

## Ultrafiltration of nitrate and heavy metal ions using cellulosic membranes

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Ultrafiltration membranes were prepared from cellulose acetate (CA) and N,N-dimethylformamide (DMF) (25:100 w/v) and their permselectivity characteristics were determined. The membranes were used for the separation of  $\text{NO}_3^-$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$  using micellar-enhanced ultrafiltration (MEUF). MEUF-based separation of nitrate and heavy metal ions was studied in order to assess the potential of MEUF for remediation of polluted wastewater. Solute rejection coefficient (*s* values) of nitrate increased from less than 34% in the absence of the cationic surfactant cetylpyridinium chloride (CPC) to more than 88% at CPC concentration above the cmc. For  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ , *s* values increased from less than 10% in the absence of the anionic surfactant sodium dodecylsulfate (SDS) to greater than 80% and 90%, respectively, at SDS concentration above the critical micelle concentration (cmc). Solute rejection increased from 13% and 28% for  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$ , respectively, to more than 85% after MEUF in the presence of 0.001 M SDS.

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**Keywords:** ultrafiltration; cellulosics membranes; nitrate removal; heavy metals

### INTRODUCTION

One of the important pressure-driven membrane processes is ultrafiltration (UF), which involves the separation of large molecular weight (MW) solutes ( $\text{MW} > 500$  Daltons) from solution. However, plain UF is not effective in separating small molecules because it can not retain solute molecules with MW less than 500 Daltons (D). In order to answer this problem Scamehorn and co-workers [1] have developed micellar-enhanced ultrafiltration.

MEUF is a membrane-based process that separates dissolved organic and inorganic compounds from water by entrapment of the solute ions or molecules in micellar aggregates. In this process surfactants are added in order to enhance the apparent solubility of hydrophobic compounds in water [2, 3]; alternatively, an ionic surfactant with an electrical charge opposite to the ionic solute to be separated is added [1, 4]. A surfactant molecule above its cmc forms aggregates called micelles which

solubilize or entrap the solute. The mixture with added surfactant is then forced through a UF membrane with pores that are small enough to reject the solute-containing micelles [5].

The present paper aims to evaluate the potential of MEUF for separating and concentrating polluting ions wastewater. CA membranes were prepared in the laboratory and used for ultrafiltration of nitrate ions in the presence of a cationic surfactant and of several metal ions in the presence of an anionic surfactant.

### EXPERIMENTAL

The UF membranes were made from CA and DMF. A mass: volume ratio of 25:100 for CA: DMF was used to prepare 25% CA membranes. The CA powder was dissolved in DMF; the resulting dope was rapidly cast and manually spread on a 20 × 20 cm. glass plate with a stainless steel spreader. The solvent

was allowed to evaporate for 1 min and the thin polymeric film in the glass plate was coagulated in a water bath at room temperature. CA membrane disks with almost the same water flux values were tested for MW cut-off, which was determined by allowing standard proteins of known MW to pass through the membranes.

CPC, a cationic surfactant, obtained from Aldrich, was dissolved in 50 ppm  $\text{KNO}_3$  solution in order to prepare 100 mL solutions of varying CPC concentration. The solutions were then ultrafiltered through the selected CA membrane disks. Samples from the retentate and the initial solution were also collected. The same procedure and conditions were used for the UF runs at 100, 200 and 300 ppm nitrate. The nitrate and CPC concentrations were determined spectrophotometrically at 211 nm and 261 nm, respectively.

Aqueous solutions of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  were prepared by dissolving  $\text{Pb}(\text{NO}_3)_2$  and  $\text{CdCl}_2$  (both analytical reagent grade) in deionized water in order to obtain concentrations of 10 ppm and 2 ppm, respectively. SDS, obtained from Sigma, an anionic surfactant, was dissolved in the prepared solutions in order to obtain 100 mL solutions of varying SDS concentration. The solutions were ultrafiltered through the selected membranes and 10-mL permeate and retentate samples were collected. The concentrations of Pb and Cd in the collected permeate were measured by atomic absorption spectrometry at 217.0 nm and 228.8 nm, respectively. The amount of SDS in the permeate was determined turbidimetrically (420 nm).

Aqueous solutions of  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$  were separately prepared by dissolving 7.80 mg  $\text{ZnCl}_2$  and 5.20 mg  $\text{HgCl}_2$  (both analytical reagent grade) in deionized distilled water to make concentrations of 3 ppm and 2 ppm, respectively. SDS was dissolved in the prepared solutions in order to obtain 100 mL solutions of varying SDS concentration in the range of 0–0.080 M. The solutions were ultrafiltered through the selected membrane and 10-mL permeate samples were collected. Samples from the retentate were also collected for analysis. Metal ion analysis was done using an atomic absorption spectrophotometer at 420 nm.

**Table 1. Permselectivity characteristics of the prepared cellulose acetate membranes.**

	Membrane			
	A	B	C	D
Water Flux ( $\text{L}/\text{m}^2\text{h}$ )				
Initial	22.56	25.51	27.96	33.51
After protein	19.33	23.88	11.32	21.81
After sample	16.01	20.21	10.25	12.33
% Rejection Coefficient				
BSA (MW 66kD)	68.00	74.30	55.90	63.90
$\alpha$ -amylase (MW 50kD)	47.02	54.00	44.6	47.50

## RESULTS AND DISCUSSION

The permselectivity characteristics of the prepared CA membranes are given in Table 1. The table shows substantial reduction of water flux after simple UF of protein and ion-containing samples, especially for membranes C and D. This indicates membrane fouling where the solute particles adhere to the membrane surface and hinder liquid permeation. However, this phenomenon usually does not significantly alter the rejection coefficient for solutes [6]. The approximate MW cut-off of the prepared membranes are also shown in Table 1 using standard proteins. The relatively low rejection values indicate that the MW cut-off of the membranes is higher than the MW (66 kD) of bovine serum albumin (BSA).

The maximum rejection of nitrate (50 ppm) was observed above the cmc value, namely 87.95% at a concentration of 0.002 M CPC. The maximum solute rejection values were 89.15% and 80.92% for 100 and 200 ppm nitrate, respectively (Fig. 1). At higher CPC concentrations (at 300 ppm nitrate concentration) a smaller rejection coefficient was observed; this may be due

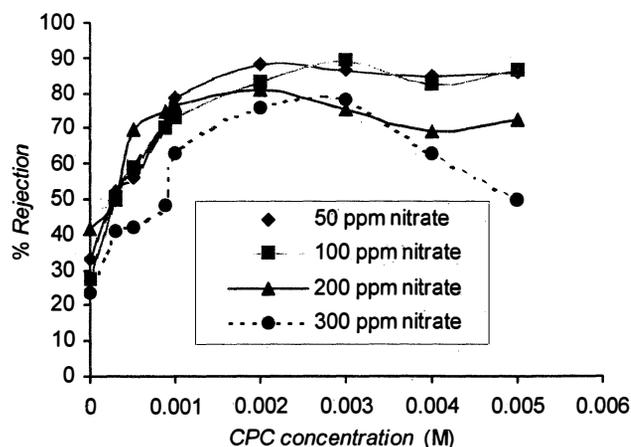


Fig. 1. Rejection of nitrate ion at varying CPC concentration.

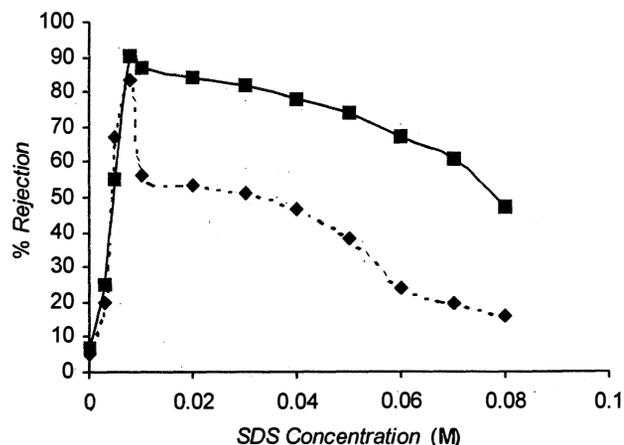


Fig. 2. Rejection of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  at varying SDS concentration.

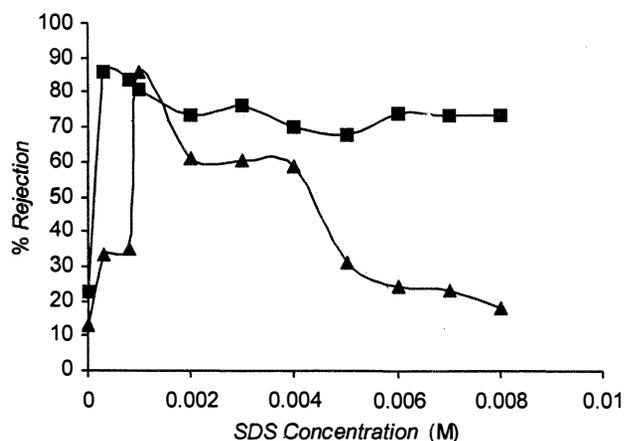


Fig. 3. Rejection of Zn<sup>2+</sup> and Hg<sup>2+</sup> at varying SDS concentration.

to the close packing of the head groups, which results in squeezing out the trapped NO<sub>3</sub><sup>-</sup> out of the micelle. Alternatively, the micellar structure could have collapsed resulting in a smaller volume available for the solute (nitrate). Thus, more free nitrate ions in solution would be present which could pass through the membrane. Figure 1 also shows that as the concentration of nitrate increases from 50 ppm to 300 ppm, the rejection coefficient decreases. Increasing the nitrate concentration from 50 to 300 ppm resulted in reduced solute rejection from 86.3% to 66.6%. At a higher concentration of nitrate the water tends to solvate the nitrate ions rather than interact with the micelle, which is much bigger in size.

Figure 2 shows the solute rejection at varying SDS concentration for Pb and Cd. At concentrations below 0.005 M, the rejection values were very low which indicate that most of the metal ions passed through the membrane. The rejection coefficient dramatically increased from 55.3% to 90.56% for Cd and from 67.30% to 83.74% for Pb as the SDS concentration was increased from 0.005 M to 0.008 M; the latter is the cmc. The strength of the anion and cation interactions with water molecules increases with ionic charge density, which is inversely proportional to the ionic radius. The atomic radii for Cd and Pb are 152 pm and 175 pm, respectively. Since Cd has a smaller atomic radius, its charge density is greater than that of Pb; thus, it is expected to have a bigger hydrodynamic/hydrated size. On the other hand, this higher charge density of Cd<sup>2+</sup> compared to Pb<sup>2+</sup> allows greater electrostatic attraction between the metal ion and the oppositely charged micelle. At moderate surfactant concentrations, which are higher than the cmc (0.008 M), a reduction of the solute rejection coefficient was observed. This can be accounted for by the close packing of the head groups, which tends to squeeze out the trapped metal; thus, the metal ions could easily pass through the membrane.

As shown in Fig. 3, the membrane showed maximal separation through MEUF of Zn<sup>2+</sup> at an SDS concentration of 0.001 M with solute rejection of 86.12% and Hg<sup>2+</sup> at 0.003 M SDS con-

Table 2. Summary of selective permeation data during MEUF of nitrate and heavy metal cations.

Ion	Surfactant	MEUF Rejection Coefficient ( $\sigma$ )	
		Surfactant Conc < CMC	Surfactant Conc > CMC
NO <sub>3</sub> <sup>-</sup>	CPC	<34%	>88%
Pb <sup>2+</sup>	SDS	<10%	>80%
Cd <sup>2+</sup>	SDS	<10%	>90%
Zn <sup>2+</sup>	SDS	<13%	>85%
Hg <sup>2+</sup>	SDS	<28%	>85%

centration with 85.86% solute rejection. Gradual reduction of % rejection values at higher SDS concentrations was observed due to the modification of the size and shape of micelles formed.

## CONCLUSION

MEUF involves addition of a surfactant above the cmc in order to entrap small solute molecules and increase their effective hydrodynamic size in solution. The resulting micelle-entrapped solute can be retained by ordinary UF membranes. This technology allows lower trans-membrane pressure and less dense membranes with bigger pore size compared to reverse osmosis (or hyperfiltration) resulting in lower costs of membrane and equipment. The MEUF technology was tested in the present paper for the separation of nitrate and several heavy metal ions in order to assess its potential for the remediation of polluted wastewater. The UF membranes were prepared from CA and DMF (25:100 w/v) and their permselectivity characteristics were studied.

MEUF-based separation of nitrate was done after adding the cationic surfactant CPC while separation of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup> and Hg<sup>2+</sup> was achieved in the presence of the anionic surfactant SDS. The solute rejection coefficient ( $\sigma$  values) dramatically increased by about 2.5- to 9.0-fold after adding the surfactant to a concentration greater than the cmc. The results, which are summarized in Table 2, show that MEUF technology has promising potential for the remediation of wastewater containing nitrate and heavy metal ions.

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