

Cross-flow micellar-enhanced ultrafiltration for removal of nitrate and chromate: competitive binding

Kitae Baek, Ji-Won Yang*

National Research Laboratory for Environmental Remediation, Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong-gu, Daejeon 305-701, South Korea

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Abstract

Feasibility of cross-flow micellar-enhanced ultrafiltration was investigated to remove chromate and nitrate from water system using a cationic surfactant, cetylpyridinium chloride (CPC). Removal of chromate with -2 as valence was higher than that of nitrate with -1 as valence in the conditions of co-existence of chromate and nitrate. Removal of nitrate was significantly inhibited by co-existence of chromate because of competitive binding to CPC micelles between chromate and nitrate, while that of chromate was only slightly inhibited by nitrate. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Groundwater contamination by inorganic pollutants such as heavy metals, chromate and nitrate has recently begun to attract widespread interests because of significant threat to human health. Nitrate and chromate are most frequently detected contaminants in groundwater. Nitrate levels have been increasing due to increased usage of nitrogenous fertilizers, changes in land-use patterns from pasture to arable, and increased recycling of domestic wastewater in low-land rivers [1]. Nitrate at the concentrations greater than 10 mg N-NO₃⁻/l can be fatal to infants under 6 months of age and pregnant women. In infants, nitrate is reduced to nitrite, which combines with hemoglobin in the blood to form methemoglobin and leads to a conditions commonly known as blue baby syndrome. The US EPA and WHO established a maximum contamination level of 10 mg N-NO₃⁻/l as a guideline [2].

Unlike other toxic heavy metals, chromate is quite soluble in the aqueous phase almost over the entire pH range, and, thus, quite mobile in the natural environment. Widespread industrial application as a metal corrosion inhibitor and high mobility are the two primary reasons why chromate

is frequently found in contaminated sites and groundwater [3]. Chromate induces coetaneous allergy and becomes carcinogenic for long exposures [4].

Recently, micellar-enhanced ultrafiltration (MEUF) has been used for the removal of various organic and/or inorganic pollutants from aqueous phase [2,5–14]. MEUF is a separation technique which involves adding surfactant to a polluted water stream. The surfactant forms micelles, which contain about 50–100 surfactant molecules, at surfactant concentration above the critical micelle concentration (CMC). If a cationic surfactant is used to remove anionic pollutants such as nitrate and chromate, the micelle has a high positive electrical potential on the surface where the charged hydrophilic groups are located. The cationic pollutants bound to the micelles, then treated in an ultrafiltration with membrane pore size small enough to block the passage of micelles [5]. The schematic diagram of MEUF process for simultaneous removal of nitrate and chromate is shown in Fig. 1.

Several research groups have tried to remove nitrate or chromate using MEUF process [5–10]. However, there are no reports on simultaneous removal of chromate and nitrate. Baek et al. reported that compounds with higher valence inhibited the removal of compounds with low valence. Ferricyanide with -3 as valence inhibited the removal of chromate with -2 as valence [11], and ferricyanide also inhibited the removal of nitrate with -1 as valence

* Corresponding author. Tel.: +82-42-869-3924;

fax: +82-42-869-3910.

E-mail address: jwyang@kaist.ac.kr (J.-W. Yang).

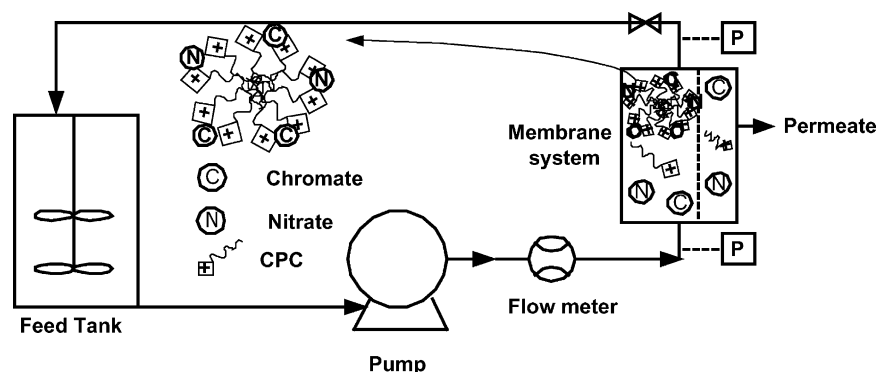


Fig. 1. Schematic diagram of cross-flow micellar-enhanced ultrafiltration for removal of nitrate and chromate.

[12]. Chromate may inhibit the removal of nitrate because chromate has -2 as valance and nitrate has -1 .

In this study, feasibility of cross-flow micellar-enhanced ultrafiltration for simultaneous removal of nitrate chromate was investigated using a cationic surfactant, cetylpyridinium chloride, especially, in the view of ionic competition between nitrate and chromate for binding to CPC micelles.

2. Materials and methods

Cetylpyridinium chloride (CPC) with purity of 99% was obtained from Aldrich (USA). Nitrate and chromate were purchased from Sigma (USA) as a form of sodium salt. Deionized water was used for the preparation of solutions.

The ultrafiltration experiments were operated in a cross-flow ultrafiltration unit (TFF, Millipore, USA). The ultrafiltration membrane was polyethersulfone with an effective area of 0.050 m^2 (Biomax, Millipore, USA). The pore size of membrane was molecular weight cut-off (MWCO) of 8000. The trans-membrane pressure was maintained at 2 bar gauge and the temperature was held constant at 25°C .

Feed solution was prepared by mixing stoichiometric amounts of CPC, nitrate, and chromate. The feed tank was initially filled with 250 ml of feed solution. At the desired time intervals, the permeate was sampled. The concentrations of CPC, nitrate, and chromate of the samples were analyzed by UV/VIS spectrophotometer (HP 8452A, USA) at wavelength of 258, 232, and 372 nm, respectively. The rejection (or removal) of nitrate, chromate, and CPC were calculated from the following equation:

$$R = \left(\frac{C_i - C_p}{C_i} \right) \times 100 \quad (1)$$

where C_i is the feed concentration of nitrate, chromate, or CPC, and C_p the concentration of each compound in the permeate. The retentate CPC concentration was measured directly using UV/VIS spectrophotometer (HP 8452A, USA).

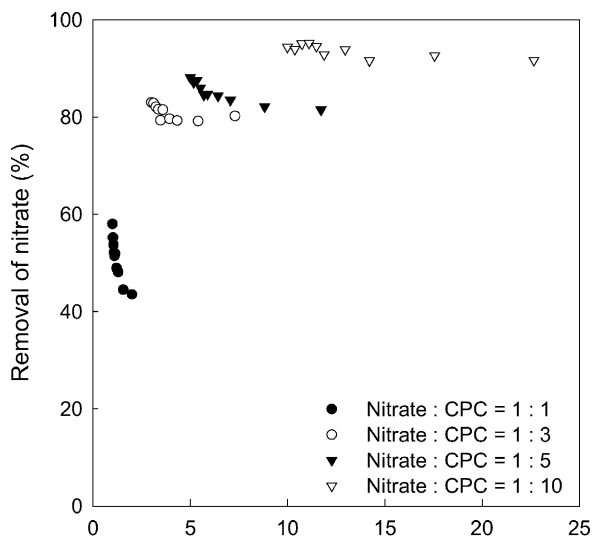
3. Results and discussion

The removal characteristics of nitrate and chromate are shown in Fig. 2 in the single pollutant system. As the molar ratio increased, the removal also increased.

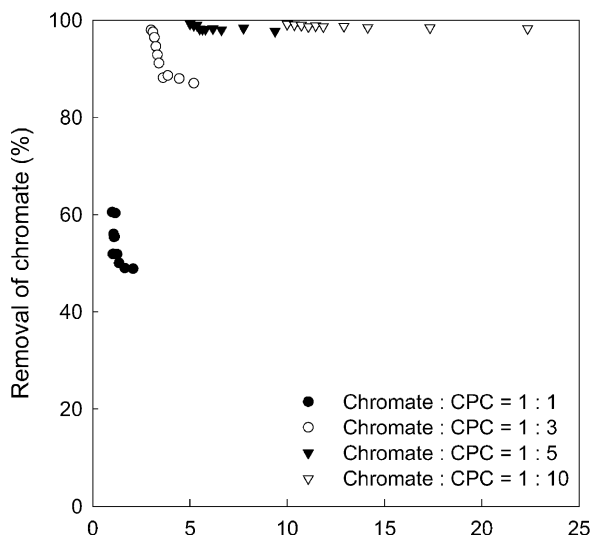
The removal characteristics of nitrate are shown in Fig. 3 in the conditions of co-existence of nitrate and chromate. The removal increased with the molar ratio of CPC, however, the removal was reduced with the increase of retentate concentration as the filtration progressed at the low molar ratio of CPC ($<1:1:3$). As the molar ratio increased from 1:1:1 to 1:1:2 and to 1:1:3 (nitrate:chromate:CPC), the initial removal of nitrate increased gradually from 30 to 49% and to 56%. The removal of nitrate increased from 56 to 78% and to 89% as the molar ratio increased from 1:1:3 to 1:1:5 and to 1:1:10, respectively, and as the concentration of retentate increased.

The removal characteristics of chromate are shown in Fig. 4 in the conditions of co-existence of nitrate and chromate. The removal increased sharply with the molar ratio of CPC, then saturated to almost 100% at molar ratio greater than 5. The initial removal of chromate was 48, 76, and 94%, respectively, at the molar ratios of 1:1:1, 1:1:2, and 1:1:3. The increase in chromate removal was much larger than that in nitrate removal at the same conditions (Fig. 2). At the molar ratio of 1:1:3, the removal of chromate already became larger than 93%.

At the molar ratio of $>1:1:5$, the chromate removal was saturated and no significant increase in the removal was observed. At the molar ratio of 1:1:5, however, the nitrate removal started to increase sharply. This phenomenon can be explained by competitive binding of chromate and nitrate to CPC micelles. Generally, ionic binding to polyelectrolytes increased as the valence of pollutants [11–13,15]. Tangvijit-sri et al. reported that the rejection of chromate and sulfate (divalent anions) was similar, however, higher than that of nitrate (monovalent anion) in the polyelectrolyte enhanced ultrafiltration [15]. In the conditions of co-existence of chromate and nitrate, chromate bound to CPC micelles preferentially to nitrate, after saturation of chromate binding, the binding of nitrate started to increase sharply. Chromate with



(A) Concentration of surfactant in the permeate (mM)



(B) Concentration of surfactant in the permeate (mM)

Fig. 2. Effect of CPC molar ratio on individual removal of nitrate (A) and chromate (B). The initial concentration of nitrate and chromate was 1 mM, respectively. Trans-membrane pressure: 2 bar gauge; operation temperature: 25 °C; membrane: polyethersulfone with molecular weight cut-off of 8000.

-2 as valence bound to CPC micelles superior to nitrate with -1 as valence.

In the MEUF process, rejection of surfactant as well as removal of pollutants should be considered because the surfactant in the permeate induced the secondary pollution in groundwater or wastewater effluent. Fig. 5 shows the rejection of CPC as a function of retentate CPC concentration. The rejection of CPC was quite high, though the rejection decreased sharply as the ultrafiltration progressed at the low molar ratio of CPC (<1:1:3). The decrease in rejection of CPC resulted from the concentration of retentate. As the molar ratio of CPC increased, the rejection of CPC increased gradually.

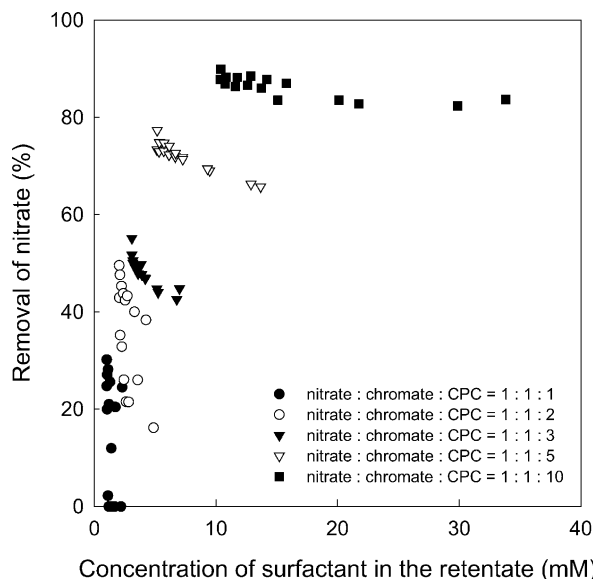


Fig. 3. Effect of CPC molar ratio on removal of nitrate in equimolar nitrate and chromate solution. The initial concentration of nitrate and chromate was 1 mM, respectively. Transmembrane pressure: 2 bar gauge; operation temperature: 25 °C; membrane: polyethersulfone with molecular weight cut-off of 8000.

Concerning the secondary pollution due to surfactant, surfactant concentration in the permeate as well as the rejection of surfactant should be investigated because the addition of large amount of surfactant for the treatment of heavy contamination caused a higher surfactant concentration in the permeate even though the same rejection of

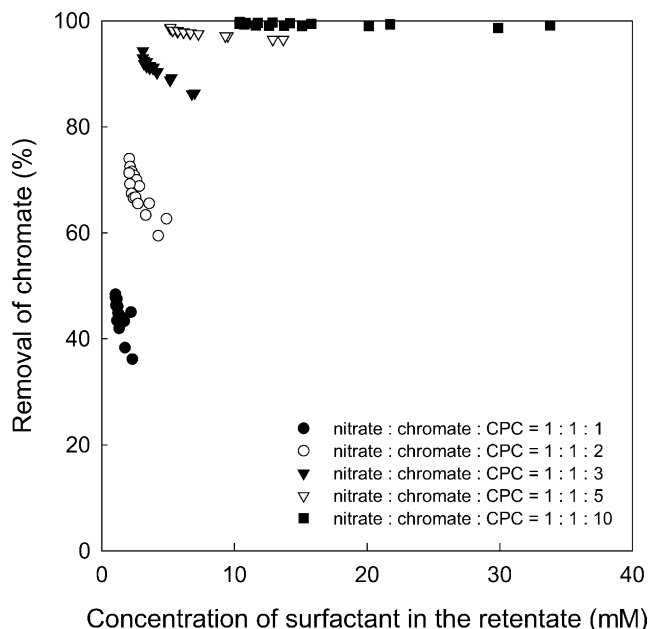


Fig. 4. Effect of CPC molar ratio on removal of chromate in equimolar nitrate and chromate solution. The initial concentration of nitrate and chromate was 1 mM, respectively. Transmembrane pressure: 2 bar gauge; operation temperature: 25 °C; membrane: polyethersulfone with molecular weight cut-off of 8000.

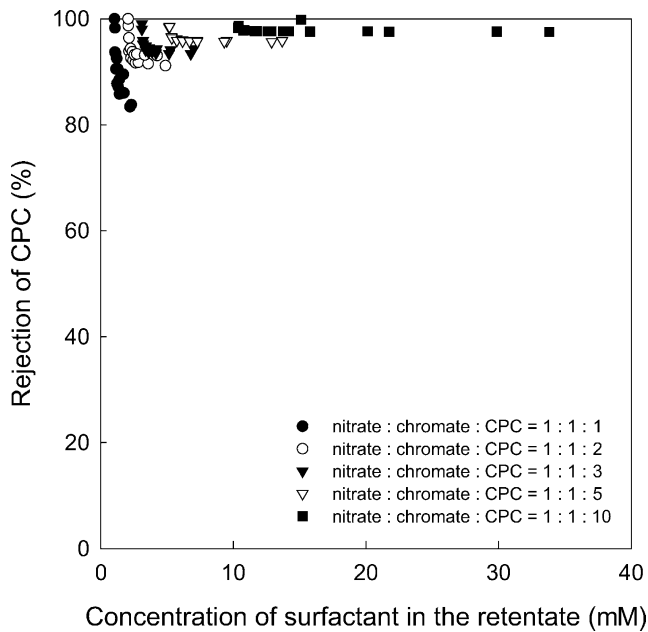


Fig. 5. Effect of CPC molar ratio on rejection of CPC in equimolar nitrate and chromate solution. The initial concentration of nitrate and chromate was 1 mM, respectively. Transmembrane pressure: 2 bar gauge; operation temperature: 25 °C; membrane: polyethersulfone with molecular weight cut-off of 8000.

surfactant was observed. The surfactant concentration in the permeate increased gradually as the concentration of CPC in the retentate increased regardless of CPC molar ratio (Fig. 6). Theoretically, the concentration of CPC in the permeate

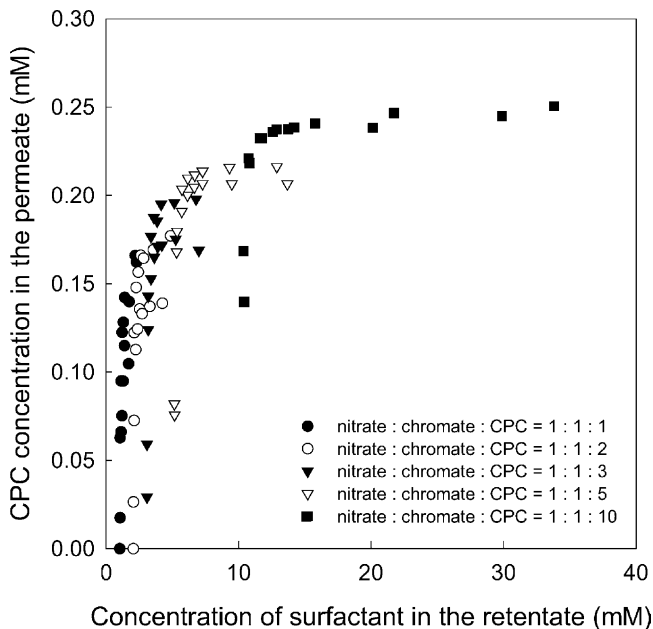


Fig. 6. Effect of CPC molar ratio on retentate concentration of CPC in equimolar nitrate and chromate solution. The initial concentration of nitrate and chromate was 1 mM, respectively. Transmembrane pressure: 2 bar gauge; operation temperature: 25 °C; membrane: polyethersulfone with molecular weight cut-off of 8000.

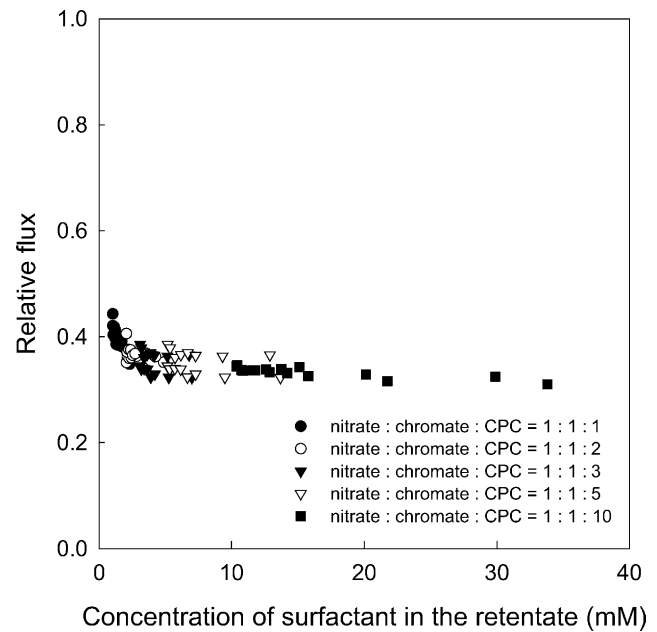


Fig. 7. Effect of CPC molar ratio on variation of relative flux in equimolar nitrate and chromate solution. The initial concentration of nitrate and chromate was 1 mM, respectively. Transmembrane pressure: 2 bar gauge; operation temperature: 25 °C; membrane: polyethersulfone with molecular weight cut-off of 8000.

can increase up to the CMC of CPC (0.9 mM), however, the concentration increased gradually up to 0.23 mM and then was saturated.

To compare the flux carried out at the different conditions, relative flux in regard to the flux of de-ionized water was introduced. As shown in Fig. 7, the relative flux was immediately lower to 40% of the flux of de-ionized water as soon as the filtration started. Even though the molar ratio of CPC increased, the flux reduction was not observed any more. The reduction in relative flux came from the fouling due to formation of secondary membrane on the surface of membrane. Even though the reduction in relative flux was large, the real flux was higher than that in the dead-end filtration (data not shown).

4. Conclusions

Cross-flow micellar-enhanced ultrafiltration was investigated to remove chromate and nitrate simultaneously. Nitrate removal was inhibited by the co-existence of chromate, while that of chromate was not significantly by co-existence of nitrate. Chromate with -2 as valence bound to CPC micelles is superior to nitrate with -1 as valence. At the molar ratio of 1:1:10 (nitrate:chromate:CPC), the removal of nitrate and chromate was 91% and >99%, respectively. The CPC concentration in the permeate was expressed as a function of retentate CPC concentration regardless of the molar ratio of CPC. Cross-flow MEUF process could be a good alternative of ion exchange or reverse osmosis for removal

of chromate and nitrate even though competitive binding occurred.

Acknowledgements

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