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Performance Evaluation of Reverse Osmosis (RO) and Nanofiltration (NF) Membranes for the Decontamination of Ammonium Diuranate Effluents

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ABSTRACT

Our earlier studies using cellulose acetate membrane for the removal of radioactive species from ammonium diuranate filtrate effluents (ADUF) indicated promising performance in terms of very good decontamination factors (*DF*) and volume reduction factors (*VRF*). In view of the inherently short membrane life of cellulose acetate membrane, studies were carried out to assess the potential of polyamide (PA) based reverse osmosis (RO), nanofiltration (NF), and ultrafiltration (UF) membranes. Experiments based on real effluents corresponding to specific activity levels of microcuries/liter containing about 4% ammonium nitrate yielded decontaminated streams containing nanocuries/liter levels of radiocontaminants both for RO and NF membranes. UF membrane failed to give reasonable decontamination factors and hence was found unsuitable for the purpose. Due to very high ammonium nitrate solute rejection of PA membranes under RO condition, it was not possible to get high volume reduction factors. However, NF membranes have shown the potential to achieve very high *VRF* with good decontamination factors owing to their poor ammonium nitrate rejection characteristics and the consequent maintenance of permeate fluxes. The studies indicate the viability of the NF process for the treatment of ammonium diuranate filtrate effluents in large scale.

Key words. Membranes; Reverse osmosis; Nanofiltration; Ultrafiltration; Ammonium diuranate effluents; Radioactive liquid waste treatment; Ammonium nitrate effluent

INTRODUCTION

Membrane processes, particularly the pressure-driven ones such as ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), etc., are finding increasing applications in water recycling and effluent treatment, besides seawater and brackish water desalination (1). Studies based on reverse osmosis for the decontamination of low level radioactive laundry wastes (2) and the decontamination of radioelements such as radium, uranium, etc. from the tailing ponds of uranium ore processing plants (3) indicate their potential applications in the nuclear industry. The US Environmental Protection Agency (USEPA), after evaluating various technologies through their Drinking Water Research Division, has recommended reverse osmosis as one of the most practical treatment methods for the removal of radium and uranium (4) from natural water. Our earlier studies using cellulose acetate membranes indicated that reverse osmosis has the potential to concentrate and decontaminate uranyl solutions (5) and ammonium diuranate filtrate (ADUF) effluents (6).

Cellulose acetate membrane, however, exhibits a relatively shorter life compared to polyamide-based membranes. Our earlier results indicated that membranes slightly porous compared to conventional RO membranes may have better performance characteristics. In view of this, experiments were planned with polyamide (PA) based reverse osmosis (RO) membranes, nanofiltration (NF) membranes, and ultrafiltration (UF) membranes.

In the processing of natural uranium, pure uranyl nitrate solution is obtained by extraction from the mother liquor. This, in turn, is converted to ammonium diuranate using ammonia following the reaction

$$\begin{aligned} &2UO_2(NO_3)_2(l) + 6NH_3(g) + 3H_2O(l) \\ &\rightarrow (NH_4)_2U_2O_7(s) + 4NH_4NO_3(l) \end{aligned} \tag{1}$$

The ADU filtrate contains radiocontaminants associated with uranium and its daughter products. The major contributors for β-activity are Th-234 and Pa-234. In the solution phase their physicochemical behavior is akin to uranium. In view of this, it is considered appropriate to evaluate the RO, NF, and UF membranes for their decontamination potential with a view to adopt them in large-scale operation.

METHODS AND MATERIALS

The experimental setup is shown in Fig. 1. The detailed procedure followed during the collection of data was earlier reported (6). For all the experiments the ADUF effluent was drawn into the feed tank under ambient conditions. Depending on the chosen experimental parameters, the feed is chemically conditioned with respect to pH and additive dosages. Thin film composite polyamide (TFCP) RO membrane and nanofiltration (NF) membranes (MTP-42), procured from HMIL, Baroda (India) and Genesis Sepratech Pvt. Ltd., Bombay (India), respectively, were used in sheet form in a plate module configuration. Ultrafiltration membranes made in-house were used. The standard characteristics of these modules are given in Table 1.

As the uranyl content of the feed, permeate, and concentrates were all very low and below dischargeable limits, no attempt was made to analyze uranium in the samples or to discuss its implications in the experimental studies. The results were analyzed only with respect to radiocontaminants, which are the critical constituents for the discharge of the treated effluents. The gross β/γ-activities were measured using standard counters, observing necessary precautions to obtain statistically significant results. The ammonium nitrate concentrations were estimated based on the nitrate concentration measurements using a nitrate ion selective electrode with necessary dilutions, whenever warranted, in a Ion-85 analyzer.

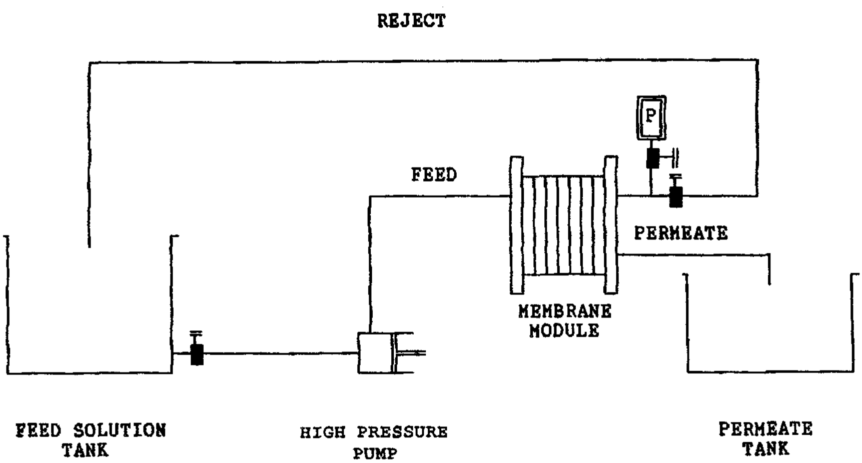

FIG. 1 Schematic flow diagram of the experimental setup.

TABLE 1
Standard Performance Characteristics of TFCP and NF Membranes Used

Characteristics	TFCP	NF	UF
Membrane constant (m/s bar) $\times 10^8$	53.2	43.2	44.4
Permeate water flux (LMD)[a]	1760	560	260
% Solute rejection[b]	97	75	15
Operating pressure (bars)	40	15	7
Area of the membrane (cm^2)	4120	820	820

[a] LMD = liters/square meter/day.
[b] With 2000 ppm sodium chloride solution.

The experiments were conducted by recirculating the concentrate in a batch-recycle mode. Various performance indicators, such as volume reduction factor (*VRF*), decontamination factor (*DF*), percent solute rejection (*SR*), etc., were calculated as follows.

$$VRF = \frac{\text{initial volume of the feed in tank}}{\text{volume of the concentrate left in the tank after the experiment}} \quad (2)$$

$$DF = \frac{\text{initial specific activity}}{\text{permeate specific activity}} \quad (3)$$

$$SR = \frac{\text{feed concentration} - \text{permeate concentration}}{\text{initial feed concentration}} \times 100 \quad (4)$$

RESULTS AND DISCUSSION

Reverse osmosis, nanofiltration, and ultrafiltration membranes separate dissolved species from the homogeneous phase, essentially based on physicochemical interaction superimposed on the size exclusion principle. Uranyl species in solution exist mostly in the coordinated state, depending upon the media. As such, we expect them to be separated well with moderately porous membranes. We could demonstrate this aspect with our experimental results by using uranyl nitrate solutions up to concentration levels of 200 mg/L with cellulose acetate membranes (5). We had observed that the addition of sulfates enhanced the solute rejection of uranyl species. Incidentally, when the experiments were tried with ADUF effluents, we could achieve fairly significant decontamination factors with respect to the associated radiocontaminants such as Th-234, Pa-234, etc. At the same time, ammonium nitrate was poorly rejected and hence most of it could be recovered in the permeate.

In membrane desalination processes it is known that synthetic polymer-based polyamide membranes exhibit higher solute rejection characteristics compared to cellulose acetate membranes (7). Accordingly, experiments were carried out with TFCP membranes to assess the reverse osmosis performance of ADUF effluents. The experimental feed had specific activity levels of about 1×10^{-3} Ci/m^3 and contained about 35,000–40,000 mg/L ammonium nitrate.

The experiments were conducted in the recycle-batch mode, leading to a buildup of ammonium nitrate concentration in the feed solution with respect to time. The concentration factors in all the experiments were not a uniform function of time due to variations in the permeate fluxes under different feed conditions. Hence the membrane behavior in terms of *DF*, *SR*, and permeate fluxes was assessed as a function of *VRF*.

PERFORMANCE OF THIN FILM COMPOSITE REVERSE OSMOSIS MEMBRANES (TFCP)

The experiments were performed following four different schemes as outlined below.

Scheme 1: Feed solution at pH 5.5–6.0 (ADUF + conc. H_2SO_4)
Scheme 2: Feed solution with antiscalent Flocon-100 (5 ppm) at pH 5.5–6.0 (ADUF + conc. H_2SO_4 + Flocon-100)
Scheme 3: Feed solution without any treatment at pH 7.0–8.0 (ADUF only)
Scheme 4: Feed solution with antiscalant Flocon-100 (5 ppm) at pH 7.0–8.0 (ADUF + Flocon-100)

During our earlier study with cellulose acetate membranes we adjusted the pH of the feed solution to about 5.5–6.0 to ensure minimum damage to the membranes, in keeping with established practices. Further, it was believed that the addition of sulfuric acid would result in the formation of complex species such as $[UO_2(SO_4)_2]^{2-}$, $[UO_2(SO_4)_3]^{4-}$, etc. (8), and hence would result in better solute rejection of uranium and its daughter products. To enable us to compare under similar conditions, data were collected with thin film composite (TFCP) membranes as per Schemes 1 and 2. Since polyamide membranes have a wider pH tolerance, it was decided to conduct experiments without pH adjustment. We have also studied the effect of the polyelectrolyte-based antiscalant Flocon-100 (Pfizer).

Figure 2 presents the observed *DF* as a function of the *VRF* for TFCP membranes under reverse osmosis conditions. It is seen that the *DF* marginally decreases with respect to *VRF*, corresponding to the experimental Schemes 1 and 2 (pH adjusted to ~5.5), while there is a noticeable increase in the *DF* with respect to the *VRF* in the case of Schemes 3 and 4 (pH 7–8). When the pH of the solution is maintained at acidic levels, the radiocontaminants are essentially in the dissolved state and hence their behavior is typical of reverse osmosis behavior of normal solutes (i.e., decrease in solute rejection with increase in concentration), following the equation

$$N_A = \left[\frac{D_{AM}}{k\delta}\right](C_2 - C_3) \qquad (5)$$

where N_A = solute flux
$[D_{AM}/k\delta]$ = solute transport parameter
C_2 and C_3 = concentration of solute at boundary and permeate solutions, respectively

For experimental Schemes 3 and 4, *DF* increases with *VRF*, which suggests that the radiocontaminants in the alkaline condition may be in

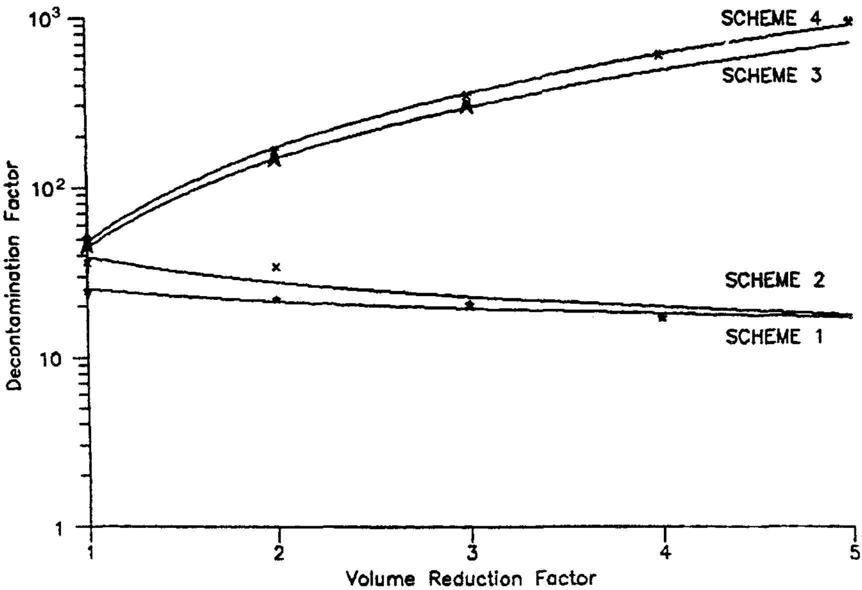

FIG. 2 Variation of *DF* with *VRF* for TFCP membranes.

the colloidal state. As the concentration increases they tend to aggregate, leading to higher sizes and hence higher decontamination. In both cases the addition of Flocon-100 was found to improve the *DF*. We could not proceed with further volume reduction (beyond 5) due to very low permeate fluxes.

Figure 3 presents the solute rejection of ammonium nitrate as a function of the *VRF* for TFCP membranes. Ammonium nitrate is rejected by about 86–89% in Schemes 1 and 2 and by about 84–86% in Schemes 3 and 4, indicating that the rejection of ammonium nitrate is relatively more in acidic conditions compared to alkaline conditions. It is generally known that decreasing pH leads to an increase in solute rejection for polyamide-based membranes, as is evident from UOP product literature for TFCP membranes. It may be due to the protonation of amide groups in the membrane, under acidic conditions, which limits the passage of cations. Further aspects in this regard are beyond the scope of the present work.

The inherently high solute rejection for ammonium nitrate is responsible for a high concentration buildup with increasing *VRF*. The permeate flux is normally governed by the equation

$$N_B = A[P - \pi(X_{A2}) + \pi(X_{A3})] \tag{6}$$

where A = pure water permeability constant

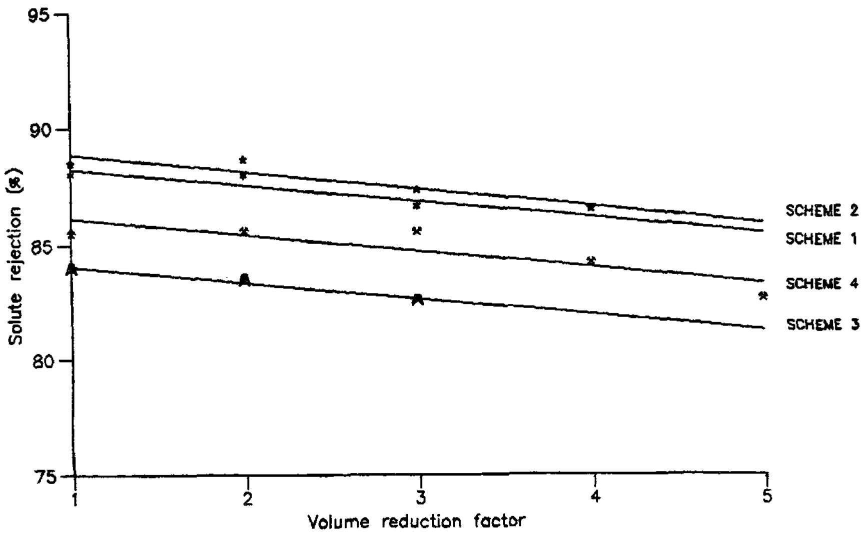

FIG. 3 Variation of ammonium nitrate solute rejection with *VRF* for TFCP membranes.

P = applied feed pressure
$\pi(X_{A2})$ = osmotic pressure of the boundary layer near the membrane surface
$\pi(X_{A3})$ = osmotic pressure of the permeate solution

Since the permeate concentrations are low due to high solute rejection, $\pi(X_{A3}) \ll \pi(X_{A2})$, with a solute rejection of 85%, the osmotic pressure of the feed solution ($\pi(X_{A1})$) and hence the boundary layer ($\pi(X_{A2})$) approach the operating pressure with increasing *VRF*, leading to a considerable fall in permeate flux.

As seen in Table 2, CA membranes can lead to higher volume reduction factors compared to TFCP membranes due to the decrease in observed flux with *VRF*. The decrease in flux is directly related to the osmotic pressure of the feed solution. Since TFCP membranes exhibit higher solute rejection, the osmotic pressure of the feed increases more rapidly compared to CA membranes. The decontamination factors observed are not of very much significance in view of their very low absolute values.

However, as an approach to zero disposal, we looked for membranes which poorly reject ammonium nitrate but still retain the daughter products of uranium. Further, the membranes should be capable of withstanding higher pH conditions in order to have the advantage of better rejection at alkaline conditions which, in turn, would reduce the cost of acid pretreatment of the effluents.

In this context, experiments were tried with ultrafiltration membranes which gave very low *DF* (<5) under untreated feed conditions. It was therefore felt appropriate to try NF membranes to assess their suitability.

TABLE 2
Performance of Cellulose Acetate and TFCP Membranes

Cellulose acetate				Polyamide (TFCP)			
VRF	*DF*	*SR* (%)	Flux (LMD)	*VRF*	*DF*	*SR* (%)	Flux (LMD)
1.0	198	43.0	506	1	50	85.33	385.0
2.7	186	41.2	428	2	165	85.64	164.0
5.2	173	37.8	389	3	352	85.61	87.5
7.6	167	34.6	311	4	598	84.25	63.0
				5	962	82.71	52.5

PERFORMANCE OF NANOFILTRATION (NF) MEMBRANES

Nanofiltration membranes have average pore sizes of 10–30 Å, an intermediate range between reverse osmosis (1–10 Å) and ultrafiltration (>30 Å). Nanofiltration (NF) has the advantage of very low solute rejection for monovalent species, probably due to their very small sizes (hydrated radii), and higher rejection for multivalent species which are large enough (i.e., more than the critical pore diameter) for rejections based on physicochemical interactions.

Figure 4 indicates the *DF* and ammonium nitrate solute rejection of NF membranes as a function of *VRF*. The solute rejection of ammonium nitrate was very low (i.e., around 16–19%) and the *DF* were nearly constant at high levels. This is due to the fact that the estimated permeate specific activities were always around background levels. However, as seen in Fig. 5, there is a distinct rise in concentrate specific activity, indicating that the radiocontaminants were well rejected.

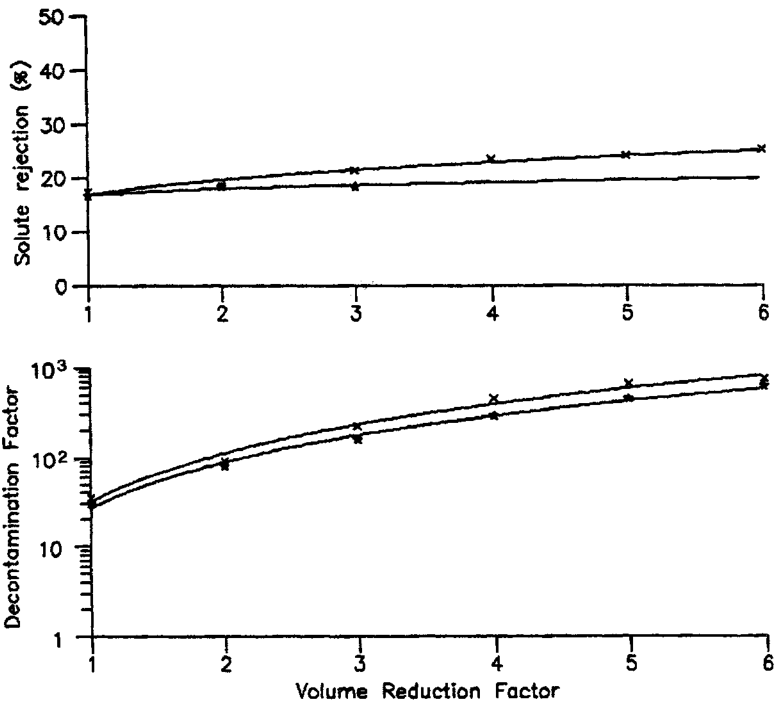

FIG. 4 Variation of *DF* and ammonium nitrate solute rejection for NF membranes.

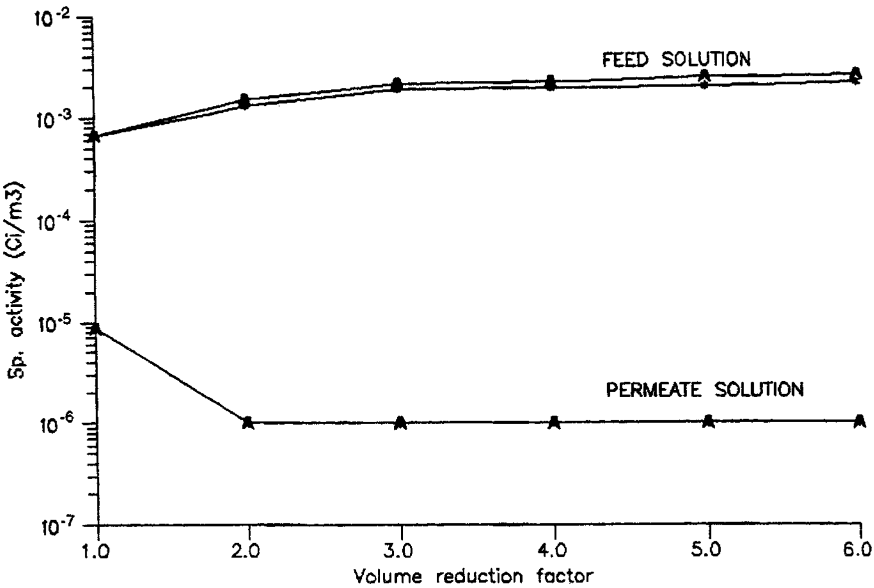

FIG. 5 Variation of recycled feed specific activity with *VRF*.

Nanofiltration membranes are known to separate preferentially bivalent species (Ca^{2+}, SO_4^{2-}, etc.) from monovalent species. In fact, negative rejection of chloride ions in the presence of sulfate ions is reported by Peterson (9). In this context, the behavior of NF membranes in the high rejection of multivalent species involving uranium and its daughter products in preference to ammonium nitrate is discernible.

The permeate flux of NF membranes is shown in Fig. 6 along with those of reverse osmosis membranes. With increasing volume reduction factors, the fall in the permeate fluxes of TFCP membranes is very significant compared to a marginal decrease in the permeate flux of nanofiltration membranes. The poor rejection of ammonium nitrate by nanofiltration membranes compared to TFCP membranes results in only small increases in feed concentration. Consequently, the net effective pressure available for fluid transport decreases only marginally, leading to the observed flux behavior. The addition of polyelectrolyte shows a marginal increase in the observed *DF* and flux rates in all experiments. Recent studies by Tabatabai et al. (10) showed that polyelectrolytes tend to increase the solute rejection of bivalent ions in UF. Since the radiocontaminants are all essentially multivalent cations, the observed increase in *DF* is quite

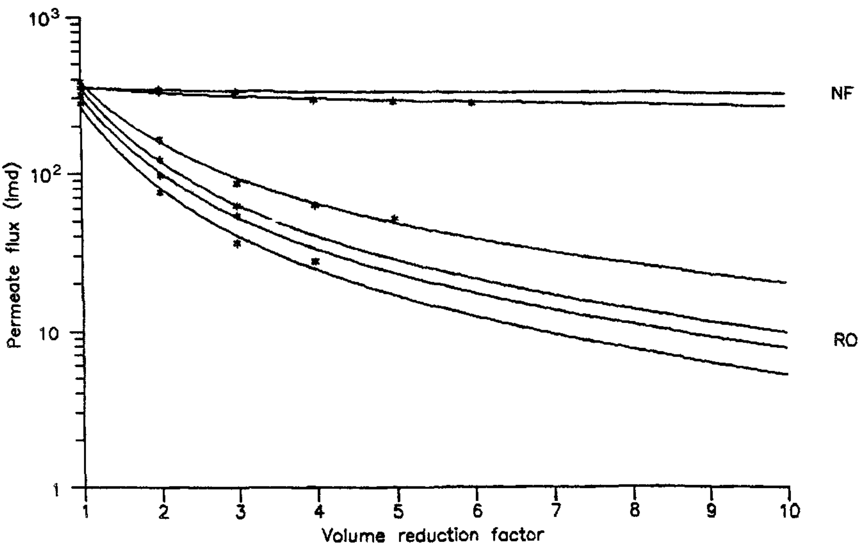

FIG. 6 Variation of permeate flux with *VRF* for RO and NF membranes.

logical. In the presence of antiscalants, the possible suspensions are not allowed to settle and hence the resistant for the flow of permeate is relatively less compared to feed without the antiscalants. Hence, there is a marginal increase in the observed flux.

CONCLUSIONS

Our experimental results clearly indicate that

1. Polyamide-based thin film composite membranes possess high solute rejection with respect to ammonium nitrate, but not a correspondingly high decontamination factor.
2. Nanofiltration membranes exhibit very poor solute rejection with respect to ammonium nitrate and have the potential to achieve high volume reduction factors. The observed decontamination factors are also very high.
3. The ammonium diuranate filtrate effluents give better decontamination without any acid treatment.
4. The practically attainable volume reduction factor of thin film composite polyamide membranes under reverse osmosis conditions is limited due to drastic reduction in fluxes.

5. Addition of the antiscalant Flocon-100 helps in maintaining a marginally higher flux rate.

The foregoing observations indicate that nanofiltration membranes are better suited for the decontamination of ammonium diuranate filtrate effluents due to near constant fluxes, high decontamination factors, and low ammonium nitrate solute rejection. The cost of treatment would also be less because it operates at lower pressures. As ammonium nitrate in the permeate stream is relatively pure, it can be recovered for further commercial use.

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