Evaluation of Phosphate Recovery from Treated Municipal Wastewater by Forward Osmosis

Mehmet Dağhan Erden1, Ozlem Ozcan2, Nuray Ateş3, Niğmet Uzal4* 💿

¹Erciyes University, Graduate School of Natural and Applied Sciences, KAYSERİ ²Abdullah Gul University, Graduate School of Engineering and Science, Department of Materials Science and Mechanical Engineering, KAYSERİ

³Erciyes University, Engineering Faculty, Department of Environmental Engineering, KAYSERİ ^{*4}Abdullah Gul University, Engineering Faculty, Department of Civil Engineering, KAYSERİ

(Alınış / Received: 19.01.2023, Kabul / Accepted: 29.03.2023, Online Yayınlanma / Published Online: 02.05.2023)

Keywords Forward Osmosis, Nutrient Recovery, Membrane Filtration, Municipal Wastewater **Abstract:** As the global population continues to grow rapidly, fertilizers are becoming increasingly crucial for ensuring the security of food supply. Because phosphate is the key component in fertilizers, there is an increasing demand for alternative phosphate (PO_4^{3-}) sources. The forward osmosis (FO) process has gained more attention recently as a promising, low-cost and low-fouling membrane process for nutrient concentration and recovery. In this study, the efficiency of the FO process was evaluated in recovering PO_4^{3-} from pre-treated municipal wastewater. The effectiveness of the FO process was investigated using two different draw solutions (MgCl₂ and NaOAc) at two different concentrations (1 and 2 M) and two different recovery rates (60% and 80%). The highest PO_4^{3-} concentration of 23.20 mg/L was obtained in FO experiments at 60% recovery rate and with the concentration of the 2 M MgCl₂ draw solution.

İleri Ozmoz ile Arıtılmış Evsel Atıksudan Fosfat Geri Kazanımının Değerlendirilmesi

Membran Filtrasyon, Evsel Atıksu ozmoz (FO) prosesi, nütrient konsantrasyonu ve geri kazanımı için umut verici, düşük maliyetli ve düşük tıkanmaya neden olan bir membran prosesi olarak son zamanlarda daha fazla dikkat çekmektedir. Bu çalışmada, ön arıtımı yapılmış evsel atıksulardan PO ₄ - ³ geri kazanımında FO prosesinin etkinliği değerlendirilmiştir. FO prosesinin etkinliği, iki farklı konsantrasyonda (1 ve 2 M) iki farklı çekme çözeltisi (MgCl ₂ ve NaOAc) ve iki farklı geri kazanım oranı (%60 ve %80) kullanılarak araştırılmıştır. FO deneylerinde en yüksek PO ₄ - ³ konsantrasyonu, 23,20 mg/L ile	Anahtar Kelimeler İleri Ozmoz, Nütrient Geri Kazanımı, Membran Filtrasyon, Evsel Atıksu	Öz: Küresel nüfus hızla artmaya devam ederken, gıda arzının güvenliğini sağlamak için gübre giderek daha önemli hale gelmektedir. Fosfat (PO ₄ - ³), gübrelerdeki ana bileşen olduğundan, alternatif PO ₄ - ³ kaynaklarına yönelik arz artmaktadır. İleri ozmoz (FO) prosesi, nütrient konsantrasyonu ve geri kazanımı için umut verici, düşük maliyetli ve düşük tıkanmaya neden olan bir membran prosesi olarak son zamanlarda daha fazla dikkat çekmektedir. Bu çalışmada, ön arıtımı yapılmış evsel atıksulardan PO ₄ - ³ geri kazanımında FO prosesinin etkinliği değerlendirilmiştir. FO prosesinin etkinliği, iki farklı konsantrasyonda (1 ve 2 M) iki farklı çekme çözeltisi (MgCl ₂ ve NaOAc) ve iki farklı geri kazanım oranı (%60 ve %80) kullanılarak araştırılmıştır. FO deneylerinde en yüksek PO ₄ - ³ konsantrasyonu, 23,20 mg/L ile %60 geri kazanım oranında ve 2 M MgCl ₂ çekme çözeltisi konsantrasyonu ile elde edilmiştir.
--	--	--

*Corresponding Author, email: ozlem.ozcan@agu.edu.tr

1. Introduction

In recent years, the sustainability of natural resources has gained a new perspective with the recovery of organic, energy and nutrients in the wastewater, beyond the principle of removal. To remove nitrogen and phosphorus from wastewater, a lot of energy and chemicals are needed [1, 2]. There is a significant opportunity for water, energy, and nutrient recovery from municipal wastewater as part of the circular economy. It was predicted that one cubic meter of municipal wastewater could provide enough supply of water for 5 to 10 people per day, enough energy to power a light bulb for an average household, and enough nutrients for at least one m² of agricultural area annually [3]. Meanwhile, phosphorus for agricultural use can only be obtained by the mining of phosphate

rock [4-6]. Predictions suggest that it could be depleted by the end of the 21st century [7], which would pose a significant danger to global food security, underscoring the importance of developing strategies to manage and ultimately overcome this potential challenge [8].

Membrane filtration has been utilized in municipal wastewater treatment to produce recovered water suitable for a number of reuse purposes. These processes are both space- and resource-efficient [9]. As a result, not only is the water recovered but also pre-concentrated phosphate in the treated wastewater is obtained, which can enhance the precipitation kinetics crucial for phosphorus mineral recovery [5, 10-12]. Pressure-driven membrane processes such as reverse osmosis and nanofiltration are used for resource recovery with high rejections after secondary treatment processes [13]. However, energy consumption and fouling are the main drawbacks of pressure-driven membrane processes [14].

Effective treatment methods for the concentration of nutrients in wastewater are needed, one alternative of that is the FO process, which is an emerging treatment process [15]. FO process has recently been used as a promising alternative for recovery due to its benefits including recovering nutrients and organic matter via natural osmotic pressure [16]. Furthermore, compared to the RO process, the fouling of the FO membrane by both organic materials and inorganic precipitates is much lower [17, 18]. However, to date, most of the studies on the FO process for concentrating treated municipal wastewater have mainly focused on the FO process's operating duration rather than the water or phosphate recovery rate achieved [19, 20].

The conception of wastewater pre-concentration has not yet been investigated to its full potential, but it presents significant potential for resource recovery processes when research on it is performed for the selection determination of draw solution type and the effectiveness of the process [21]. Therefore, this study aims to investigate the performance of the FO process in terms of the recovery of phosphate from pre-treated municipal wastewater. The effect of draw solution type, concentration, and process recovery rate on the phosphate recovery potential were evaluated.

2. Materials and Method

2.1. Materials

In FO experiments, the performances of two different draw solutions, sodium acetate (NaOAc) and magnesium chloride (MgCl₂), were evaluated in terms of phosphate recovery at concentrations of 1 M and 2 M. The municipal wastewater taken from Kayseri Municipality Wastewater Treatment Plant and has been used in the FO tests after treating with a hybrid process that consist of direct ceramic microfiltration and anaerobic fluidized bed membrane bioreactor. Table 1 shows the feed sample characterization.

рН	7.9±0.15
Conductivity (mS/cm)	1.50 ± 0.1
COD (mg/L)	69±5
PO ₄ -3 (mg/L)	11.2±1.5
Cl ⁻ (mg/L)	168±51

Table 1. Characterization of the feed sample used in FO tests

The commercial flat-sheet membrane (FTS H2O, Sterlitech, USA) was used in FO tests. Table 2 shows the specifications of FO membrane used for phosphate recovery.

Table 2. Specifications of FO membrane					
Membrane material	Cellulose Triacetate (CTA)				
pH range	3-7				
Max. operating Temperature	50 °C				
Maximum Chlorine	2 ppm				
Minimum transmembrane pressure	5 psi				
Max. inlet pressure	75 psi				

2.2. Experimental

FO tests were performed at three stages: i) evaluation of the draw solution type using MgCl₂ and NaOAc at 2M concentration, ii) evaluation of recovery rate for 2M MgCl₂ at 60% and 80 recovery rates, iii) evaluation of draw solution concentration for 1 M and 2 M of MgCl₂. FO tests were performed using a lab-scale FO system as shown in Figure 1. FO system was operated at a rate of approximately 1L/min flow using the peristaltic pump for draw and feed side. The membrane module has an active membrane area of 60 cm². During the tests, the changes in weight were monitored in order to calculate the flux. Temperature was kept constant ($25\pm3^{\circ}C$) during the tests.

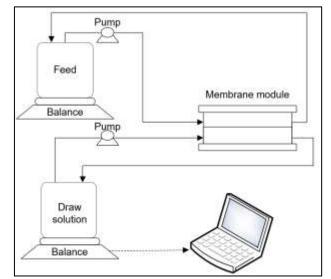


Figure 1. The schematic representation of the experimental setup

The flux values were calculated based on equation 1

$$J = \Delta V / (S \times \Delta t) \tag{1}$$

where, J is the flux, ΔV is the volumetric change, S is the effective membrane area, and Δt is the operating time. The reverse salt flux (RSF, g/m².h) was calculated according to Equation 2.

$$RSF = V_f / (C_f \times C_i) / S \times t$$
⁽²⁾

Here, Cf is the initial feed solution ion concentration, V_f is the initial feed solution volume, C_i is the feed solution ion concentration at the end of the experiment, S is the effective membrane area, and t is the operating time.

3. Results

In this study, the performance of the FO process was tested for the recovery of phosphate from pre-treated municipal wastewater. The FO experiments were conducted using two different draw solutions (MgCl₂ and NaOAc) at two different concentrations (1 and 2M) and for two different recovery rates (60 and 80%).

Table 3 shows the characteristics of the concentrated feed samples of the FO experiments for two different MgCl₂ and NaOAc draw solutions. It is seen that the increase in MgCl₂ concentration from 1 M to 2 M not significantly affected the PO₄³⁻ concentration efficiency at the 60% recovery rate. However, the PO₄³⁻ concentration of concentrated feed reached 23.2±0.1 mg/L at 60% recovery rate for 2M MgCl₂ and 14.3±7.4 mg/L for 2M NaOAc draw solution. The PO₄³⁻ concentration capacity was decreased from 23.2 mg/L to 12.4 mg/L by the increase in recovery rates from 60 to 80% for the same 2 M MgCl₂ draw solution concentration.

Table 3. Characterization of concentrated feed samples of the FO experiments for two different draw solutions
(MgCl ₂ and NaOAc) at two different concentrations (1 and 2 M) and for two different recovery rates (60 and 80%).

Parameters	2 M NaOAc (60%)	2 M MgCl ₂ (60%)	2 M MgCl ₂ (80%)	1 M MgCl ₂ (60%)
рН	8.1±0.1	8.2±0.2	8.4±0.3	7.9±0.0
Conductivity (mS/cm)	3.6±0.4	3.3±0.4	6.9±0.3	3.6±0.1
COD (mg/L)	180±34	198±71	340±48	259±28
PO4 ³⁻ (mg/L)	14.3±7.4	23.2±0.1	12.4±3.8	23.0±0.0
Cl ⁻ (mg/L)	487±51	527±42	593±136	659±43

Figure 2 illustrates the pure water, feed and RSF fluxes in FO experiments. Feed fluxes were 7.5 ± 0.2 and 9.0 ± 1.2 LMH at 60% and 80% recovery rate of 2M MgCl₂ draw solution, respectively. However, when the recovery rate was raised from 60% to 80%, RSF increased from 12.2 ± 4.2 to 30.2 ± 5.3 g/m².h for MgCl₂ draw solution. When the concentration of the draw solution was decreased from 2 M to 1 M MgCl₂, the flux was reduced from 7.5 ± 0.2 LMH to 6.6 ± 1.3 LMH. Considering the effect of draw solution type (MgCl₂ and NaOAc) at 60% recovery rate and 2 M concentration, higher RSF and lower feed flux are attained.

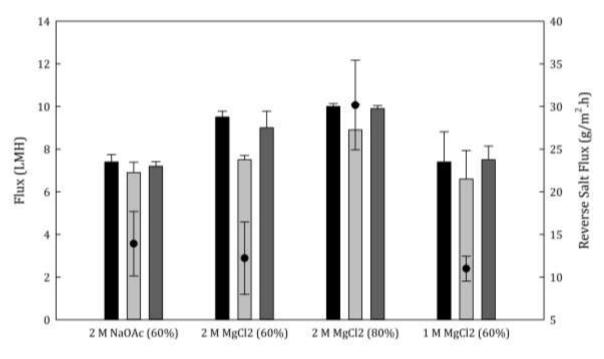


Figure 2. The pure water, feed and RSF flux values for FO experiments

4. Discussion and Conclusion

In this study, pre-treated municipal wastewater was concentrated using CTA membranes. The FO membrane rejects PO₄-³, thus ensuring a stable and reliable removal [12]. Thus, the PO₄-³ concentration increased as the draw solution concentration was increased. The highest PO₄³⁻ concentration of 23.20 mg/L was obtained in FO experiments at 60% recovery rate and with the concentration of the 2 M MgCl₂ draw solution. In the literature, RSF values were found to range from 0.2 to 7.72 g/m² h in FO studies were performed with MgCl₂ draw solution for nutrient recovery [9, 22, 23]. In this study, the FO tests performed with 60% recovery and at the concentration of the 2 M MgCl₂ draw solution where the greatest PO₄³⁻ concentration was obtained, the RSF value was 12.2±4.2 g/m² h However, RSF can be useful for nutrient recovery, even if typically viewed as a challenge in the FO process. Using the reverse magnesium flux mechanism, Xie et al. (2014) intentionally used MgCl₂ as a draw solution to

increase magnesium concentration in the feed solution [5]. Furthermore, the requirement of Ca²⁺ and/or Mg²⁺ addition for providing the struvite precipitation is eliminated due to the enrichment of these ions by the FO membrane [24, 25]. In addition, the feed solution pH can rise on its own thanks to the bidirectional diffusion of solutes that occurs during the FO tests. According to the research conducted by Xie et al. (2014) and Ansari et al. (2016), it was revealed that the precipitation of struvite and calcium phosphate both benefited directly from the bidirectional transfer of Mg²⁺/Ca²⁺ and proton (H⁺) [5, 26]. Therefore, not only is an increase in the rate of phosphate recovery attained, but also an improvement in the efficiency of further struvite precipitation methods in highly concentrated wastewater when using 2 M MgCl₂ instead of NaOAc as a draw solution.

Acknowledgment

The authors gratefully acknowledge the Scientific and Technological Research Council of Turkey for the financial support (Project No: 119Y134) Scientific Research Foundation of Erciyes University (Project No: FYL-2022-11861).

References

[1] Zeeman, G., et al. Anaerobic treatment as a core technology for energy, nutrients and water recovery from source-separated domestic waste(water). 2008. Water science and technology : a journal of the International Association on Water Pollution Research. 578 1207-1212.

[2] Sun, D., et al. Energy-neutral sustainable nutrient recovery incorporated with the wastewater purification process in an enlarged microbial nutrient recovery cell. 2018. Journal of Power Sources. 384 160-164.

[3] Lee, Y., et al. Towards Energy Self-Sufficient Water Reclamation Plants. 2013. PUB Technology Review, London.

[4] Elser, J. and Bennett, E. A broken biogeochemical cycle. 2011. Nature. 4787367 29-31.

[5] Xie, M., Nghiem, L. D., Price, W. E., and Elimelech, M. 2014. Toward resource recovery from wastewater: extraction of phosphorus from digested sludge using a hybrid forward osmosis-membrane distillation process. Environmental Science & Technology Letters. 12 191-195.

[6] Jørgensen, M. K., Sørensen, J. H., Quist-Jensen, C. A., and Christensen, M. L. 2018. Wastewater treatment and concentration of phosphorus with the hybrid osmotic microfiltration bioreactor. Journal of Membrane Science. 559 107-116.

[7] Reijnders, L. 2014. Phosphorus resources, their depletion and conservation, a review. Resources, conservation and recycling. 93 32-49.

[8] Vardanyan, A., Kafa, N., Konstantinidis, V., Shin, S. G., and Vyrides, I. 2018. Phosphorus dissolution from dewatered anaerobic sludge: Effect of pHs, microorganisms, and sequential extraction. Bioresource technology. 249 464-472.

[9] Singh, N., et al. 2019. Dewatering of sewage for nutrients and water recovery by Forward Osmosis (FO) using divalent draw solution. Journal of Water Process Engineering. 31 100853.

[10] Ali, A., Quist-Jensen, C. A., Macedonio, F., and Drioli, E. 2015. Application of membrane crystallization for minerals' recovery from produced water. Membranes. 54 772-792.

[11] Quist-Jensen, C. A., Macedonio, F., and Drioli, E. 2016. Membrane crystallization for salts recovery from brine—an experimental and theoretical analysis. Desalination and Water Treatment. 5716 7593-7603.

[12] Qiu, G., Law, Y.-M., Das, S., and Ting, Y.-P. 2015. Direct and complete phosphorus recovery from municipal wastewater using a hybrid microfiltration-forward osmosis membrane bioreactor process with seawater brine as draw solution. Environmental science & technology. 4910 6156-6163.

[13] Arola, K., Van der Bruggen, B., Mänttäri, M., and Kallioinen, M. 2019. Treatment options for nanofiltration and reverse osmosis concentrates from municipal wastewater treatment: A review. Critical Reviews in Environmental Science and Technology. 4922 2049-2116.

[14] Díez, B. and Rosal, R. A 2020. critical review of membrane modification techniques for fouling and biofouling control in pressure-driven membrane processes. Nanotechnology for Environmental Engineering. 52 1-21.

[15] Jafarinejad, S. 2021. Forward osmosis membrane technology for nutrient removal/recovery from wastewater: Recent advances, proposed designs, and future directions. Chemosphere. 263 128116.

[16] Shaffer, D. L., Werber, J. R., Jaramillo, H., Lin, S., and Elimelech, M. Forward osmosis: Where are we now? 2015. Desalination. 356 271-284.

[17] Rastogi, N. K. 2020. Forward osmosis: Principles, applications, and recent developments. Current Trends and Future Developments on (Bio-) Membranes. 3-35.

[18] Chiao, Y.-H., et al. 2022. Comparison of Fouling Behavior in Cellulose Triacetate Membranes Applied in Forward and Reverse Osmosis Industrial & Engineering Chemistry Research. 6141 15345-15354.

[19] Yadav, S., et al. 2020. Organic fouling in forward osmosis: a comprehensive review. Water. 125 1505.

[20] Almoalimi, K. and Liu, Y.-Q. 2022. Fouling and cleaning of thin film composite forward osmosis membrane treating municipal wastewater for resource recovery. Chemosphere. 288 132507.

[21] Ansari, A. J., Hai, F. I., Price, W. E., Drewes, J. E., and Nghiem, L. D. 2017. Forward osmosis as a platform for resource recovery from municipal wastewater - A critical assessment of the literature. Journal of Membrane Science. 529 195-206.

[22] Pramanik, B. K., Hai, F. I., Ansari, A. J., and Roddick, F. A. 2019. Mining phosphorus from anaerobically treated dairy manure by forward osmosis membrane. Journal of Industrial and Engineering Chemistry. 78 425-432.

[23] Singh, N., Petrinic, I., Hélix-Nielsen, C., Basu, S., and Balakrishnan, M. 2019. Influence of Forward Osmosis (FO) membrane properties on dewatering of molasses distillery wastewater. Journal of Water Process Engineering. 32 100921.

[24] Carlsson, H., Aspegren, H., Lee, N., and Hilmer, A. 1997. Calcium phosphate precipitation in biological phosphorus removal systems. Water Research. 315 1047-1055.

[25] Song, Y., Hahn, H. H., and Hoffmann, E. 2002. Effects of solution conditions on the precipitation of phosphate for recovery: A thermodynamic evaluation. Chemosphere. 4810 1029-1034.

[26] Ansari, A. J., Hai, F. I., Price, W. E., and Nghiem, L. D. 2016. Phosphorus recovery from digested sludge centrate using seawater-driven forward osmosis. Separation and Purification Technology. 163 1-7.