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PHOSPHATE FRACTIONATION FROM WASTEWATER BY A SELECTRODIALYSIS PROCESS

PHÂN TÁCH PHOTPHATE TỪ NƯỚC THẢI BẰNG QUÁ TRÌNH SELECTRODIALYSIS

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ABSTRACT

Phosphate recovery by crystallization has been a concern in recent years. However, to obtain a high efficiency in crystallization, the phosphate concentration in the influent stream is an important factor to control. This study aims at the fractionation and concentration of phosphate from synthetic water in selectrodialysis to increase the concentration as a pretreatment prior to crystallization. A lab-scale ion exchange membrane electrodialysis system (selectrodialysis) was used to perform the experiments. The results of selectrodialysis show that an increase in current density, initial pH of the product, and initial feed concentration of phosphate led to an increase in phosphate concentration in the product. The phosphate concentration in the product can reach 16 mM with a purity of phosphate 44%, the current efficiency to transport phosphate and chloride was 26.6% for a standard anion exchange membrane and 63% for a monovalent selective anion exchange membrane. Therefore, this study proves that the selectrodialysis is feasible and effective to fractionate phosphates from monovalent ions in the mixture.

***Keywords**: Selectrodialysis; phosphate fractionation; wastewater, ion exchange membrane, phosphate recovery.*

TÓM TẮT

Thu hồi Phosphate bằng quá trình kết tinh đã được quan tâm trong những năm gần đây. Tuy nhiên, để đạt được hiệu quả cao trong quá trình kết tinh, nồng độ phosphate đầu vào là một yếu tố quan trọng. Nghiên cứu này nhằm mục đích phân tách và làm đậm đặc phosphate từ nước thải bằng màng selectrodialysis để tăng nồng độ như là một quá trình tiền xử lý trước khi thực hiện quá trình kết tinh. Hệ thống màng thẩm tích (selectrodialysis)với qui mô phòng thí nghiệm được thiết lập. Các kết quả của việc phân tách phosphate cho thấy với sự gia tăng cường độ dòng điện, pH ban đầu, và nồng độ phosphate dòng vào dẫn đến sự gia tăng nồng độ phosphate trong dòng sản phẩm. Nồng độ phosphate trong dòng sản phẩm có thể đạt tới 16 mM với độ tinh khiết của phosphate 44%, hiệu quả vận chuyển phosphate và chloride là 26.6% đối với màng trao đổi anion và 63% đối với màng trao đổi anion hóa trị một. Do đó, nghiên cứu này chứng minh rằng việc phân tách phosphate từ nước thải là khả thi và có hiệu quả.

***Từ khóa:** Selectrodialysis; phân tách phosphate; nước thải, màng trao đổi ion, thu hồi phosphate.*

1. INTRODUCTION

Phosphorus (P) is an essential and limited element, therefore phosphate recovery from wastewater is to be considered an important aspect in sustainable development [1]. The most developed technique that can be applied to recover phosphate is precipitation/ crystallization as struvite and calcium phosphate [2-4]. Calcium phosphate can be directly used in the phosphoric acid and fertilizer production. Struvite can be formed by addition of ammonia and magnesium to phosphate to obtain a precipitate of magnesium ammonium phosphate ($MgNH_4PO_4$) and has a slow release mechanism.

However, this precipitation technology still has drawbacks since low feed concentrations lead to low supersaturation levels, and a low efficiency. The minimum P concentration required for good precipitation is 50 mgP/L at neutral pH [5], while the concentration of phosphate in municipal wastewater is low (from 18.5 to 48.3 mgP/L) [6]. Consequently, to achieve a high recovery efficiency, new techniques are to be developed in order to concentrate phosphate prior to the precipitation process.

Biological treatment [7-8], adsorption [9-10], ion exchange [11-12] and nanofiltration [13-14] are common methods to concentrate and recover phosphate from wastewater. Kodera et al. (2013) [8] used anaerobic treatment to increase the phosphate concentration from 5 to 100 mgP/L by using a biofilm enriched with polyphosphate accumulating organisms. Biological treatment was carried out in a sequencing batch reactor (SBR), an anaerobic anoxic oxic (A2O) reactor and an oxidation ditch. During the anaerobic phase, phosphate taken up in aerobic conditions is released. Xiong and Peng (2008) [9] used ferrihydrite-modified diatomite, which was made by modifying the surface of raw diatomite including NaOH treatment and ferrihydrite deposition, as phosphorus adsorbent. With increased surface area and surface charge, the maximum adsorption capacity of ferrihydrite-modified diatomite increased from 10.2 mg P/g of raw diatomite to 37.3 mg P/g at pH 4 and from 1.7 mg P/g to 13.6 mg P/g at pH 8.5. The use of ion exchange for this application was studied by Kumar et al. (2007) [11]. The adsorption capacity of a Dow 3 N Cu loaded resin was 17.5 mg P/mL resin. The ion exchange process for phosphate recovery has been further enhanced by using the regenerated stream with a desorption efficiency of 85% of adsorbed phosphate to produce struvite. However, these methods have some obstacles. The anaerobic condition to achieve the release of ortho-phosphate is not easy to control. Adsorption and ion exchange need a regeneration procedure to release the phosphate from adsorbents and ion exchange resins, which leads to a higher operational cost and a more complicated process. This study aims at the fractionation and concentration of phosphate from synthetic water using selectrodialysis to increase the phosphate concentration prior to crystallization.

2. METHODS

2.1. An experimental model

A lab-scale ion exchange membrane electrodialysis system (selectrodialysis) from PCCell GmbH, Germany was used to perform the experiments. Three pieces of anion exchange membranes (PC-AM), three pieces of monovalent selective anion exchange membrane (PC-MVA) and four pieces of cation exchange membranes (PC-CM) were used in the stack, each with an effective surface area of 64 cm^2, dividing the stack into four types of compartments: electrode rinsing, feed, product, and brine (Fig.1). The membrane characteristic and operational conditions for selectrodialysis were described in Table 1 and Table 2, respectively. The current and the applied pH in the product adjusted by adding NaOH 6M were kept constant during 6h continuous operation in the experiment.

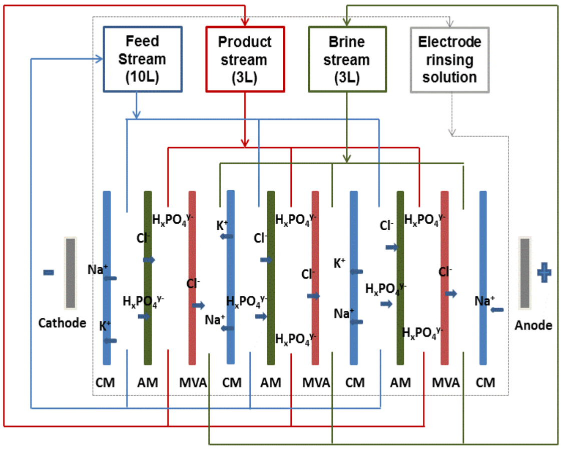

Figure 1. *Cell configuration of selectrodialysis*

Table 1. *Characteristics of PCA membranes*

Membrane	Thickness (mm)	Ion exchange capacity (meq/g)	Chemical stability (pH)	Selectivity $^{(1)}$/ Water splitting $^{(2)}$	Area resistance (Ω.cm^2)
PC-CM	0.13	1	0 – 11	>96%$^{(1)}$	0.75 – 3
PC-AM	0.09 – 0.13	1.5	0– 9	>93%$^{(1)}$	1 – 1.5
PC-MVA	0.1	1	0 – 7	> 97%$^{(1)}$	N/A

Table 2. *Operational conditions for selectrodialysis*

Current density, A.m-^{2}	pH of the product	Initial ion concentration in the feed, mM	Initial ion concentration in the product and brine, mM
46.9	8	$H_xPO_4^{y-}$ = 3; Cl^- = 17	$H_xPO_4^{y-}$ = 0 Cl^- = 20
46.9	12	$H_xPO_4^{y-}$ = 3; Cl^- = 17	
31.3	10	$H_xPO_4^{y-}$ = 3; Cl^- = 17	
62.5	10	$H_xPO_4^{y-}$ = 3; Cl^- = 17	
31.3	8	$H_xPO_4^{y-}$ = 5; Cl^- = 15	
62.5	8	$H_xPO_4^{y-}$ = 5; Cl^- = 15	
31.3	10	$H_xPO_4^{y-}$ = 7; Cl^- = 13	
46.9	12	$H_xPO_4^{y-}$ = 7; Cl^- = 13	

2.2. Analytical methods

Samples of the solution from the different compartments of the selectrodialysis unit were taken at 30 min intervals. The pH was determined by using an Orion pH meter model 420A, while the conductivity was measured by using an Orion Star A212 conductivity meter. Anion concentrations were determined by ion chromatography (Dionex ICS-2000).

3. RESULTS AND DISCUSSION

3.1 Phosphate pre-concentration profile in product stream

The profile of phosphate concentration in the product was shown in Fig.2. When comparing the increase of the phosphate concentration in the product operating at pH 12 and pH 8, the phosphate concentration at higher pH increases faster than at lower pH. One possible method that makes monovalent selective anion exchange membranes have the selectivity for monovalent ions is the addition of a small negatively charged polyelectrolyte layer on the surface of membrane, making it more difficult for multivalent ions to pass [15]. As phosphate was more present in the divalent form at increasing pH value, more phosphate was kept in the product.

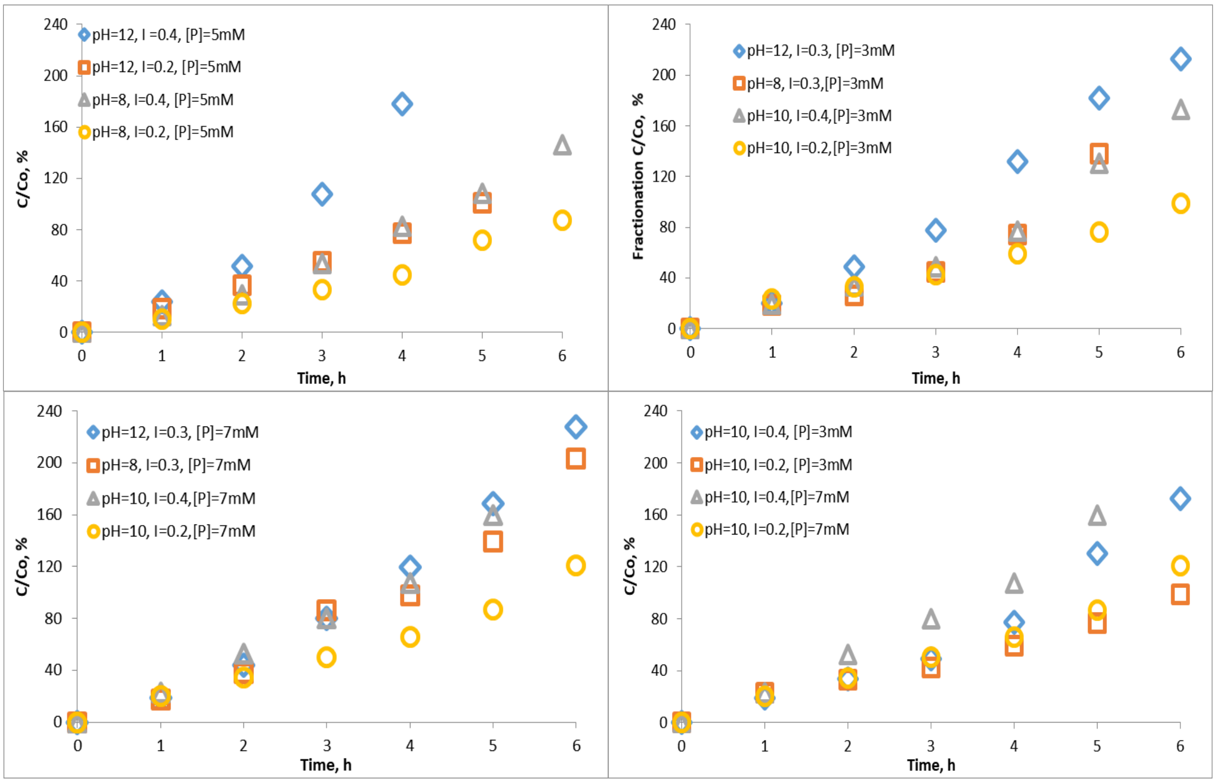

Figure 2. *Change of phosphate concentration as a function of time in the product of a selectrodialysis unit*

Moreover, it can be seen that the use of a higher current density leads to a higher phosphate concentration in the product stream. This result is not unexpected as the ions carry themselves the current, higher current densities result in high mass transfers. An increase in the initial phosphate feed concentration also resulted in an increase of the phosphate concentration in the product compartment. However, the final phosphate product concentrations respectively were 2.3 and 2.1 times the initial concentration in the feed of 7 mM and 3 mM, which proves that selectrodialysis has the possibility to pre-concentrate phosphate even at a low concentration in the feed.

Besides that, the removal percentage of phosphate from the feed to the product stream was also higher at a higher current density: 66.2% for the experiment at i = 62.5 A.m^{-2} after 330 min and 40.5% at i = 31.3 A.m^{-2} after 360 min of operation. The phosphate concentration in the brine was with 1.65 mM higher at i = 62.5 A.m^{-2} than with 1.11 mM at i = 31.3 A.m^{-2}. Similarly, starting from a phosphate feed concentration of 5 mM and applying a product pH 8, the phosphate concentration in the brine at a current density of 62.5 A.m^{-2} increased from 0 mM to 7.7 mM and only from 0 mM to 4.8 mM at i = 31.3 A.m^{-2}. This result is not unexpected as the ions carry themselves the current, higher current densities result in high mass transfers.

3.2 Chloride removal profile in product stream

Fig. 3 shows the profile of the chloride concentration in the product stream as a function of time. The chloride concentrations in the product stream decreased at pH 10 and pH 8, but initially increased at pH 12. At pH 8 of the product stream and i = 46.9 A.m-2, the chloride concentration decreased from 20 mM to 17.4 mM (Fig. 3). More chloride went from the product stream to the brine stream since the MVA membranes are selective for monovalent ions.

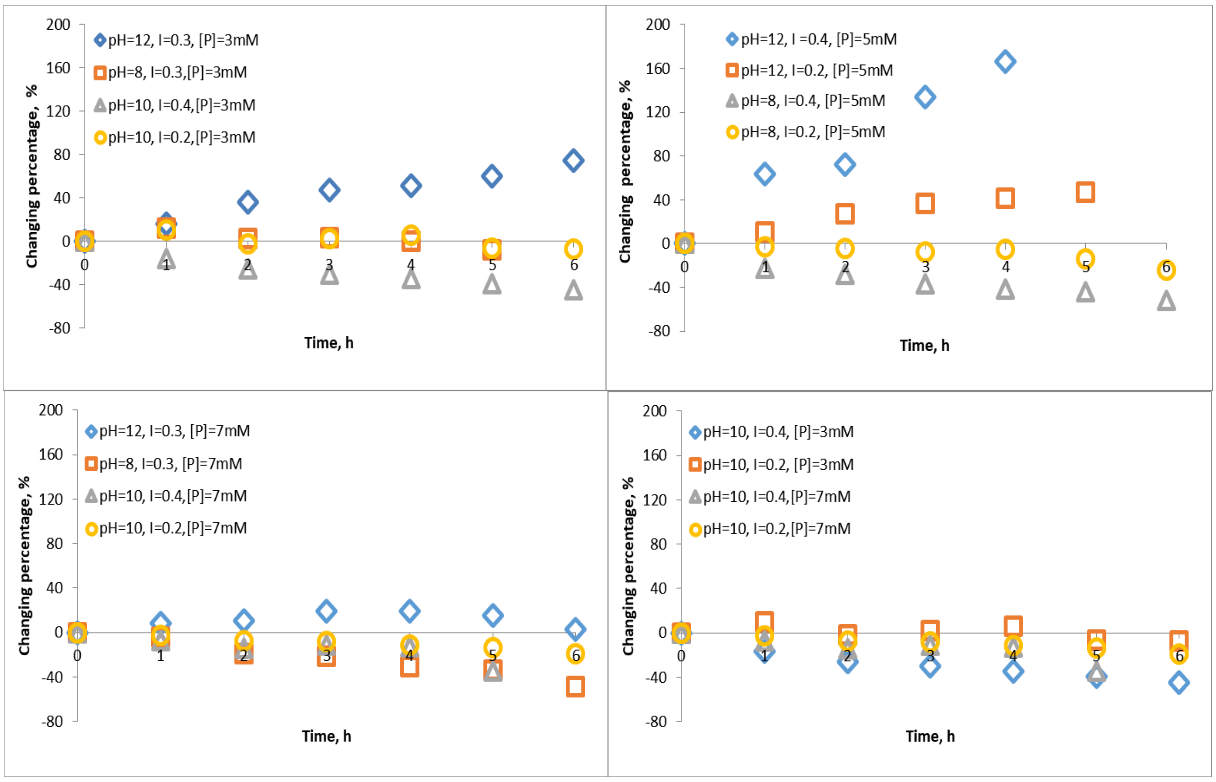

__Figure 3.__ Change of chloride concentration as a function of time in the product of a selectrodialysis unit

However, the chloride concentration increased from 20 mM to 35 mM after 330 min at pH 12 in the product stream (Fig. 3). This is probably due to the high pH in the product stream, which caused a lot of hydroxide ions (OH-) to be present in the product stream. Under the effect of the electrical field, these ions (OH-) were transferred to the brine stream instead of the chloride ions, and so part of the chloride ions that came from the feed stream to the product stream were kept in the product stream.

4. CONCLUSION

A promising and sustainable renewable source of phosphate was obtained by an integrated selectrodialysis/crystallization process, in which selectrodialysis was first used to pre-concentrate the phosphate before crystallization in a fluidized pellet reactor. An increase in current density, initial pH of the product, and initial feed concentration of phosphate led to an increase in phosphate concentration in the product of selectrodialysis. The phosphate concentration in the product can reach 16 mM with a purity of 44%, the current efficiency to transport phosphate and chloride was 26.6% for a standard anion exchange membrane and 63% for a monovalent selective anion exchange membrane.

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REFERENCES

[1] Cordell, D., Rosemarin, A., Schröder, J.J. and Smit, A.L., 2011. *Towards global phosphorus security: A systems framework for phosphorus recovery and reuse options.* Chemosphere 84, 747 - 758.

[2] Warmadewanthi and Liu, J.C., 2009. *Recovery of phosphate and ammonium as struvite from semiconductor wastewater*. Sep. Purif. Technol. 64, 368 - 373.

[3] Okano, K., Uemoto, M., Kagami, J., Miura, K., Aketo, T., Toda, M., Honda, K. and Ohtake, H., 2013. *Novel technique for phosphorus recovery from aqueous solutions using amorphous calcium silicate hydrates (A-CSHs)*. Water Res. 47, 2251 - 2259.

[4] Korchef, A., Saidou, H., Amor, M.B., 2011. *Phosphate recovery through struvite precipitation by CO2 removal: Effect of magnesium, phosphate and ammonium concentrations*. J. Hazard.Mater. 186, 602 - 613.

[5] Carlsson, H., Aspegren, H., Lee, N. and Hilmer, A., 1997. *Calcium phosphate precipitation in biological phosphorus removal systems.* Water Res. 31, 1047 - 1055.

[6] T. D. Ha, T. T. V. Nga, T. H. Son, The application of A/O-MBR system for domestic wastewater treatment in Hanoi, *Journal of Science and Technology*, 50, pp. 40-47, 2012.

[7] Korsak, L., Moreno, L., 2006. *Water Pollution VIII: Modelling, Monitoring and Management,* WIT Press, Southampton, UK.

[8] Kodera, H., Hatamoto, M., Abe, K., Kindaichi, T., Ozaki, N., Ohashi, A., 2013. *Phosphate recovery as concentrated solution from treated wastewater by a PAO-enriched biofilm reactor*. Water Res. 47, 2025 - 2032.

[9] Xiong, W., Peng, J., 2008. *Development and characterization of ferrihydrite-modified diatomite as a phosphorus adsorbent.* Water Res. 42, 4869 - 4877.

[10] Wahab, M.A., Hassine, R.B., Jellali, S., 2011. *Posidonia oceanica (L.) fibers as a potential low-cost adsorbent for the removal and recovery of orthophosphate*. J. Hazard.Mater. 191, 333 - 341.

[11] Kumar, M., Badruzzaman, M., Adham, S. and Oppenheimer, J., 2007. *Beneficial phosphate recovery from reverse osmosis (RO) concentrate of an integrated membrane system using polymeric ligand exchanger (PLE).* Water Res. 41, 2211 - 2219.

[12] Wu, R.S.S., Lam, K.H., Lee, J.M.N. and Lau, T.C., 2007. *Removal of phosphate from water by a highly selective La(III)-chelex resin*. Chemosphere 69, 289 - 294.

[13] Disha, V.J., Aravindakumar, C.T. and Aravind, U.K., 2012. *Phosphate Recovery by High Flux Low Pressure Multilayer Membranes*. Langmuir 28, 12744 - 12752.

[14] Hong, S.U., Ouyang, L. and Bruening, M.L., 2009. *Recovery of phosphate using multilayer polyelectrolyte nanofiltration membranes*. J. Membr. Sci. 327, 2 - 5.

[15] Strathmann, H., 2004. *Ion-Exchange Membrane Separation Processes,* First ed. Elsevier B.V., Amsterdam, The Netherlands.

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