

## Chromate removal from wastewater using micellar enhanced crossflow filtration: effect of transmembrane pressure and crossflow velocity

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**Abstract:** Removal of chromate from wastewater was investigated using Micellar Enhanced Crossflow Ultrafiltration Technique (MEUF) with cationic surfactant, didecyldimethylammonium bromide (DDAB). The variation of chromate, surfactant rejections, and permeate flux with time were measured as a function of transmembrane pressure drop ( $\Delta P$ ), and crossflow velocity, while maintaining DDAB/chromate, membrane pore size, and pH of the feed solution constant. The method was found to be effective in removing chromate from wastewater. It was observed that the efficiency of chromate removal increased with increasing transmembrane pressure drop ( $\Delta P$ ), and crossflow velocity. It was found that fouling of the membrane by surfactant is very rapid at the high crossflow velocity.

**Keywords:** crossflow, ultrafiltration, micellar enhanced ultrafiltration, chromate removal, wastewater treatment.

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### 1. Introduction

The term "ultrafiltration (UF)" is usually applied to a membrane separation process where the solute dimensions are significantly larger than the solvent dimension. Ultrafiltration has been used extensively for product recovery and pollution control in the chemical, electronic, electrocoating, as well as in the food, pharmaceutical and biotechnical industries (Juang & Liang, 1993). It was reported that heavy metal ions, dissolved organic and other ions might be effectively and economically removed from aqueous solution by Micellar enhanced ultrafiltration (MEUF) (Christian *et al.*, 1988; Dunn *et al.*, 1987; Morel *et al.*, 1991; Scamehorn *et al.*, 1994; Keskinler *et al.*, 1997; Daniş & Keskinler, 2002). MEUF is a separation technique which involves adding surfactant to a polluted water stream. The surfactant forms roughly spherical aggregates called micelles which contain about 50 to 100 molecules (Klepac *et al.*, 1991). The interior of the micelle contains the hydrocarbon chain of the surfactant and forms a hydrophobic environment. Organic pollutants in the water dissolve or solubilize in micelles primarily through hydrophobic association and interaction with the surfactant head groups. If an anionic surfactant is used, the micelle has a high negative electrical potential on the surface where the charged hydrophilic groups are located. If a cationic surfactant is used, multivalent anionic species in solution will bind to the micelle instead. The solution is then treated in an ultrafiltration device with membrane pore size small enough to block the passage of micelles.

Chromium, which is very toxic in the industrial wastewater, is usually found in the forms of chromate ions ( $\text{CrO}_4^{2-}$ ) and dichromate ions ( $\text{Cr}_2\text{O}_7^{2-}$ ) depending on pH level. However, chromate

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ions exist as a stable anionic species throughout relatively wide pH ranges. Removal of chromate (or indeed other heavy metal ions) from water can also be achieved using reverse osmosis, electrodialysis or electrodeposition techniques which require high operating pressures and/or consume large amounts of energy. Therefore, the current technique, like MEUF (Christian *et al.*, 1988), may be considered as an energy-efficient separation technique, especially if the high surfactant concentration levels could be tolerated.

The basic sludge of removal of surfactants and/or polymeric surfactants from water is also available (Akay, Wakeman, 1994a; Akay, Wakeman, 1994b; Akay, Wakeman, 1994c; Akay and Wakeman, 1996a). In this study, we investigated the removal of chromate ions from wastewater using the surfactant enhanced crossflow filtration. Furthermore, the mechanisms of permeate flux decay, chromate, and surfactant rejections in crossflow filtration were investigated as depending on time

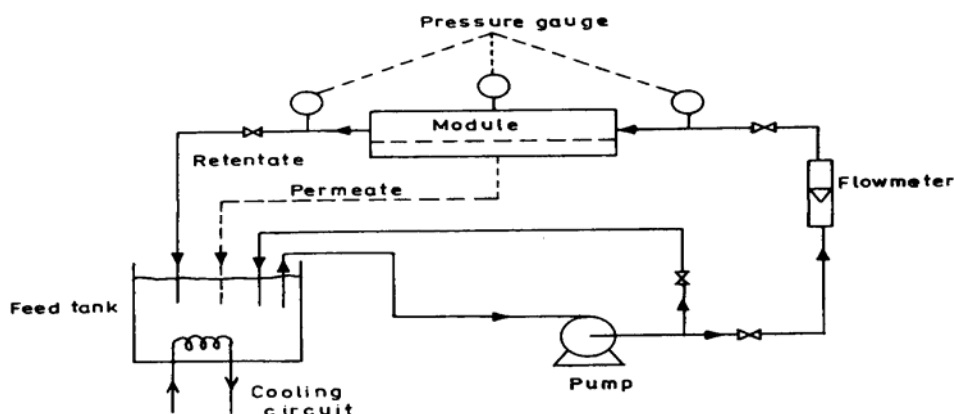
## 2. Experimental

### 2.1. Materials

Potassium chromate (Merck, certified analytical grade), cationic surfactant, didecyldimethylammonium bromide (Aldrich, certified analytical grade) were used as received. Distilled and deionized water was used for preparation of all the solutions. The ultrafiltration membrane was anisotropic cellulose acetate membrane with 0.2  $\mu\text{m}$  pore diameter size.

### 2.2 Apparatus and Techniques

The experimental apparatus is shown in Figure 1 consisted of a flow circuit in which 20 litres of distilled water containing a known amount of surfactant and chromate ions (feed solution) was pumped continuously through a crossflow filtration cell at a predetermined crossflow velocity and transmembrane pressure drop. The desired filtration conditions were maintained by two manually operated valves. The temperature of the process solution was kept constant at 30°C by using a plate type heat exchanger placed in the feed tank, which had its own cooling circuit. The filtration equipment consisted of a filtration cell which was constructed from plastic and stainless steel. Flat sheet membranes of 28 cm<sup>2</sup> effective surface area were placed into the cell to form a one sided rectangular filtration channel of length 70 mm, width 40 mm and 1.975 mm thickness. The filtrate produced was returned to the feed tank so that the feed surfactant concentration remained constant.



**Figure 1.** Schematic diagram of the crossflow filtration apparatus

The feed solution was prepared at 30°C in the feed tank containing 20 litres distilled water while recirculating the by-pass line with the filter line shut. The desired amount of concentration in the process solution was obtained by adding a certain amount of active surfactant slowly into the feed tank. Then at the end of a 60 minutes recirculation period a certain amount of chromate was slowly added into the feed tank in order to obtain a known chromate concentration in the process solution. The recirculation was continued for another 60 minutes prior to the start of the filtration process. During filtration, permeate flow rate, feed flow rate, temperature and transmembrane pressure drop values were recorded. Permeate and feed conductivities were monitored. There were no significant variations in pH (pH=7.10) and in the conductivities of the feed solution and permeate. The permeate samples were collected at predetermined time intervals and later analysed for their surfactant and chromate concentrations. The permeate flux was determined gravimetrically.

### 2.3. Surfactant and chromate concentrations determination

Chromate concentrations were determined at 540 nm with an UV-Visible recording spectrophotometer of type Shimadzu UV160A (APHA, 1985). Surfactant concentration was determined by Organic Carbon Analyser (Beckman 915A) with UNICAM 4815 computing integrator.

#### 2.3.1. Calculation of the chromate and surfactant rejections

The efficiency of the ultrafiltration process is defined by the conventional rejection coefficients,  $R_S$  and  $R_C$  for CTAB and chromate rejections respectively. For the surfactant rejection (Danış, 2005)

$$R_S = 1 - \frac{C_{SP}}{C_{SF}} \quad (1)$$

where  $C_{SP}$  and  $C_{SF}$  are the surfactant concentrations in the permeate and feed streams, respectively and for the chromate rejection:

$$R_C = 1 - \frac{C_{CP}}{C_{CF}} \quad (2)$$

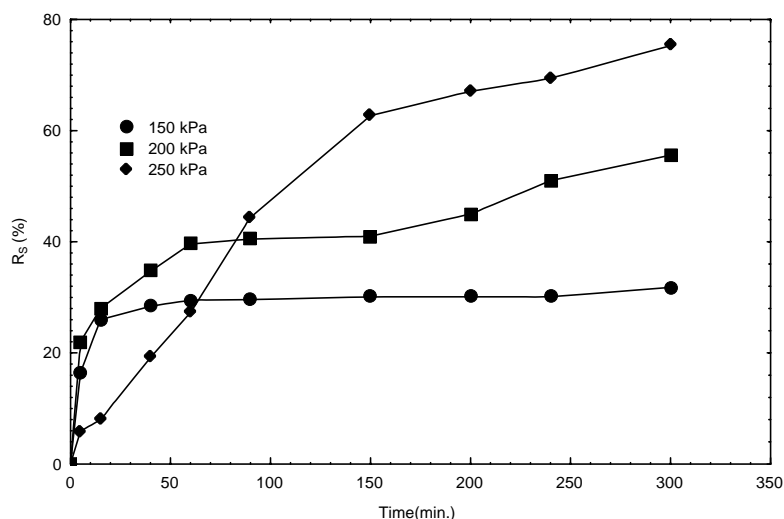
where  $C_{CP}$  and  $C_{CF}$  are the chromate concentrations in the permeate and feed streams, respectively.

## 3. Results and Discussion

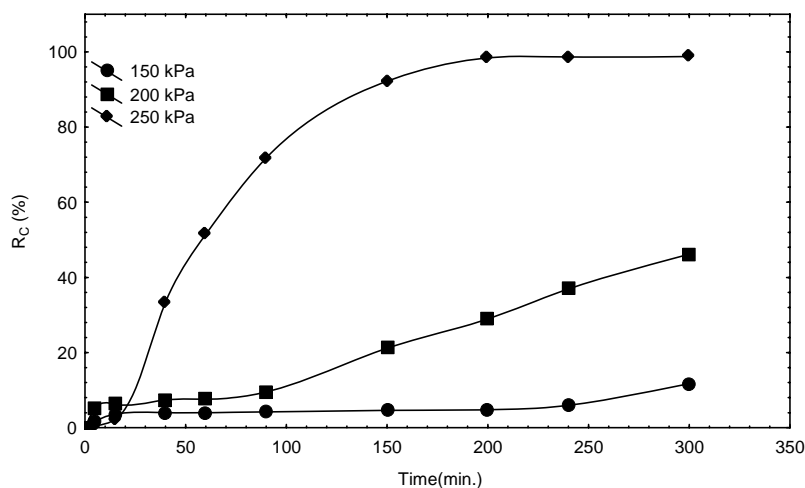
### 3.1 The effect of transmembrane pressure drop ( $\Delta P$ ) on the rejections and permeate flux

In order to investigate the effect of  $\Delta P$ , the experiments carried out at 30 mM surfactant concentration and observed finding showed that the rejections of DDAB and chromate increased with increasing pressure, as indicated Figs. 2 and 3. The rejections of DDAB and chromate seem to be lower because of not being blocked into the membrane pores at low pressure (e.g. with decreasing  $\Delta P$ ). At increased  $\Delta P$  pressure, membrane pores have been completely blocked into and the secondary membrane layer has been formed on the surface and makes it possible to reach to the stable conditions in a short time. Fig. 4 indicates effect of applied pressure on permeate flux decay. As seen in figure 4, there was a small decreasing in flux at the application of 30 mM concentration because of membrane pores at low  $\Delta P$  are unfilled with micelles. At the beginning there is a fast rate of permeate flux decay and then very slow flux decay exists. In high  $\Delta P$ s, higher flux decay was observed than that of 150 kPa. After certain filtration time,

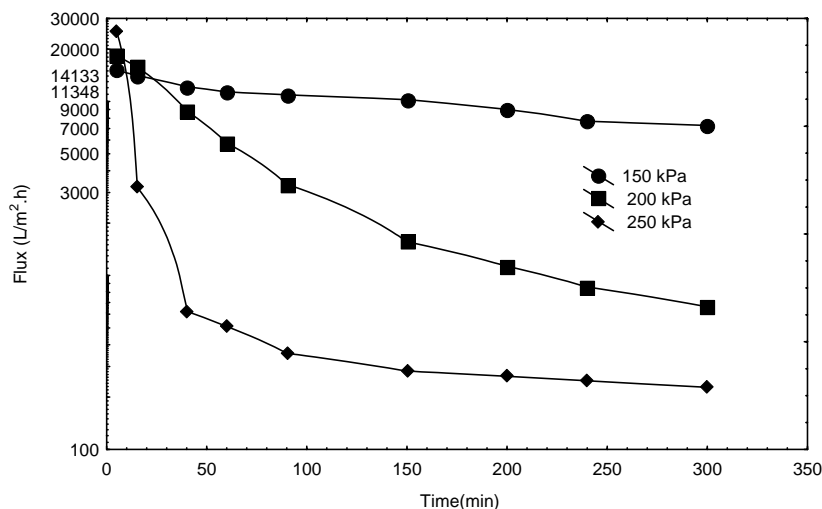
noticeable changes at increasing pressure were not observed as seen Fig. 4. Pressure drop does not significantly affect the steady state permeate flux and rejection coefficient, as shown in Figs. 2,3 and 4. The permeate flux reduces and rejections increases due to the developing secondary membrane on the surface and within the pores of the membrane. This case explains that the flux will be able to independent than the pressure after a certain period of filtration time.



**Figure 2.** The variation of DDAB rejection with time as function of  $\Delta P$ . (pH=7.10, DDAB/chromate=150, T=30°C, membrane pore size=0.2  $\mu\text{m}$ , v=6m/s)



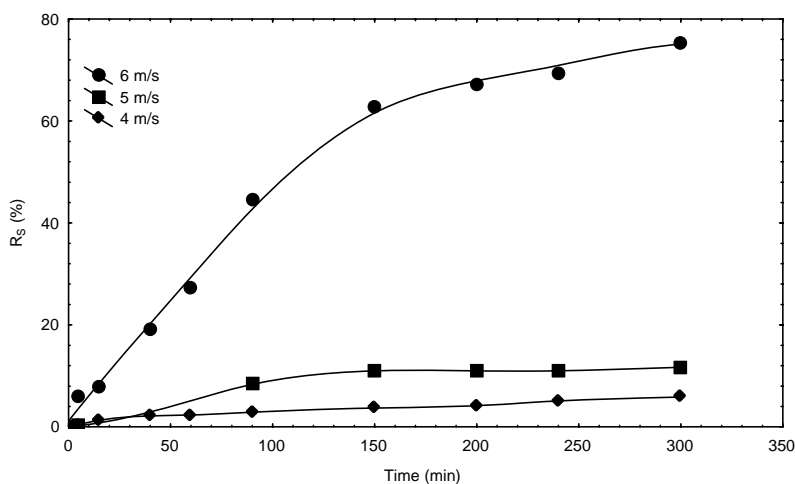
**Figure 3.** The variation of chromate rejection with time as function of  $\Delta P$ . (pH=7.10, DDAB/chromate=150, T=30 °C, membrane pore size=0.2 $\mu\text{m}$ , v=6 m/s)



**Figure 4:** The variations of permeate flux with time as function of  $\Delta P$ . (pH=7.10, DDAB/chromate=150,  $T=30^{\circ}\text{C}$ , membrane pore size= $0.2\mu\text{m}$ ,  $v=6\text{m/s}$ )

### 3.2 The effect of crossflow velocity on the rejections

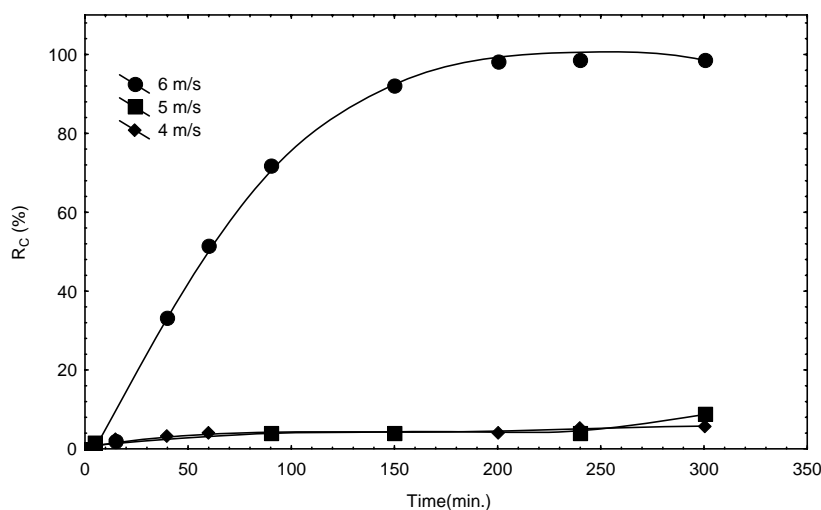
The effects of crossflow velocity on DDAB and chromate rejections are shown in Figs. 5 and 6 respectively. As illustrated in the figures, while the rejections of the DDAB and chromate increase with increasing crossflow velocity, for crossflow velocities 4 and 5 m/s, it is observed that the rejections of the DDAB and chromate have an important gradual decrease.



**Figure 5:** The variation of DDAB rejection with time as function of crossflow velocity. (pH=7.10, DDAB/chromate=150,  $T=30^{\circ}\text{C}$ , membrane pore size= $0.2\mu\text{m}$ ,  $\Delta P=250\text{ kPa}$ )

It is supposed that this surprising case related to the deformation of surfactant micelles. These finding are the same with the investigations made with quaternary ammonium chloride (dioctadecyl dimethyl ammonium chloride) including double hydrophilic head groups as DDAB by Akay & Wakeman (1996b). It is observed that the increases are similar to performance of process with accelerating crossflow velocity. We consider that deformation rate is to be extreme owing to accumulating of surfactant into the pore entrance because of no flowing higher on the membrane surface at low crossflow velocities. Hence, it is an expected case that membrane

pores are to be filled with different sizes micelles due to a deformation and the low flow on the membrane surface is not cause an important surfactant deposition.



**Figure 6:** The variation of chromate rejection with time as function of crossflow velocity. (pH=7.10, DDAB/chromate=150, T=30°C, membrane pore size=0.2 $\mu$ m,  $\Delta P$ =250 kPa).

#### 4. Conclusions

It was observed that the chromate ions could be effectively removed from wastewater using cellulose acetate membranes and cationic surfactant such as DDAB. The efficiency of the separation process is independent of the initial chromate concentration in the feed and the rejection coefficients for the surfactant and chromate are strongly dependent on DDAB/chromate ratio, transmembrane pressure drop ( $\Delta P$ ) and crossflow velocity. It was found that the surfactant rejection is adversely affected by the increase of transmembrane pressure drop ( $\Delta P$ ) and crossflow velocity. The secondary membrane can entirely control the permeate flux and rejection of the surfactant or other solutes. It is therefore important to understand the dynamics of the secondary membrane development and the mechanisms of permeate flow and rejection behaviour of these types of "composite membranes". The results were shown that the secondary membrane formation mechanism is significantly influenced by DDAB/chromate ratio, transmembrane pressure drop ( $\Delta P$ ) and crossflow velocity.

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