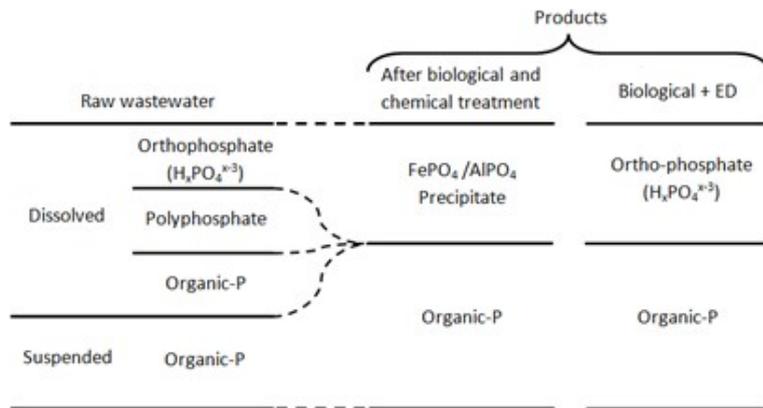


FIGURE 6. THE CHEMICAL STATE OF PHOSPHORUS AS IT ARRIVES IN THE WASTEWATER TREATMENT PLANT (RAW WASTEWATER) TO THE CHEMICAL STATE IN WHICH PHOSPHORUS LEAVES THE WASTEWATER TREATMENT PLANT AFTER BIOLOGICAL AND CHEMICAL TREATMENT AS WELL AS A COMBINATION OF BIOLOGICAL AND ELECTRODIALYSES.

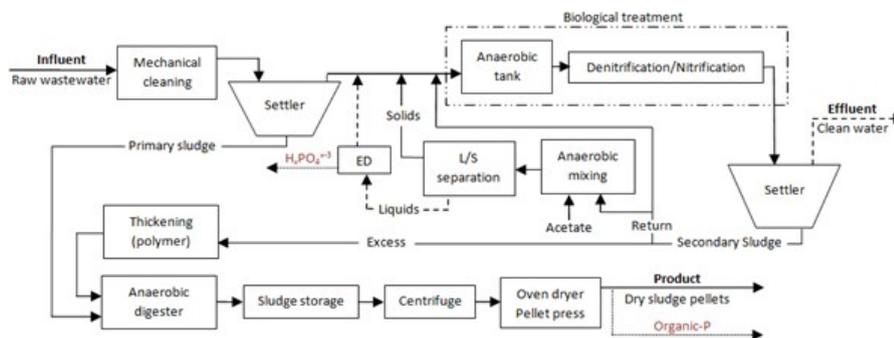


FIGURE 7. A SCHEMATIC DRAWING OF THE DANISH BJERGMARKEN WWT SYSTEM LAYOUT WHERE VFA'S ARE ADDED UNDER ANAEROBIC CONDITIONS TO A SIDE-STREAM OF THE SECONDARY SLUDGE THAT WOULD NORMALLY BE RETURNED DIRECTLY TO THE BIOLOGICAL TREATMENT (RETURN). LIQUIDS AND SOLIDS ARE SEPARATED (L/S SEPARATION) AND THE PHOSPHORUS RICH LIQUID IS TREATED USING ED (ED), OBTAINING CONCENTRATED ORTHOPHOSPHATE SOLUTION ( $H_xPO_4^{x-3}$ ).

## 2.4 Project objective

The overall aim of this study is to investigate the effectiveness of the new idea of recovering phosphorus from wastewater by combining the biological processes stimulating phosphorous release and electrodiolytic recovery and estimate the power consumption for such process.

## **2.5 Project layout**

The experimental work was separated into three parts: batch experiments (chapter 3), lab-scale electrodiolytic experiments (chapter 4) and benchscale electrodiolytic experiments (chapter 5).

Batch experiments were conducted to investigate optimal conditions, which would result in the highest release of phosphorus from secondary sludge by stimulation using VFA's under anaerobic condition, while simultaneously keeping the organic matter content low.

Lab-scale electrodiolytic experiments were conducted to investigate the experimental benefit of preferential extraction of mono- or multivalent cations, using mono or multi valent cation exchange membranes.

Based upon the results of these experiments, larger, benchscale electrodiolytic experiments were designed and conducted where a phosphorus rich solution, obtained from anaerobically treated secondary sewage sludge, was subjected to electrodiolytic extraction. Different currents and flow speeds were tested in order to find the optimal conditions, meaning highest phosphorus extraction against the lowest energy cost.

# 3. Batch experiments

Batch experiments were conducted to investigate optimal conditions that would result in the highest release of phosphorus from secondary sludge, obtained from the Bjergmarken Renseanlæg, Denmark, (Figure 8), while at the same time keeping the organic matter content low. Next to the availability of oxygen, the main parameter determining the release or uptake of phosphorus from phosphorus accumulating organisms under anaerobic conditions is the presence of volatile fatty acids. Dry matter, which at this stage in the wastewater treatment process can be considered an indication of the total amount of (active) microorganisms in the sludge (Metcalf & Eddy, Inc., 2002), was measured by the wastewater treatment plant. The pH of the sludge was monitored during the batch experiments. The pH of the solution was not manually changed as the optimal pH for phosphorus release under anaerobic conditions was already present in the collected sludge samples (pH ~ 7) (Metcalf & Eddy, Inc., 2002).



FIGURE 8. AERIAL VIEW OF THE BJERGMARKEN RENSEANLÆG (WASTEWATER TREATMENT PLANT) OPERATED BY ROSKILDE FORSYNING A/S, THE MAIN LOCATION WHERE SAMPLES FOR THE EXPERIMENTS IN THIS STUDY WERE OBTAINED.

## 3.1 Materials and methods

### 3.1.1 Sampling primary and secondary sludge

Primary sludge, with a dry matter content of around 3.2%, was sampled in a 10 liter jerry can from the Bjergmarken WWTP, ran by Roskilde Forsyning A/S. The sludge was hydrolyzed by sealing the jerry can air tight, creating anaerobic conditions, and allowing an incubation under room temperature for 48 hours.

Secondary sludge, with a dry matter content of around 1.82%, was sampled using 25 liter jerry cans from the Bjergmarken WWTP, while the sludge was aerated (see Figure 2, 'nitrification/denitrification'). Due to the aerobic conditions, most of the phosphate in the secondary sludge was bound within the phosphorus accumulating organisms in the sludge.

### 3.1.2 Sample preparation for influence of acetate concentration

#### Samples of 500 ml secondary

sludge were transferred to 500 ml plastic bottles. Sodiumacetate (99.9% pure) in concentrations of 1.0 and 2.0 g/l were added to 14 bottles; two sets

with 7 bottles for each concentration. For comparison, another set of 7 bottles with secondary sludge and no sodium acetate were included.

The bottles were capped and mixed thoroughly, by turning over the bottles by hand. Hereafter the samples remained stationary for different durations (one sample from each set at each duration) 0, 1, 2, 3, 4, 6 and 8 hours. After their respective reaction time, the sludge samples were transferred to 500 ml containers, which were centrifuged at 4500 RPM for 5 minutes to separate the solid and liquid phases of the sludge. The liquid phase was decanted and mechanically filtered (pore-size 0.45  $\mu\text{m}$ ).

The samples were analyzed for the following parameters using the following techniques:

- |                                                                               |                                                                           |
|-------------------------------------------------------------------------------|---------------------------------------------------------------------------|
| - P, Al, Fe, Ca K, Mg and Na concentrations                                   | using inductively coupled plasma optical emission spectrometry (ICP-OES); |
| - $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{NO}_3^-$ and $\text{PO}_4^{3-}$ | using Ion Chromatography (IC);                                            |
| - Dissolved organic matter (DOM)                                              | using UV-254 nm absorption;                                               |
| - Total organic carbon (TOC)                                                  | using a Total Organic Matter Analyzer;                                    |
| - pH and conductivity                                                         | using a radiometer analytical electrode.                                  |

The procedures are described in 3.1.4

### 3.1.3 Sample preparation for influence of volatile fatty acids created by hydrolyzed primary sludge

Preparing samples for influence of volatile fatty acids on the phosphorous release and TOC created by hydrolyzed primary sludge, 500 ml samples of secondary sludge were transferred to 500 ml plastic bottles. Hydrolyzed primary sludge was added to 20 bottles in amounts of 0, 25, 50, and 100 ml, 5 bottles for each concentration. The bottles were capped and after mixing thoroughly, turning over the bottles by hand. Hereafter the samples remained stationary for 0, 2, 4, 8 and 24 hours (Figure 9).

After their respective reaction time, the sludge samples were transferred to 500 ml containers, which were centrifuged at 4500 RPM for 5 minutes to separate the solid and liquid phases of the sludge. The liquid phase was decanted and mechanically filtered (pore-size 0.45  $\mu\text{m}$ ). The samples were analyzed for the above (chapter 3.1.2) described parameters.



FIGURE 9. THE 4 BOTTLES OF SECONDARY SEWAGE SLUDGE AFTER 24 HOURS CONTAINING 0, 25, 50 AND 100 ML OF 48 HOUR HYDROLYZED PRIMARY SLUDGE.

### 3.1.4 Sample preparation and analytical methods

#### *Total concentrations by ICP-OES*

After filtration, 20 ml of the liquid phase of each sample was transferred to a Teflon bottle where 5 ml of 1:1 HNO<sub>3</sub> was added. The bottles were heated to 200 kPa (120°C) for 30 minutes. The P, Al, Fe, Ca, K, Mg and Na concentrations were measured in the aqueous phase by ICP-OES. The samples were analyzed in duplicate.

#### *Anion concentrations in filtrate by IC*

After filtration, 20 ml of each wastewater sample was transferred into a plastic container, capped and analyzed for Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> using ion chromatography (IC).

#### *TOC and DOM*

The amount of organic matter in the liquid phase was determined using two different methods: (I) determination of dissolved organic matter (DOM) and (II) determination of the amount of non-purgabele organic carbon (NPOC).

The first method was the determination of dissolved organic matter (DOM) in the liquid sample through UV absorbance measurements at 254 nm. Light with a wavelength of 254 nm is absorbed by organic compounds, specifically aromatic, in water samples. Before and after filtration, 5 ml of the samples were transferred to a plastic cuvet with a width of 1 cm. Light with a 254 nm wavelength was passed through the cuvet. The intensity of the attenuated light was measured and divided by a pure water measurement, before a logarithm is calculated. The measurement was reported as absorbance per path length (abs/cm). The higher the amount of DOM in the liquid, the higher the abs/cm will be. The spectrometer was calibrated using a cuvet filled with milli-Q-water.

The second method of determining the amount of organic matter in the liquid phase was through determining the amount of non-purgabele organic carbon (NPOC). After filtration, the liquid samples were diluted 10 times by transferring 3 ml sample, using an eppendorf pipette, to a glass tube, which was then filled up to 30 ml using milli-Q-water. Two droplets of 17% phosphoric acid were added, decreasing the pH to 2 or 3, in order to conserve the organic matter. This also removed carbonic acid, which is in equilibrium with carbon dioxide (CO<sub>2</sub>). A cap was added to the tube, which was subsequently mixed by turning over the glass tube several times. Using a Shimadzu Total Organic Carbon Analyzer TOC-vwp with auto sampler the samples were analyzed for NPOC. Inside the Shimadzu TOC analyzer, the solution was first sparged for 3 minutes using nitrogen gas, stripping the CO<sub>2</sub> from the water phase and eliminating the inorganic carbon (IC) component. The total carbon (TC) remaining in the sample after sparging is called the NPOC. When the total amount of volatile organic substances (benzene, toluene, chloroform, etc.) in the solution is low, which is generally the case for natural environmental water, public water and purified water, the NPOC can be considered a measure for the total organic carbon (TOC). After stripping the CO<sub>2</sub>, the oxidation reagent (a solution 60 gram sodium persulfate and 15 ml (85%) phosphoric acid brought up to a volume of 500 ml using milli-Q-water) is added. The remaining organic carbon is converted to CO<sub>2</sub> and measured by an infra-red detector.

The first method (UV-254nm absorbance) requires relatively little effort compared to the second method (TOC). During the batch experiments, both parameters were measured. After the experiments, both parameters were compared in order to investigate if a trend between both parameters could be established for wastewater, allowing for quicker measurements of the amount of organic matter through UV-254nm absorption.

## 3.2 Results and discussion

### 3.2.1 Influence of Acetate Concentration

Phosphorus release from secondary sludge under anaerobic conditions was observed to be highest when adding sodium acetate in concentrations of 1.0 and 2.0 g/l (Figure 10). This is comparable to the release as described in literature (Metcalf & Eddy, Inc., 2002). The pH of the solution remained relatively constant, whereas the conductivity changed according to the amount of sodium acetate added to the sludge. An increase of organic matter in the liquid phase of the sludge was also observed in the TOC, but less so in the UV-254nm absorption.

The latter can be explained by the fact that acetate is not aromatic and will not absorb light at the UV-254 nm wavelength as efficiently.

Over time, both TOC and UV-254 increased in a linear trend, confirming that organic matter was released from the microorganisms under anaerobic conditions. After approximately 4 to 6 hours, the highest amount of phosphorus was released from the secondary sewage sludge for both the 1.0 and 2.0 g/l sodium acetate concentrations. Since organic matter is continuously released after this point in time, as observed by the continuous increase in TOC and UV-254 nm absorption, 4 to 6 hours of experimental seems to be the most optimal duration of the secondary sludge incubation, to avoid high organic matter concentrations.

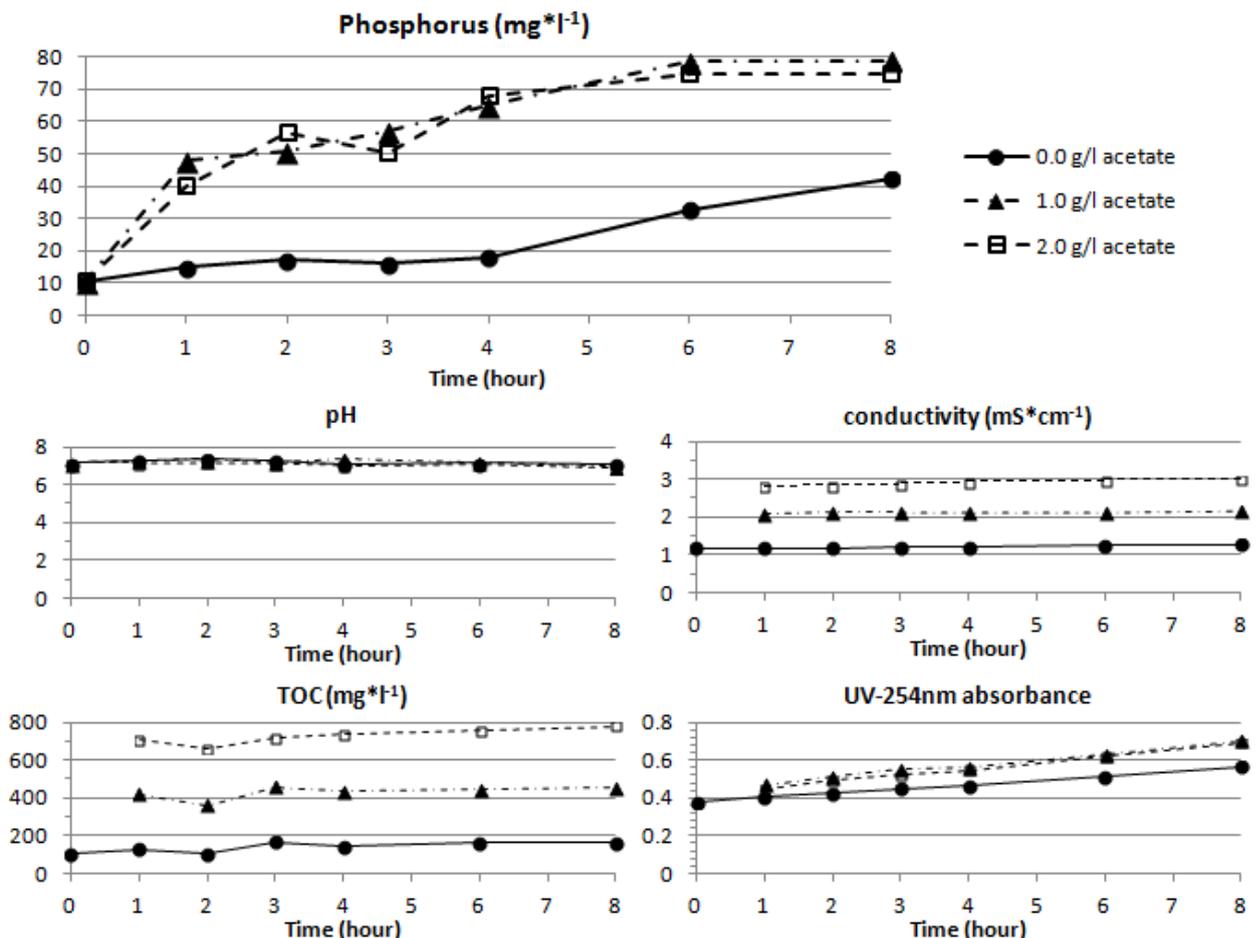


FIGURE 10. THE PHOSPHORUS CONCENTRATION ( $\text{mg/l}$ ), pH, CONDUCTIVITY, TOC ( $\text{mg/l}$ ) AND UV-254 ABSORBANCE IN THE LIQUID PHASE OF THE (SODIUM) ACETATE STIMULATED SECONDARY SLUDGE, SODIUM ACETATE CONCENTRATIONS OF 0.0, 1.0 AND 2.0 g/l AFTER CENTRIFUGATION AND FILTRATION VERSUS TIME.

### 3.2.2 Influence of VFA's created by hydrolyzed primary sludge

The fastest phosphorus and highest release from secondary sludge using hydrolyzed primary sludge occurred when 100 ml of primary sludge was added to 500 ml of secondary sludge (PS-100) and incubated over 4 hours. These parameters, phosphorus release rate and concentration, decrease when lower amounts of hydrolyzed primary sludge are used.

The higher release of phosphorus in PS-100 is likely due to the fact that 100 ml of hydrolyzed primary sludge in total contains more VFA's. Furthermore, the remaining (active) microorganisms in the primary sludge will continue to produce more VFA's while the secondary sludge incubates than in a secondary sludge where less primary sludge was added.

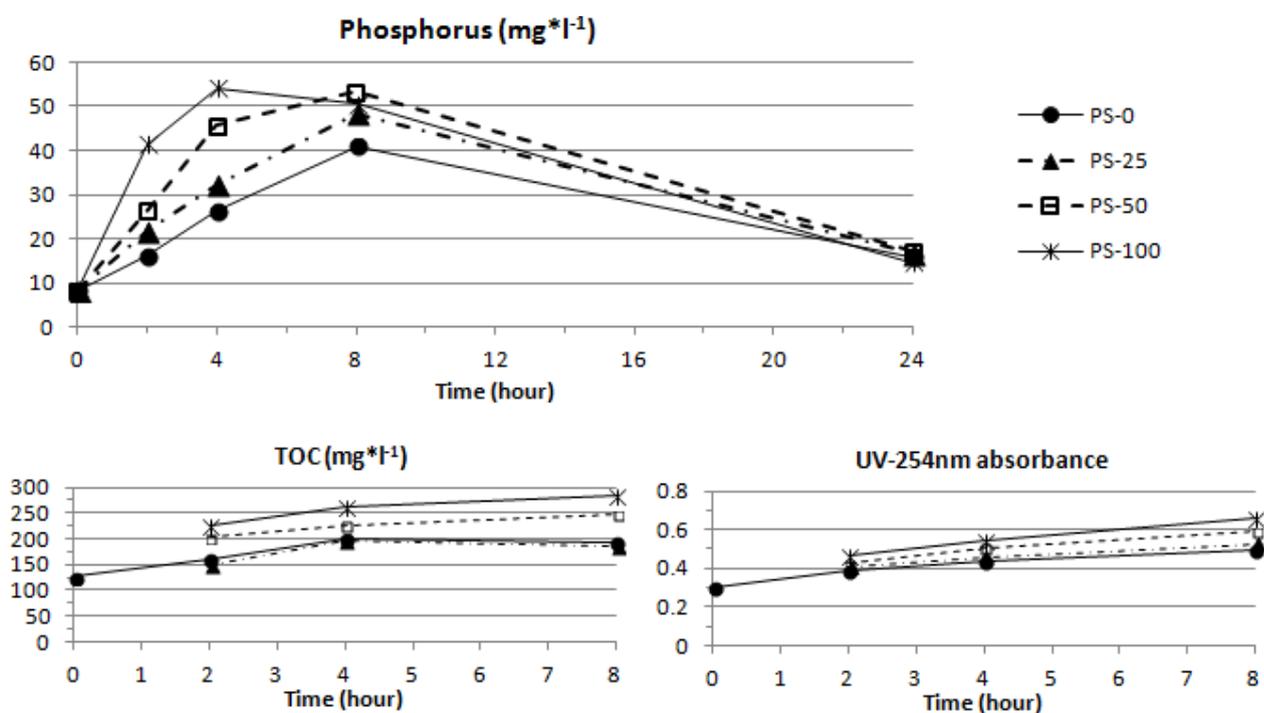


FIGURE 11. THE PHOSPHORUS CONCENTRATION (mg/l), TOC (mg/l) AND UV-254 ABSORBANCE IN THE LIQUID PHASE OF THE SECONDARY SLUDGE AFTER HYDROLYZED PRIMARY SLUDGE STIMULATED THE RELEASE OF PHOSPHORUS UNDER ANAEROBIC CONDITIONS VERSUS TIME.

Organic matter, measured by both TOC and UV-254nm absorbance, however, also increased with a higher amount of hydrolyzed primary sludge added (figure 11). An exception is observed in the case of 25 ml of hydrolyzed primary sludge (PS-25). Although TOC and UV-254nm increased over time in this experiment, they remained virtually similar to the secondary sludge where no hydrolyzed primary sludge was added (PS-0). After 8 hours of incubation, the concentration of phosphorus in the secondary sludge reaches a level similar to that of PS-100.

### 3.2.3 UV-254nm absorbance (DOM) versus TOC

There is a tendency for linear relationship between the TOC concentration in and the UV-254nm absorption (Figure 12) of the liquid phase of anaerobically stimulated secondary sludge. UV-254nm light is mainly absorbed by (aromatic) organic compounds, which are released into the liquid phase of the secondary sludge. Under anaerobic conditions there seems to be a release of aromatic organic carbon that has a linear correlation with the total amount of organic matter released.

The increase in the TOC concentration caused by the addition of the (sodium) acetate does not reflect strongly in the UV-254nm absorbance, due to the fact that acetate as organic matter is not aromatic in nature. If sodium acetate is used to stimulate the release of phosphorus from secondary sludge, however, a correction factor needs to be applied to account for the added carbon in the form of acetate.

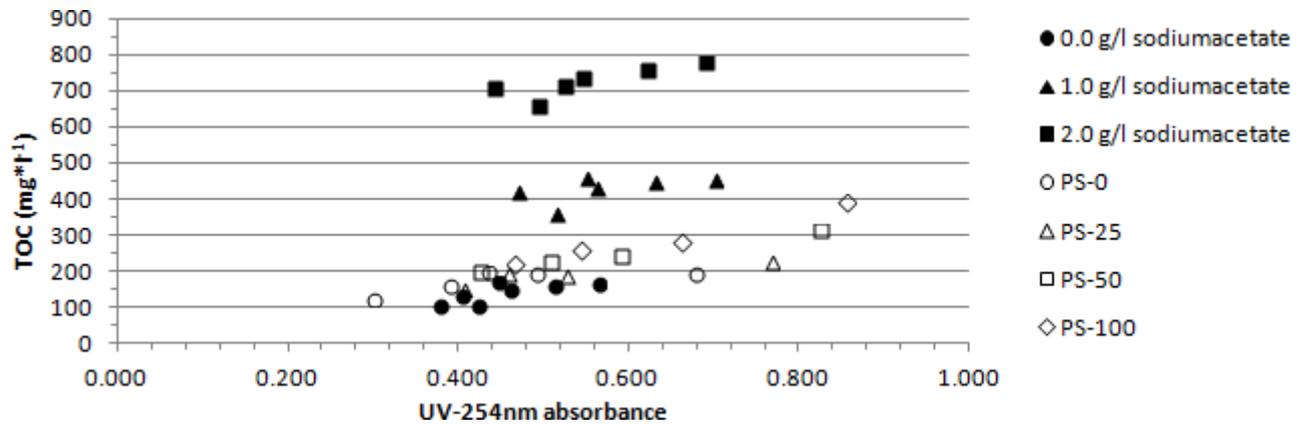


FIGURE 12. THE TOTAL ORGANIC CARBON (TOC) IN mg/l VERSUS UV-254NM ABSORBANCE IN ALL THE PREVIOUSLY DESCRIBED BATCH EXPERIMENTS.

Despite removing most (visible) organic matter from the liquid phase of the secondary sludge after centrifugation, flocks of organic matter still remained in the solution (Figure 13). This organic matter could be problematic to the next project phases as it may contribute to further fouling and decreasing of efficiency of phosphorus extraction during the electrodynamic experiments.

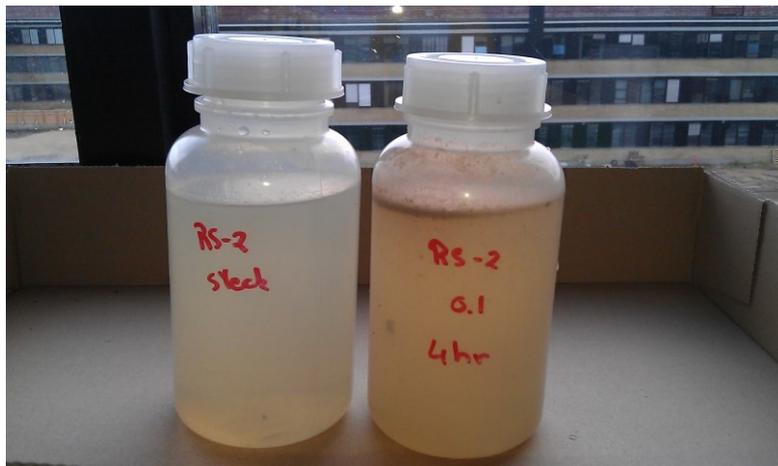


FIGURE 13. THE LIQUID PHASE OF 'FRESH' SECONDARY SLUDGE AFTER CENTRIFUGATION (RS-2 STOCK) AND THE LIQUID PHASE OF SECONDARY SLUDGE AFTER ADDITION OF 1.0 g/l (0.1 g/100 ml, 4 HOUR INCUBATION UNDER ANAEROBIC CONDITIONS AND CENTRIFUGATION (RS-2 0.1 4HR).

### 3.2.4 Summary from batch experiments

The most optimal conditions for the release of phosphorus from secondary sludge, when sodium acetate is used as volatile fatty acid source, was when 1.0 g/l of sodium acetate was added to the sludge and it has incubated under anaerobic conditions for approximately 4 to 6 hours.

The most optimal conditions for the release of phosphorus from secondary sludge is when 25 ml of 3.2% dry matter containing primary sludge hydrolyzed for 48 hours is used as volatile fatty source and the secondary sludge has incubated for approximately 8 hours.

A linear tendency exists between the amount of TOC and UV-254nm absorbance in the liquid phase of the secondary sludge, allowing for an approximation of the TOC using UV-254nm absorbance. If sodium acetate is used to stimulate the release of phosphorus from secondary sludge, however, a correction factor needs to be applied to account for the added carbon in the form of acetate.

# 4. Lab-scale electro dialytic experiments

The lab-scale experimental setup shown in figure 3 and figure 14, and it is in essence a smaller version of the bench-scale experiment described and tested in next chapter. Although it is more difficult to directly upscale the lab-scale setup into a wastewater treatment system, it allows the study of parameters that influence the electro dialytic processes, thus the phosphorus extraction, relatively quickly and generally requires less preparation.

The lab-scale experimental setup was used to study the effect of using monovalent or multivalent cation exchange membranes.

Monovalent cation exchange membranes (MCEM's) promote the transport of monovalent cations (i.e.  $\text{Na}^+$ ) over the membrane, whereas multivalent cation exchange membranes do not distinguish between mono- or multivalent cations (e.g.  $\text{Ca}^{2+}$  and  $\text{Fe}^{3+}$ ). The monovalent cation exchange membranes are by far most often used in different electro dialytic processes.

The objective in testing the monovalent ion exchange membranes is that the concentrate (the solution with the extracted phosphate) in the bench-scale setup comes into contact with the extracted cations. This can cause unwanted precipitation of phosphates with the multivalent cations, e.g. as precipitation of calcium-, iron-, aluminum- or magnesium phosphates. Since precipitation does not occur as easily in combination with monovalent cations, it may be beneficial to promote the extraction of monovalent cations by using monovalent cation exchange membranes.



FIGURE 14. THE LABORATORY SCALE 3-COMPARTMENT ELECTRODIALYTIC CELL SETUP AS USED IN THE LABSCALE EXPERIMENTS.

## 4.1 Materials and methods

### 4.1.1 Preparation of artificial solution

An artificial solution was created to simulate the concentrations of the cations calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ) and sodium ( $\text{Na}^+$ ) as found in the liquid phase of secondary sludge in the

preliminary experiments. For the artificial stock solution 4.15 gram of  $\text{CaCl}_2$ , 17.79 gram of  $\text{NaCl}$  and 0.98 gram  $\text{MgCl}_2$  were dissolved in 2 liter of milli-Q-water.

#### 4.1.2 Laboratory scale electro dialytic cell setup

Electro dialytic experiments with the phosphorus rich wastewater and the artificial solution were conducted in laboratory cells with three compartments as shown in Figure 3 and Figure 14. The cell parts were made of Plexiglas with an internal diameter of 8 cm. The compartment with the wastewater had a length of 10 cm and the electrode compartments 5 cm. Compartment II contained 350 ml of wastewater or solution. A overhead stirrer was used to keep concentration gradients from building up at the membranes and had two plastic fins sized 3 cm by 4 mm and a constant rotational velocity. The stirrer also prevent concentration gradients to build up in the wastewater compartment near the membranes.

A multivalent cation exchange membrane (Ionics CR67 HUY N12116B) or monovalent cation exchange membrane (Excellion<sup>TM</sup> I-100 cation membrane) was placed between the wastewater/solution compartment and the catholyte. An anion exchange membrane (Ionics 20 SZRA B02249C) was placed between the wastewater compartment and the anolyte. The electrolyte solutions in the electrode compartments were 500 ml 0.01M  $\text{NaNO}_3$  (pH~2) solution, circulating between the compartment and a flask to increase the total volume and to remove the gases produced from the electrode processes.

A constant direct current of 100 mA ( $2.0 \text{ mA/cm}^2$ ) was applied over a period of 24 hours. Samples of 10 ml were taken from the compartment with the artificial solution and the cathode compartment after 0, 1, 2, 3, 4, 5, 6, 8, 16 and 24 hours. In these samples, conductivity and pH were measured. The samples were also analyzed for calcium, magnesium and sodium using ICP-OES. At the sampling time the voltage and current were measured.

#### 4.1.3 Results and discussion

The concentration of Na in the middle compartment in the multivalent cation exchange membrane setup (AEM/CEM) is higher than the concentration of Na in the middle compartment in the monovalent cation exchange membrane setup (AEM/MCEM) (Figure 15). Until 6 hours into the experiment a higher concentration of  $\text{Na}^+$  is observed in the catholyte of the monovalent-CEM setup than for catholyte of the multivalent-CEM. A similar, but reversed, trend is also observed for the  $\text{Ca}^{2+}$  concentration in the cathode compartment. The  $\text{Ca}^{2+}$  in the cathode compartment of the monovalent-CEM is lower than the concentration of  $\text{Ca}^{2+}$  in the cathode compartment of the multivalent-CEM.

The concentration of  $\text{Mg}^{2+}$  in the middle or cathode compartment is too low to observe a clear distinction between the concentrations found in the middle or cathode compartment for the monovalent-CEM and multivalent-CEM setup.

The extracted concentrations of the cations towards the cathode compartment are comparatively closer together in the multivalent-CEM setup compared to the monovalent-CEM setup.

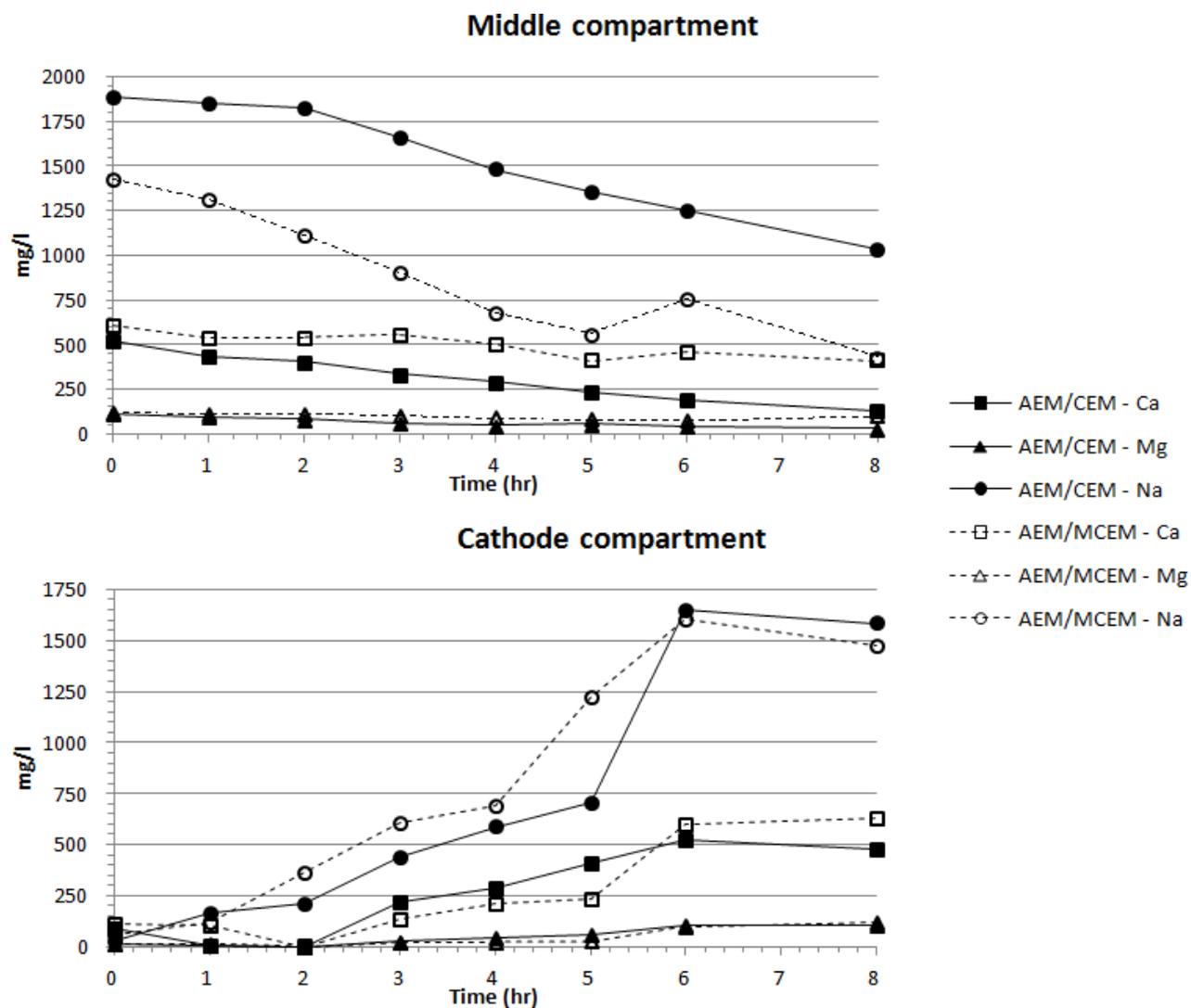


FIGURE 15. THE CONCENTRATIONS (IN mg/l) OF CALCIUM, MAGNESIUM AND SODIUM IN THE MIDDLE AND THE CATHODE COMPARTMENTS OF THE LABSCALE SETUP DURING ELECTRODIALYTIC EXTRACTION.

#### 4.1.4 Summary from lab scale ED

The effect of the monovalent-CEM becomes apparent in the results where  $\text{Na}^+$  is preferentially transported over the membrane compared to  $\text{Ca}^{2+}$ , however, the observed effect of the preferential flow of monovalent cations through the monovalent-CEM, did not differ to an extent where the effect became interesting compared to the extraction of these cations when using the multivalent-CEM. Because the relatively small difference, it was decided to use the multivalent-CEM (Ionics CR67 HUY N12116B) in the bench-scale experiments.

## 5. Bench-scale experiments

The benchscale electro dialytic cell setup is a version of the electro dialytic cell that can be relatively easily upscaled and used during the wastewater treatment. It consists of multiple stacked layers of membranes and compartments (Figure 16 and Figure 18). Increasing the amount of compartments increases extraction efficiency due to the higher surface area of the membranes exposed to the electric field.

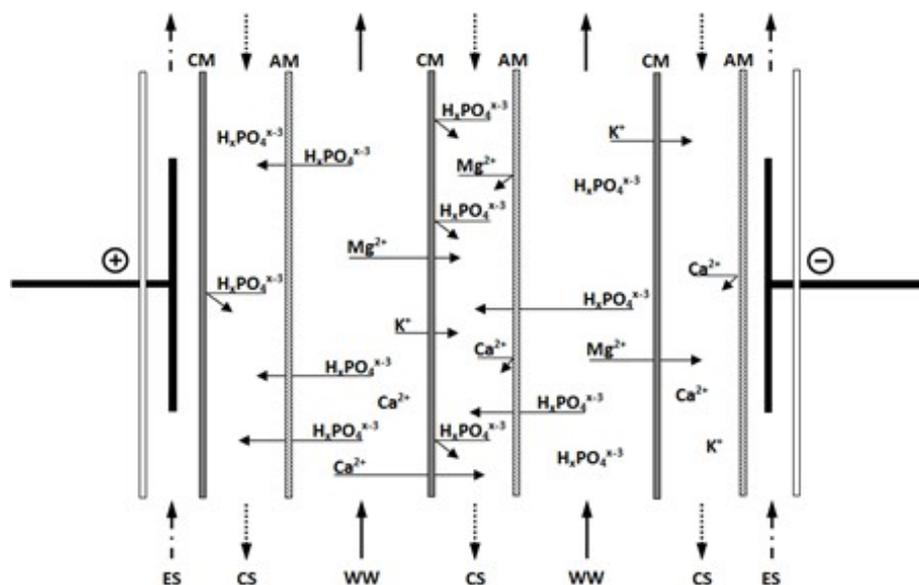


FIGURE 16. A SCHEMATIC DRAWING OF THE BENCHSCALE ELECTRODIALYTIC EXPERIMENTAL SETUP. PHOSPHORUS (IN THE FORM OF ORTHOPHOSPHATE) AND OTHER ANIONS ARE EXTRACTED FROM THE WASTEWATER (WW) INTO THE CONCENTRATE SOLUTION (CS) THROUGH THE ANION EXCHANGE MEMBRANE (AEM). THE CATIONS ARE EXTRACTED FROM THE WW THROUGH THE CATION EXCHANGE MEMBRANES (CEM) INTO THE CS.

The flow speed of the wastewater and the current were the main parameters investigated in this setup.

Flow speed and current are major important to the extraction rates of both phosphorus and organic matter. A relatively low flow speed and a high current allows for quicker extraction of phosphorus, but at the same time also that of (dissolved) organic matter. Due to the relatively smaller molecular size of phosphorus (as orthophosphate) compared to dissolved organic matter molecules or flocks, its migration in a solution under an electric field should be faster than the migration of most (dissolved) organic matter. Therefore, an optimum flow speed/current ratio should exist where the highest amount of phosphorus would be extracted against the least amount of fouling by extraction of organic matter.

The aim of the bench-scale experiments was to find these optimal conditions and use these to carry out a first evaluation of the cost-efficiency of electro dialysis in support of biological wastewater treatment processes.



FIGURE 17. A PHOTO OF THE BENCHSCALE ELECTRODIALYTIC CELL SETUP AS USED IN THE EXPERIMENTS. THE ELECTRODIALYSIS STACK IS TO THE LEFT.

## 5.1 Materials and methods

### 5.1.1 Sampling of secondary sludge and preparation of phosphorus rich solution

Secondary sludge, with a dry matter content of around 0.75%, was sampled using 25 liter jerry cans from the Bjermarken WWTP while the sludge was being aerated (see Figure 1, 'nitrification/denitrification'). Sodium acetate was added in an approximate concentration of 1.0 g/l. The jerry cans were capped, to ensure anaerobic conditions, and turned over several times by hand to ensure thorough mixing of the acetate in the sludge. The sludge was left to incubate for 4 hours, after which it was transferred to 500 ml containers and centrifuged at 4500 RPM for 5 minutes. The liquid phase was decanted until 5 liter of 'phosphorus rich' solution was gathered for each subsequent experiment.

### 5.1.2 Bench-scale electro dialytic experiments

The bench-scale electro dialytic cell (as schematically drawn in Figure 16) was assembled. The assemblance of the stack started with an anion exchange membrane (AEM) (Ionics CR67HUY N12116B) at the cathode (-), followed by a spacer to allow the flow of the concentrate solution through the stack, followed by cation exchange membrane (CEM) (Ionics 20 SZRA B02249C) and another spacer to allow for the flow of the wastewater through the setup. This segment, AEM, spacer, CEM and spacer, was repeated, finishing off the stack with a CS compartment. A total of 5 compartments for the wastewater and 6 compartments for the concentrate solution were created. The flow of the wastewater and concentrate solution was divided over these compartments (Figure 19).

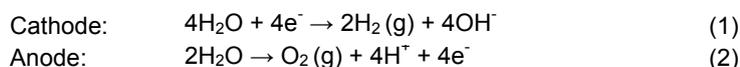
Four bench-scale experiments (BS-1 to BS-4) were carried out (Table 1). During each experiment, 5 liter of the prepared 'phosphorus rich' solution was treated using electrodialeses. The current (mA) through the stack and flow speed (ml/min) were the parameters differing between experiments, see (Table 1).

**TABEL 1.** EXPERIMENTAL CONDITIONS OF THE BENCHSCALE EXPERIMENTS.

Experiment	Current (mA)	Flowspeed of wastewater (ml/min)
BS-1	82	400
BS-2	82	800
BS-3	322	400
BS-4	322	800

The applied currents of 82 and 322 mA in this particular stack setup, with a total exposed surface membrane area of approximately 322.5 cm<sup>2</sup>, is equivalent to a current density of 0.25 or 1.0 mA/cm, respectively.

The concentrate solution (CS) and electrolyte solutions (ES) consisted of 1 liter of 0.01M NaNO<sub>3</sub> (pH~2), which was pumped through their respective compartments. Due to the following half reactions at the electrodes



the pH in the electrode solutions had to be adjusted to around 7 every 20 minutes using 1:1 HNO<sub>3</sub> at the cathode and 1 ml of 10% NaOH at the anode. The wastewater and concentrate solution were sampled by taking 20 ml samples every 20 minutes for the first 2 hours. After the first 2 hours, samples were taken every 30 minutes.

After each experiment was carried out, the wastewater compartment of the benchscale setup was rinsed to remove residual organic matter from the membranes. A 1 liter solution of 5% NaOH was used, followed by a 1 liter solution of 5% HNO<sub>3</sub> and finally by 1 liter of demineralized water. Each solution was pumped through the wastewater compartment for approximately 20 minutes.

### 5.1.3 Sample preparation for analyses

The extracted samples were prepared for analyses similarly as described in Chapter 3.1.4 for the batch experiments. The following parameters were measured in the WW and CS:

- P, Al, Fe, Ca K, Mg and Na using inductively coupled plasma optical emission spectrometry (ICP-OES);
- Cl<sup>-</sup> and PO<sub>4</sub><sup>3-</sup> using Ion Chromatography (IC);
- Dissolved organic matter (DOM) using UV-254 nm absorption;
- Total organic carbon (TOC) using a Total Organic Matter Analyzer;
- pH and conductivity using a radiometer analytical electrode.

## 5.2 Results and discussion

Phosphorus concentrations (55 to 80mg/l) as obtained in the batch experiments after acetate/hydrolyzed sludge addition to secondary sludge under anaerobic conditions (Figure 10 and Figure 11) were not obtained in the bench-scale experiments where only approximately 16 mg/l was reached.

The quality of the secondary sludge obtained from the wastewater treatment plants (WWTP's) seemed to vary significantly with each sampling day. This can be explained by the many parameters that influence effective wastewater treatment at the WWTP. For example, rain and other discharges can significantly lower the amount of dry matter, an indication of the amount of active microorganisms, in a time span of days (Metcalf & Eddy, Inc., 2002). In the case of the above described experiments, this resulted in dry matter concentrations in the secondary sludge varying between 0.75% to 1.82% (compared to 3.2% dry matter in the batch experiments) and likely the resulting lower concentration of phosphorus.

Figure 18 shows the phosphorous concentration in wastewater and concentrate solution over time. The phosphate concentration in the wastewater decreases over time and increases in the concentrate solution in every experiment. The slightly higher initial phosphorus concentration in the BS-1 experiment could be explained by the lower pH of the wastewater (Figure 19). Although a lower pH results in a higher release of phosphorus from the microorganisms it can similarly be detrimental to the growth rate of such microorganisms (Metcalf & Eddy, Inc., 2002), thus neutral pH is to be preferred.

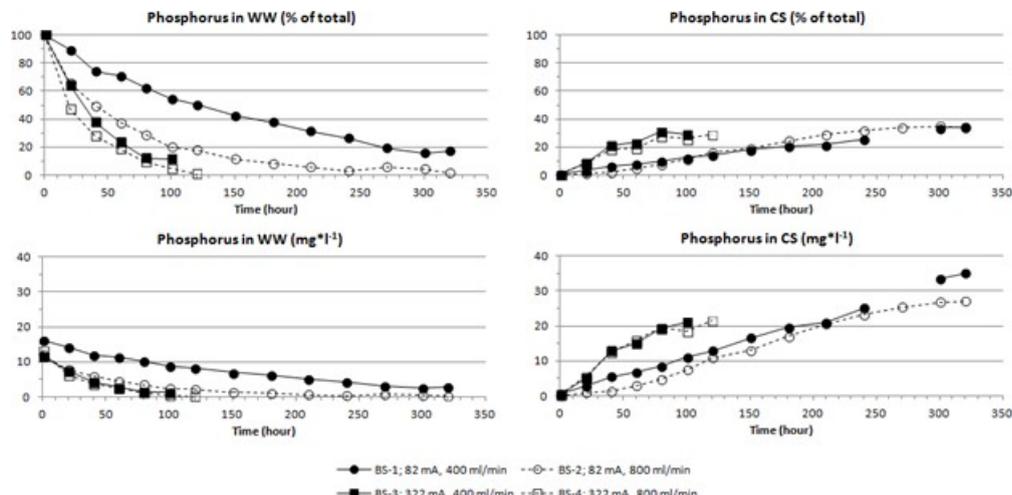


FIGURE 18. PHOSPHORUS IN mg/l AND AS PERCENTAGE OF TOTAL PHOSPHORUS ORIGINALLY PRESENT IN THE WW BEFORE ED EXTRACTION IN BOTH THE WASTEWATER AND THE CONCENTRATE SOLUTION THROUGHOUT THE DURATION OF THE BENCHSCALE EXPERIMENT.

The phosphorous concentration was higher in the wastewater all through the experiments with a flow speed of 800 ml/min (BS-1 and BS-3) compared to 400 ml/min (BS-2 and BS-4). Thus, the higher flow speed gave a better extraction of phosphorous.

This trend was particularly clear in the amount of phosphorus extracted from the wastewater during the experiments with the lower current (82 mA). This trend could be explained by the fact that at a higher flow speed, more of the phosphorus molecules (as orthophosphate) are extracted compared to the relatively larger molecular complexes of the organic matter. While the extraction of phosphorous was better at high flow speed, the transport of phosphorous into the concentrate solution was not influenced by the flow speed, but solely on the current applied.

Phosphorus was effectively concentrated in the concentrate solution with concentrations increasing to about 20 to 35 mg/l in the concentrate solution compared to initial concentrations of around 16 mg/l in the wastewater (Figure 18).

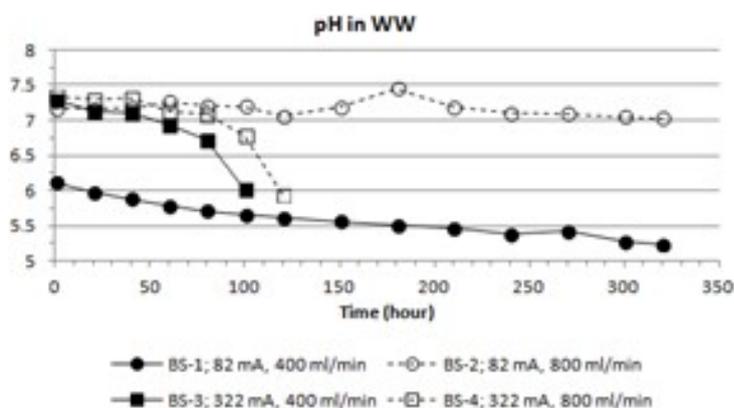


FIGURE 19. THE pH OF THE WASTEWATER (WW) COMPARTMENT DURING THE BENCHSCALE EXPER

With a constant current during the experiment, the energy cost of the extraction and concentration (expressed in kilowatt or kW) is determined by the voltage. The energy cost of phosphorus extraction and concentration is higher using a higher current (Figure 20). Furthermore, when the phosphorus concentration in the wastewater reaches approximately 3 mg/l for the 322 mA experiments (BS-3 and BS-4), a sharp increase in voltage (and consequently energy cost) is observed. A significantly smaller increase in voltage is observed in the experiments with a current of 82 mA (BS-1 and BS-2). The voltage increase in these experiments remains relatively linear. The same trends are observed in the plot of conductivity against voltage, with a sharp increase in voltage for the 322 mA experiments when the conductivity reaches approximately 0.6 mS/cm.

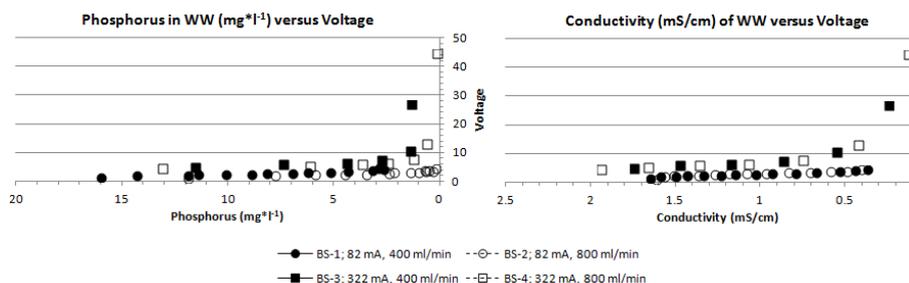


FIGURE 20. THE PHOSPHORUS CONCENTRATION IN mg/l IN THE WASTEWATER PLOTTED AGAINST THE VOLTAGE. WITH A CONSTANT CURRENT, THE VOLTAGE IS THE VARIABLE IN THE EXPERIMENTS THAT INDICATES THE ENERGY COST OF PHOSHPORUS EXTRACTION.

Fouling of the anion exchange membranes by organic matter in the bench-scale experiments was not completely prevented (Figure 21).



FIGURE 21. THE ANION EXCHANGE MEMBRANES AFTER CLEANING AND EXPERIMENTS IN THE BENCHSCALE STACK.

A (visible) organic matter residue was observed in the 5% NaOH solution used to rinse the wastewater compartment after the experiments (Figure 22). This has likely to do with the flocks of organic matter remaining in the liquid phase of the secondary sludge after separation of liquids and solids through centrifugation (Figure 14). If a layer of organic matter was present on the AEM, effectively creating a negatively charged layer on the membrane, the transport of anions, such as orthophosphates, through the AEM could be inhibited. This could explain the near complete extraction of phosphorus from the wastewater, while only approximately 35% of the total amount of phosphorus was found in the concentrate solution (Figure 18). The phosphorus may be bound in this layer rather than being transported into the anolyte as intended.



FIGURE 22. THE (VISIBLE) ORGANIC MATTER RESIDUE THAT WAS RETRIEVED FROM THE MEMBRANES AFTER RINSING WITH A 1 LITER 5% NAOH SOLUTION.

### 5.3 Summary from bench scale experiments

The concentration of phosphorus in the liquid phase of the sewage sludge obtained by acetate stimulation under anaerobic conditions prepared to the bench scale experiments was lower than the concentrations obtained during the batch experiments, 16 mg/l versus 55 to 80 mg/l, respectively. This is likely caused by the lower amount of dry matter, and thus active microorganisms in the sewage sludge used in preparation to the bench-scale experiments, as compared to the batch experiments.

Phosphorus extraction was highest in the experiments with a flow speed of 800 ml/min (BS-1 and BS-3) compared to 400 ml/min (BS-2 and BS-4). This trend was particularly clear in the amount of phosphorus extracted from the WW during the experiments with the lower current (82 mA). A current (322 mA compared to 82 mA) results in a higher phosphorus extraction rate but results in a higher voltage and consequently a higher energy cost.

Phosphorus was concentrated in the CS with concentrations rising to about 20 to 35 mg/l in the concentrate solution compared to starting concentrations of around 16 mg/l in the wastewater (Figure 19). However, a large amount of phosphorous (about 70%) was captured in the thin layer of organic matter fouling the anion exchange membrane.

When the phosphorus concentration in the wastewater reaches approximately 3 mg/l, and the conductivity reaches approximately 0.6 mS/cm for the 322 mA experiments, a sharp increase in voltage (and consequently energy cost) is observed. A significantly smaller increase in voltage is observed in the experiments with a current of 82 mA (BS-1 and BS-2).

The process needs optimization compared to the bench-scale experiments conducted here. Especially in relation to increasing the initial phosphorous concentration. Optimization will influence the power consumption positively for the electrodialytic process. However, to give an indication of the range in the current experiments the two cases (322 mA, 120 hours, 4V and 5 liters) and (82 mA, 240 hours, 2.5 V and 5 liters) corresponds to a power consumption of 32 kWh/m<sup>3</sup> and 12 kWh/m<sup>2</sup>.

### 5.4 Recommendations

When future experiments are conducted, the following recommendations are made to improve the experimental setup:

- Since phosphorus release from secondary sludge in the WWTP depends highly upon the amount of active organisms in the wastewater (sludge), which is in turn influenced by a multitude of (to us uncontrollable) parameters, it is suggested that for the experiments secondary sewage sludge should be obtained from a more stable environment. An example of such an environment could be a laboratory version of a secondary sewage sludge reactor where under controlled circumstances PAO's are grown.
- While centrifugation of the secondary sludge results in most (visible) organic matter to be settled and removed from the liquid phase, flocks of the organic matter were still present after decanting the remaining liquid phase. In order to improve the liquid-solid separation after addition of the VFA's and the four hour incubation period, a 'tumble'-filter could be used instead (Figure 23). A 'tumble'-filter is a rotating filter through which the secondary sludge can be lead after incubation under anaerobic conditions. The filter separates the liquid and solid phase of the sludge but prevents clogging of the membrane by the nature of its rotating motion, constantly exposing a new, cleaned part of the membrane to the sludge stream. Figure 24 shows the placement of the electrodialytic treatment in the WWWT plant.
- Volatile fatty acids can be generated through the partial hydrolysis of primary or secondary sludge in a specialized reactor. This resource of VFA's could also be used to stimulate release of phosphorus during anaerobic conditions to which secondary sludge is exposed before treatment using ED. This in turn avoids the use of external chemicals such as sodium acetate and allows the WWTP to be self-sufficient.

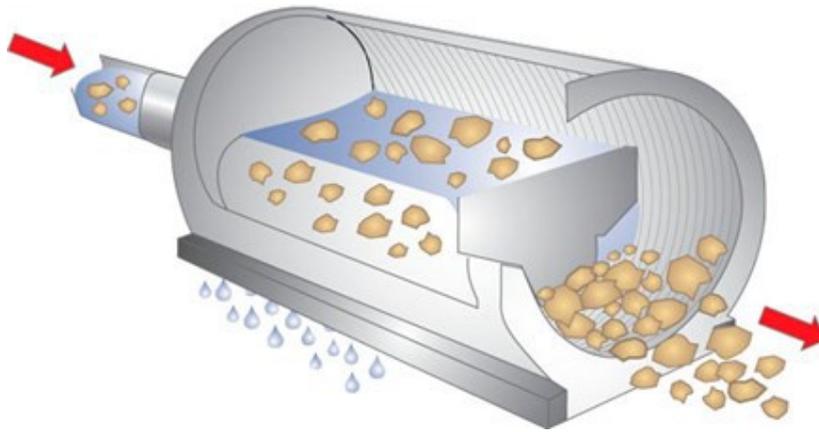


FIGURE 23. AN EXAMPLE OF A SO-CALLED 'TUMBLE'-FILTER AS IT COULD BE APPLIED IN WASTEWATER TREATMENT (PICTURE BY DIRECTINDUSTRY).

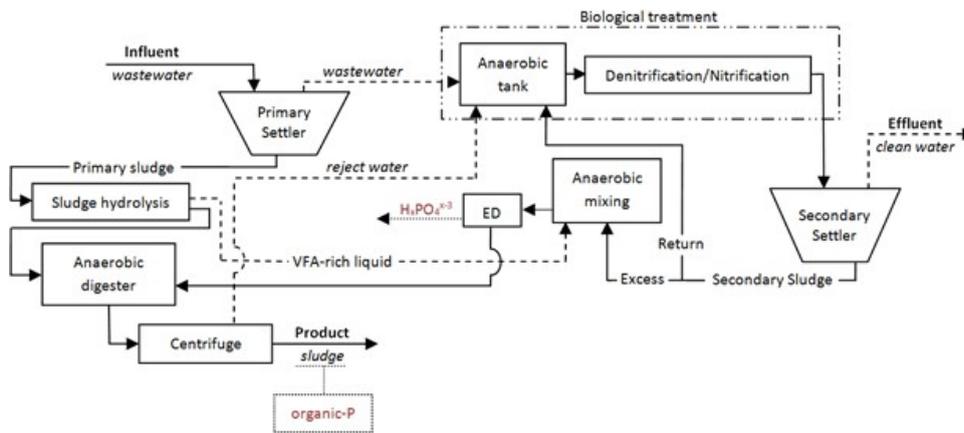


FIGURE 24. A SCHEMATIC DRAWING OF THE DANISH BJERGHOLM WWTW SYSTEM LAYOUT WHERE VFA'S (OBTAINED FROM HYDROLYSIS OF PRIMARY SLUDGE) ARE ADDED UNDER ANAEROBIC CONDITIONS TO A SIDE-STREAM OF THE SECONDARY SLUDGE.

## 6. Conclusions

From the batch experiments, it was concluded that solution most rich in phosphorus to be used in the benchscale electrolysytic experiments can best be created using sodium acetate. In the timespan of the experiments it was the most readily available source of volatile fatty acids, compared to hydrolyzed primary sludge, which would release the highest amount of phosphorus in the smallest amount of time.

Separation of mono-valent and multi-valent cations during electrolysis by the use of a monovalent cation exchange membrane did not work sufficiently. The regular multivalent cation exchange membranes were thus used in the bench-scale experiments, as it was found from lab scale electrolysytic experiments that the preferential flow of cations over a monovalent cation exchange membrane was not significant enough to warrant the investment.

The highest phosphorus extraction over the least amount of time was observed when using a current density of  $1.0 \text{ mA/cm}^2$  compared to a current density of  $0.25 \text{ mA/cm}^2$ . However, the most optimal conditions of extracting phosphorus was observed under a current density of  $0.25 \text{ mA/cm}^2$  with a flow speed of  $400 \text{ ml/min}$  as compared to a flow speed of  $800 \text{ ml/min}$ . This is likely due to the smaller size of the orthophosphate molecules as compared to the organic matter molecules, which therefore, using a higher flowrate are more easily influenced by the electric field and extracted from the solution.

Since the concentration of phosphorus in the bench scale experiments was low, approximately  $16 \text{ mg/l}$  compared to  $55$  to  $80 \text{ mg/l}$  in the batch experiments, the phosphorus to be recovered was low. It was furthermore found, that a significant amount of phosphorus (70%) was captured on a thin layer of organic matter fouling the anion exchange membrane. Still a concentration from wastewater ( $16 \text{ mg P/l}$ ) to the concentrate (up to  $35 \text{ mg P/l}$ ) was obtained.

The process needs optimization, which will influence the cost for the process. The lowest current tested ( $82 \text{ mA}$ ) resulted in longer treatment time than the high current ( $322 \text{ mA}$ ), and overall the lower current resulted in the lowest power consumption. The treatment as tested in the bench-scale experiment was in the best experiment  $12 \text{ kWh/m}^3$ .



## **Improving Phosphorus recovery by supplementing existing Danish wastewater treatment with electrodialysis**

The overall aim of this study is to investigate the effectiveness of the new idea of recovering phosphorus from wastewater by combining the biological processes stimulating phosphorous release and electro-dialytic recovery and estimate the power consumption for such process.



Environmental  
Protection Agency  
Haraldsgade 53  
DK-2100 København Ø

[www.mst.dk](http://www.mst.dk)