## MEUF를 이용한 크롬(VI)과 nitrate의 동시제거에 관한 연구

양지원 • 백기태

# 한국과학기술원 생명화학공학과 환경복원연구실

#### Simultaneous removal of chromate and nitrate using micellar enhanced ultrafiltration

Ji-Won Yang and Kitae Baek

Department of Chemical and Biomoleucular Engineering, KAIST

#### **Introduction**

The increasing contamination of groundwater by toxic inorganic compounds is a serious environmental problem. These inorganic pollutants are of considerable concerns because they are non-biodegradable, highly toxic and have probable carcinogenic or other negative effects.

Chromate is one of the most common groundwater contaminants at industrial sites and military facilities due to its widespread use as a metal corrosion inhibitor. In the environment, the stable oxidation states of chromium are Cr(III) and Cr(VI). While Cr(III) is an essential element for living beings, playing an important role in carbohydrate metabolism, Cr(VI) becomes carcinogenic for long exposures. Hence, Cr(VI) incurs a significant risk to human health when released into the environment.

Nitrate, which caused blue baby syndrome to a baby less than 6 months, has been a major pollutant in groundwater due to development of agricultural fertilizers. Nitrate contamination of groundwater supplies is increasingly breaching safety levels in developed and developing countries. The maximum level of nitrate in water supplied for human consumption is about 10 mg/l.

Micellar enhanced ultrafiltration (MEUF) has been shown to be an effective method to remove chromate or nitrate from aqueous phase (Yildiz et al, 1996; Morel et al., 1994;Tangvijitsri et al., 2002;Gzara & Dhahbi, 2001;Christian et al., 1988). Figure 1(A) shows the conceptual diagram of MEUF for removal of nitrate and chromate with a cationic surfactant. These researches on removal of chromate or nitrate have focused on single pollutant system. In the real field, however, a pollutant co-exists with other pollutants. In multi-pollutants systems, removal or binding phenomena is changed due to competition between one pollutant and the other pollutant.

In the present study an attempt is made to remove chromate anions and nitrate simultaneously from aqueous solutions by micellar enhanced ultrafiltration using cetylpyridinium chloride (CPC). The influence of some operating parameters in the permeate flux and rejection of chromate, nitrate, and CPC is detailed. The process is investigated as a function of molar ratio of surfactant to pollutant.

#### **Materials and Methods**

Cetylpyridinium chloride (CPC), sodium nitrate, and sodium chromate were purchased from Simga chemicals (USA). Deionized water was used in preparing all solution. Ultrafiltration experiments were executed with stirred cell (Millipore, 8400, USA). The schematic diagram of experimental apparatus was shown in Figure 1(B). The membrane area was 45.6 cm2, regenerated cellulose acetate with molecular weight cut-off (MWCO) 3000 and 10,000 and transmembrane pressure was adjusted to 2 bar. Feed solutions were mixed adequately during at least 12 hours.

The inlet reservoir was initially filled with a 100 ml feed solution, and during first 3 min the permeate was wasted for leaching steady state. To evaluate the filtration efficiency in removal of chromate and nitrate from the feed solution, the following equation (rejection or removal efficiency) was expressed as

$$R = \left[1 - \frac{C_p}{C_i}\right] \times 100$$

where R is the percent removal rate, Cp the concentration of chromate or nitrate in the permeate, and Ci the initial feed concentration.

For the comparison of the fluxes measured in different conditions, relative fluxes to fluxes of deionized water were used. The analysis of nitrate, CPC, and chromate in permeate solution is carried out through UV-visible spectrophotometer (HP 8452 A, USA) at 232, 258, and 372 nm.

#### **Results and Discussion**

Figure 2 shows the rejection of chromate under co-existence of nitrate as a function of molar ratio of nitrate to chromate and CPC. Rejection of chromate increased from 70% to 95% as the molar ratio of nitrate : chromate : CPC increased from 1 : 0.1 : 0.55 to 1 : 0.1 : 2.2. At the concentration of CPC greater than the molar ratio of 1 : 0.1 : 2.2, the increase in chromate rejection was negligible. The rejection of chromate according to molar ratio of CPC to chromate decreased significantly in the multi-pollutant system compared to single pollutant system. The rejection decreased from 98% to 70% at the similar molar ratio of CPC to chromate (i.e. 5 to 1) under co-existence of nitrate because chromate competed with nitrate to bond on CPC micelles. Chromate ion has greater binding power than nitrate ion in chromate/nitrate/CPC system because binding power is proportion to number of charges ( Tangvijistri et al., 2002). There was no significant difference in chromate rejection between membrane with MWCO of 10,000 and that with of MWCO 3,000 because the size of CPC micelle is big enough not to pass through the membrane pore. However, flux in MWCO of 10,000 was 3 times greater than that in MWCO of 3,000. This means that the filtration system fitted with MWCO 10,000 is beneficial compared to the system with MWCO 3,000 in the point of treatment capacity.

Figure 3 shows the nitrate rejection under co-existence of chromate as a function of molar ratio of nitrate to chromate and CPC. The nitrate rejection increased gradually as the molar ratio increased. The rejection in nitrate/chromate/CPC system was similar to that in nitrate/CPC system because the concentration of nitrate in the feed was 10 times greater than the concentration of chromate. As a result, the effect of chromate on nitrate

화학공학의 이론과 응용 제8권 제2호 2002년

rejection was negligible, but the effect of nitrate on the chromate rejection was significant because of competition. There was no significant difference in chromate rejection between membrane with MWCO 10,000 and that with MWCO 3,000 because the size of CPC micelle is big enough not to pass through the membrane pore.

#### **Conclusions**

MEUF could removed chromate and nitrate simultaneously to 99% and 90%, respectively. Rejection of chromate under co-existence of nitrate was inhibited by higher concentration of nitrate, while the rejection of nitrate was not because the concentration of nitrate was high enough compared to chromate concentration. There is no significant difference in rejection of nitrate and chromate between membrane with MWCO of 10,000 and membrane with MWCO of 3,000 because the size of CPC micelle is big enough not to pass through the membrane pore. As a result, the rejection of CPC was high enough and the concentration of CPC in the permeate was low enough. MEUF process could be a alternative to treat groundwater contaminated with nitrate and chromate.

#### **Acknowledgement**

Finantial support for this work was provided by MOST through National Research Laboratory program.

### **References**

Christian, S.D., Bhat, S.N., Tucker, E.E., Scamehorn, J.F., El-Sayed, D.A., *AIChE J.*, **34** (2), 189-194 (1988). Gzara, L., Dhahbi, M, *Desalination*, **137**, 241-250 (2001).

Morel, G., Graciaa, A., Lachaise, J., J. Membr. Sci., 56, 1-12 (1991).

Tangvijistri, S., Saiwan, C., Soponvuttikul, C., Scamehorn. J.F., *Sep. Sci. Technol.*, **37**(5), 993-1007 (2002). Yildiz, E., Pekdemir, T., Keskinler, B., Cakici, A., Akay, G., *Trans IChemE*, **74**(A7), 189-194 (1996).



Figure 1. Conceptual diagram of MEUF (A) and Schematic diagram of experimental apparatus (B)

화학공학의 이론과 응용 제8권 제2호 2002년



Figure 2. Rejection of chromate in the chromate/nitrate/CPC system. Initial concentration of chromate and nitrate was 10 mM and 1 mM, respectively. Ultrafiltration was carried out at the stirred cell fitted with MWCO 10,000 (left figure) and MWCO 3,000 (right figure) under 2 bar.



Figure 3. Rejection of nitrate in the chromate/nitrate/CPC system. Initial concentration of chromate and nitrate was 10 mM and 1 mM, respectively. Ultrafiltration was carried out at the stirred cell fitted with MWCO 10,000 (left figure) and MWCO 3,000 (right figure) under 2 bar.