Exploration of Ethylenediaminetetraacetic Acid Disodium (EDTA-2Na) Salt as Novel Draw Solution for Forward Osmosis Process on Dewatering of High Nutrient Sludge

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ABSTRACT

A novel draw solution - Ethylenediaminetetraacetic acid disodium (EDTA-2Na) was explored on dewatering of high nutrient sludge by forward osmosis (FO) performance process. This study used flat-sheet cellulose triacetate FO membranes with effective membrane area of 92.95 cm^2 under membrane orientation of active layer facing feed solution and cross flow rate of 6.4 cm/s to draw water from wasted sludge using EDTA-2Na as draw solution. Results show that using EDTA-2Na as draw solution produced high water flux and lower reverse solute flux as compared with conventional inorganic salt (i.e., NaCl, $MgSO_4$) and final sludge concentration reached 34,700 mg/L after 11 hours of operation. Moreover, nutrients and organic compounds in activated sludge were also successfully removed by FO membrane with approximately 97% of NH_4^+- N and 99% of PO_4^{3-}-P due to steric effect of FO membrane and multi barrier layer of sludge forming on membrane surface. The overall performance indicates that EDTA-2Na is a bright prospect as draw solution in the potential application.

Keywords: *Forward osmosis, sludge dewatering, osmotic pressure, EDTA-2Na.*

INTRODUCTION

Forward osmosis (FO) is known as an advanced technology with excellent advantages such as low fouling, without aid pressure and high rejections of many polluted components as well. Unlike RO, FO utilises an osmotic pressure gradient to draw the water from feed solution across a semi permeable membrane to minimise operation cost and increased lifetime of membrane significantly. Hence, current researches have focused on using FO membrane for wastewater treatment (Li, 2012) or sludge dewatering (Nguyen, Chen, Yang, & Hau, 2013) recorded to be both technical and having economical feasibility. Cornelissen, Harmsen, de Korte, Ruiken et al. (2008) carried out a combination of conventional MBR with forward osmosis membrane in a single biological tank (innovative osmotic membrane bioreactor (OMBR) to treat municipal wastewater using traditional inorganic salt (i.e. NaCl) as draw solution. Although promising results have been recorded with high water flux (J_w = 9.7 L/m^2 h at 20 ± 2 °C with 1.5 M NaCl), the most critical drawback is high salt leakage (J_s= 23 g/m^2h), which affects negatively on microbiological activity. To overcome the disadvantage of the influence of inorganic salt for bioreactor, Yong, Phillip, & Elimelech (2012) investigated the reverse flux of neutral draw solute-glucose-across an asymmetric forward osmosis membrane. This method was able to obtain low reverse salt flux; however, the measured water flux for the glucose system (around 4.7 L/m^2h with

1M glucose) is one-half the water fluxes measured for the sodium chloride system. Besides, synthesis of magnetic nanoparticles as draw solutions on FO process provided a new way to design draw solutions (Bai, Liu, & Sun, 2011; Ge, Su, Chung, & Amy, 2011; Ling, Wang & Chung, 2010), but observed particle aggregation during recycling via magnetic separators is troublesome. As aforementioned, until now, the development of FO technology in water treatment is still hindered by the unavailability of suitable draw solutions. Thus, the objective of this study is to explore novel draw solution – Ethylenediaminetetraacetic acid disodium (EDTA-2Na) salt that can generate a high water flux with a minimal reverse salt diffusion. Fundamentally, EDTA exhibits high charged compounds in high pH condition according to equation (1-4):

$H_4EDTA \leftrightarrow H_3EDTA^- + H^+$ $pKa_1=1.99$ (1)
$H_3EDTA^- \leftrightarrow H_2EDTA^{2-} + H^+$ $pKa_2=2.67$ (2)
$H_2EDTA^{2-} \leftrightarrow HEDTA^{3-} + H^+$ $pKa_3=6.16$ (3)
$HEDTA^{3-} \leftrightarrow EDTA^{4-} + H^+$ $pKa_4=10.26$ (4)

Obviously, ions of trivalent and tetravalent are much easier to remain at the draw solution side which limits the diffusion of the counterion. More specially, high charged compounds of draw solution will be easily regenerated with the aid of nanotrafiltration. In this work, the critical effects of pH value and flow rate on FO performance process using EDTA-2Na as draw solution were determined. Moreover, the research also investigated simultaneously dewaterability of sludge and nutrient removal for waste activated sludge.

MATERIALS AND METHODS

Materials

Laboratory-grade EDTA-2Na (purity of 99.0%) was purchased from Sigma-Aldrich Co., Germany. NaOH and D-glucose, NH_4Cl and K_2HPO_4 were purchased from Merck Co. Ltd., Germany to adjust pH value and nutrient concentrations of activated sludge. Commercial asymmetric cellulose triacetate (CTA) membranes (Hydration Technology Inc., Albany, OR, USA) were used and classified as cartridge type for all FO experiments. The FO membrane thickness is approximately 50 μm with measured contact angle of 61^0 and membrane has been recorded to be negatively charged at typical feed waters (Cartinella, Cath, Flynn, Miller et al., 2006). Samples of activated sludge were collected at the secondary sedimentation tank of new Taipei wastewater treatment plant in Taiwan with mixed liquor suspended solid (MLSS) concentration 10,000 mg/L. And then raw sludge was added glucose, NH_4Cl and K_2HPO_4 solution to produce synthetic sludge with NH_4^+-N of 100 mg/L, PO_4^{3-}-P of 100 mg/L and dissolved organic carbon (DOC) of 200 mg/L as presented in Table 1.

Table 1: Characteristics of synthetic sludge and draw solution

Synthetic sludge using as feed solution							
MLSS (mg/L)	SVI (ml/g)	TDS (mg/L)	EC (μs/cm)	pH	NH_4^+-N (mg/L)	PO_4^{3-}-P (mg/L)	DOC (mg/L)
10,000	62	868	1328	7.2	100	100	200
EDTA-2Na using as draw solution							
pH	4.5	6.0	7.0	8.0			
NaOH, (M)	0	0.10	0.23	0.35			
TDS (g/L)	16.40	19.87	22.30	23.70			

Experimental Set-Up

The experimental set-up used in this work is shown in Figure 1 and operated in batch experiments. The FO test cell was designed with symmetric channels on both sides of feed solution and draw solution, in which each channel was 6.5 cm wide, 14.3 cm long and 0.2 cm deep. The total active FO membrane area for mass transfer was 92.95 cm^2. Two peristaltic pumps (Master Flux L/S Drive, Model 7518-00) were used to continuously circulate the flow of draw solution and feed solution on both sides of the FO membrane. The fluctuation of room temperature during experiment was in the range of $25\text{-}28^0$C. Conductivity and pH sensors were installed in the feed solution and draw solution containers to monitor the change in conductivity and pH of two solutions.

Moreover, mass transport across the membrane was determined by measuring the weight change of the draw solution container with scale, which was used for calculation of water flux.

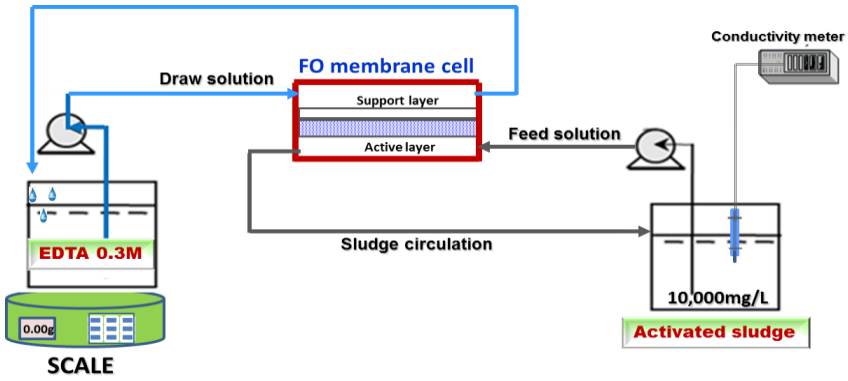

Figure 1: Schematic illustration of the high nutrient sludge dewatering FO system

Measurement of Water Flux and Reverse Solute Flux

The water flux, J_w *(L/m^{2}h)*, across the membrane was calculated by measuring the change in mass of the draw solution container versus time as follow: $J_w = (m^* 10) /(d^*A^*t)$ (5)
Where m is total increase mass of draw solution container (g), d is the density of draw solution with respective operating time (g/mL), A is the effective FO membrane area (cm^2) and t is the time (h).
The reverse solute flux, J_s *(g/m^{2}h)*, of EDTA-2Na salt was determined by the conversion of its electrical conductivity measured using a calibrated conductivity meter when EDTA-2Na dissociates in its aqueous solution as follow: $J_s= (C_t * V_t - C_o * V_o)/(A*t*100)$ (6)
where C_t and V_t are the concentration and volume of feed solution measured at time of t, respectively, C_0 and V_0 are the initial concentration and volume of feed solution.

Analytical Methods

The concentration of Na^+, PO_4^{3-}-P and NH_4^+-N was analysed by Ion Chromatography (a Dionex ICS - 90) and by a UV–Vis spectrophotometer (HACH Model DR-4000, Japan). DOC samples were prepared by using filter paper with pore size of 0.45 µm then measured by using Aurora 1010C TOC Analyzer purchased from O.I. Analytical Corporation in USA. The concentrations of MLSS was analysed using methods 2540 D described in *Standard Methods for the Examination of Water and Wastewater* (APHA, 2005). The conductivity value was monitored by conductivity meter (Sension156, Hach, China).

RESULTS AND DISCUSSION

Effect of pH on Water Flux and Salt Reverse Flux

Figure 2(a) shows the effect of the pH on the water flux and salt flux using DI water as a feed solution and 0.3 M EDTA-2Na as a draw solution for the FO performance process. The results recorded that when pH values of draw solution raised from 4.5 to 8, water fluxes increased from 6.89 to 7.64 L/m^{2}h. A key reason is that adding 0.10 - 0.35M of NaOH to adjust pH 6-8 of draw solution respectively, consequently increasing free Na^+ and osmotic pressure as well. More specially, Figure 2 (b) shows that when the flow rates were raised from 130 to 500 mL/min, water fluxes were gradually increased from 6.02 to 6.67 L/m^{2}h, respectively. An explanation for this phenomenon would be that the increasing velocity of draw solution reduced the external concentration polarisation (ECP) effect, and thus increased water flux.

Moreover, reverse salt fluxes had slightly increasing trends in pH of 4.5-7 and decreased at pH 8 then. Obviously, by pH values of 4.5-7, free Na^+ ions increased in draw solution to be main reason for increasing salt concentration in feed solution. Because FO membrane with mean pore radius of 0.37 nm (Xie et al., 2012) can remove most of the high valent ions and organic contaminants, but some monovalent ions as Na^+ with hydrated radius of 0.36 nm (Israelachvili, 2010) is able to pass through the FO membranes into feed solution container. In addition, increase salt fluxes in pH range of 4.5-7 were insignificant (from 0.16 to 0.19 g/m^2h) since the higher pH condition was used, the higher charged compounds of EDTA was recorded according to equation (1-4), resulting in increasing the Donan equilibrium effect where the reverse diffusions of cation and anion should be equal on a molar – equivalent basis as shown in Fig 3. Hence, it limited the diffusion of Na^+ ions through FO membrane even with high concentration of Na^+ in draw solution. In contrast, salt flux of pH 8 (J_s = 0.18 g/m^2h) was lower than that of pH 7 (J_s= 0.19 g/m^2h) due to appearing 14.4% of complex between $EDTA^{3-}$ and Na^+ at pH 8 as presented in Figure 4, which declined free Na^+ ions significantly. This clearly demonstrates that the higher pH was used, the higher water flux was achieved and the lower salt leakage was recorded. In other words, at 0.3 M of EDTA-2Na with pH 8, complex formation between EDTA and Na had much lower salt flux than that using NaCl and $MgSO_4$ solutions (i.e., Js of 10.7 g/m^2h from 0.5 M NaCl; 24.1 g/m^2h from 1 M NaCl; and 0.9 g/m^2h from 0.6 M $MgSO_4$) (Achilli, Cath & Childress, 2010; Su and Chung, 2011). Therefore, pH 8 is the optimum value for EDTA-2Na as draw solution on FO performance process.

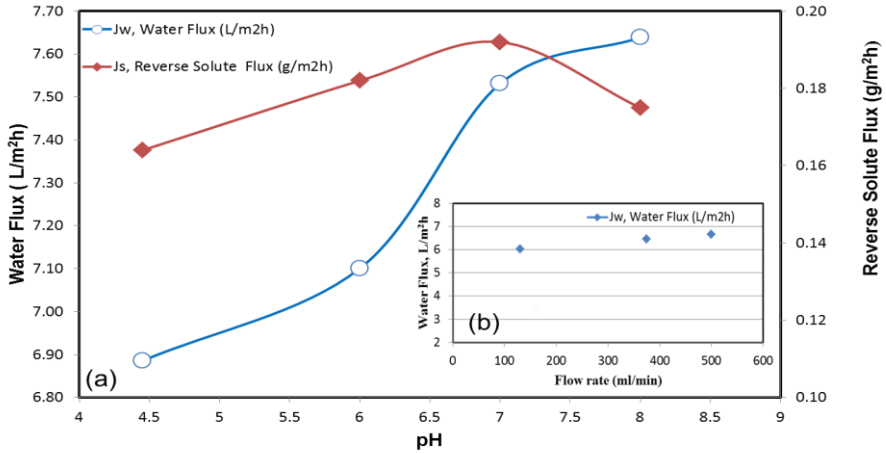

Figure 2: (a) Water flux and salt flux of different pH values (feed: DI water; draw solution: 0.3 M EDTA-2Na; membrane orientation: active layer facing the draw solution and flow rate: 500 mL/min). (b) Water flux of different flow rates (feed: DI water; draw solution: 0.3 M EDTA-2Na; and pH:7)

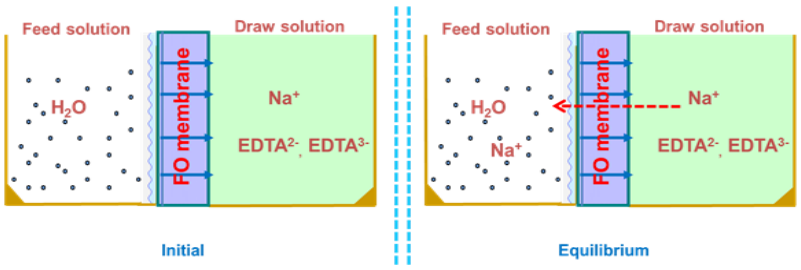

Figure 3: Ionic equilibrium across a semipermeable membrane

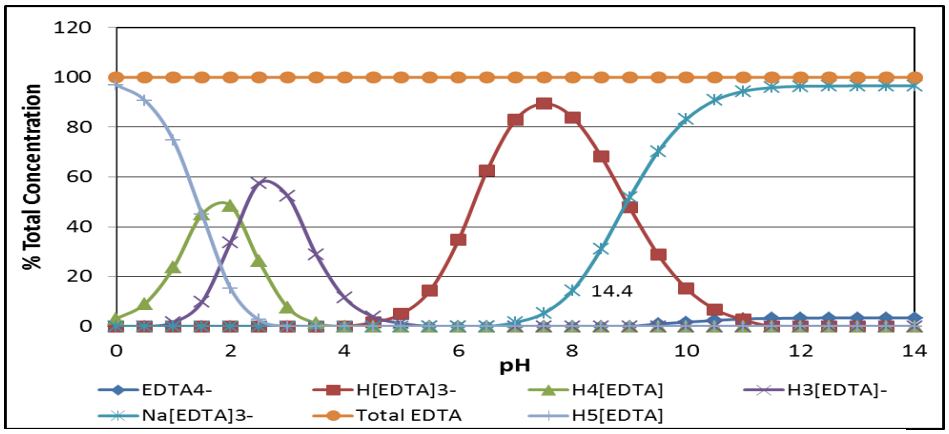

Figure 4: Complex formation between EDTA and Na from Mineql+ for EDTA concentration of 0.3 M and NaOH concentration of 0.35 M (reproduced from the data of Mineql+)

Sludge Dewatering

Figure 5 presents the variation in the water flux versus dewatering time using EDTA-2Na 0.3M as draw solution and initial sludge concentration of 10,000 mg/L as feed solution. It is observed that when dewatering time raised from 1 to 11 hours, water flux was gradually decreased from 5.87 to 2.68 L/m^{2}h. A possible reason for the change is that the laboratory set-up was conducted in batch mode, which results in the dilution of the draw solution therefore decreasing the water flux with the extension of experimental time. Furthermore, both increasing deposition of sludge cake layer on the FO membrane surface and salt concentration in feed solution prevented and decreased water flux during sludge dewatering time. On the other hand, the result recorded that when activated sludge was used as feed solution and 0.3 M EDTA-2Na as draw solution at pH 8, the reversed salt flux was less than 0.1 g/m^{2}h, indicating the positive effect of sludge cake layer on salt leakage. Based on the experimental results, sludge concentrations of feed solution depended on the permeable water volume into FO membrane. From Figure 6, it can be shown that the MLSS concentration increased quickly with dewatering time and after 11 hours of operation, the MLSS concentration reached 34,700 mg/L with nearly constant water flux of 2.68 L/m^{2}h from an initial sludge concentration of 10,000 mg/L.

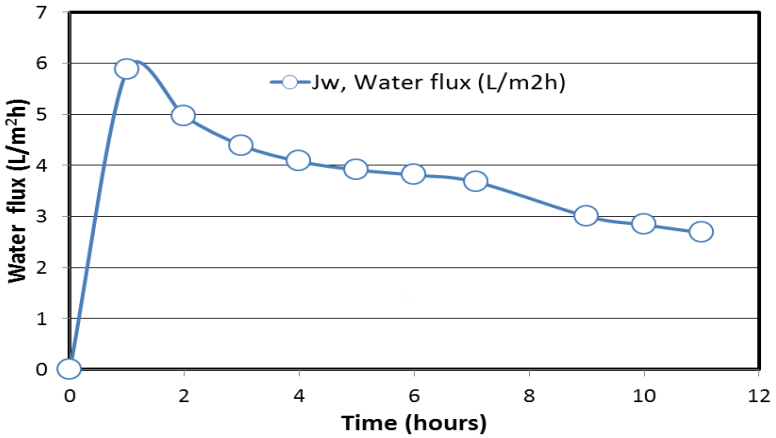

Figure 5: Variations in water flux versus time for sludge dewatering process (feed: activated sludge of MLSS 10,000 mg/L; draw solution: 0.3 M EDTA-2Na; pH: 8, membrane orientation: active layer facing the feed solution and flow rate: 500 mL/min)

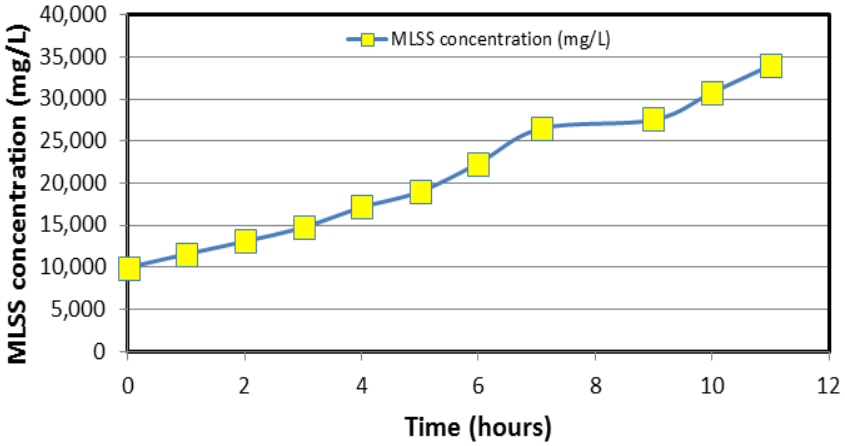

Figure 6: Variations in sludge concentration versus time (feed: activated sludge of MLSS 10,000 mg/L; draw solution: 0.3 M EDTA-2Na; pH: 8, membrane orientation: active layer facing the feed solution and flow rate: 500 mL/min)

Nutrient Removal on Sludge Dewatering of FO Membrane

Rejection of NH_4^+-N and PO_4^{3-}-P was calculated using initial concentrations in the feed solution and final concentrations in the diluted draw solution. Results pointed out that removal of nutrient compounds on sludge dewatering process by FO membrane was high with approximately 97% of NH_4^+-N and 99% PO_4^{3-}-P. A possible reason is that activated sludge often contained colloids and other functional groups that may adsorb NH_4^+ as well as PO_4^{3-} (Guo, Ngo, & Li, 2012), and then formed a multi-barrier layer of sludge on the membrane surface. As a result, nutrient compounds were completely rejected by steric effect of FO membrane.

For clarification, PO_4^{3-}-P removal was higher than that of NH_4^+-N due to both the effect of hydrated radius and charged repulse. According to Kiriukhin and Collins (2002), hydrated radius of NH_4^+-N was 0.104 nm while PO_4^{3-}-P was 0.339 nm and obviously, larger hydrated radius is higher removal efficiency. Moreover, pH of feed solution was always remained about 7.2, and at pH >7, CTA membrane is negatively charged (Cartinella et al., 2006) and easy to attach NH_4^+ ions on surface membrane and into water flux by electrostatic attractions, but CTA membrane pushes PO_4^{3-} ions by electrostatic repulsions.

CONCLUSIONS

The research demonstrated the feasibility of applying EDTA-2Na in FO process. The good solubility and high charged formation of EDTA at pH 8 not only provide effective osmotic pressure to draw water from wasted sludge, but also reduce salt leakage significantly as compared with traditional inorganic salts. In addition, FO experiments record that the MLSS concentration reached 34,700 mg/L after 11 hours of operation and nutrient compounds were removed with high efficiency approximately 97% of NH_4^+-N and 99% of PO_4^{3-}-P.

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