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Concentration of ammonium diuranate effluent by reverse osmosis and forward osmosis membrane processes

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ABSTRACT

In this study, both reverse osmosis (RO) and forward osmosis (FO) experiments are conducted to concentrate simulated inactive ammonium diuranate (ADU) filtered effluent solution (by mixing uranyl nitrate and ammonium nitrate) using indigenously developed cellulose acetate blend (CAB) and thin-film composite polyamide (TFCP) membranes. Both the membranes are prepared and characterized in terms of pure water permeability and solute rejection for 2000 ppm NaCl feed, water contact angle and surface average roughness. Subsequently, testing of volume reduction and concentration of simulated ADU effluent solution are carried out using custom made RO and FO testing systems. It is found that in RO process, the performance in terms of volume reduction factor and concentration factor with respect to uranium for both CAB and TFCP membranes are comparable but the CAB membranes show better performance than the TFCP membranes in FO modes. The concentration of ammonium nitrate is less in RO concentrate than in the FO concentrates. Similar experiments with the feed solution having different concentration of uranium (1–20 ppm) with same concentration of ammonium nitrate show that in FO, almost no leaching of uranium is found to the draw solution side but in RO, some of the uranium starts passing to the permeate side, particularly at lower concentration of uranium in the feed.

Keywords: Cellulose acetate blend; Forward osmosis; Membrane; Radioactive waste treatment; Reverses osmosis; Thin-film composite polyamide

1. Introduction

"Concentrate-and-contain" is one of the principles employed in the management of radioactive wastes particularly for the wastes that arise in relatively large volumes but contain low-specific-activity components [1]. The treatment methods include volume reduction of the concentrate, which can then be safely stored in a radioactive "cemetery" after solidification. However, if separation of radioactive compounds present in the waste and reuse of the bulk solution is possible, it always gives added value to the overall process [2]. General methods used to treat such low level and medium level liquid wastes are chemical precipitation,

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sedimentation, ion exchange, thermal evaporation and distillation, electro-coagulation, photocatalytic degradation, biological methods, membrane processes, etc. [3–7].

Membrane processes have gained wide acceptance and made significant inroads against competing technologies in this areas, because of their flexibility in design, performance reliability, cost competitiveness, and eco-friendliness [8]. In addition, membrane process is capable of separating radioactive components from the inactive solution. It gives dual advantages namely, recovery of valuables like uranium from the concentrated stream in one hand and in other hand the dilute inactive solution that can be reused and it gives huge economical advantages to the system. Membrane processes like reverse osmosis (RO) and ultrafiltration are being used in the treatment of radioactive laundry, laboratory effluents, removal of uranium from contaminated water, and some other applications in nuclear industry [9–13]. Supported and emulsion liquid membrane techniques were also used quite frequently for separation and recovery of uranium and other radioactive elements [14–16]. Concentration of low- and medium-level radioactive wastes with three-stage RO pilot plant has also been studied [17]. It is also shown that cellulose acetate-based RO membranes can be used for the decontamination of radioactive streams containing high concentrations of ammonium nitrate [18]. In recent times, forward osmosis (FO) is being used as alternate to RO in application areas for the concentration of low volume high value product [19,20]. From point of view of energy economy, it is the best alternative to RO and based on the use of chemical process modeling software (HYSYS), energy savings of FO compared to current technologies including RO and thermal processes, on an equivalent work basis, are projected to range from 72 to 85% [21].

Concentrated brine generated from sea water desalination plant are used as draw solutions in FO [22] experiments. It gives double benefits—the nuclear waste can be "concentrated" by facilitating low-energy simple treatment and in same time, dilution of the concentrated brine in draw solution side takes place which is otherwise problematic in disposal. So, membrane processes like RO and FO can be applied for concentration of filtered solution of the ammonium diuranate (ADU) precipitate generated on processing of natural uranium by the ammonium dicarbonate precipitation route. The pure uranyl nitrate solution obtained after extraction from the mother liquor is treated with ammonia and the ADU precipitates [18]. After filtration of the ADU precipitate, the solution (ADU filtrate) contains radiocontaminants associated with uranium and its daughter products (specific activities of about $10^{-3}\,\mathrm{Ci/m^3}$ beta/gamma emitters) and significant quantities of ammonium nitrate (~40,000 ppm). However, in inactive laboratory, both RO and FO experiments are conducted to concentrate simulated ADU-filtered solution (only uranium as uranyl nitrate and ammonium nitrate) using cellulose acetate blend (CAB) and thin-film composite polyamide (TFCP) membranes. The objectives of this research are firstly to prepare and characterize CAB and TFCP RO membranes and secondly, to evaluate their performances in terms of volume reduction factor and concentration factor utilizing a simulated ADU effluent solution (containing only uranyl nitrate and ammonium nitrate). The effects of different concentration of uranium (1–20 ppm) with same ammonium nitrate on membrane performances in both RO and FO have also been studied.

2. Experimental

2.1. Materials

For preparation of CAB membranes, cellulose acetate (CA) (Mn = 50,000), and cellulose triacetate (CTA) (Mn = 72,000–74,000) polymers are procured from Aldrich, India. Solvents like 1,4-dioxane, acetone, and methanol are of analytical reagent grade obtained locally and used without further purification. Polysulfone polymer is obtained from M/s. Solvay Specialities India Pvt. Ltd., India for preparation of support for thin-film composite (TFC) membrane. The reagent grade N-methyl pyrrolidone (NMP) is used as solvent for making polysulfone support membranes and is procured from Sisco Research Laboratories, India. 1,3-phenylene diamine (MPDA) and 1,3,5-benzene tricarbonyl chloride or trimesoyl chloride (TMC).

2.2. Preparation of membranes

Cellulose acetate (CA) and cellulose triacetate (CTA) polymers are dissolved separately in 1,4-dioxane and acetone mixture. Then both the solution mixed together and then methanol is added to the mixed polymer solution and kept agitated for complete dissolution. Over a smooth glass plate, the polymer solution obtained is spread over a nonwoven polyester-spun bonded fabric support (Viledon grade H1006 obtained from M/s. Freudenberg Nonwovens India Pvt. Ltd.), using a knife edge. The membrane after casting kept for 75–80 s in air as evaporation time and then immersed in a demineralized water bath maintained at 1–2˚C temperature for an hour.

The membrane obtained after gelling is repeatedly washed with demineralized water and then annealed at 75℃ water for 10 min. Subsequently, it is stored in refrigerator cooled water (~7℃) till further use.

In the first step, polysulfone support membranes are prepared and then subsequently, a thin-film coating of polyamide is given over the support membrane by *in situ* polymerization technique. The preparation method of the polysulfone membrane is similar to the CAB membrane preparation, but at room temperature gelling and without evaporation time and annealing. Subsequently, the wet water saturated support membrane is immersed in a 2.0% (w/v) aqueous solution of amine for 60 s. Then the aqueous amine saturated support membrane is positioned vertically to drain the excess reagent, till the surface looks free of amine solution. Then it is immersed in hexane solution of TMC for 30 s for formation of TFCP membranes. This membrane obtained is then dried under infrared (IR) light for 10 min or till the surface of the composite membranes looks completely dry.

2.3. Experimental methods

The membranes are characterized in terms of pure water permeability and solute rejection for NaCl feed, surface hydrophilicity, and surface average roughness. NaCl separations by all the membranes are determined using 2000 ppm NaCl feed at 15 kg/cm^2 pressure. Separation performance in terms of flux and salt rejection is calculated by taking the average of three readings taken for three membrane samples prepared separately. Hydrophilicity of all the membranes is determined by measuring pure water contact angles using the sessile drop method on a standard drop shape analysis system (DSA100, KRüSS GmbH, Germany). The average roughness of the membranes is measured using an atomic force microscope (AFM) (NT-MDT-Multimode 3, Ireland), equipped with a standard silicon nitride cantilever.

Volume reduction studies have been carried out by both RO and FO processes. The volume reduction factor is defined as the ratio of the initial volume of the feed in the tank to the volume of the concentrate left in the tank after the experiment. Final results are calculated by taking the average of three readings taken for three membrane samples prepared separately. In RO, the feed is pumped across a given membrane using a reciprocating pump and the pressure (40 kg/cm^2) is applied using a pressure regulating valve. The reject is recycled back to the feed and hence, concentration of feed increases with time. In FO, the feed is allowed to flow through one side of the membrane surface and at the same time a solution with a higher osmotic pressure than the feed (draw solution) is kept flowing in the other side. So the feed is getting concentrated with time and draw solution gets diluted. Draw solution used for this FO experiment is concentrated seawater brine with salt concentration of 68,000–70,000 ppm from seawater desalination plant at Trombay, Mumbai. The schematics of testing procedures in RO and FO modes are given in Fig. 1.

3. Results and discussion

3.1. Physico-chemical characterizations of the membranes

The pure water permeability of CAB and TFCP membranes is evaluated at 15 kg/cm^2 pressure on the

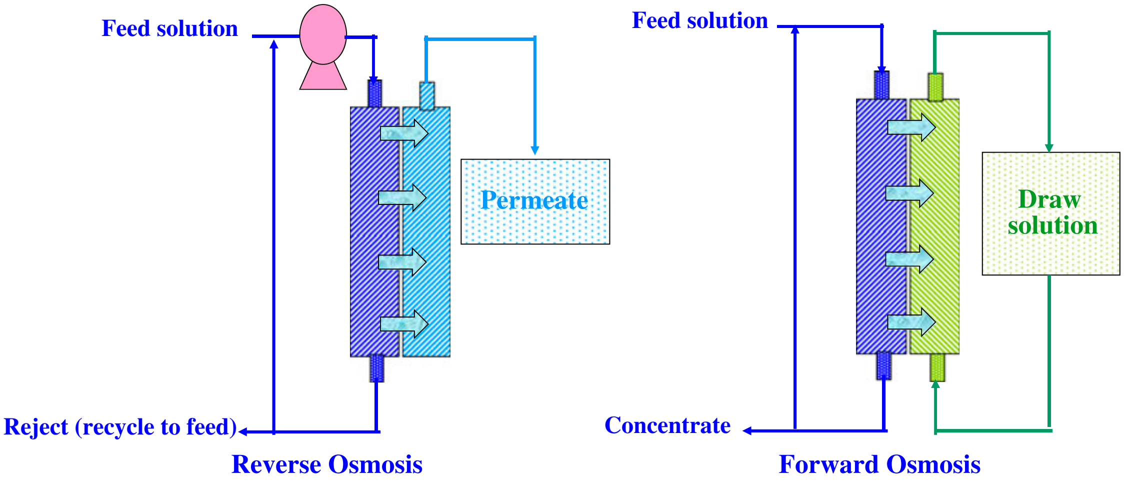

Fig. 1. Schematic of testing procedures of membranes in reverse osmosis and forward osmosis modes.

Table 1
Characterization data of CAB and TFCP membranes

Membrane	Cellulose acetate blend	Composite polyamide
Pure water permeability ($\mathrm{L\,m^{-2}\,d^{-1}}$)*	470 ± 20	496 ± 24
Salt rejection (%)*	85.0 ± 3.2	87.8 ± 3.0
Average surface roughness (nm)	64 ± 10	92 ± 12
Water contact angle (°)	48 ± 3	65 ± 4

Note: *Applied pressure: 15 kg/cm^2. Feed: 2000 ppm NaCl. Feed temperature: 25°C.

Table 2
Performance of CAB and TFCP membranes in terms of volume reduction in RO and FO processes

Time (min)	VRF by RO		VRF by FO	
	CAB	TFCP	CAB	TFCP
60	1.27 ± 0.06	1.3 ± 0.05	1.19 ± 0.03	1.16 ± 0.04
120	1.7 ± 0.08	1.73 ± 0.06	1.34 ± 0.03	1.21 ± 0.06
240	2.35 ± 0.07	2.4 ± 0.06	1.45 ± 0.03	1.32 ± 0.06
360	3.35 ± 0.09	3.4 ± 0.08	1.58 ± 0.04	1.40 ± 0.06

pre-pressurized membrane at 25 kg/cm^2 for 4 h. Subsequently, pure water is changed to 2000 ppm NaCl solutions to check the salt separation capability of the membranes. The separation data are collected when the product flux remained constant over 45 min. The pure water permeability along with the NaCl rejection data for both the membranes are given in Table 1. These membranes are also characterized in terms of water contact angle values and average surface roughness, and the results are also given in the same Table 2-D and 3-D atomic force microscopic views of the membranes are shown in Fig. 2.

The TFC polyamide (TFCP) membranes are relatively more permeable and give better salt rejection than CAB membrane under identical testing condition. In general, TFCP membranes are more permeable than asymmetric membranes, due to the thinner barrier layer present in TFCP membranes. But in the present case, both membranes are tailor-made with similar water permeability and salt rejection values in order to better perform a comparison of ADU concentrations under actual applications. However, their water contact angles and surface roughness are found to be different. CAB membranes are more hydrophilic (low water contact angle) with a smoother membrane surface (less surface average roughness), than the TFCP membranes.

3.2. Volume reduction factor (VRF) of CAB and TFCP membranes

The simulated ADU filtrate (as feed) is prepared by adding 24.8 ppm uranyl nitrate (contains ~15 ppm uranium) with 40,000 ppm aqueous solution of ammonium nitrate (NH_4NO_3) and initial feed volume taken is 10 L. In RO modes, NH_4NO_3 rejection is 40.0 and 43.2%, whereas uranium rejection is 99.2 and 99.5% by CAB and TFCP membranes, respectively. Hence, 60% NH_4NO_3 for CAB and 56.8% for TFCP membrane can be recovered from the respective permeates with very less contamination of uranium. So, if the experiment could be conducted with actual radioactive species in ADU, decontamination could have been very high. In FO modes, NH_4NO_3 leaches to the draw solution side through the membrane for both membranes. From the mass balance, it is found that in the CAB membrane, leaching of NH_4NO_3 is 15.0% and in TFCP membrane it is 12.5%. However, the uranium leaching to the draw solution side is zero for both membranes.

Performance of CAB and TFCP membranes in terms of volume reduction factor in RO and FO processes using simulated ADU feed is provided in Table 2. In RO, the volume reduction factor is marginally more in the TFCP membrane than the CAB membrane, which is quite obvious as the water permeation rate is more in TFCP than CAB membranes under the same applied pressure (Table 1). But in FO, CAB membranes show a better volume reduction than the TFCP membranes. So, performance difference on concentration of ADU feed in FO and RO could be due to the difference in hydrophilicity and surface roughness of the membranes used. Accordingly, their interaction with water molecules and transport would be different. In RO, water passes through the membrane due the difference in pressure gradient but in FO, it is due to the concentration gradient. The volume reduction in FO mode can be increased by circulating fresh draw solution every time, rather than recirculation of diluted draw solution with time.

3.3. Effects of uranium concentration on membrane performances

The simulated ADU filtrates (as feed) are prepared independently by adding 1.7–33 ppm uranyl nitrate (contains ~1–20 ppm uranium) with 40,000 ppm aqueous solution of ammonium nitrates to study the effect of uranium concentration on the CAB membrane performances. This study was conducted to check whether membrane processes like RO and FO are suitable for concentration of uranium at low concentration or not. So, the concentration of uranium is quantified

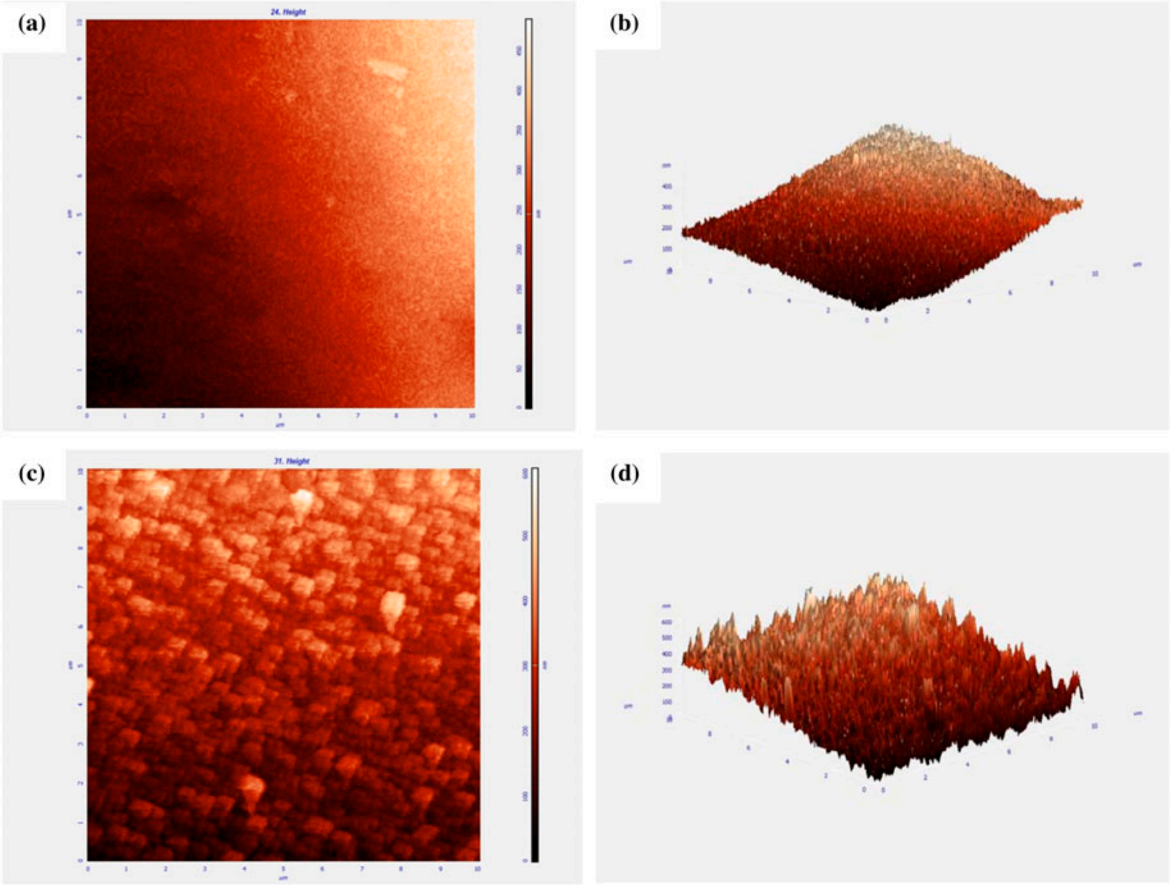

Fig. 2. AFM images of CAB [(a) 2D, (b) 3D] and TFCP [(c) 2D, (d) 3D] membranes.

(analyzed using ICP-MS and ICP-AES) in both RO and FO concentrates and presented in Table 3. In the RO experiment, uranium rejection is 99.0% or more when uranium concentration in feed is more than 10 ppm and around 97.5% when uranium concentration in feed is around 4 ppm. However, in the FO experiment, the uranium leaching to the draw solution side is very marginal at all concentrations of uranium in the feed. However, it is evident that flux in FO is less than that in RO. But still FO may be preferable in concentration of radioactive waste as almost no contamination would leak to the other side of the membrane.

Table 3
Uranium rejection/retention in RO and FO processes by CAB membranes

Conc. of uranium (ppm)	% rejection in RO	% retention in FO
1	96.6 ± 0.4	99.9 ± 0.06
4	97.5 ± 0.2	99.9 ± 0.06
10	99.0 ± 0.1	99.9 ± 0.06
15	99.2 ± 0.1	99.9 ± 0.06
20	99.3 ± 0.2	99.9 ± 0.06

4. Conclusions

TFCP and CAB membranes are two potential membranes that can be used in osmosis applications both in RO and FO. In the case of low to medium level radioactive waste treatment, both RO and FO can offer a means for decontaminating the radioactive effluents by concentrating the activity in smaller volumes (reject in RO and concentrated feed in FO) and making the larger volumes (permeate in RO and diluted draw solution in FO) suitable for direct disposal.

Experiments with simulated ADU-filtered effluent solution (containing only uranyl nitrate and ammonium nitrate) show the performance with respect to the volume reduction factor for both CAB and TFCP membranes are comparable in the RO mode, but the CAB membranes show better performance than the TFCP membranes in the FO mode. Concentration of ammonium nitrate is less in the RO concentrate, than in the FO concentrates because 40.0–43.2% ammonium nitrate is passed through the membranes. In FO, almost no leaching of uranium is found in the draw solution side but in RO, some of the uranium starts passing to the permeate side particularly at low concentrations of uranium in the feed. For concentration of actual radioactive effluent, the activity of the concentrated solutions would increase with time and this will certainly limit the stability of the polymeric membranes.

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