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PHOSPHATE RECOVERY FROM WASTEWATER USING SELECTRODIALYSIS AND CRYSTALLIZATION PROCESS

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ABSTRACT

Stimulated by the depletion of phosphate resources and the need to avoid eutrophication, phosphate removal/ recovery has been studied in recent years. The aim of this study is to investigate the feasibility of phosphate recovery from wastewater by the hybrid system consisting of pellet reactor and selectrodialysis. The phosphates will be pre-concentrated in the selectrodialysis and then be recovered by a crystallization process where it will precipitate on to sand grains as calcium phosphate in a pellet reactor. The results of selectrodialysis show that the co-existing ions in the wastewater affect the fractionating phosphate from wastewater; however, the efficiency is still good enough to obtain the high phosphate concentration in the product. The phosphate concentration in the product can reach 4 mM after 10h. After that, the pellet reactor was run to precipitate calcium phosphate, the efficiencies fluctuated between 70 and 80% during the period of the experiments. That proved that it is possible to recover phosphate as calcium phosphate from wastewater with high efficiency.

Keywords: *Phosphate; selectrodialysis; crystallization; wastewater treatment; recovery.*

1. INTRODUCTION

Phosphorus is an essential element for life but its existence in the earth is limited. The phosphates are extracted from non-renewable resources, they cannot be manufactured or synthesized from other products, and are used to cultivate food for animals and humans [1]. During the last decade, the demand for phosphorus increased a lot. This is caused by the growing world population and therefore, leading the increase in the demand for food and higher usage of fertilizers. The agricultural intensification has led to the replacement of the traditional phosphorus cycle by a linear throughput system - recovering phosphorus from wastewater.

Besides, high phosphate concentrations can have a big impact on the environment. By increasing the food demand, the fertilizer normally may be used higher than the requirement for growth, residue of phosphate may end up in landfill, rivers and oceans. In some cases, the phosphate concentration in the soil has reached saturation level and the excess of phosphates will run off into the surface waters. The discharge of too much phosphate into the surface waters can cause eutrophication. This excess of phosphate (more than 0.1 mg P/L) in the water causes an algae bloom, an enhanced growth of algae, which in turn causes the biodiversity to be declined [2].

From the two aforementioned reasons, the most important one for phosphate recovery is the depletion of phosphorus in the future [3]. Several studies point out that the phosphorus mining causes a depletion of phosphorus over 100 to 400 years from now. Most of the phosphate minerals can be found in China and Morocco. Also the United-States, South-Africa and Jordania are one of the most important producers of phosphate. The problem on world scale is that there is an unbalance in phosphate streams over the world. Most of the cultivated plants in Africa and South-America are exported to Europe and America where these are consumed. This causes a deficiency of nutrients (phosphates) in the soil of the poorer countries and an accumulation of phosphates in the soil and water stream in the richer countries. This accumulation leads to problems like the previously mentioned eutrophication.

In 2011-2012, 60 % of the MAP-measuring points did not meet the norm for the phosphate concentration of surface water in agricultural areas in Flanders. Compared to nitrate levels, only 28% did not meet the norm. Thus, phosphates cause an even bigger challenge than nitrates (do). The norm for yearly average phosphate concentration in surface water is 0.1 mg P/L.

Based on these considerations, new technologies have been developed and are being investigated, to recuperate phosphate and utilize it in a sustainable way [4]. A promising and sustainable renewable source of phosphate can be obtained through crystallization of calcium phosphate in wastewater. Many different processes were proposed for pre-concentration of phosphate to increase the precipitation efficiency, such as adsorption [5], ion exchange [6], biological treatment and membrane filtration [7-8]. And methods for higher phosphate concentrations are precipitation and crystallization [9]. The recovery of phosphates by crystallization as calcium phosphate or as magnesium ammonium phosphate (struvite), are two of the major technologies developed over the years [10]. Until now the struvite process has been more applied because it removes at the same time both ammonium and phosphate from the waste stream [11]. The advantages of these processes compared to the traditional biological removal, is that the recovered products can be used as alternative for agriculture fertilizers instead of being captured in sludge.

Recently, a novel electrodialysis, denoted “selectrodialysis”, can be used for separating the multivalent ions from monovalent ions by standard anion exchange membrane and monovalent selective anion exchange membranes [12-13]. This study aims at the fractionation and concentration of phosphate from synthetic water using selectrodialysis to increase the phosphate concentration prior to crystallization process to recover phosphate as calcium phosphate from wastewater.

2. MATERIALS AND METHODS

2.1. Selectrodialysis

Selectrodialysis is based on conventional electrodialysis, in which an extra monovalent anion exchange membrane (MVA) is added to the 2 standard anion (AM) and cation exchange membranes (CM). This MVA membrane is added in order to achieve a fractionation between the multivalent phosphate and monovalent chloride ions. [12-13]. Due to the applied electrical field, the anions (chloride, nitrate, sulphate, carbonate and phosphate) move across anion exchange membranes while the cations (sodium, potassium, calcium and magnesium) move across cation exchange membranes. Since monovalent selective anion exchange membranes are set between anion and cation exchange membrane, the multivalent ions such as sulphate, carbonate and phosphate are kept in the product compartment (Fig. 1).

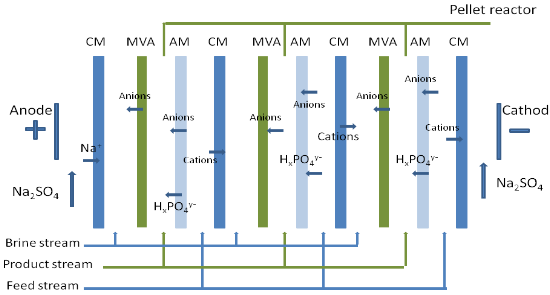

Figure 1. *Selectrodialysis membrane stack*

Synthetic wastewater containing phosphate and other ions (chloride, carbonate, sulfate) was used as feed. The product and brine stream both only contained chloride ions. the influence of commonly present ions in wastewater, like $SO_4^{2-}SO_4^{2-}$ and $CO_3^{2-}\ CO_3^{2-}$, is investigated. The electrode rinsing solution is 3L Na_2SO_4 0.1M solution. All 4 streams are recirculated to the membrane stack back to the vessel. The feed, product and brine stream have a flow rate of 20L/h, except the electrode rinsing solution with flow rate of 100L/h.

The influence of other ions coexisting in the wastewater was studied as 3 experiments:

Run 1 was performed at pH=10; I=0.3A and feed concentration of 28 mM Cl^-, 6 mM CO_3^{2-}, 3 mM PO_4^{3-}, 2 mM SO_4^{2-}. The product and brine concentration was around 25 mM Cl^-.

Run 2 was performed at pH=10; I=0.3A and the feed, product and brine stream had the same composition as the feed stream in run 1.

Run 3 was performed at pH=10; I=0.2A and feed concentration of 28 mM Cl^-, 6 mM CO_3^{2-}, 3 mM PO_4^{3-}, 2 mM SO_4^{2-}. The product and brine concentration was around 25 mM Cl^-. All the experiments were run for a period of 600 minutes.

The pH is controlled by adding an alkaline solution of NaOH to the product stream. Each hour, samples are taken of which the conductivity is measured and further analyzed (via ion chromatography Dionex ICS -2000) to see how the concentration of the specific ions (phosphate, chloride) in each stream changed over time.

2.2. Pellet reactor

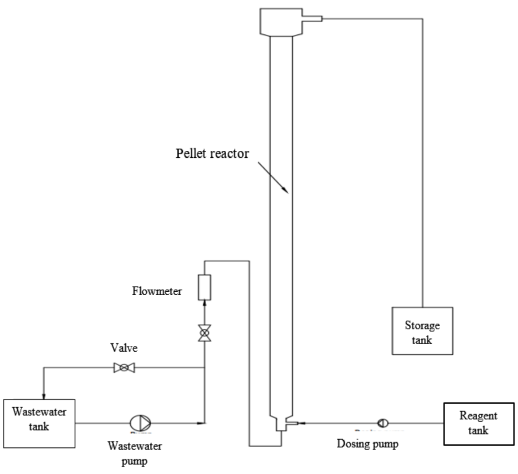

Figure 2. *Pellet reactor configuration*

The lab-scale pellet reactor is columnar with conical reactors on the top of columnar, 150 mm body height and a diameter of 16 mm (Fig.2). The water was pumped vertically upwards the fluidized bed through an inlet water tube of (D =5 mm) without recirculation with a flow rate of 18 L/h. At the same time, a mixture of $Ca(OH)_2$ with a flow rate of 1 L/h was injected at a point 3 cm away from the bottom of the pellet reactor (D = 2 mm) to adjust the operational conditions.

3. RESULTS AND DISCUSSIONS

3.1. Phosphate profile in the product stream

During the second phase of the experiments, run 1-3, the influence of commonly present ions in wastewater, like $SO_4^{2-}SO_4^{2-}$ and $CO_3^{2-}CO_3^{2-}$, is investigated. All the experiments were run for a period of 600 minutes.

Figures 3 represents the concentration profiles of PO_4^{3-}, Cl^-, CO_3^{2-} and SO_4^{2-} for the three different runs. Because this study aims to find out what the influence of other ions was on the fractionation of PO_4^{3-}, and Cl^- only the product stream is considered.

Run 1:

After 600 min, the PO_4^{3-} concentration increased from 0 mM to 2.54 mM. Taking the initial feed concentration of 3 mM, this corresponds to an efficiency of 84.7%. In the previous study [14] (pH=10 and I=0.2A) for the synthetic water reached an efficiency of 96.8% after 6 hours. Therefore, when comparing the obtained results, it is seen that the synthetic water (without other ions) reaches already after 6 hours, and at a lower driving force (I=0.2A), a higher efficiency. The Cl^- concentration had only a small decrease, from 25.08 mM to 23.77 mM, achieving a decrease of 5.2%. The CO_3^{2-} concentration increased from 0 mM to 8.27 mM. Taking the initial feed concentration (5.1 mM) into account, the efficiency is 162.1%. The SO_4^{2-} concentration increased from 0 mM to 2.37 mM, with an initial feed concentration of 2.08 mM, an efficiency of 114% was reached.

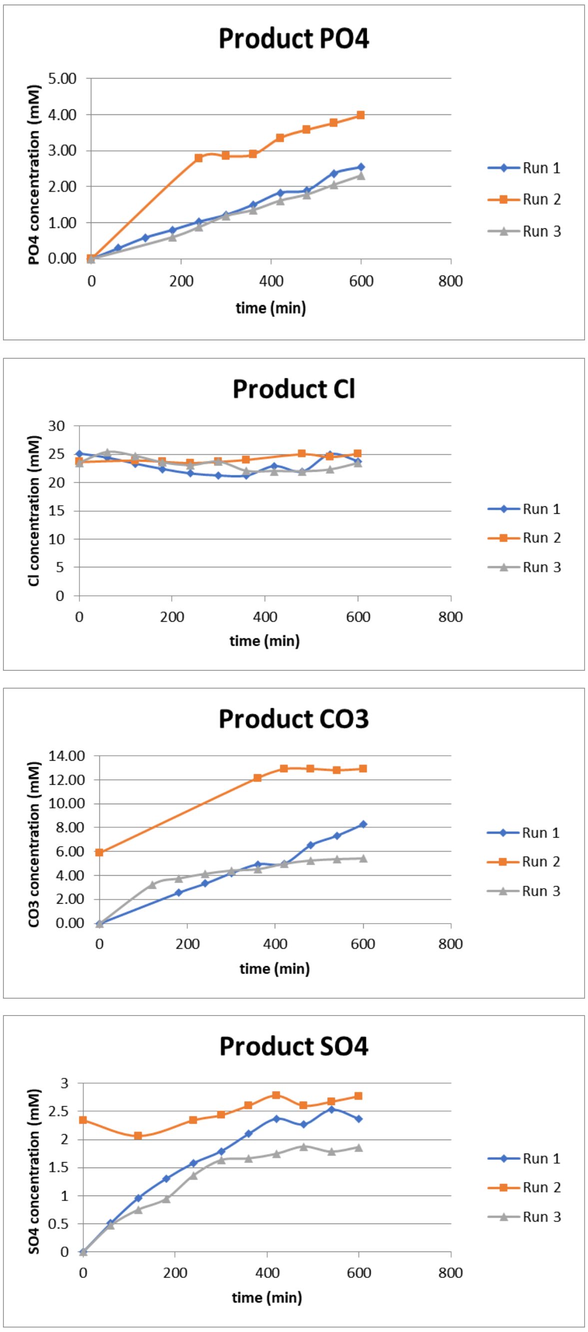

Figure 3. *Ions profile a function of time in the product stream*

Run 2:

After 600 min, the PO_4^{3-} concentration increased from 3.15 mM to 3.97 mM. Taking the initial feed concentration of 3.15mM, this corresponds to an efficiency of 26%. The experiment described in [14] (pH=10 and I=0.2A) for the synthetic water, the pre-concentrating efficiency reached 96.8% after 6 hours. Therefore, when comparing the results, it is seen that the synthetic water (without other ions) reaches already after 6 hours, and at a lower driving force (I=0.2A), a higher efficiency. The Cl^- concentration had only a small increase, from 23.65mM to 25.13mM, achieving an increase of 6.3%. The CO_3^{2-} concentration increased from 5.87 mM to 12.89 mM, corresponding efficiency of 119.6%. The SO_4^{2-} concentration increased from 2.34 mM to 2.77 mM, an efficiency of 118.4% was reached.

Run 3:

After 600 min, the PO_4^{3-} concentration increased from 0 mM to 2.3 mM. When the initial feed concentration was 2.99 mM, this corresponds to an efficiency of 77%. Previous experiment with pH=10 and I=0.2A [14] for the synthetic water, the efficiency reached 96.8% after 6 hours. Therefore, when comparing the results between the synthetic solution and wastewater, it can be seen that the synthetic water (without other ions) reaches a higher efficiency after 6 hours. The Cl^- concentration stayed almost constant, from 23.48 mM to 23.42 mM, achieving a decrease of 0.3%. The CO_3^{2-} concentration increased from 0 mM to 5.4 mM. Taking the initial feed concentration (5.5 mM) into account, the efficiency is 98.2%. The SO_4^{2-} concentration increased from 0 mM to 1.86 mM, with an initial feed concentration of 2.0 mM, an efficiency of 93% was reached.

The conclusion is that the efficiencies for run 1 are a bit higher compared to the efficiencies of run 3 due to the somewhat larger driving force (I=0.3A for run 1 vs. I=0.2A for run 3). Also, when comparing run 1 with run 2 or run 3 with run 2, it can be seen that for all three runs, Cl^- stayed constant (only small increase or decrease). Higher PO_4^{3-} efficiencies were obtained for run 1 (84.7%) and run 3 (77%) compared to only 26% for run 2. Thus, larger separation between PO_4^{3-} and Cl^- is reached for run 1 and 3. The small separation in run 2 is probably due to scaling on the AM and MVA membrane, since wastewater was used in all three streams. Again, due to the higher current in run 1 a larger separation is reached compared to run 2.

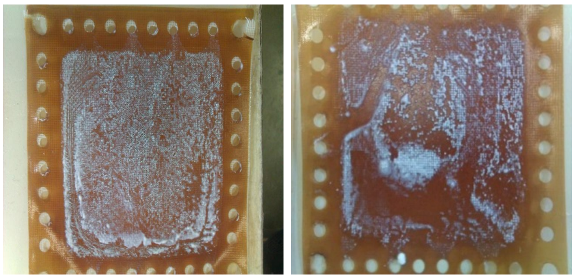

Figure 4. *Scaling on the MVA membranes*

The experiments also showed that when comparing run 1 (pH=10; I=0.2A) from the synthetic solution with the three runs for the wastewater, higher efficiencies for the PO_4^{3-} are reached (even after less hours of running or at lower current). This is probably because of scaling. Since there are other ions present in solution, like Ca^{2+}, Mg^{2+}, CO_3^{2-} and SO_4^{2-}, they can form products and precipitate on the membranes. This causes more resistance for the anions to be transported to the next stream and as such the separation between PO_4^{3-} and Cl^- becomes harder. In figure 4, a picture of the MVA membranes after doing the experiment with wastewater is given. The scaling of $CaCO_3$, $CaSO_4$ may occur on the surface of membranes. Thus, it is probably better to use to correct pre-treatment, in order to remove the Ca^{2+}, Mg^{2+} and CO_3^{2-} ions from the influent and avoid scaling in the SED.

3.2. Phosphorus recovery in a pellet reactor

After pre-concentrating phosphate from wastewater, the wastewater with high concentration was run continuously in the pellet reactor to crystallize calcium phosphate. The pellet reactor was run with the operational parameters: flow rate of 18 L/h, pH = 10, ratio of $[Ca^{2+}]:[PO_4^{3-}] = 2/3$, initial phosphate concentration of 3 mM. As can be seen, with the synthetic wastewater, even with the effect of other ions, the efficiencies fluctuate between 70 and 80% during the period of the experiments. That proved that, with suitable conditions, it is possible to recover phosphate as calcium phosphate from wastewater with high efficiency.

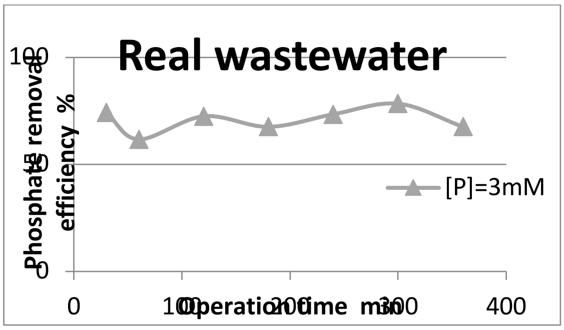

Figure 5. *Phosphate recovery in the synthetic wastewater*

The pellets are analyzed before and after each experiment. This analysis of the collected pellets afterwards is done using microscopic analysis SEM. Figure 6 shows that the changing in the roughness of the surface of the sand proved calcium phosphate are precipitated and crystallized on the seeding materials in the pellet reactor.

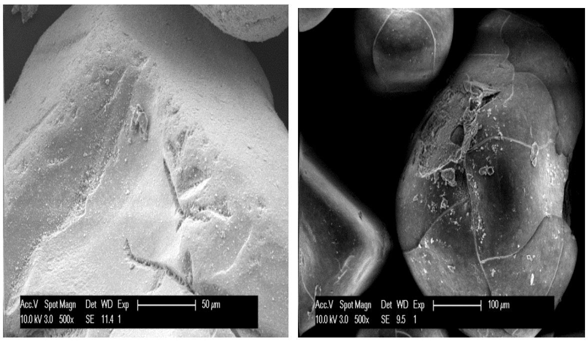

Figure 6. *SEM of pellet before and after pellet reactor treatment*

4. CONCLUSION

Selectrodialysis can be used as a pretreatment step in order to increase the removal efficiency in the pellet reactor. Higher PO_4^{3-} efficiencies were obtained for run 1 (84.7%) and run 3 (77%) compared to only 26% for run 2. However, scaling of $CaCO_3$, $CaSO_4$ may occur on the surface of membranes. Thus, it is probably better to use to correct pre-treatment, in order to remove the Ca^{2+}, Mg^{2+} and CO_3^{2-} ions from the influent and avoid scaling in the SED. When pre-concentrating phosphate, the efficiency of selectrodialysis was high so the product from the selectrodialysis can be directly fed into the crystallization process without pH adjustment. After that, the pellet reactor was used to recover phosphate from wastewater by crystallization in a seeding material. The recovery efficiency is from 70 – 80% during the period of the experiments.

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