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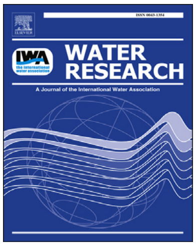

Ferric and cobaltous hydroacid complexes for forward osmosis (FO) processes

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ABSTRACT

Cupric and ferric hydroacid complexes have proven their advantages as draw solutes in forward osmosis in terms of high water fluxes, negligible reverse solute fluxes and easy recovery (Ge and Chung, 2013. Hydroacid complexes: A new class of draw solutes to promote forward osmosis (FO) processes. Chemical Communications 49, 8471–8473.). In this study, cobaltous hydroacid complexes were explored as draw solutes and compared with the ferric hydroacid complex to study the factors influencing their FO performance. The solutions of the cobaltous complexes produce high osmotic pressures due to the presence of abundant hydrophilic groups. These solutes are able to dissociate and form a multi-charged anion and Na^+ cations in water. In addition, these complexes have expanded structures which lead to negligible reverse solute fluxes and provide relatively easy approaches in regeneration. These characteristics make the newly synthesized cobaltous complexes appropriate as draw solutes. The FO performance of the cobaltous and ferric-citric acid (Fe-CA) complexes were evaluated respectively through cellulose acetate membranes, thin-film composite membranes fabricated on polyethersulfone supports (referred as TFC-PES), and polybenzimidazole and PES dual-layer (referred as PBI/PES) hollow fiber membranes. Under the conditions of DI water as the feed and facing the support layer of TFC-PES FO membranes (PRO mode), draw solutions at 2.0 M produced relatively high water fluxes of 39–48 LMH ($L\ m^{-2}\ hr^{-1}$) with negligible reverse solute fluxes. A water flux of 17.4 LMH was achieved when model seawater of 3.5 wt.% NaCl replaced DI water as the feed and 2.0 M Fe-CA as the draw solution under the same conditions. The performance of these hydroacid complexes surpasses those of the synthetic draw solutes developed in recent years. This observation, along with the relatively easy regeneration, makes these complexes very promising as a novel class of draw solutes.

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1. Introduction

Freshwater shortage has been becoming a global problem nowadays (Crow, 2012). To alleviate the water scarcity, clean water production through seawater desalination and wastewater reclamation has received much attention. Pressure-driven membrane processes have been employed for water production, among which reverse osmosis (RO) is the most popular technology for seawater desalination (Escobar and der Bruggen, 2011; Lee et al., 2011). However, RO processes are energy intensive due to the involvement of high pressure. In addition, low water recovery, high concentration polarization and severe membrane fouling are ubiquitous in RO processes. Furthermore, the discharge of RO retentate is troublesome because of its unfriendly impact on environment. Hence, a sustainable and environmental friendly water production technology that consumes less energy is needed urgently.

Forward osmosis (FO) is an emerging technology for wastewater reclamation and seawater desalination (Cath et al., 2006; Qin et al., 2012; Zhao et al., 2012; Kim et al., 2013). Unlike RO, the FO process is driven by the osmotic pressure difference between two solutions separated by a semipermeable membrane. The semipermeable membrane allows water to spontaneously pass through it but rejects the solutes. Hence, the FO process can be operated at low or negligible pressures. Moreover, FO has additional advantages such as high rejections to a variety of contaminants and low fouling propensities (Mi and Elimelech, 2010; Li et al., 2011a,b; Liu and Mi, 2012; Gu et al., 2013). Despite these strongpoints, however, FO still faces the challenges of the unavailability of high performance FO membranes and suitable draw solutes with characteristics of low cost and easy recovery (Chung et al., 2012).

Some FO membranes with good performance of high water fluxes and low reverse solute fluxes have recently been developed (Han et al., 2012; Song et al., 2011; Sukitpaneenit and Chung, 2012), while exploring an appropriate draw solute is still challenging. Many categories of commercial compounds from gases, nutrients to salts have been explored as draw solutes (Ge et al., 2013). These conventional draw solutes, however, have problems of severe reverse solute fluxes during FO processes and/or high energy consumption during regeneration (Achilli et al., 2010). Synthetic draw solutes explored in recent years have shown promise in terms of negligible reverse solute fluxes or low-energy consumption during regeneration (Ge et al., 2011; Li et al., 2011a,b; Ling et al., 2010; Yen et al., 2010; Stone et al., 2013; Ge et al., 2012; Ge and Chung, 2013; Han et al., 2013). However, most of them produce much lower water fluxes than those conventional draw solutes. Meanwhile, some were synthesized through a series of complicated chemical reactions (Yen et al., 2010); some have problems of particle aggregation (Ge et al., 2011; Ling et al., 2010), high viscosity (Ge et al., 2012) or difficult recycling (Achilli et al., 2010). These characteristics make them impractical in FO processes. Therefore, it is essential to explore novel draw solutes having features of high water flux, low reverse solute flux, and relatively easy regeneration.

Compared to recent synthetic draw solutes, hydroacid complexes are promising as draw solutes, as demonstrated in our early study (Ge and Chung, 2013). Not only have they reasonably high water fluxes and negligible reverse solute fluxes, but also they can be recycled relatively easily. Among this new class of draw solutes, the ferric-citric acid (Fe-CA) complex has the best performance when using the HTI cellulose triacetate membrane in the FO process. To study the factors influencing the FO performance of hydroacid complexes, novel monomer and dimer cobaltous citric acid complexes (referred as Co–CA and Co2-CA, respectively) were synthesized and used as draw solutes. Performance comparisons were made among these cobaltous complexes and Fe-CA under different experimental conditions. For fair comparison and exploration of their applicability to different FO membranes, three types of FO membranes were employed during tests, namely, cellulose acetate, thin-film composite membranes fabricated on polyethersulfone supports (TFC-PES) and polybenzimidazole PES (PBI/PES) dual layer hollow fiber membranes. This study may give insights for the exploration of new draw solutes and pave the way to advance the FO technology.

2. Materials and methods

2.1. *Starting materials*

$Fe(NO_3)_3 \cdot 9H_2O$ (99%), $Co(NO_3)_2 \cdot 6H_2O$ (98%) and citric acid (99%) were purchased from Sigma–Aldrich. NaOH (99%) and NaCl (99.5%) were supplied by Merck. Ethanol (99%) was obtained from Acros Organics. All the chemicals above were used as received. DI water from a Milli-Q (Millipore, USA) system was used in all experiments.

2.2. *Experimental*

2.2.1. *Syntheses*

Synthesis of $Na_4[Co(C_6H_5O_7)_2]$ (Co-CA): $Co(NO_3)_2 \cdot 6H_2O$ (10 mmol, 2.9 g) and citric acid (20 mmol, 3.84 g) in DI water (30 mL) were stirred overnight at 50 °C. Then NaOH (1.0 M) was added dropwise until pH ∼ 8. The resultant solution was then stirred for 3 h and concentrated to ∼10 mL under vacuum. Cold ethanol was added to precipitate the product. It was then purified 3 times from H_2O/EtOH. The purple solid of $Na_4[Co(C_6H_5O_7)_2] \cdot 2H_2O$ was dried under vacuum (yield > 95%) and ready for characterization and performance tests. Elemental analysis: calcd: C 25.5, H 2.5, O 45.3%; found: C 25.8, H 2.4, O 44.9%.

Synthesis of $Na_2[Co_2(C_6H_5O_7)_2(H_2O)_4]$ (Co2-CA) is similar to that of Co-CA except that the ratio of $Co(NO_3)_2 \cdot 6H_2O$ to citric acid is 1:1. Calcd for Co2-CA ($Na_2[Co_2(C_6H_5O_7)_2(H_2O)_4] \cdot H_2O$): C 22.8, H 3.2, O 54.1%; found: C 23.3, H 3.0, O 53.7%. Fe-CA was synthesized according to the reported procedures in our previous study (Ge and Chung, 2013).

2.2.2. *Relative viscosity of Fe-CA, Co-CA and Co2-CA*

The relative viscosity of Fe-CA, Co-CA and Co2-CA, η_r, compared to DI water is calculated using Equation (1) (McNaught and Wilkinson, 1997):

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t\rho}{t_0\rho_0} \tag{1}$$