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A cage-like supramolecular draw solute that promotes forward osmosis for wastewater remediation and source recovery



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ABSTRACT

Draw solute is a key element of forward osmosis (FO) technology. Here we design a cage-like supramolecular material of N-(hexamethylenetetramine) propane-1-sulfonate (HMTA⁺ – SO₃) for the simultaneous wastewater remediation and protein enrichment via FO processes. HMTA⁺ – SO₃ reclaims water efficiently with a transfer rate of 36.0 LMH at 1.0 M without reverse solute diffusion, outperforming the conventional NaCl draw solute that produces a smaller water flux coupled with severe solute leakage. The good performance originates from the innate nature of HMTA⁺ – SO₃ that can create a sufficiently high osmotic pressure to drive the FO process and form a supramolecular network with H₂O via hydrogen-bonding to prevent solute leakage. Protein enriched by HMTA⁺ – SO₃ remains intact in structure but those concentrated by typical NH₄HCO₃ or NaCl draw solutes are either contaminated or denatured resulting from the severe reverse solute diffusion in the FO process. HMTA⁺ – SO₃ can be readily collected quantitatively via precipitation purification and reused with reproducible results. The HMTA⁺ – SO₃ facilitated FO process for protein-containing wastewater treatment reported here may ultimately find use in processing other high-value-added compounds.

1. Introduction

Wastewater from the food and pharmaceutical industries usually contains high-value-added compounds. Isolating these valuable substances from wastewater not only reduces the risks of environmental contamination, but also avoids the cost of resource generation [1-3]. Ovalbumin (OVA) is a commonly recognized high value-added substance and widely used in nutraceutical, medical, dietary supplements and food fields [4,5]. Pure OVA enrichment has become a recent research focus [6-8]. Protein purification is usually achieved by conventional technologies such as freeze drying [9], salt precipitation [10], isoelectric precipitation [11], and membrane separation (nanofiltration (NF) [12], reverse osmosis (RO) [13] and electro-dialysis [14]). However, problems including low protein recovery efficiency, intensive energy input, protein denaturation and secondary protein contamination are widely presented with those methods. Alike other proteins, OVA is heat sensitive and highly reactive with the presence of functional -COOH and -OH groups. Typical thermal or chemistry approaches may alter its structure. Thus there is an urgent need to develop a green and cost-effective technology for OVA recovery from contaminated water.

Here we propose a relatively emerging membrane technology,

namely, forward osmosis (FO) for simultaneous water purification and OVA recovery. This technology relies on the osmotic differential across membrane to drive water transfer from the feed side to draw solution to achieve solute-water separation [15-17]. FO can be operated under ambient conditions without applied pressures. Obviously, a key point for FO is to select a draw solute that is able to generate a sufficient osmotic pressure to drive the FO process. Meanwhile a suitable draw solute needs to have a reasonable size to minimize solute leakage, and is stable and reusable [18,19]. Guided by these criteria, we herein report a novel draw solute of N-(hexamethylenetetramine) propane-1-sulfonate $(HMTA^+ - SO_3)$ for the simultaneous OVA enrichment and wastewater remediation via FO (Fig. 1). Experimental results indicate that $HMTA^+ - SO_3^-$ has a high water recovery efficiency with water permeability of 36.0 LMH at 1.0 M coupled with negligible solute leakage resulted from the ability to produce a high osmotic pressure and formation of a polymeric network. Contrary to the commonly used NH4HCO3 and NaCl draw solutes which either contaminate or react with OVA when used for FO OVA concentration, $HMTA^+ - SO_3^-$ remains the structure of OVA intact. Moreover, The HMTA⁺ – SO_3^- draw solute can be quantitatively recovered via precipitation and reused for next FO cycles with reproducible results. The HMTA⁺ - SO₃⁻ promoted FO

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Fig. 1. The novel $HMTA^+ - SO_3^-$ draw solute in (a) is applied to FO processes for wastewater remediation and protein enrichment; $HMTA^+ - SO_3^-$ can be completely recovered via solvent precipitation (in (b)). Protein enriched by $HMTA^+ - SO_3^-$ remains intact while those by conventional draw solutes are either contaminated or denatured in structure (in (c)).



Fig. 2. (a) The synthesis scheme of $HMTA^+ - SO_3^-$, (b) The single crystal structure and self-assembly process of $HMTA^+ - SO_3^-$.

process demonstrates a facile and viable approach in recycling valuable substances and wastewater treatment simultaneously, and can be potentially used to treat wastewaters containing other high value-added substances.

2. Experimental

2.1. Materials

NaCl (99.5%) and NH_4HCO_3 (99.0%) were purchased from Sinopharm Chemical Reagent Co. Ltd. and deployed as conventional draw solutes for reference. Poly(ether sulfone) (PES, Solvay Advanced



Fig. 3. ¹H NMR spectra of HMTA⁺ – SO_3^- and the HMTA precursor.



Fig. 4. FTIR spectra of the HMTA and HMTA⁺ - SO₃⁻.

Polymer), sulfonated poly(ether sulfone) (sPES, Solvay Advanced Polymer) were used to prepare the substrates of FO membrane. m-Phenylenediamine (MPD, Macklin) and 1,3,5-benzenetricarboxylic chloride (TMC, Micxy) were deployed to synthesize the dense polyamide (PA) layer of the FO membrane. Hexamethylenetetramine (HMTA, 99.5%, Aladdin), 1,3-propane sulfone (99.5%, Aladdin), EtOH (99.7%, Sinopharm Chemical Reagent) were used respectively as the raw materials and solvent to synthesize the draw solute of HMTA⁺ – SO₃⁻. OVA (99.0%, Aladdin) was used to simulate the OVA containing wastewater. Deionized (DI) water produced by a Milli-Q unit (Millipore, U.S.A.) was used throughout the experiments.

2.2. Preparation of HMTA⁺ – SO_3^-

 $\rm HMTA^+ - SO_3^-$ was synthesized from hexamethylenetetramine (HMTA) and 1,3-propane sulfone at room temperature. Briefly, HMTA (14.0 g, 0.1 mol) and 1,3-propane sulfone (48.8 g, 0.4 mol) were loaded separately to a 250 mL flask containing 100 mL EtOH. A colorless homogenous solution was obtained instantly and stirred constantly for 72

h at room temperature. White precipitate was formed gradually in the course of reaction which was then separated by filtration, washed with EtOH, and dried in vacuum successively to give the target compound with a yield >96%. ¹H NMR (400 MHz in D₂O): δ 2.14–2.25 (m, 2H, CH₂CH₂SO₃), 2.99 (t, J = 7.0 Hz, 2H, CH₂SO₃), 3.06–3.17 (m, 2H, N⁺CH₂), 4.64–4.74 (dd, J = 12.9 Hz, 6H, NCH₂N), 5.18 (s, 6H, NCH₂N⁺).

2.3. Characterizations of HMTA⁺ - SO_3^-

Nuclear magnetic resonance (NMR) spectroscopy, fourier transform infrared (FTIR) spectroscopy and single-crystal X-ray crystallography analysis were used to determine the chemical composition and molecular structure of HMTA⁺ – SO₃⁻. The physicochemical properties of HMTA⁺ – SO₃⁻ were systematically studied by analyzing its relative viscosity over DI water, osmotic pressure, conductivity, acid-base properties, and particle size distribution.

The chemical composition and molecular structure of HMTA⁺ – SO₃⁻ were characterized respectively by nuclear magnetic resonance (NMR) spectroscopy (Bruker ACF300 300 MHz FT NMR spectrometer), fourier transform infrared (FTIR) spectroscopy (iS10 Nicolet spectrophotometer) with a wavenumber range of 4000–400 cm⁻¹, and single-crystal X-ray crystallography analysis via a Bruker SMART CCD diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å). A single crystal of HMTA⁺ – SO₃⁻ was grown by slow diffusion of ethanol into the concentrated HMTA⁺ – SO₃⁻ aqueous solution and suitable for analysis in one week.

The physicochemical properties of $HMTA^+ - SO_3^-$ were studied by analyzing its relative viscosity over DI water, osmotic pressure (OSMOMAT 3000 freezing point osmometer, Gonotec 3000, Germany), conductivity (LEICI conductivity meter, DDSJ-308F, Shanghai), acidbase properties (Horiba pH meter D-54, Japan), and particle size distribution (NanoBrook-Omni measurements under the dynamic light scattering mode).

The relative viscosity (η) of HMTA⁺ – SO₃⁻ solution against that of DI water was calculated using equation (1)

$$\eta = \frac{\eta_D}{\eta_W} = \frac{t_D \rho_D}{t_W \rho_W} \tag{1}$$

where t_D and t_W (s) are the respective flowing times of the draw solution and DI water which are determined by using an Ubbelohde viscosity meter (SYP1003-III, Shanghai) at 25 °C; their individual densities, ρ_D and ρ_W (g/cm³) are measured by a DMA 35 portable density meter.

2.4. FO processes

The FO performance of $HMTA^+ - SO_3^-$ was evaluated via a commercial bench-scale FO system (Suzhou Faith Hope Membrane Technology Co., Ltd.). The home-made thin-film composite (TFC) flat sheet membranes based on either polyether sulfone (PES) [20] or sulfonated polyether sulfone (sPES) [21] substrates, denoted as TFC-PES and TFC-sPES membranes, respectively, were used in FO experiments [22]. The FO performance of $HMTA^+ - SO_3^-$ was evaluated via a commercial bench-scale FO system (Suzhou Faith Hope Membrane Technology Co., Ltd.). The flow rates of feed and draw solutions were both controlled at $0.3~{\rm L~min^{-1}}$ through a peristaltic pump (Changzhou Kejian, BT00–600 M). The home-made thin-film composite (TFC) flat sheet membranes based on either PES or sPES substrates, denoted as TFC-PES and TFC-sPES membranes, respectively, were used in FO experiments. The testing membrane area was 4.5 cm². Feed solution was made from either DI water or OVA solution, while draw solution was prepared from the self-synthesized HMTA⁺ - SO₃⁻ or commercial NaCl and NH₄HCO₃. Experimental temperature was maintained at 25 \pm 0.5 $^\circ C$ all the time.

Water flux, J_W (L/m² h, denoted as LMH), in FO processes was determined by the volume change in per unit time and area on the draw



Fig. 5. (a) Comparisons in the relative viscosity and osmotic pressure of $HMTA^+ - SO_3^-$, NaCl and NH_4HCO_3 , (b) Comparisons in the relative viscosity and osmotic pressure between 1.0 M $HMTA^+ - SO_3^-$ and other synthetic draw solutes at their highest studied concentrations. Cation starch (30 wt%) [22], P(SSA-co-MA)-Na: poly (4-styrenesulfonic acid-co-maleic acid) sodium (0.25 g/ml) [23], P444-DMBS: tetrabutyl phosphonium-2,4-dimethylbenzensulfonate (70 wt%) [25], PASPNa: poly (aspartic acid sodium salt) (0.3 g/ml) [29], CP: carboxylate polyelectrolyte (0.21 g/ml) [30].

solution side and calculated by equation (2).

$$J_W = \frac{\Delta V}{A \times \Delta t} \tag{2}$$

where ΔV (L) is the volume of water permeating to the draw solution, A (m²) is the effective membrane area and Δt (h) is the testing time.

Reverse flux, J_S (g/m²h, denoted as gMH), was determined by the concentration and volume changes of the feed solution in per unit time and area and calculated by equation (3).

$$J_s = \frac{C_D V_D - C_0 V_0}{A \times \Delta t} \tag{3}$$

where C_D (g/L) and V_D (L) are the respective draw solute concentration and solution volume on the feed side, C_0 (g/L) and V_0 (L) are the individual initial draw solute concentration and solution of the feed when FO experiments start. A standard curve describing the relationship of draw solute concentration and conductivity was built prior to FO experiments. C_0 and C_D were then converted from the conductivities before and after FO tests which were measured by a conductivity meter (DDSJ-308F, Rex Electric Chemical, China).

2.5. Characterizations of FO membrane

The structural, physicochemical and morphological properties of the TFC-PES and TFC-sPES membranes were characterized systematically. Water contact angle was measured by a sessile drop method with a goniometer (Precise Test, China). Membrane morphology was studied on a field emission scanning electron microscope (FESEM, Nova Nano-SEM 230, FEI, USA). The roughness was studied on atomic force microscopy (AFM, Agilent, USA).

2.6. Protein-containing wastewater treatment

OVA solutions with varying concentrations were used to simulate the

protein-containing wastewater. The OVA solution before and after FO experiments was characterized by FTIR and circular dichroism (CD) spectroscopy to identify any possible structural changes. HMTA⁺ – SO₃⁻ promoted FO processes for water reclamation and OVA enrichment were investigated by using HMTA⁺ – SO₃⁻ (1.0 M) as the draw solution and OVA at 100 ppm, 500 ppm and 1000 ppm as the respective feed solutions. Both solutions were used with an initial volume of 1.0 L. As the most frequently used draw solutes in FO, NaCl and NH₄HCO₃ were also investigated under the same conditions for reference. All FO experiments were conducted at room temperature and lasted for 10 h. Conductivity and pH values in the feed solution were recorded in every 30 min. The OVA solution before and after FO experiments was characterized by FTIR and circular dichroism (CD) spectroscopy to identify any possible structural variations.

3. Results and discussion

3.1. Synthesis and characterizations of HMTA⁺ – SO_3^-

HMTA, a versatile commercial substance widely used in industry, was quaternized by 1,3-propane sulfonate on one of the tertiary amine groups via a clean one-step reaction under ambient conditions to give the highly soluble HMTA⁺ – SO₃⁻ in a quantitative yield (> 96%) (Fig. 2 (a)).

The synthesis of HMTA⁺ – SO_3^- is more facile and economical than those of other synthetic draw solutes, such as poly (4-styrenesulfonic acid-co-maleic acid) sodium (P(SSA-co-MA)-Na) [23], sodium alginate–graphene oxide (SA-GO aerogel) [24], tetrabutyl phosphonium-2, 4-dimethyl-benzensulfonate (P₄₄₄₄-DMBS) [25], sodium hexacarboxylatophenoxy phosphazene [26] which are all prepared via complicated procedures with a variety of chemicals involved.

Single-crystal X-ray crystallography analysis reveals that $HMTA^+ - SO_3^-$ consists of a cage-like structure of HMTA with 1,3-propane sulfonate pendant covalently bonded to one of the tertiary amine moieties (Fig. 2(b)), consistent with the proposed formula of $HMTA^+ - SO_3^-$.



Fig. 6. Comparisons of the TFC-PES and TFC-sPES membranes: (a) Membrane composition, (b) Water contact angle and surface roughness, (c) Morphology of the cross section.

Being rich in tertiary amine N atoms and sulfonate O atoms both of which are typical functional sites to interact with water molecules via hydrogen-bond, HMTA⁺ – SO₃⁻ can form a three-dimensional (3D) supramolecular network bridged by water molecule [27], as verified by the single-crystal X-ray crystallography analysis (Fig. 2(b)). Notably, the properties of HMTA⁺ – SO₃⁻ functionally resemble those found in conventional NaCl and NH₄HCO₃ draw solutes, but are structurally distinct from these small ionic pairs in terms of the 3D polymeric feature in water. Such unique characteristics will promote water transfer while inhibit solute reverse diffusion when HMTA⁺ – SO₃⁻ used as a draw solute in FO and make it ideal for FO applications.

The ¹NMR spectra of HMTA⁺ – SO₃⁻ and the HMTA precursor were recorded on NMR spectroscopy (¹H at 400 MHz in D₂O) (Fig. 3). Signals from the protons in NCH₂N⁺ (H_{a1}, 5.18 ppm) of HMTA⁺ – SO₃⁻ shift downfield compared to that in the HMTA precursor (H_a, 4.55 ppm). This is caused by the strong electron-withdrawing effects of the quaternary ammonium group in HMTA⁺ – SO₃⁻. The resonances of protons in NCH₂N of HMTA⁺ – SO₃⁻ are affected by the rigid cage structure and possess different stereoisomers, which induces the original signal peak in HMTA (4.55 ppm) to split into multiple signals (4.64–4.74 ppm).

The functional groups in HMTA⁺ – SO₃⁻ were analyzed by FTIR (Fig. 4). Bands at 1190 cm⁻¹ and 530 cm⁻¹ present in HMTA⁺ – SO₃⁻ but absent in the raw material of HMTA are from the S–O stretching vibration absorption. Peaks at 1465 cm⁻¹, 1379 and 1239 cm⁻¹, 685 cm⁻¹, which exist in both HMTA and HMTA⁺ – SO₃⁻, are attributed to the C–H angular mode (δ_{C-H}), out-of-plane oscillation (ω_{C-H}) and

oscillating vibration mode ($\rho_{C\text{-H}}$), respectively. Absorptions in the range of 960–1100 cm $^{-1}$ are from the C–N expansion vibration mode ($\nu_{C\text{-N}}$) [18,19,28]. The spectroscopic properties indicate the successful grafting of 1,3-propane sulfonate pendant on HMTA to synthesize the target HMTA $^+$ – SO $_3^-$ product.

3.2. Physicochemical properties of HMTA⁺ - SO₃⁻

The acidity and basicity, viscosity and osmotic pressure of HMTA⁺ – SO_3^- solution are investigated thoroughly because these properties impact FO separation greatly and hence are important considerations in evaluating the suitability of HMTA⁺ – SO_3^- as a draw solute. The HMTA precursor and conventional draw solutes of NaCl and NH₄HCO₃ are also investigated for comparison (Fig. 5).

A concentrated solution produces a higher osmotic pressure and relative viscosity for all compounds. This is because of the colligative properties of osmotic pressure and more number of solute particles present in per unit area of solution with concentration enhancement. Having greatly increased osmotic pressures and pH values in weak acidity (pH ~ 6.0), HMTA⁺ – SO₃⁻ is more suitable than its precursor HMTA (pH ~ 8.5) to be a draw solute. The osmotic pressure and viscosity of HMTA⁺ – SO₃⁻ are similar to those of NaCl and NH₄HCO₃ at low concentrations but increase faster with concentration enhancement. Comparisons indicate that HMTA⁺ – SO₃⁻ at 1.0 M produces a much higher osmotic pressure coupled with a smaller viscosity than other recently reported draw solutes at their saturation concentrations, such



Fig. 7. A comparison in the FO performance of HMTA⁺ – SO₃⁻, NaCl and NH₄HCO₃: TFC-PES membrane under (a) FO mode and (b) PRO mode; TFC-sPES membrane under (c) FO mode and (d) PRO mode. Experimental conditions: DI water as the feed solution, test duration 30 min and at 25 ± 0.5 °C.

as cation starch (30 wt%) [22], poly (4-styrenesulfonic acid-co-maleic acid) sodium (P(SSA-co-MA)-Na, 0.25 g/mL) [23], tetrabutyl phosphonium-2,4-dimethylbenzen-sulfonate (P₄₄₄₄-DMBS, 70 wt%) [25], poly (aspartic acid sodium salt) (PASPNa, 0.3 g/ml) [29], carboxylate polyelectrolyte (CP, 0.21 g/mL) [30], (Fig. 5(b)).

A draw solute with a higher osmotic pressure and smaller viscosity is desired because these features ensure a higher driving force and less concentration polarization in FO processes. With this regard, $\rm HMTA^+ - SO_3^-$ is more suitable as a draw solute than those as compared above.

3.3. $HMTA^+ - SO_3^-$ as a draw solute in FO

With the aforementioned desirable properties, $HMTA^+ - SO_3^-$ fulfills the requirements of an ideal draw solute [15–19]. The performance of $HMTA^+ - SO_3^-$ as an FO draw solute is evaluated thoroughly via the self-made TFC-PES and TFC-sPES membranes with properties shown in Fig. 6 [21,31].

NaCl and NH_4HCO_3 are also investigated for reference. Systematic studies reveal that the performances of draw solutes are all affected remarkably by their innate characteristics and experimental conditions such as membrane properties, operation mode, and solution concentration (Fig. 7).

 $\rm HMTA^+ - SO_3^-$ produces a higher water flux at a higher concentration due to an increased osmotic pressure to drive water transfer (Fig. 7). The PRO mode (Draw solution facing the active layer) constantly surpasses the FO mode with higher water permeation when experimental conditions remain the same. Facing the porous substrate side (FO mode), $\rm HMTA^+ - SO_3^-$ may be entrapped in the membrane interior, causing internal concentration polarization (ICP) which detrimentally influences the FO process and leads to a lower water flux, as also observed elsewhere [32–34]. $\rm HMTA^+ - SO_3^-$ performs better via the TFC-sPES membrane than the TFC-PES membrane with remarkably improved water permeation rates and constantly negligible reverse solute

diffusion. The TFC-sPES membrane has a smoother surface, a sponge-like inner structure [35] and more hydrophilic substrate due to the presence of sulfonate groups all of which benefit water transfer compared to a finger-like configuration of the TFC-PES membrane (Fig. 6). This indicates that HMTA⁺ – SO_3^- can perform better when a more ideal FO membrane is available.

 $HMTA^+ - SO_3^-$ produces water fluxes in between those of NaCl and NH4HCO3 under the same conditions. However, unlike NaCl and NH₄HCO₃ both of which have severe solute leakage, HMTA⁺ - SO₃⁻ exhibits negligible reverse solute diffusion in FO (Fig. 7). NaCl and NH₄HCO₃ both have ionic particles possessing hydrated diameters in the range of 0.25–0.45 nm which is comparable to the pore size distribution of FO membranes (Fig. 8) [36]. In contrast, HMTA⁺ – SO₃⁻ contains a cage-like HMTA and a 1,3-propane sulfonate pendant which makes it possessing a larger molecular structure (Fig. 2(a)). Meanwhile, the exposed N and O atoms in HMTA⁺ - SO₃⁻ are proton acceptors which promote the formation of a polymeric HMTA⁺ - SO₃⁻ network bridged by water via hydrogen-bonding (Fig. 8(a)), as proven by the single crystal X-ray diffraction (Fig. 2(b)). As a result, the polymeric HMTA⁺ - SO_3^- has a much bigger size than the pore size of the membranes (Fig. 8 (b)), accounting for the negligible reverse solute flux of $HMTA^+ - SO_3^$ in FO. Thus as a draw solute, $HMTA^+ - SO_3^-$ not only avoids contamination to the feed solution, but also reduces the costs caused by replenishing draw solutes lost in FO due to reverse diffusion. Therefore $HMTA^+ - SO_3^-$ is advantageous especially in FO applications where feed solutes are sensitive to contaminants but need be recycled for reuse.

We then systematically studied the HMTA⁺ – SO_3^- facilitated FO processes in purifying high value-added compounds, OVA as a representative here, through the TFC-sPES membrane. Conventional NaCl and NH₄HCO₃ draw solutes are also investigated as a benchmark (Fig. 9). Water permeation rate decreases constantly when changing the feed from DI water to OVA solutions with a growing concentration. A concentrated feed solution reduces the transmembrane osmotic pressure



Fig. 8. (a) Chemical and single crystal structures of the polymeric HMTA⁺ – SO_3^- , (b) Hydration diameter distribution of HMTA⁺ – SO_3^- in water (left) and pore size distribution of the TFC-PES and TFC-sPES membranes (right).



Fig. 9. Comparisons in the long-term FO performance of $HMTA^+ - SO_3^-$, NaCl and NH_4HCO_3 via the TFC-sPES membrane: (a) Water flux, (b) Reverse flux. Experimental conditions: DI water or OVA at different concentrations as the feed, FO mode.

differential and driving force which results in a declined water transfer rate. Extending the operation time (up to 10 h) leads to a steady decline in water flux. This is primarily ascribed to the membrane fouling caused by OVA which becomes severe over time (Fig. 9(a)) [37]. Nevertheless, with an average water flux of 15.0 LMH against 1000 ppm OVA, $\rm HMTA^+ - SO_3^-$ can efficiently enrich industrial-scale quantities of OVA from its dilute solution. Similar to the situation where DI as the feed, both NaCl and $\rm NH_4HCO_3$ produce significant reverse salt fluxes in concentrating OVA, whereas $\rm HMTA^+ - SO_3^-$ has negligible reverse diffusion even in a longer operation duration (Fig. 9(b)), which ensures the high purity of OVA product after FO enrichment.

3.4. Effects of draw solution on protein

The impact of draw solute on the OVA enriched via FO processes is evaluated from the changes of OVA properties before and after experiments. Screening tests reveal that the conductivity, acid-base properties, FTIR and CD spectra of OVA solution alter significantly with different



Fig. 10. Effects of different draw solutes on the feed properties: (a) Feed conductivity as a function of testing duration, (b) The proposed structure of OVA after coordinated with Na⁺ ions, (c) The changes in pH value of the feed OVA, (d) FTIR spectra of pure and concentrated OVA, (e) CD spectra of pure and concentrated OVA.

substances as the FO draw solutes, which are summarized in Fig. 10.

Regardless of DI water or OVA as the feed solution, conductivities on the feed side remain unchanged with $HMTA^+ - SO_3^-$ as the draw solute but increase significantly over time when NaCl or NH4HCO3 as the draw solutes owing to their severe salt leakage (Fig. 10(a)). Moreover, NaCl impacts the feed conductivity of DI water and OVA differently from $\rm NH_4HCO_3.$ Cationic $\rm Na^+$ is a good electron acceptor, while OVA as a typical protein carries a large number of carboxylic acid groups which can react with Na⁺ via complexation. Na⁺ ions are then coordinated to the carboxylic sites of OVA (Fig. 10(b)), as frequently observed when both species are present in an aqueous solution [38,39]. Consequently, the overall ionic number decreases once the coordination reaction occurs between Na⁺ ions and carboxylic acid groups, leading to a decrease in the feed conductivity after an initial increase. When the complexation reaction reaches equilibrium, the feed conductivity proceeds to increase with sodium ions permeating to the feed more than those coordinating with carboxyl moieties. Unlike Na⁺, NH₄⁺ has a quaternized N atom which is coordination saturated and has no empty orbitals to accept electron donor groups [40]. As a result, NH₄HCO₃ diffusing to the OVA feed solution exists in free anions and cations which leads to a constant increase in feed conductivity [33]. Different from both NaCl and NH_4HCO_3 , $HMTA^+ - SO_3^-$ imposes no effects on the feed conductivity whether DI water or OVA as the feed in view of the negligible reverse diffusion (Figs. 1(c) and Figure 10(a)).

Corresponding to the changes in conductivity, OVA solutions enriched by different draw solutes also exhibit different acid-base properties (Fig. 10(c)). Compared with the original solution, the OVA solution enriched by NH₄HCO₃, NaCl and HMTA⁺ – SO₃⁻ becomes more basic, more acidic and unchangeable, respectively. The presence of NH₄HCO₃ in the OVA solution due to severe leakage increases the pH value. NaCl as a neutral substance does not affect the OVA acid-base properties, but complexation between Na⁺ and carboxylic acid groups promotes the dissociation of the latter and releases H⁺ [38,41], leading to a decrease in the pH value of solution. Given the negligible reverse diffusion, HMTA⁺ – SO₃⁻ does not impact the OVA acid-base properties. FTIR analysis reveals that there is no obvious change in the spectra of OVA enriched by NH₄HCO₃ and HMTA⁺ – SO₃, but a new peak in 546 cm⁻¹ appears with NaCl as the draw solute (Fig. 10(d)). This absorption is considered from the vibration of Na–O bonds [38,42], manifesting the complexation reaction of Na⁺ with the carboxylic groups in OVA. Accordingly, an apparent detour around 220 nm in the CD spectra and a noticeable change in α -helix are observed for the OVA solution concentrated via the NaCl facilitated FO (Fig. 10(e)), further validating the occurrence of reaction between Na⁺ and OVA. NH₄HCO₃ contaminates the OVA solution but does not change its structure which makes no difference in the studied spectra. Contrary to NH₄HCO₃ and NaCl, the HMTA⁺ – SO₃⁻ draw solute remains the OVA intact, demonstrating the superiorities of HMTA⁺ – SO₃⁻ over those frequently used draw solutes.

3.5. $HMTA^+ - SO_3^-$ regeneration

To maximize the advantages of FO technology, draw solute after FO processes is preferred to be recycled for reuse. Conventional draw solutes such as NH₄HCO₃ and NaCl are usually discharged directly after FO or regenerated via either thermal [43] or RO processes [42]. Synthetic draw solutes proposed recently can be recycled via either single membrane distillation (MD) [44], NF [45], and RO [46] or membrane-based integrated processes [47,48]. These technologies are also workable to regenerate HMTA⁺ – SO₃⁻ in this study. Meanwhile, HMTA⁺ – SO₃⁻ can also be recycled via solvent precipitation due to its insoluble properties in most of common organic solvents. Solvent precipitation has become a common process to purify substances in the chemical industry nowadays in view of the mild operational conditions without applied pressure [49, 50]. HMTA⁺ – SO₃⁻ can thus be regenerated readily via an ethanol-induced precipitation process on account of its insolubility in ethanol and the miscible property of ethanol with water. Adding ethanol to the HMTA⁺ - SO₃⁻ aqueous solution can completely precipitate $HMTA^+ - SO_3^-$ out of water. After successive experiments of filtration, washing with ethanol and vacuum dry, $HMTA^+ - SO_3^-$ is ready for reuse in the following FO processes. The ethanol and water mixture can be conveniently separated by pervaporation at 35 °C [51]. The recycled ethanol can be reused to precipitate HMTA⁺ – SO₃⁻. Without issues frequently encountered in recycling other draw solutes, such as agglomeration [52], decomposition [53] and loss [54], HMTA⁺ – SO₃⁻ can be fully collected and provide reproducible results when reused in FO.

4. Conclusions

From readily available raw materials, $HMTA^+ - SO_3^-$ is synthesized via a convenient one-step reaction under mild conditions. Containing both anionic sulfonate and cationic quaternized amine groups, $HMTA^+ - SO_3^-$ has good water solubility and can produce a high osmotic pressure to drive FO processes. With a cage-like HMTA and supramolecular structure in water, $HMTA^+ - SO_3^-$ causes negligible reverse diffusion while provides a reasonable high water flux in FO experiments. These characteristics coupled with high recyclability make $HMTA^+ - SO_3^-$ more efficient in water recovery than other synthetic draw solutes, and superior to conventional draw solutes in enriching impurity-sensitive substances. This study provides an inspiration for designing materials as FO draw solutes to treat wastewater and simultaneously enrich high value-added substances from it.

Declaration of competing interest

No conflict of interest with this submission.

CRediT authorship contribution statement

Xialu Liao: Formal analysis, Writing - original draft. Wen-Hua Zhang: Formal analysis. Qingchun Ge: Conceptualization, Writing original draft.

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