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**Forward osmosis for oily wastewater reclamation: Multi-charged oxalic
acid complexes as draw solutes**

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ABSTRACT

Forward osmosis (FO) has demonstrated its merits in hybrid FO seawater desalination. However, FO may have a potential for other applications if suitable draw solutes are available. In this study, a series of novel draw solutes based on oxalic acid (OA)-transitional metal complexes are presented. Influential factors of FO performance have been systematically investigated by varying the transitional metals, cations of the complex draw solutes as well as the experimental conditions. Compared to NaCl and other recently synthesized draw solutes, the OA complexes show superior FO performance in terms of high water fluxes up to 27.5 and 89.1 LMH under the respective FO and PRO (pressure retarded osmosis) modes, both with negligible reverse solute fluxes. The features of octahedral geometry, abundant hydrophilic groups and ionic species are crucial for the OA complexes as appropriate draw solutes with satisfactory FO performance. Among the synthesized OA complexes, the ammonium salt of chromic complex ($\text{NH}_4\text{-Cr-OA}$) outperforms others due to the presence of more ionic species in its complex system. $\text{NH}_4\text{-Cr-OA}$ also performs better than the typical NaCl draw solute in FO oily wastewater treatment with higher water recovery and negligible reverse fluxes. Dilute solutions of OA complexes have been reconcentrated through membrane distillation (MD) and reused to new round of FO processes. The OA complexes have demonstrated their suitability and superiority as a novel class of draw solutes for the FO process in this study.

Keywords: Forward osmosis; Draw solute; Hydroacid complex; Water treatment; Oil-water separation.

1. Introduction

Oily wastewater discharged from the oil and gas industry without proper treatment is a major environmental problem in many areas (Ahmadun et al., 2009; Gryta et al., 2001). A range of physical, chemical and biological processes such as flotation, adsorption, coagulation and flocculation, and biological treatment have been employed to treat oily wastewater prior to its discharge (Ahmadun et al., 2009; Gryta et al., 2001; Escobar and der Bruggen, 2011; Pintor et al. 2016; Chakrabarty et al., 2008; Abbasi et al., 2010). However, these methods have drawbacks such as low efficiency, high cost, potentially toxic chemical involvement and recontamination. Moreover, they are unable to remove small oil droplets and emulsified oil effectively (Ahmadun et al., 2009; Gryta et al., 2001; Chakrabarty et al., 2008; Abbasi et al., 2010) to meet the requirements set by the environmental regulations where the total oil and grease in discharge water should be in the range of 10 – 15 mg/L (Abbasi et al., 2010).

Depending on the size and charged conditions of the components in oily water, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), have been used to treat oily water (Ahmadun et al., 2009; Gryta et al., 2001; Escobar and der Bruggen, 2011; Pintor et al. 2016; Chakrabarty et al., 2008; Abbasi et al., 2010). Compared to the aforementioned conventional methods, membrane separation has the advantages of high efficiency for oil removal, low costs and no chemical additives. However, these pressure-driven membrane processes suffer from severe fouling in oil-water separation. Not only does fouling lower the separation efficiency but also increases operational cost and shortens membrane life. Therefore, a more effective membrane technology for the reclamation of oily wastewater is urgently needed.

Compared to the MF, UF and NF processes, RO and forward osmosis (FO) are superior in oil-water separation in terms of the rejection at the molecular level due to their small membrane pore sizes. FO is better than RO in terms of its osmotically driven feature with low fouling propensity (Zhang et al., 2014; Li et al., 2014; Lutchmiah et al., 2014; Cath et al., 2006; Zhao et al., 2012; Liu and Mi, 2012; Li et al., 2012). However, FO has its own drawbacks. To effectively compete with RO, FO must (1) employ high performance FO membranes, (2) use effective draw solutes and (3) demonstrate economical feasibility in draw solute regeneration (Ge et al., 2013). Significant progress has been made on high performance FO membranes over the past decade (Duong et al., 2014; Coday et al., 2015; Fane et al., 2015; Sukitpaneenit and Chung, 2012). However, the exploration of draw solutes with characteristics of good FO performance and relatively easy regeneration progresses slowly (Ge et al., 2013; Li and Wang, 2013). Although a wide range of draw solutes, such as gases, sugars, inorganic and organic salts, have been proposed over the past few decades (Ge et al., 2013; Long and Wang, 2016; Long et al., 2016), most draw solutes still encounter one or more problems such as low water flux, severe salt leakage, high viscosity, and difficulties in regeneration (Ge et al., 2013; Li and Wang, 2013).

Oxalic acid (OA)-transition metal complexes have octahedral configurations in the metal centers and can ionize into multiple ionic species in their aqueous solutions (Ge and Chung, 2015). Such features make them appropriate as draw solutes for FO processes. OA complexes have been preliminarily investigated in our previous studies and proven their superiority as draw solutes for FO in terms of high water fluxes, insignificant solute leakage and easy recovery (Ge and Chung, 2015; Ge et al., 2016). To further explore the factors influencing the FO performance of draw solutes made from OA complexes, novel OA complexes were proposed as draw solutes for FO and applied to wastewater reclamation in this study. Therefore, the objectives of this

paper are to (1) design and synthesize a series of highly soluble novel draw solutes based on OA complexes; (2) systematically study their suitability as draw solutes in the FO process as a function of transitional metals, cations of the complex draw solutes, membranes, and experimental conditions; and (3) investigate their effectiveness for oily wastewater reclamation via the FO process. This study may provide useful insights to design better draw solutes for FO treatment of oily wastewater.

2. Materials and Methods

2.1. Starting materials

Oxalate compounds of $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 6\text{H}_2\text{O}$ (98%), $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (98%), $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (99%) and $\text{H}_2\text{C}_2\text{O}_4$ (98%), dichromate substances of $\text{K}_2\text{Cr}_2\text{O}_7$ (99%), $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (99.5%) and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (99.5%), other materials of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (99%), H_2O_2 (30 wt. % in H_2O), petroleum (18% aromatics basis with a boiling point of 180-220 °C) and Tween 80 surfactant were purchased from Sigma-Aldrich. NaOH (99%) and NaCl (99.5%) were supplied by Merck. Acetone (99%) was obtained from Acros Organics. Commercial CTA HTI flat sheet membranes (Batch No. 060327-3, Hydration Technologies Inc., OR, USA) and self-made thin-film composite (TFC) FO membranes fabricated on polyethersulfone (PES) hollow fibers (TFC-PES) were used for FO experiments (Sukitpaneenit and Chung, 2012). All the chemicals were used as received. DI water from a Milli-Q (Millipore, USA) system was used in all experiments.

2.2. Experimental

Syntheses of OA Complexes

K₃[Fe(C₂O₄)₃] (referred to as **K-Fe-OA**) Fe(NH₄)₂(SO₄)₂·6H₂O (0.05 mol, 20g) was dissolved in 50 mL DI water. 100 mL of 1 M H₂C₂O₄ was added stepwise to the solution. A yellow precipitate of iron (II) oxalate (FeC₂O₄) was formed immediately. After constantly stirring for 30 minutes at 40°C, 6.3 g H₂C₂O₄ (0.07 mol) and 70 mL 2 M NaOH were respectively added to the FeC₂O₄ suspension. After 10 minutes stirring, 8 mL of 30 % H₂O₂ was added dropwise. The mixture was heated to boiling until no more bubbles came out. With the addition of 30 mL 1 M H₂C₂O₄, a green solution was achieved. The resultant solution was continuously stirred for 30 minutes and then concentrated to ~30 mL using a rotary evaporator. Cold acetone was added to precipitate the product and purified 3 times from H₂O/acetone. Green powders of K₃[Fe(C₂O₄)₃]·2H₂O were obtained after vacuum drying (yield > 95%) and ready for characterization and performance tests. Elemental analysis: calcd: C 15.2, H 0.82, O 47.4 %; found: C 15.6, H 0.86, O 47.1%.

(NH₄)₃[Cr(C₂O₄)₃] (**NH₄-Cr-OA**) (NH₄)₂C₂O₄ (0.11 mol, 15.6 g) and H₂C₂O₄ (0.37 mol, 32.9 g) in 100 mL DI water were stirred to form a clear orange red solution. (NH₄)₂Cr₂O₇ (0.05 mol, 12.6 g) powders were added to the solution in small portions with vigorous stirring. The color of the resultant solution changed from clear red to dark blue gradually, indication the occurrence of the reaction. After stirring for two more hours, the solution was concentrated to ~20 mL through a rotary evaporator. Cold acetone was added to precipitate the product. It was then purified 3 times from H₂O/acetone. Dark blue powders of (NH₄)₃[Cr(C₂O₄)₃]·H₂O were obtained after vacuum drying (yield > 95%) and ready for characterization and performance tests. Elemental analysis: calcd: C 18.6, H 3.6, O 53.6%; found: C 18.8, H 3.5, O 54.0%.

The synthesis of **K₃[Cr(C₂O₄)₃]** (**K-Cr-OA**) is similar to that of **NH₄-Cr-OA** except that (NH₄)₂C₂O₄ and (NH₄)₂Cr₂O₇ were replaced with K₂C₂O₄ and K₂Cr₂O₇, respectively. Elemental

analysis: calcd for $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$: C 15.4, H 0.85, O 47.8%; found: C 15.8, H 0.86, O 48.3%. $\text{Na}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ (**Na-Fe-OA**) and $\text{Na}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ (**Na-Cr-OA**) were synthesized according to the literature (Ge and Chung, 2015; Ge et al., 2016).

Determination of the Physicochemical Properties of the OA Complex Solution

The relative viscosity of the oxalic acid complex draw solutions compared to that of DI water, η_r , as a function of concentration was calculated using equation (1):

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t\rho}{t_0\rho_0} \quad (1)$$

where t (s) is the elution time of the complex solution measured by a AVS 360 inherent viscosity meter, ρ ($\text{g} \cdot \text{mL}^{-1}$) is the density of the complex solution measured by a DMA 35 potable density meter, and t_0 (s) and ρ_0 ($\text{g} \cdot \text{mL}^{-1}$) are the elution time and density of DI water, respectively.

The osmotic pressures of the complex solutions were measured using a model 3250 osmometer (Advanced Instruments, Inc.). This device employed a freezing-point depression method to measure the osmolality of a solution which was derived from the total solute concentration. The osmolality was then converted to the osmotic pressure of the solution.

2.3. Characterizations of OA Complexes

Elemental analyses were performed on a Perkin-Elmer PE 2400 CHNS Elemental Analyzer. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Perkin-Elmer FT-IR Spectrometer Spectrum 2000 in the range of 4000 to 400 cm^{-1} to determine the functional groups. The solid KBr method was used to obtain the FTIR spectra. Thermogravimetric analysis

(TGA) with a TGA 2050 thermogravimetric analyzer (TA Instruments, New Castle, DE) was used to measure the composition of the OA complexes. The TGA experiments were conducted under N₂ from 30 to 700 °C at a heating rate of 10 °C/min.

2.4. FO processes

For HTI flat sheet membranes, a crossflow permeation cell was designed in a frame configuration with an effective membrane area of 8.0 cm². It consisted of a rectangular channel on each side of the membrane, while the feed and draw solutions flowed co-currently through their respective cell channels at a velocity of 6.4 cm·s⁻¹. The TFC-PES hollow fiber membranes with properties shown **Table 1** were used for hollow fiber membrane measurements. The flow rates along the lumen and shell sides were 10 mL·min⁻¹ and 300 mL·min⁻¹, respectively. Each FO module packed with 5 pieces of TFC-PES hollow fibers with 14.5 cm in length was used in FO processes. The effective membrane areas calculated from the lumen and shell sides are 19.5 cm² and 23.0 cm² respectively. The temperatures of both feed and draw solutions were maintained at 23 ± 0.5 °C. Draw solutions were prepared from the synthesized oxalic acid complexes. DI water and oily wastewater were used as the feeds. The original volumes of the feed and draw solutions were 1.0 L unless otherwise stated. Two operation modes; namely, PRO mode and FO mode, were employed during the experiments. All data were obtained from 3 parallel tests.

The water flux, J_w , (L·m⁻²·hr⁻¹, abbreviated as LMH) was calculated from the volume change of the feed solution using equation (2).

$$J_w = \frac{\Delta V}{A \Delta t} \quad (2)$$

where ΔV (L) is the volume change of the feed solution over a predetermined time Δt (hr) and A is the effective membrane surface area (m²). The reverse solute flux, J_s (gMH), in FO refers to

the draw solute permeating from the draw solution to the feed side. Since the complexes dissociate and are conductive in their aqueous solutions, a standard curve of conductivity as a function of known solution concentration was established prior to the FO experiments. Hence, the concentration of draw solutes permeating to the feed solution was obtained from the curve through the conversion of its electrical conductivity measured using a calibrated conductivity meter (Oakton Instruments, Vernon Hills, IL). The value of J_s was determined from the increase in the feed conductivity (Ge and Chung, 2013):

$$J_s = \frac{(C_t V_t) - (C_0 V_0)}{\Delta t} \frac{1}{A_m} \quad (3)$$

where C_0 ($\text{mol} \cdot \text{L}^{-1}$) and V_0 (L) are the initial salt concentration and the initial volume of the feed, respectively, while C_t ($\text{mol} \cdot \text{L}^{-1}$) and V_t (L) are the salt concentration and the volume of the feed over a predetermined time Δt (h), respectively.

2.5. Oily Water Emulsion Preparation and Analyses

The oil-water emulsions were prepared by mixing petroleum and Tween 80 in a ratio of 9 to 1 in 500 mL DI water. The mixture was then blended by a high speed blender (Waring Products Division, Torrington, CT, USA) for 3 minutes to acquire a stable emulsified oil-water solution. The resultant emulsion was diluted to a desirable concentration with DI water. Fresh oil-water stock solutions were prepared each day to minimize the effects of possible oil droplet aggregation.

The oil rejection (R , %) in the FO process was determined by equation (4) (Zhang et al., 2014):

$$R = \left(1 - \frac{C_d \times V_d / V_p}{C_f} \right) \times 100\% \quad (4)$$

where C_d (ppm) is the oil concentration in the draw solution at the end of an FO test, V_d (L) is the final volume of the draw solution, V_p (L) is the volume of the permeate water, and C_f (ppm) is the oil concentration in the feed solution. C_d was measured using an ultraviolet (UV) spectrometer with the aid of the standard UV absorption curve of oil-water solutions at 270 nm (Zhang et al., 2014; Li et al., 2014; Duong et al., 2014). The standard curve was developed by measuring UV absorptions of a series of oil-water solutions with known concentrations.

2.6. Recycling of OA complex after FO

The draw solution of OA complex was diluted after FO due to water transport from the feed side to draw solution. A membrane distillation (MD) setup with home-made PVDF composite hollow fiber membranes was employed to recycle the draw solute in this study (Ge et al., 2016).²¹ The dilute draw solution after FO processes (50 ± 0.5 °C) were circulated through the shell side of the MD module at the flow rate of $500 \text{ mL}\cdot\text{min}^{-1}$, while cold DI water (20 ± 0.5 °C) as the permeate solution co-currently flowed through the lumen side of the PVDF hollow fiber at the flow rate of $200 \text{ mL}\cdot\text{min}^{-1}$. The water flux was calculated by equation (2) and the solute concentration in the permeate was determined by equation (3).

3. Results and Discussion

3.1. Syntheses and characterizations

A series of OA complexes were synthesized via one-pot reaction with quantitative yields for all substances. **Table 2** shows the proposed structures and formula of these OA complexes. The real structures of Na-Fe-OA and Na-Cr-OA have been confirmed by the X-ray single crystal chromatography (Ge and Chung, 2015) (**Table 3(a)**) and are consistent with the proposed ones.

The compositions of the OA complexes were determined by elemental analyses, FTIR and TGA prior to FO experiments.

The FTIR spectra confirm the coordination between the oxalic acid ligand and Cr^{3+} or Fe^{3+} metal centers. **Fig. 1** displays the FTIR spectra of the chromic complexes. The OA spectrum is included for comparison. The peaks at ~ 3500 are from the O-H groups in the crystal water molecules or N-H groups in the case of $\text{NH}_4\text{-Cr-OA}$. Characteristic absorptions at $1650 \sim 1700 \text{ cm}^{-1}$ and $1260 \sim 1273 \text{ cm}^{-1}$ correspond to C=O and C-O of the carboxyl groups, respectively (Ge and Chung, 2015; Palma et al., 2007). The coordination with the transitional metal centers at the hydroxyl site leads to a lower stretching frequency of C=O from the oxalic acid (1700 cm^{-1}) to the chromic complex ($\sim 1680 \text{ cm}^{-1}$) due to the fact that the electrophilic Cr^{3+} core weakens the electron cloud density of C=O via conjugation. The absorption at $\sim 540 \text{ cm}^{-1}$ is attributed to the presence of the metal-oxygen bond (Cr-O), as verified in those of similar complexes (Das et al., 2008). The analytic results affirm the successful coordination between the oxalic acid ligand and the metal cores.

The TGA experiments reveal the composition of these OA complexes. **Fig. 2** illustrates the representative TGA spectra of the chromic complexes. Due to the presence of crystal water molecules in all complexes, the thermal decomposition of the OA complexes occurs in two stages. The first-stage weight loss is mainly related to the release of H_2O molecules that takes place at $50 \sim 120^\circ\text{C}$. The second-stage weight loss is associated with the decomposition of unhydrated intermediates that occurs at much higher temperatures of $270 \sim 450^\circ\text{C}$. As a result, small volatile molecules of H_2O , CO or CO_2 were evaporated and non-volatile metallic oxides left as residues. The TGA spectra disclose the thermal stability of the chromic complexes in the

order of $\text{K-Cr-OA} > \text{Na-Cr-OA} > \text{NH}_4\text{-Cr-OA}$. The chromium complexes exhibit higher thermal stability than their iron analogues, in agreement with other complex draw solutes explored previously (Ge and Chung, 2013). The thermal decomposition mechanism of the OA complexes is also the same as those with similar structures reported elsewhere (Patron et al., 2003). As tabulated in **Table 4**, the experimental weight losses are very close to the calculated ones for all OA complexes, indicating the validity of the proposed structures for the OA ferric and chromic complexes.

3.2. Physicochemical Properties of the OA Complexes

pH and Solubility of OA and Its Complexes. Oxalic acid has a pH value of 0.8 - 1.2 when its concentration ranges from 0.5 to 2.0 M. This acidic property inhibits it from being a draw solute directly as most membranes, such as commonly used cellulose acetate/triacetate membranes (Zou et al., 2011; McCutcheon et al., 2006; Zhao and Zou, 2011) and TFC membranes (Zhang et al., 2014; Li et al., 2014; Duong et al., 2014; Fane et al., 2015), are unable to tolerate such acidic conditions and will undergo structural damage. As a consequence, inconsistent results will be incurred in FO experiments. Unlike the oxalic acid ligand, its ferric and chromic complexes are neutral (pH 6.8 ~ 7.5) in their aqueous solutions because the carboxyl groups in oxalic acid convert to carboxylates in the OA complexes via the coordination with metal cores (**Table 3(a)**).

Besides the change in acid-base properties, the solute solubility also varies remarkably when proceeding from oxalic acid to its complexes. The OA complexes exhibit better solubility than the oxalic acid under the same conditions. This is ascribed to a higher degree of dissociation of carboxylic groups which leads to more ionic species present in the complex solutions.

1 Interestingly, the chromic complexes are more soluble than their ferric analogues. This may be
2 due to different dissociation abilities of the OA complexes. Both Cr and Fe elements belong to
3 the fourth period and Cr is in front of Fe in the periodic table. The valence electron number in the
4 outermost 3d electron shell is 3 for Cr^{3+} and 5 for Fe^{3+} . As a result, the former has a smaller
5 radius and stronger electron-withdrawing property than the latter. This is in agreement with the
6 data derived from the X-ray single crystal diffraction analysis (Ge and Chung, 2015). As shown
7 in **Table 3(b)**, the bond lengths between the metal core and the coordinated oxygen are in the
8 range of 1.96 - 1.98 (Å) and 2.00 - 2.03 (Å) for the respective Cr-O and Fe-O in the OA
9 complexes, indicating a stronger interaction between the chromic core and the carboxyl group.
10 Therefore, the chromic complex exhibits a stronger degree of dissociation and higher solubility
11 than its ferric analogue. Their effects on conductivity and osmotic pressures will be discussed
12 below.

13 Both their neutral property in aqueous solutions and higher solubility make OA complexes
14 more suitable as draw solutes than their oxalic acid precursor.

15
16 **Relative Viscosity of the OA Complexes.** As the viscosity of a draw solution impacts FO
17 performance, the relative viscosity (η_r) of the OA complexes to water is studied prior to the FO
18 tests. The relative viscosity as a function of draw solution concentration is depicted in **Fig. 3**.
19 Because of solubility constraints, some OA complexes are unable to be investigated over the
20 entire range of 0.5 – 2.0 M. For each complex, η_r increases with increasing solution
21 concentration and a greater increment is observed at higher concentrations. For both chromic and
22 ferric complexes, the viscosity changes with the variation of cation and follows the order of K-
23 M-OA > Na-M-OA > NH_4 -M-OA (M = Cr or Fe) at the same concentration. Chromic and ferric

complexes have similar relative viscosity at the same concentration when their cations are the same. The OA complexes exhibit a slightly higher viscosity than the NaCl draw solute (Ge and Chung, 2015) but a lower relative viscosity than other synthetic draw solutes reported in the literature (Patron et al., 2003; Ge et al., 2012). Since the viscosity of a draw solute is associated with its diffusion coefficient and inversely proportional to its FO water flux, the draw solutes made from OA complexes may outperform those synthetic draw solutes with higher viscosity when other experimental conditions are the same. The effects of viscosity variation on the FO performance of OA complexes will be discussed in the following section.

Osmotic Pressures of OA Complexes. According to the principles of the FO process, the gradient of osmotic pressure across FO membranes is the driving force. **Fig. 4** shows the osmotic pressures of the OA complex solutions as a function of their concentrations.

These OA complexes can produce high osmotic pressures due to the fact that each one of them can dissociate into a multi-charged anion and $K^+/Na^+/NH_4^+$ cations in aqueous solution. Based on the Van't Hoff equation (Ge et al., 2013; Ge et al., 2016), the osmotic pressure of a solution is colligative and proportional to the ionic numbers in it. Hence, consistent with **Fig. 4**, the osmotic pressure increases with increasing solution concentration for each complex. However, the relationship between the osmotic pressure and concentration is not rectilinear, especially at high concentrations. This is associated with the dissociation degree of the OA complexes. The OA complexes are able to fully dissociate in dilute solutions but the ionization degree decreases and the ionic number reduces with an increase in concentration, resulting in a slightly non-linear relationship between the osmotic pressure and solution concentration.

For both chromic and ferric complexes, the osmotic pressure follows the order of K-M-OA < Na-M-OA < NH₄-M-OA (M = Cr or Fe) at the same concentration, opposite to the order of their viscosity (**Fig. 3**). Meanwhile, the chromic complexes generate higher osmotic pressures than their corresponding ferric analogues. This is in line with the aforementioned dissociation degrees of the OA complexes and consistent with their solubility. The osmotic pressures produced by these OA complexes are much higher than those of recently developed synthetic draw solutes such as magnetic nanoparticles (Ge et al., 2013; Bai et al., 2011; Ge et al., 2016), polyelectrolytes (Ge et al., 2012), hydrogels (Li et al., 2011) and many others (Ge et al., 2013).

3.3. FO Performance

The attributes of high water solubility and dissociation into multiple ionic species make the OA complexes attractive candidates as draw solutes. **Fig. 5** shows their FO performance as a function of concentration and testing mode via the commercial HTI membrane using DI water as the feed. The water flux increases with increasing concentration for all OA complexes regardless of the operation of FO (draw solution flowing against the membrane support layer) or PRO (pressure retarded osmosis) (draw solution flowing against the membrane active layer) mode. A higher water flux is achieved for each OA complex under the PRO mode than the FO mode due to the adverse effect of internal concentration polarization (ICP) present in the latter, as reported in the literature (Cath et al., 2006; Zhao et al., 2012; Liu et al., 2016). For both chromic and ferric complexes, the ammonium salts perform best followed by the sodium salts and then the potassium salts in their respective series. This order is consistent with the trend of their osmotic pressures (**Fig. 4**), but inversely proportional to the order of their viscosity (**Fig. 3**). **Fig. 5** also discloses that the chromic complexes consistently outperform their ferric analogues under the

1 same testing conditions. The specific solute fluxes (J_s/J_w) in FO for both chromic and ferric
2 complexes are in the range of 0.02 ~ 0.07 g/L, indicating the negligible loss of draw solutes in
3 treating one liter of feed solutions. Compared to other recently developed draw solutes (Ge et al.
4 2013; Bai et al., 2011; Li et al., 2011), these OA complexes exhibit superiorities as a novel class
5 of draw solutes in view of much higher FO water fluxes under the same testing conditions.

6 **Fig. 5(c) and 5(d)** display insignificant reverse solute fluxes for all OA complexes even
7 though salt leakages increase slightly with an increase in solution concentration. All OA
8 complexes have a reverse solute flux lower than 0.8 g/MH in all experiments, which is much
9 lower than the values of other draw solutes measured under the same conditions (Ge et al. 2013;
10 Sukitpaneenit and Chung, 2012). The insignificant reverse solute fluxes are primarily attributed
11 to the unique spatial configuration of these OA complexes. As depicted in **Table 3(a)**, the X-ray
12 single crystal structures generated from the cif files (Ge and Chung, 2015) show that both Cr^{3+}
13 and Fe^{3+} are 6-coordinated in their OA complexes with an octahedral shape in the metal center.
14 The expanded structure significantly reduces the reverse diffusion of OA complex molecules to
15 the feed solution in the FO process. Moreover, there are abundant free oxygen atoms at the ends
16 of the carboxylic groups in each OA complex that are prone to form H-bonds with the
17 surrounding water molecules. As a consequence, the OA complexes may form a large network
18 with neighboring water molecules via H-bonds. Both the octahedral configuration and the
19 network forms between the OA complexes and water molecules contribute to their minimal
20 reverse fluxes in FO experiments.

21 To study the membrane influence on the FO performance of the OA complex draw solutes, a
22 self-made TFC-PES hollow fiber FO membrane is also employed in this study. This membrane
23 had previously shown its superiority to several FO membranes, such as cellulose acetate (CA)

membranes, commercial HTI membranes, and TFC flat sheet membranes for seawater desalination (Sukitpaneemit and Chung, 2012). $\text{NH}_4\text{-Cr-OA}$ and $\text{NH}_4\text{-Fe-OA}$ are chosen in this study because they exhibited the best performance in their respective series. For comparison, NaCl is also tested as a reference draw solute.

Fig. 6 compares the FO performance between the OA complexes and NaCl using the TFC-PES hollow fibers. Both $\text{NH}_4\text{-Cr-OA}$ and $\text{NH}_4\text{-Fe-OA}$ outperform NaCl under the PRO mode, while $\text{NH}_4\text{-Cr-OA}$ performs best among these three draw solutes due to the presence of more ionic species in its complex system at the same molar concentration. The superiority of the ammonium salts over NaCl is less impressive under the FO mode because they have comparable water fluxes. This may be attributed to the fact that the OA complexes have a larger structure which possibly leads to a lower diffusion coefficient and hence induces more severe ICP than NaCl. Nevertheless, $\text{NH}_4\text{-Cr-OA}$ still has a higher water flux than NaCl under the studied conditions. In addition, compared to NaCl, all OA complexes under both the FO and PRO modes exhibit insignificant reverse fluxes (**Fig. 6(b)**). Therefore, the use of these OA complex draw solutes may not only reduce the risk of secondary contamination from the draw solutions but also minimize the replenishment cost of draw solutes.

A comparison between **Fig. 5** and **6** indicates that the TFC-PES hollow fiber has much better FO performance than the HTI flat sheet membrane in terms of higher water flux and lower reverse solute flux. This may be due to the fact that the TFC-PES membrane has a smaller pore size, a thinner dense active layer and a more porous support than the HTI membrane (Sukitpaneemit and Chung, 2012), all of which are conducive to better FO performance. Therefore, the FO performance of these draw solutes can be further improved when a more ideal FO membrane is used.

FO treatment of oily wastewater. Since the combination of $\text{NH}_4\text{-Cr-OA}$ and TFC-PES membranes shows the best FO performance, 1.0 M $\text{NH}_4\text{-Cr-OA}$ and TFC-PES hollow fibers are selected to study the FO treatment of oily wastewater. Three petroleum water emulsions at concentrations of 500, 1500 and 3000 ppm are employed as the feeds. NaCl (1.0 M) is also employed as the benchmark because it has been often used as the draw solute in oil-water separation (Zhang et al., 2014; Li et al., 2014; Duong et al., 2014; Coday et al., 2015). **Fig. 7** illustrates the effects of oil concentration and operation mode on FO performance within a 30-min duration for each test.

For both $\text{NH}_4\text{-Cr-OA}$ and NaCl, the water fluxes decrease when replacing DI water with oily wastewater as the feed solution under both FO and PRO modes because the former reduces the effective osmotic driving force across the membrane and more easily causes concentration polarization than the latter. The PRO mode shows a bigger drop in water flux than the FO mode at higher oil concentrations due to the more severe fouling problem under the PRO mode. Similar to the previous observation when using DI water as the feed (**Fig. 6**), **Fig. 7** displays that $\text{NH}_4\text{-Cr-OA}$ surpasses NaCl with better FO performance in terms of a higher water flux and a negligible reverse solute flux under the same experimental conditions. Meanwhile, a much lower specific solute fluxes (J_s/J_w) of less than 0.01g/L for $\text{NH}_4\text{-Cr-OA}$ is observed than NaCl (around 0.2 g/L) during the entire experiments.

As fouling is a more severe problem in oily wastewater reclamation than in the treatment of many other wastewaters (Gryta et al., 2001; Escobar and der Bruggen, 2011; Pintor et al. 2016; Chakrabarty et al., 2008; Coday et al., 2015; Liu et al., 2016; Bui and McCutcheon, 2013; She et al., 2016), a series of 10-hour oil-water separation experiments are also conducted to investigate

the efficiency and sustainability of $\text{NH}_4\text{-Cr-OA}$ for the reclamation of oily wastewater. For comparison, 1.0 M $\text{NH}_4\text{-Cr-OA}$ and NaCl are both employed as draw solutes; meanwhile, both DI water and 500 ppm oily wastewater are used as feeds. Each feed has an initial volume of 1.0 liter and the tests are under the FO mode. To minimize the dilution effect, the draw solute concentration was maintained at 1.0 M during the entire test with the aid of a conductivity meter.

The FO performance as a function of time is summarized in **Fig. 8**. The water fluxes are nearly constant when using DI as the feed and $\text{NH}_4\text{-Cr-OA}$ or NaCl as draw solutes. Consistent with previous results, $\text{NH}_4\text{-Cr-OA}$ induces a higher water flux than NaCl . A distinctive trend is observed when DI water is replaced with the 500 ppm oily water. Both water fluxes decline in the first four hours for both draw solutes. After that, water fluxes change slightly because the FO process reaches a stable state. This phenomenon suggests that the membrane fouling caused by the oil droplets gradually achieves equilibrium in the first four hours and does not cause notable fluctuations in water flux afterward (Long et al., 2016). This phenomenon has been observed in other FO studies of oil-water separation (Zhang et al., 2014; Li et al., 2014; Duong et al., 2014).

Fig. 8(b) shows the evolution of draw solute concentration in the feed solutions as a function of time due to the reverse diffusions of draw solutes. The $\text{NH}_4\text{-Cr-OA}$ concentrations in both feeds increase slightly with time but their final values are still very low because of the large $\text{NH}_4\text{-Cr-OA}$ molecules. The reverse diffusion of $\text{NH}_4\text{-Cr-OA}$ might occur due to the defects of the TFC-PES membrane, as demonstrated in other studies using polyelectrolytes as draw solutes.²⁹ In contrast, the NaCl concentration in both feeds increases dramatically due to the significant NaCl reverse diffusions, in line with those displayed in **Fig. 3** and **4**. The NaCl concentration in the feed water is higher than that in oily water due to a slightly lower NaCl

reverse diffusion in the latter. This is consistent with the aforementioned observation in **Fig. 7(d)**.

As shown in **Fig. 8(c)**, the final oil concentrations in the feeds increase to almost two times of the initial concentration after 10-h experiments for both $\text{NH}_4\text{-Cr-OA}$ and NaCl cases. However, a more concentrated oil-water solution and a higher feed recovery are achieved when using $\text{NH}_4\text{-Cr-OA}$ as the draw solute. The efficient water recovery together with the negligible reverse solute diffusion in the oily wastewater treatment demonstrates the advantage of $\text{NH}_4\text{-Cr-OA}$ as a novel draw solute. In addition, based on the UV absorption analyses of all $\text{NH}_4\text{-Cr-OA}$ draw solutes, the oil rejection is higher than 99.5% in all FO experiments, demonstrating the effectiveness of the $\text{NH}_4\text{-Cr-OA}$ promoted FO technology in the reclamation of oily wastewater.

3.4. OA Complex regeneration

MD was proven to be effective to regenerate OA complex from its diluted solution in our previous study (Ge et al., 2016). As all of the OA complexes in this study exhibit good thermal stability (**Fig. 2**), the regeneration of OA complexes after the FO experiments were also carried out through MD processes in this work. **Fig. 9** shows the water flux and solute rejection as a function of $\text{NH}_4\text{-Cr-OA}$ concentration. A slight decline in water flux was observed with the concentration of $\text{NH}_4\text{-Cr-OA}$ solution increase. This may be due to the increased viscosity and decreased water activity of the feed solution which results in a reduction in effective vapor pressure and hence water flux. Temperature polarization may also contribute to the reduction in water flux.

No variation in conductivity was detected on the permeate side of MD under all experimental conditions, indicating a complete rejection of $\text{NH}_4\text{-Cr-OA}$ in the MD recycling process (**Fig. 9**).

When the recycled $\text{NH}_4\text{-Cr-OA}$ was reused in the new rounds of FO experiments, reproducible experimental results were obtained, demonstrating the good stability and reusability of OA complexes.

4. Conclusions

In summary, the simple but efficient one-pot synthesis approach as well as the attributes of good water solubility, expanded structures and abundant ionic species in aqueous solutions makes the OA complexes attractive as draw solutes for the FO process. The high water fluxes, negligible reverse solute fluxes and efficient water recovery in the FO treatment of oily wastewater demonstrate the suitability and practicality of using OA complexes as draw solutes. This work may provide useful insights to design better draw solutes as well as to explore the OA complexes for other FO applications.

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Table 1. Properties of TFC-PES hollow fiber membranes

Membrane	OD/ID (mm)	Pure water permeability (LMH/bar)	Mean pore radius (nm)	Molecular weight cut off (Da)	Rejection to NaCl (%)
TFC-PES	1080/840	1.64	0.28	213	83.04

<p>Oxalic acid (OA) ($\text{C}_2\text{H}_2\text{O}_4$)</p>			
different cation	<p>K-Fe-OA ($\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$) MW = 473</p>	<p>Na-Fe-OA ($\text{Na}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$) MW = 425</p>	<p>NH₄-Fe-OA ($(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$) MW = 410</p>
	<p>K-Cr-OA ($\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$) MW = 469</p>	<p>Na-Cr-OA ($\text{Na}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$) MW = 421</p>	<p>NH₄-Cr-OA ($(\text{NH}_4)_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot \text{H}_2\text{O}$) MW = 388</p>
	different anion		

Table 2. Structures and molecules of the OA complexes and their OA precursor

(a)

X-ray single crystal structures

(b)

Bond length (Å)							
Fe-O1	2.01	Fe-O2	2.00	Cr-O1	1.97	Cr-O2	1.97
Fe-O5	2.00	Fe-O6	2.03	Cr-O5	1.96	Cr-O6	1.97
Fe-O9	2.03	Fe-O10	2.00	Cr-O9	1.98	Cr-O10	1.96

Table 3. (a) X-ray single crystal structures of anionic Na-Fe-OA and Na-Cr-OA; (b) Bond lengths between the transition metals and their connected oxygen atoms

Noted: the serial number of the oxygen atoms is generated directly from the original CIF files

Sample	Decomposition stage	Decomposition temperature (°C)	Observed weight loss (%)	Calculated weight loss (%)
K-Cr-OA	I (H ₂ O)	70 ~ 114	8.0	7.7
	II (organic ligand)	360 ~ 450	44.2	46.0
Na-Cr-OA	I (H ₂ O)	55 ~ 96	8.4	8.6
	II (organic ligand)	343 ~ 422	52.3	51.3
NH ₄ -Cr-OA	I (H ₂ O)	50 ~ 120	4.7	4.6
	II (organic ligand)	270 ~ 292	88.3	88.1

Table 4. Weight losses in the 1st and 2nd stages of the OA chromic complexes in TGA measurements

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	<p>K-Cr-OA ($\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$) MW = 469</p>	<p>Na-Cr-OA ($\text{Na}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$) MW = 421</p>	<p>NH₄-Cr-OA ($(\text{NH}_4)_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot \text{H}_2\text{O}$) MW = 388</p>
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Noted: the serial number of the oxygen atoms is generated directly from the original CIF files

Fig. 1. FTIR spectra of OA and OA chromic complexes.

Fig. 2. Spectra of TGA measurements of the OA chromic complexes

Sample	Decomposition stage	Decomposition temperature (°C)	Observed weight loss (%)	Calculated weight loss (%)
K-Cr-OA	I (H ₂ O)	70 ~ 114	8.0	7.7
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Table 4. Weight losses in the 1st and 2nd stages of the OA chromic complexes in TGA measurements

(a)

(b)

Fig. 3. Relative viscosity as a function of draw solute concentration

(a)

(b)

Fig. 4. Osmotic pressure as a function of draw solute concentration

Fig. 5. The FO performance comparison of oxalic acid complexes through HTI membranes: (a) water flux of Fe-OA; (b) water flux of Cr-OA; (c) reverse flux of Fe-OA; (d) reverse flux of Cr-OA. DI water as the feed solution.

(a)

(b)

Fig. 6. Performance comparison via TFC-PES membranes: (a) water fluxes of NH₄-Fe-OA, NH₄-Cr-OA and NaCl; (c) reverse fluxes of NH₄-Fe-OA, NH₄-Cr-OA and NaCl. DI water as the feed solution.

Fig. 7. The FO performance comparison of $\text{NH}_4\text{-Cr-OA}$ and NaCl in oily wastewater treatment via TFC-PES membranes: (a) water flux under the PRO mode; (b) water flux under the FO mode; (c) reverse flux under the PRO mode; (d) reverse flux under the FO mode. Oily wastewater as the feed solution.

Fig. 8. 10-h FO performance of $\text{NH}_4\text{-Cr-OA}$ and NaCl via the TFC-PES membranes: (a) water flux; (b) solute concentration in the feed; (c) feed water recovery. 1M $\text{NH}_4\text{-Cr-OA}$ or NaCl as the draw solution, DI water or 500 ppm oily wastewater as the feed, under FO mode.

Fig. 9. Water flux and solute rejection in the recycle of $\text{NH}_4\text{-Cr-OA}$.

1. Forward osmosis (FO) for oily wastewater reclamation
2. Multi-charged oxalic acid complexes as draw solutes for FO
3. Oxalic acid complexes: high water flux with insignificant salt leakage in FO
4. Oxalic acid complexes: regenerated by MD and applied to FO for oil-water separation