

## **Modified polyethersulfone membranes for micellar enhanced ultrafiltration of chromium**

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### **Abstract**

Separation performances of micellar enhanced ultrafiltration process in Cr(III) and Cr(VI) removal has been evaluated. The neat as well as sulfonated and aminated derivatives of polyethersulfone were tested as the material for membrane preparation while hexadecylpyridine chloride and sodium dodecyl sulfate served as surfactant. It was shown that modified membranes can better reject both forms of chromium in the micellar enhanced ultrafiltration than their neutral analogues. In all cases, the surfactants should be applied at the amounts that give 5 critical micelle concentration. Any additives that reduce the cmc value are also profitable from the operational point of view.

Keywords: sulfonated polyethersulfone, aminated polyethersulfone, environmental protection, membrane separation

### **1. Introduction**

The increasing contamination of water by various pollutants has turned to be a serious environmental problem today. The growing concentration of heavy metals in aquatic systems has forced plenty of governments to establish some restrictive limits that, in turns, have promoted the search for new separation technologies. That phenomenon can be observed for chromium removal. This element exists in the nature mostly in two states - as trivalent and hexavalent species. While Cr(III) is an essential element for living beings, playing an important role in carbohydrate metabolism, Cr(VI) becomes carcinogenic when the living creature is long exposed to it. For that reason, Cr(VI) incurs a significant risk to human health when released into the environment [Bagchi et al., 2002]. To overpass that problem, the metal finishing industry has increased the use of trivalent chromium electroplating baths to replace hexavalent chromium ones. Although the effluents generated in these processes are less toxic than Cr(VI), they are still highly dangerous to the environment and must be treated prior to disposal.

Membrane separation processes play today an important role in the field of wastewater treatment. This well consolidated technology has become the central point of industry interest due to its low operative costs, conceptual simplicity, modularity, flexibility to quality of treated water, and productivity in relation to other separation techniques [Mulder, 1991]. In order to separate ions, reverse osmosis (RO) or nanofiltration (NF) is being commonly used. However, the permeate fluxes in RO and NF are not so high and both processes require to use the high transmembrane pressure. That operation turns them to more expensive membrane processes. The next pressure driven process - ultrafiltration (UF) – needs smaller transmembrane pressure and its operational cost is not so high. It has been shown that ultrafiltration is efficient in removal larger molar substances (polymers, colloids) that size ranging from 2 to 100 nm and molecular weight is larger than 500 Da. However, the pore size of any ultrafilter is too large to reject small molecules like inorganic ions.

The micellar enhanced ultrafiltration (MEUF) has been shown to be a promising method to remove of low levels of toxic heavy metal ions from industrial effluents. In MEUF an ionic surfactant at a concentration higher than the critical micelle concentration (cmc) is added to the aqueous stream containing the dissolved solutes. The negatively or positively charged micelles cause the cations or anions, respectively, to bind at the micelle interface. Micelles containing absorbed ions are then separated by UF using membrane of suitable porosity, capable of retaining micelles [Scamehorn et al. 1994; Juang et al., 2003; Baek et al., 2004].

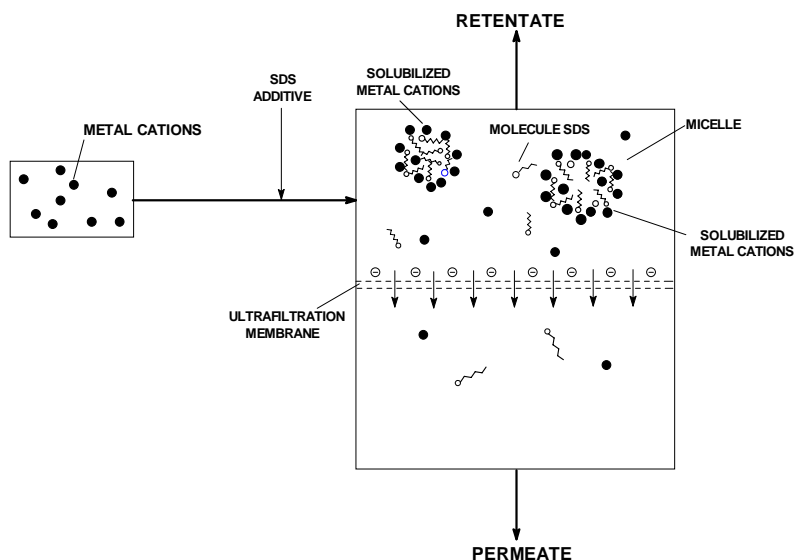


Figure 1: Schematic of metal cations separation by MEUF

To enhance selectivity in MEUF, it has developed ligand-modified micellar enhanced ultrafiltration (LM-MEUF) [Paulenovà et al. 1996; Fillipi et al., 1997]. This method involves addition of an amphiphilic ligand and surfactant to the contaminated solution under conditions where most of the surfactant is presented as micelles. The ligand has a high degree of solubilization in the micelles and shows tendency to complex the target metal ion.

Thermo-resistant polymers of good mechanical strength, biological and chemical stability and film-forming properties are the most frequently used materials for membrane preparation. Among them polyethersulfone (PES) is a popular one in last time. However, it has hydrophobic character that facilitates adsorption of many substances during filtration processes. Deposition of solute on/in membrane causes the negative effect – a significant drop of the permeate flux. This harmful phenomenon is called membrane fouling [Jönsson and Jönsson, 1995]. There are many ways to protect membrane from fouling. One of them is introduction of ionic groups to the membrane materials by chemical [Poźniak et al., 1995, 2002a; Guan et al. 2005; Turkiewicz et al. 2006; Poźniak 2006a] or plasma treatment [Bryjak et al. 2000, 2004; Poźniak et al. 2006b; Wavhal et al. 2002]. Porous ion exchange membranes prove to be very useful in ultrafiltration of charge-bearing solutes. The improvement in solute rejection and decrease in the membrane fouling ability are the main profits coming from the use of such membranes.

The aim of the present work is to evaluate a chance to prepare membranes from aminated and sulfonated polyethersulfone and to detect the usefulness of porous ion exchange membranes in the micellar enhanced ultrafiltration for removal of Cr(III) and Cr(VI) ions from aqueous media.

## 2. Experimental

### 2.1. Modification of polyethersulfone

Sulfonation of polyethersulfone (Ultrason E2020P,  $M_w=58$  kDa, from BASF) was carried out using a mixture of chlorosulfonic acid (CSA) and 1,2-dichloroethane (at room temperature, 90 min). The initial molar ratio of CSA to PES was 3:1.

PES was chloromethylated using a mixture of methyl chloromethyl ether (50 moles per mer PES) with  $\text{SnCl}_4$  (5 moles per mer PES). The reaction was conducted within 24 hours at room temperature. The membranes were formed directly from the chloromethylated derivatives. Aminolysis of chloromethylated membranes was performed in 50 vol.-% solution of 1,2-diaminoethane in 1:1 mixture of water and methanol. The reaction was completed within seven days at room temperature.

### 2.2. Preparation of membranes

Porous asymmetric membranes were formed by phase-inversion method from: 13.5%-wt. solution of PES (neutral membrane), 30%-wt. solution of sulfonated PSU (cation exchange membrane) and 17%-wt. solution of chloromethylated PES in N,N-dimethylformamide (after amination - anion exchange membrane). In all cases, water was used as a coagulation medium.

The ion exchange capacity was estimated on the basis of acid-base titration method [Hamza et al., 1995]. Porosity was determined gravimetrically and average pore diameter was calculated according to the Ferry-Faxen relationship [Bodzek, 1983].

### 2.3. Micellar enhanced ultrafiltration

The Amicon 8200 dead-end cell with filtration surface area of  $19.6 \text{ cm}^2$  was used. The transmembrane pressure was equal to 0.1 MPa.

Mixtures of  $\text{Cr}_2(\text{SO}_4)_3$  ( $1 \text{ mmol/dm}^3$ ) and sodium dodecyl sulfate, SDS, (16.2, 40.5 and  $81 \text{ mmol/dm}^3$  – that is equivalent to 2, 5 and 10 x critical micelle concentration)

were filtered through PES and SPES membranes. Additionally, mixtures of SDS and  $\text{Cr}_2(\text{SO}_4)_3$  ( $1 \text{ mmol/dm}^3$ ) with ligand ethylenediaminetetraacetic acid, EDTA, ( $4 \text{ mmol/dm}^3$ ) were filtrated through the same membranes.

Through PES and APES membranes mixtures of  $\text{K}_2\text{CrO}_4$  ( $1 \text{ mmol/dm}^3$ ) and hexadecylpyridine chloride, CPC, ( $1.76, 4.4$  and  $8.8 \text{ mmol/dm}^3$  - that is equivalent to 2, 5 and 10 x critical micelle concentration) were filtered.

Concentrations of CPC and chromate in permeate were determined using spectrophotometer UV/VIS (SPECORD M40, Zeiss, Jena) at 258 nm and 372 nm, respectively, according to [Baek et al., 2004]. Permeate chromium (III) concentration was measured by atomic absorption (AAnalyst 100, Perkin-Elmer). SDS concentration in the permeate was determined by the two phase titration method, according to [Heinerth, 1976]

To evaluate the filtration efficiency in removing the chromium ions from the feed solution, we have used the flux of permeate (J) and the rejection (R) expressed as:

$$J = \frac{V}{S \cdot t} \text{ dm}^3/\text{m}^2\text{h} \quad (1)$$

where: V – volume of permeate, S – active surface of membrane, t – time of filtration,

$$R = \left(1 - \frac{C_p}{C_f}\right) \cdot 100\% \quad (2)$$

where:  $C_p$  and  $C_f$  - the chromium ions concentration in the permeate and in the initial feed, respectively.

### 3. Results

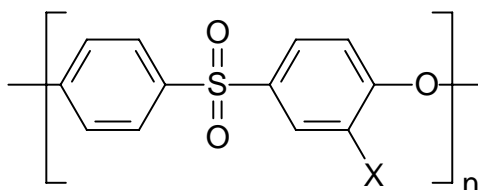
For the purpose of this study three kinds of membrane have been obtained; they are similar in physical structure but differ in chemical composition (Table 1).

Table 1: Properties of ultrafiltration membranes

| Membrane | Ion exchange capacity<br>mmol/g | Average pore diameter<br>nm | Membrane porosity<br>% | Rejection of surfactant*<br>% |
|----------|---------------------------------|-----------------------------|------------------------|-------------------------------|
| PES      | 0.00                            | 13                          | 72                     | 75                            |
| SPES     | 0.79                            | 18                          | 79                     | 97                            |
| APES     | 0.88                            | 12                          | 76                     | 99                            |

\* concentration of CPC or SDS equal to 10 x cmc

Chemical modification of polyethersulfone allowed to anchor positive or negative groups on the membrane surface.



X = -H,  $-\text{SO}_3^-$ , or  $-(\text{CH}_2)_2\text{N}^+-\text{CH}_2\text{CH}_2\text{NH}_2$

When micelle diameter is greater than pore size the porous membrane obtained from PES, APES and SPES can be used for MEUF process. This assumption seems to be fulfilled as rejection parameter of both tested surfactants at concentration of 10 x cmc reached the great values. Hence, all of them can be applied for chromium removal by means of membrane enhanced ultrafiltration process. The results of Cr(III) removal by MEUF and LM-MEUF are shown in Tables 2 and 3, respectively.

Table 2: Chromium (III) flux and rejection in MEUF process

| SDS concentration<br>mmol/dm <sup>3</sup> | PES membrane                           |        | SPES membrane                          |        |
|---|--|--------|--|--------|
|   | J<br>dm <sup>3</sup> /m <sup>2</sup> h | R<br>% | J<br>dm <sup>3</sup> /m <sup>2</sup> h | R<br>% |
| 16.2                                      | 46                                     | 48     | 68                                     | 61     |
| 40.5                                      | 37                                     | 65     | 51                                     | 91     |
| 81.0                                      | 23                                     | 73     | 37                                     | 99     |

Table 3: Chromium (III) flux and rejection in LM-MEUF process

| SDS concentration<br>mmol/dm <sup>3</sup> | PES membrane                           |        | SPES membrane                          |        |
|---|--|--------|--|--------|
|   | J<br>dm <sup>3</sup> /m <sup>2</sup> h | R<br>% | J<br>dm <sup>3</sup> /m <sup>2</sup> h | R<br>% |
| 8.1                                       | 65                                     | 67     | 78                                     | 90     |
| 16.2                                      | 47                                     | 73     | 71                                     | 99     |
| 40.5                                      | 41                                     | 76     | 55                                     | 99     |

It can be seen that Cr(III) is rejected much better at sulfonated membrane than at its neutral analogue and that the rejection reached level of 91% when SDS concentration was kept as high as 5 x cmc (40.5 mmol/dm<sup>3</sup>). The use of higher surfactant concentration results in complete rejection of chromium.

Addition of EDTA to the MEUF system caused one more profitable effect – 90% rejection was reached for 1 x cmc concentration of SDS (8.1 mmol/dm<sup>3</sup>) while permeation of Cr(III) ions was blocked for 5 x cmc concentration. This phenomenon can be rationalized as follows: removal of chromium ions by means of MEUF and LM-MEUF hybrid systems is based on electrostatic binding of ions to oppositely charged micelles [Scamehorn et al. 1994]. After addition of EDTA to SDS solution (acidic mixture) the critical micelle concentration of SDS is lowered significantly. It reached the value 0.9 mmol/dm<sup>3</sup> that is about 10 times lower than cmc for neat SDS in distilled water [Paulenovà et al. 1996, 1998]. Additionally, mixed micelles of ligand and surfactant are more rigid and therefore rejection of micelles is higher what is favorable for chromium (III) removal. When the amount of surfactant is reduced the higher permeate flux is observed – it is one more benefit of the use the LM-MEUF process.

Solubilization of Cr(VI) was performed by means of CPC – cationic surfactant. To reduce tendency to deposit surfactant on the membrane surface aminated polyethersulfone membrane was used. The results are juxtaposed in Table 4.

Similarly to the case of Cr(III), the best results were obtained for membrane bearing the charge. It is indicated that the concentration of surfactant on the level of 5 x cmc (4.4 mmol/dm<sup>3</sup>) guarantee high rejection of chromium (VI).

Table 4: Chromium (VI) flux and rejection in MEUF process

| CPC concentration mmol/dm <sup>3</sup> | PES membrane                        |     | APES Membrane                       |     |
|--|-------------------------------------|-----|-------------------------------------|-----|
|  | J dm <sup>3</sup> /m <sup>2</sup> h | R % | J dm <sup>3</sup> /m <sup>2</sup> h | R % |
| 1.76                                   | 66                                  | 47  | 79                                  | 74  |
| 4.40                                   | 54                                  | 68  | 69                                  | 95  |
| 8.80                                   | 45                                  | 77  | 58                                  | 97  |

#### 4. Conclusion

Polyethersulfone membranes and mostly its aminated and sulfonated derivatives can be applied for separation of chromium (III) and (VI) ions by means of MEUF and LD-MEUF. It is suggested to use 5 x cmc concentrations of surfactants to reach the satisfactory level of chromium rejection. The best Cr(III) ions separations were observed for LM-MEUF process with EDTA as ligand. However, the charge bearing membranes are more effective in the processes that its neutral analogue.

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