

Chromate Removal from Wastewater using Micellar Enhanced Ultrafiltration and Activated Carbon Fibre Processes; Validation of Experiment with Mathematical Equations

Rabindra Bade and Seung Hwan Lee[†]

School of Civil and Environmental Engineering, Kumoh National Institute of Technology, 1 Yangho-dong, Gyeongbuk, 730-701, Korea

Received May 2008, accepted June 2008

Abstract

In this study, chromate and cetylpyridinium chloride (CPC) removal from artificial wastewater was monitored by using micellar enhanced ultrafiltration (MEUF) and activated carbon fibre (ACF) adsorption hybrid processes. For the efficient chromate removal, molar concentration of the CPC should be five times that of chromate and it should be at least one critical micelle concentration (CMC). The MEUF was found to be effective in the chromate removal while ACF in the CPC adsorption to produce chromate and CPC free effluents. The chromate and CPC removal was 99.8% from MEUF-ACF process. Effluent chromate concentration was exponentially correlated with molar ratio of CPC to chromate and pH.

Keywords: Activated carbon fibre, Cetylpyridinium chloride, Chromate, Micellar enhanced ultrafiltration, Mathematical equation

1. Introduction

Environmental pollution control laws are becoming more stringent and toxic compounds removal from wastewater is becoming more crucial before discharging it to environment. Chromium compounds are widely used in textile, leather tanning, wood preserving and electroplating industries.^{1,2} Wastewater from those industries contains huge amount of chromium. It has several adverse effects on environment and even in wastewater treatment plants.^{3,4}

Micellar enhanced ultrafiltration (MEUF) is a promising technology which combines the high flux of ultrafiltration (UF) with the high efficiency of reverse osmosis.⁵ In this process, surfactants aggregate and form micelles when they are present in the solution at the concentration above critical micelle concentration (CMC). This process can remove hydrophobic organics by the solubilization in micelle⁶ and inorganic nutrients, multivalent ions by electrostatic adsorption on micelle.^{7,8} Metal ions together with micelle are retained on membrane surface when it is passed through ultrafilter having pore size smaller than the size of micelle.^{9,10} In the MEUF process, cationic or anionic surfactants are used for the separation of metal ions.

Cetylpyridinium chloride (CPC) and cetyltrimethyl ammonium bromide (CTAB) were used to remove chromate, nitrate and ferricyanide.^{3,5,11} Over 93% of As (V) removal was reported using CPC.^{12,13} Over 95% of Cu²⁺, Zn²⁺, Cr³⁺ and 96% of cadmium, zinc, copper, and calcium were removed with sodium dodecyl sulphate (SDS).¹⁴⁻¹⁶ Similarly, 95% cadmium removal was observed using one cmc of SDS.¹⁷ Akita et al. (1997)¹⁸ had reported almost complete removal of Zn, Cu and Fe using SDS. Nickel removal of 100% was reported using SDS.¹⁴ Attractive removal was achieved by MEUF process for the mixture of metal ion and organics without affecting each others removal.

In adsorption process, powdered activated carbon (PAC), granular activated carbon (GAC) and activated carbon fibre (ACF) have been used for the removal of organics from wastewater. Compared to PAC and GAC, ACF has a uniform micropore structure, faster adsorption kinetics and lower pressure drop.¹⁹ Several researchers have studied on heavy metal removal using MEUF^{3,11} but no study have been conducted using high molecular weight cut-off (MWCO) membrane and the removal of CPC that contained in the permeate. Performance of MEUF-ACF hybrid processes on chromate and CPC removals from wastewater at various conditions were studied. Experimental results were then verified with mathematical equation using regression analysis.

[†] Corresponding author
E-mail: dlee@kumoh.ac.kr
Tel: +82-54-478-7632, Fax: +82-54-478-7629

2. Materials and Methods

Sodium chromate with 99% assay and CPC with 98% assay were received from Sigma-Aldrich Co. Ltd. They were used without further purification. Hollow fibre ultrafilter (UF) membrane was made of polyacrylonitrile material and its inside and outside diameter were 0.8 mm and 1.4 mm, respectively. Membrane module was cross-flow type and has an effective surface area of 0.055 m². The membrane has molecular weight cut-off (MWCO) of 100 KD and flow direction was from inside to outside. Weight of the ACF, having BET surface area of 1000 m²/g, was 30 g/cartridge. Distilled water was used for the preparation of feed solution and cmc for the CPC was taken as 0.9 mM.⁵⁾

MEUF-ACF experimental unit is shown in Fig. 1. Preliminary experiments on the MEUF were conducted for one hour and based on their results the MEUF-ACF experiments were run for 5 hr. During this process, flushing and backwashing were done with distilled water at each 30 and 10 min interval, respectively for 5 sec. All experiments were carried out at ambient laboratory temperature (22°C-25°C). After each experiment the membrane was subsequently flushed and backwashed with distilled water and cleansed with 0.05 M NaOH and 0.25% HCl. Cartridge filter and ACFs were also cleaned subsequently by soaking them in distilled water and 2% HCl. Collected samples were analyzed for the CPC and the chromate using UV/VIS spectrophotometer at the wave length of 258 nm and 372 nm, respectively.⁵⁾ In all the experiments retentate pressure of 0.14 MPa was applied. Statistical Package for Social Scientists (SPSS) and Matlab softwares were used to develop mathematical equation and simulation curve.

3. Results and Discussion

3.1. Optimum Molar Ratio and Effect of pH on the Chromate Removal

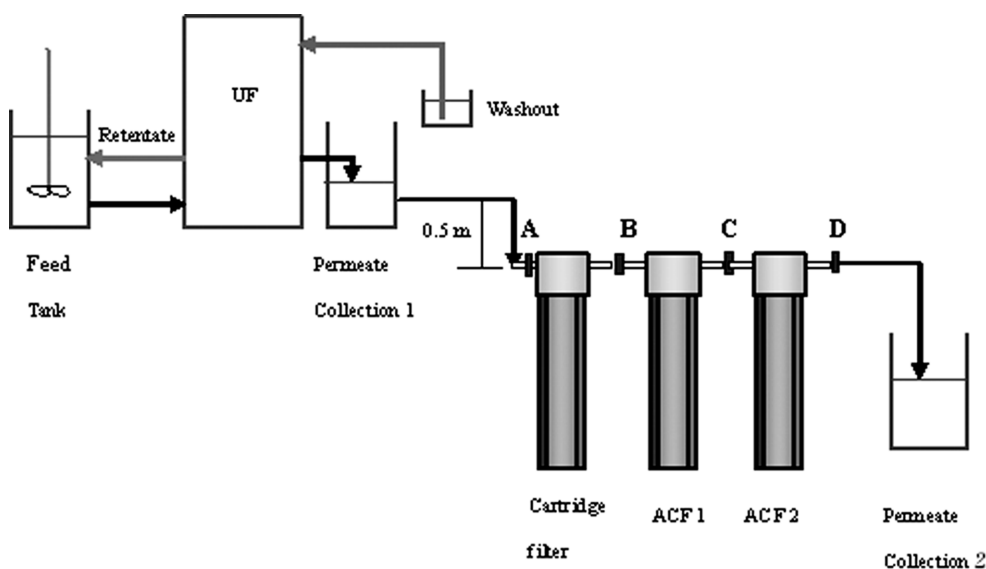


Fig. 1. Experimental set-up of MEUF combined with ACF for chromate removal from wastewater.

To find the effect of molar ratio of the chromate to the CPC, a series of experiment was conducted at various molar ratio of the chromate to the CPC for the operation period of one hour. Fig. 2 shows that the chromate removal increased with the increase of molar concentration of CPC. Average chromate removal was found to be 92.6%, 98.6%, 99.1% and 99.5%, respectively for molar ratio of 1:3, 1:5, 1:7 and 1:10. Optimum molar ratio was 1:5. At a higher CPC concentration, higher removal efficiency for the chromate and the CPC was resulted while filtering the solution through the UF membrane. To find the effect of pH, another series of experiment was carried out at various pH. Chromate removal efficiency ranged from 87% to 69% at the pH of 5.5 to 9.0 (Fig. 3). At a higher pH, there was competition between OH⁻ group and chromate ions to get the micelle surface resulting in the decrease of removal efficiency. Chromate removal efficiency increased with the decrease of pH.

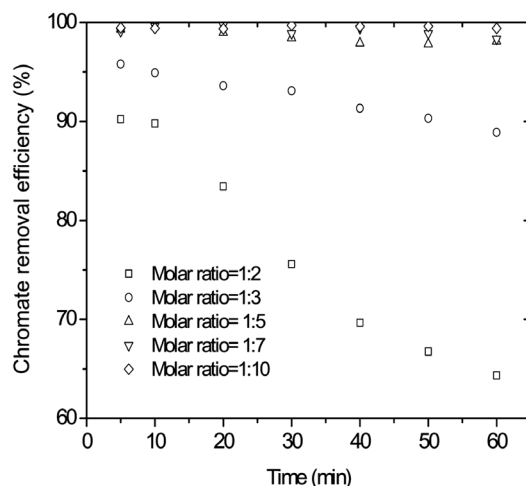


Fig. 2. Effect of molar ratio of chromate to CPC on chromate removal (Initial permeate flux = 43.75 L/m².h, Initial chromate conc. = 20 mg/L, Retentate pressure = 0.14 MPa, pH = 7).

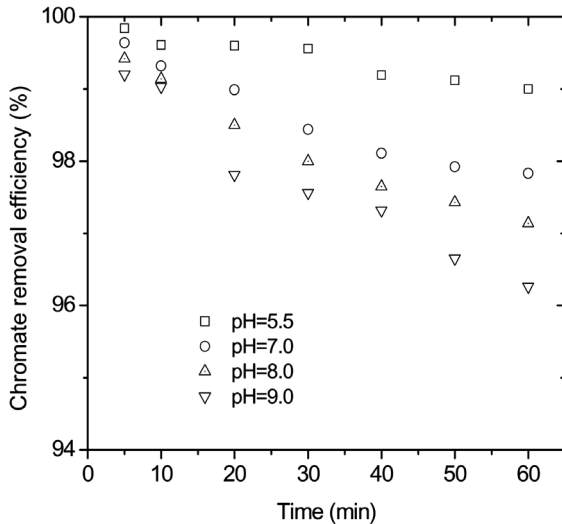
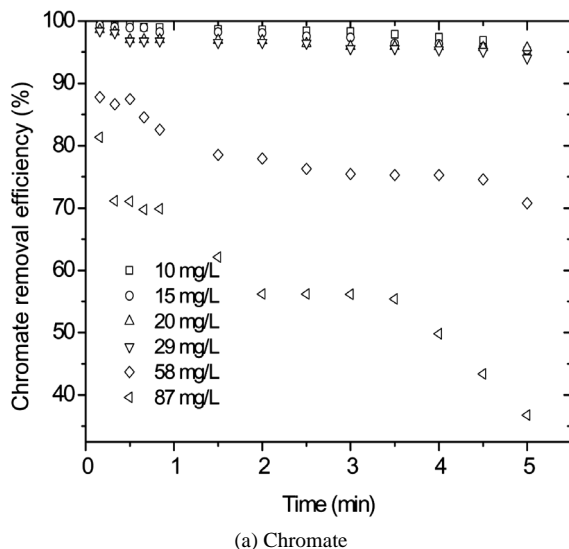


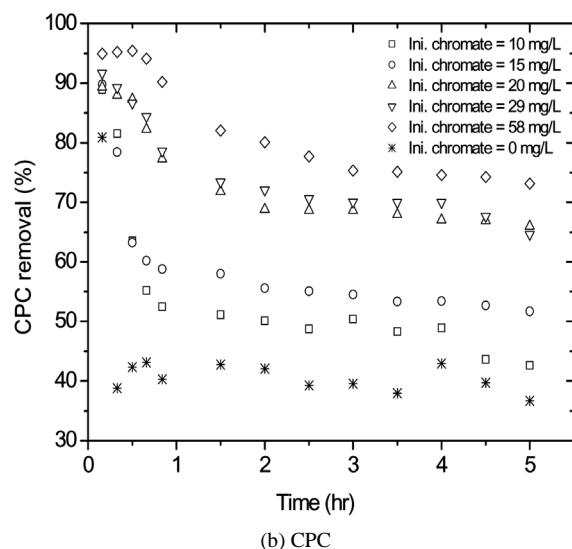
Fig. 3. Effect of pH on chromate removal (Initial permeate flux = 43.75 L/m².h, Initial CPC conc. = 1 cmc, Retentate pressure = 0.14 MPa, Initial chromate concentration = 20 mg/L).

3.2. Effect of Initial Chromate Concentration

To investigate the effect of initial chromate concentration on its removal, the other series of experiment was carried out for five hours at various initial chromate concentrations. Fig. 4(a) shows that average chromate removal ranged from 96% to 98%. Corresponding permeate concentration was 0.24 mg/L, 0.33 mg/L, 0.71 mg/L and 1.27 mg/L, respectively for the initial chromate concentration of 10 mg/L, 15 mg/L, 20 mg/L and 29 mg/L, respectively. It implies that the chromate removal decreases with the increase of its initial concentration at one cmc CPC while CPC removal increased. It is mainly due to more competition among chromate ions to get the binding surface with micelle. Similar results on chromate removal were presented by other researchers.³⁾



(a) Chromate



(b) CPC

Fig. 4. Effect of initial chromate concentration on chromate and CPC removal (Initial permeate flux = 32.9 L/m².h, Ini. CPC concentration = 1 cmc, Retentate pressure = 0.14 MPa, pH = 7).

The CPC removal from the 100 KD MWCO membrane was 49%, 55%, 72% and 73%, respectively for the respective initial chromate concentration of 10 mg/L, 15 mg/L, 20 mg/L and 29 mg/L (Fig. 4(b)). The CPC removal increased at the higher initial chromate concentration due to the formation of more micelle with the presence of counter ions. The CPC removal in the absence of the chromate was only 40% at one cmc of the CPC and the removal increased to 80% in the presence of chromate in similar condition (Fig. 4(b)).

The chromate and the CPC removals from different units of MEUF-ACF process are as shown in Fig. 5. From the entire process over 99.5% of the chromate and 99.8% of the CPC removal was observed. Corresponding chromate concentration remained at 0.01 mg/L to 0.31 mg/L and the CPC concentration was less than 2 mg/L, respectively. The ACF was found to be effective adsorbent for the CPC adsorption even at the higher concentration.

3.3. Effect of CPC Concentration

Another series of experiment was carried out at the different initial CPC concentration varying from 0.5 cmc to 1.0 cmc of CPC for the initial chromate concentration of 15 mg/L. Fig. 6(a) shows that the chromate removal increases with the increase of the initial CPC concentration. Average chromate removal was 98%, 95%, and 80%, respectively at 1.0 cmc, 0.75 cmc, and 0.5 cmc of the CPC. The result showed the highest removal at 1.0 cmc of the CPC. CPC concentration on the membrane surface can exceed cmc although retentate contains no micelle resulting the rejection of CPC at less than one cmc. Similar results on copper, zinc and manganese removals were also reported.^{15,20)} Even with the larger MWCO membrane of 100 KD, the rejection were not low compared to previous studies with 10KD, 8KD membranes at the molar ratio of 1:5. Average CPC removal was in the order of 49%, 53% and 56%, respectively for 0.5 cmc,

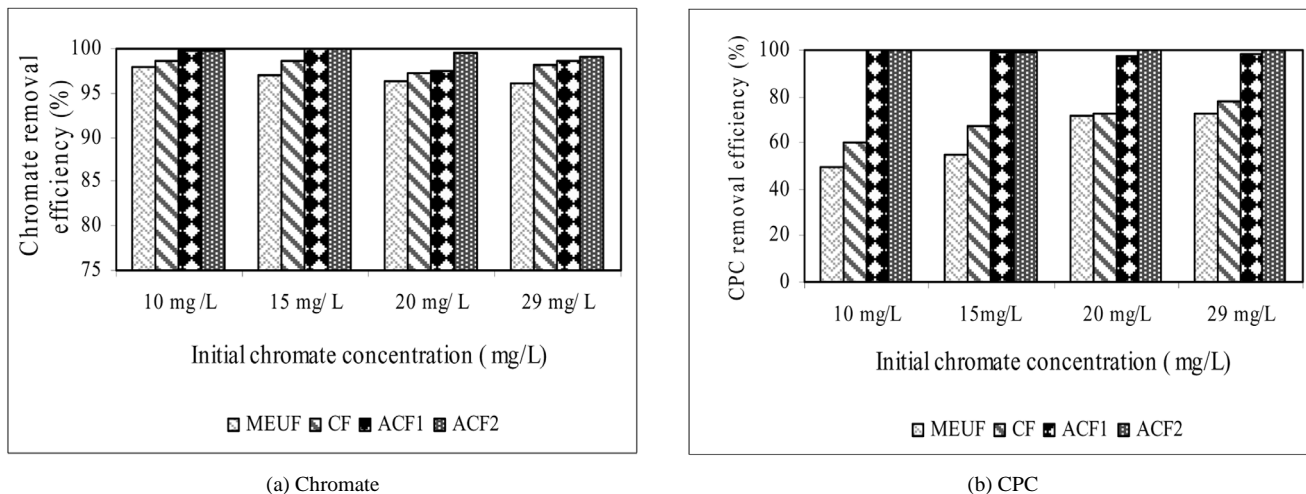


Fig. 5. Comparative removal of chromate and CPC from different units of MEUF-ACF process (Initial permeate flux = 32.9 L/m².h, Initial CPC concentration = 1 cmc, Retentate pressure = 0.14 MPa, pH = 7).

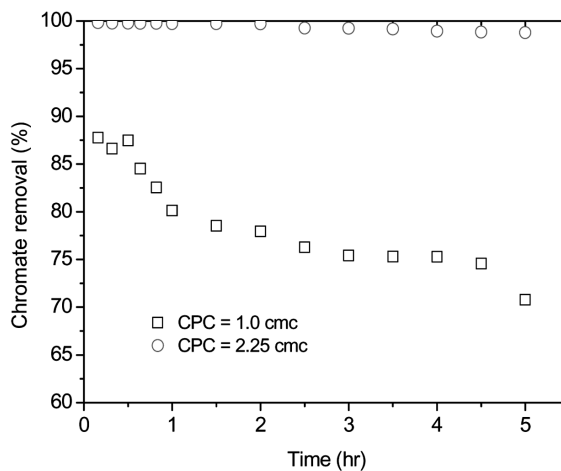
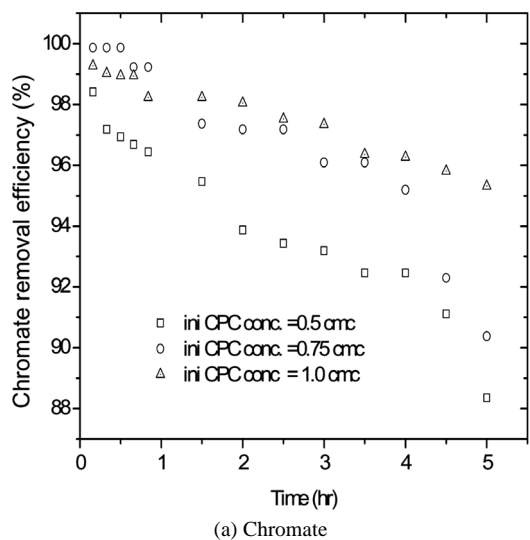
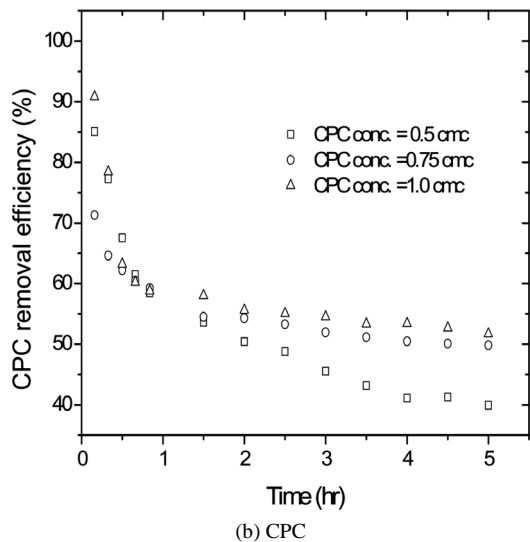


Fig. 6c. Effect of initial CPC concentration on chromate removal from MEUF (Initial permeate flux = 32.9 L/m².h, initial chromate concentration = 58 mg/L, Retentate pressure = 0.14 MPa, pH = 7).



0.75 cmc and 1 cmc of CPC (Fig. 6(b)). The CPC at the permeate increased with time because of passing of some of monomer CPC. Table 1 shows that the chromate and the CPC removal efficiency reached to 99.9% from the overall process.

Efficiency of the 100 KD UF membrane was studied for the chromate concentration of 58 mg/L (0.5M) for the operation period of 5 hr. Average chromate removal was 80% at one cmc while 99.8% removal efficiency was achieved at 2.25 cmc of the CPC (Fig. 6(c)). It further verifies that the molar ratio of 1:5 and the cmc of CPC in the solution can remove chromate efficiently.

The 300 KD UF membrane showed the chromate removal efficiency of 97% for the initial chromate concentration of 15 mg/L at the similar condition (Fig. 7). While combining the process with ACF adsorption, both the chromate and the CPC removal reached to 99.9%. It can be inferred that as long as the cmc of CPC is maintained higher chromate removal efficiency can be achieved and the remaining chromate and the CPC can be well adsorbed on to the ACF.

Fig. 6a, b. Effect of initial CPC concentration on chromate and CPC removal from MEUF (Initial permeate flux = 32.9 L/m².h, Initial chromate concentration = 15 mg/L, Retentate pressure = 0.14 MPa, pH = 7).

Table 1. Comparative removal efficiency of chromate and CPC from different units of MEUF-ACF

CPC concentration (cmc)	CPC removal (%)				Chromate removal (%)			
	MEUF	CF	ACF1	ACF2	MEUF	CF	ACF1	ACF2
0.50	48.8	52.7	72.3	98.8	93.3	93.5	98.0	98.9
0.75	53.3	59.8	97.4	98.8	96.0	97.8	99.9	99.9
1.0	55.3	66.9	98.9	99.2	97	98.7	99.9	99.9

(Initial permeate flux = 32.9 L/m².h, Chromate concentration = 15 mg/L, Retentate pressure = 0.14 MPa, pH = 7)

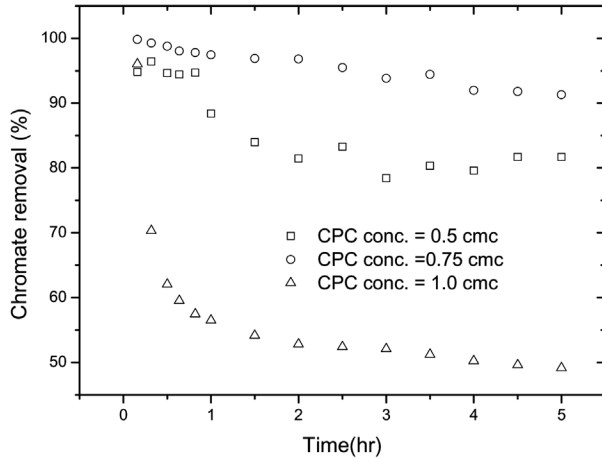


Fig. 7. Chromate removal at different initial CPC concentration (300KD).

3.4. Mathematical Equations for One Hour MEUF Experiment

Experimental data were analyzed using SPSS programme for correlating the effluent chromate concentration with molar ratio of CPC to chromate and pH of the solution. Exponential relation of the chromate concentration with the molar ratio of CPC to the chromate and pH of feed solution is represented in Eq. (1).

$$C_e = \exp(-1.762 - 0.158A + 0.173B) \quad (1)$$

Where,

C_e = Effluent chromate concentration, mg/L

A = molar ratio of CPC to chromate

B = pH of the feed solution

The equation (1) is graphically represented in Fig. 8(a). Simulation of experimental and predicted results showed the correlation of 0.89 (Fig. 8(b)). Maximum and average deviations were found to be 0.07 mg/L and 0.02 mg/L, respectively. The relation of effluent chromate concentration with three dependent variables is represented by Eq. (2). It has the correlation coefficient of 0.89, which implies an exponential function is suitable for the prediction of the effluent chromate concentration.

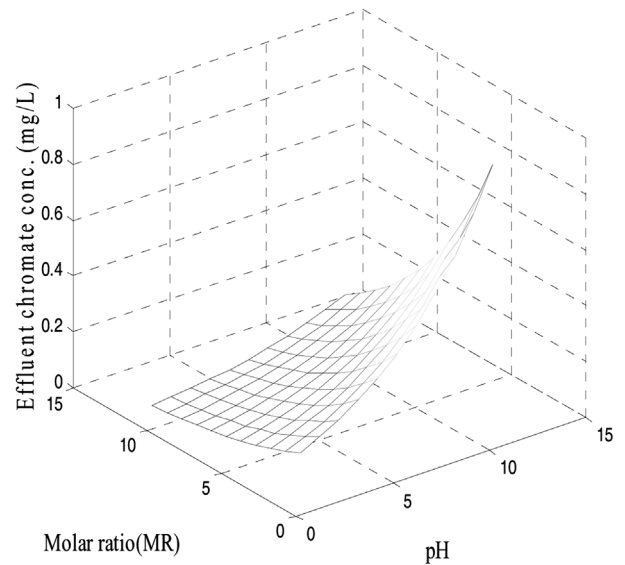
$$C_e = \exp(-2.576 + 0.027t - 0.198A + 0.189B) \quad (2)$$

Where,

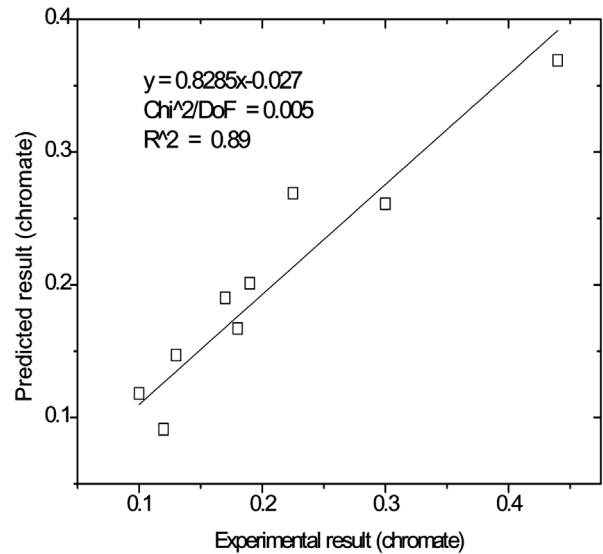
A = molar ratio of CPC to chromate

B = pH of the feed solution

t = time in minutes



(a) Graphical representation of correlation

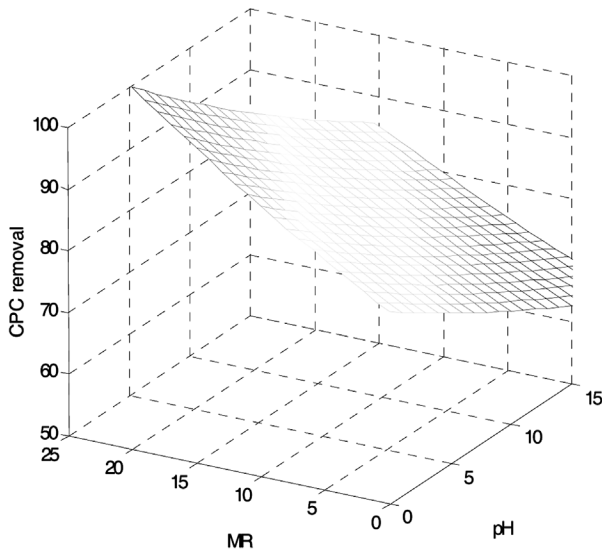


(b) Simulation of predicted and experimental results

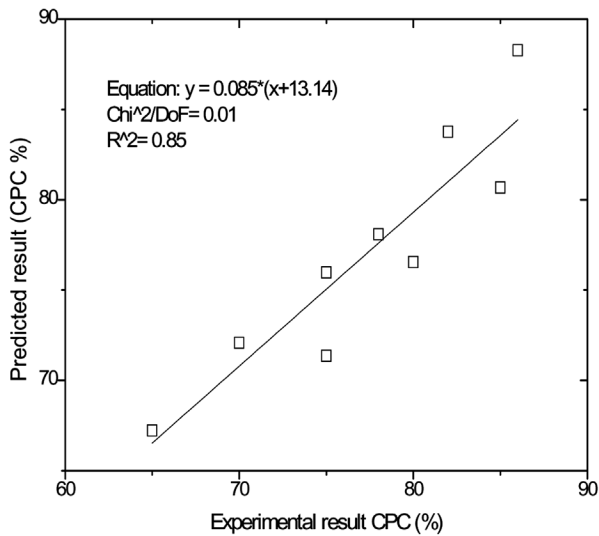
Fig. 8. Simulation for the effluent chromate concentration as function of molar ratio and pH.

Similarly, predicting equation for the CPC removal with respect to the molar ratio and the pH is represented by Eq. (3), it has a correlation coefficient of 0.85. The equation is represented graphically in Fig. 9(a). Fig. 9(b) shows the comparative results of the experimental and the predicted data.

$$C_{re} = \exp(4.373 + 0.03A - 0.035B) \quad (3)$$



(a) Graphical representation of correlation



(b) Simulation of predicted and experimental results

Fig. 9. Simulation for CPC removal efficiency (%) as functions of molar ratio and pH.

Where,

$$C_{re} = \text{CPC removal (\%)}$$

4. Conclusions

The chromate removal was over 97% from the MEUF process with the high MWCO membrane of 100KD when the CPC concentration was over one cmc and the molar ratio of the chromate to the CPC was 1:5. CPC removal from the MEUF was ranged from 50% to 70%. It shows that the MEUF process efficiently removes chromate but it produces the CPC rich effluent. By the addition of ACF unit, both the chromate and the CPC removals increased up to 99.8%. The MEUF was found to be effective in the chromate removal while the ACF in the CPC adsorption to produce chromate and CPC free effluent. Effluent chromate concentration was exponentially correlated with molar ratio of

CPC to chromate and pH.

Acknowledgement

This work was supported by The Korean Research Foundation Grant funded by the Korean government (KRF-2004-D00451). The authors are grateful for the provision of UF membrane unit from Chemicore Inc., Korea.

Nomenclature

- A = molar ratio of CPC to chromate
- B = pH of the feed solution
- C_e = Effluent chromate concentration, mg/L
- C_{re} = CPC removal (%)
- t = time in minutes

References

1. Shu, L., Lee, S. H., and Jegatheesan, V., "A case study on waste minimization and wastewater treatment in starch and noodle factories," *Environ. Eng. Res.*, **7**(2), 75-84 (2002).
2. Kim, S. W., and Lim, J. L., "Development of adsorbent using by-products from Korean medicine for removing heavy metals," *Environ. Eng. Res.*, **121**, 1-7 (2007).
3. Gzara, L., and Dhahbi, M., "Removal of chromate by micellar-enhanced ultrafiltration using cationic surfactants," *Desalination*, **137**(1-3), 241-250 (2001).
4. Lee, S. H., and Jang, J. H., "Preliminary study on the development of phosphorus removal process by converter and furnace slags," *Journal of the Korean Society of Water and Wastewater*, **18**(2), 137-144 (2004).
5. Baek, K., and Yang, J. W., "Competitive bind of anionic metals with cetylpyridinium chloride micelle in micellar-enhanced ultrafiltration," *Desalination*, **167**, 101-110 (2004).
6. Wiltek, A., Koltuniewicz, A., Kurczerwski, B., Mariola, R., and Hatalski, M., "Simultaneous removal of phenols and Cr^{3+} using micellar-enhanced ultrafiltration process," *Desalination*, **191**(1-3), 111-116 (2006).
7. Tung, C. C., Yang, Y. M., Chang, C. H., and Maa, J. R., "Removal of copper ions and dissolved phenol from using micellar-enhanced ultrafiltration with mixed surfactants," *Waste Manage.*, **22** (7), 695-701 (2002).
8. Baek, K., and Yang, J.-W., "Simultaneous removal of chlorinated aromatic hydrocarbons, nitrate, and chromate using micellar-enhanced ultrafiltration," *Chemosphere*, **57**, 1091-1097 (2004).
9. Keskinler, B., Danis, U., Cakici, A., and Akay, G., "Chromate removal from water using surfactant-enhanced cross-flow ultrafiltration," *Sep. Sci. Technol.*, **32**(11), 1899-1920 (1997).
10. Fell, A., Jagatheesan, Sadler, and Lee, S. H., "Baseline measurements on the performance of four constructed wetlands in tropical Australia," *Environ. Eng. Res.*, **10**(6), 316-327 (2005).
11. Ghosh. G., and Bhattacharya, P. K., "Hexavalent chromium

- ion removal through micellar enhanced ultrafiltration,” *Chem. Eng. J.*, **119**(1), 45-53 (2006).
12. Beolchini, F., Pagananelli, F., Michelis, I. De, and Veglio, F., “Treatment of concentrated arsenic (V) solutions by micellar enhanced ultrafiltration with high molecular weight cut-off membrane,” *J. Hazard. Mater.*, **148**(1-2), 2007.
 13. Iqbal, J., Kim, H.-J., Seok, J., Baek, K., and Yang, J.-W., “Removal of arsenic from ground water by micellar-enhanced ultrafiltration (MEUF),” *Chemosphere*, **66**(5), 970-976 (2007).
 14. Yurlova, L., Kryvoruchko, A., and Kornilovich, B., “Removal of Ni (II) ions from wastewater by micellar enhanced ultrafiltration,” *Desalination*, **144**(1-3), 255-260 (2002).
 15. Juang, R. S., Xua, Y. Y., and Chen, C. L., “Separation and removal of metal ions from dilute solution using micellar enhanced ultrafiltration,” *J. Memb. Sci.*, **218**(1-2), 257-267 (2003).
 16. Liu, C. K., and Li, C. W., “Simultaneous recovery of copper and surfactant by an electrolytic process from synthetic solution prepared to stimulate concentrate waste stream of a micellar enhanced ultrafiltration process,” *Desalination*, **169**(2) 185-192 (2004).
 17. Xu, K., Zeng, G. M., Huang, J.-H., Fang, Y.-Y., Huang, G., Li, J., Xi, B., and Liu, H., “Removal of Cd²⁺ from synthetic wastewater using micellar-enhanced ultrafiltration with hollow fiber membrane,” *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **294**(1-3), 140-146 (2007).
 18. Akita, S., Yang, L., and Takeuchi, H., “Micellar enhanced ultrafiltration of gold (III) with nonionic surfactant,” *J. Membr. Sci.*, **133**(2), 1-13 (1997).
 19. Park, S. J., and Kim, Y. M., “Influence of anodic treatment on heavy metal ion removal by activated carbon fibres,” *J. Colloid Interf. Sci.*, **278**(2), 276-281 (2004).
 20. Bade, R., and Lee, S. H., “Micellar enhanced ultrafiltration and activated carbon fibre hybrid processes for copper removal from wastewater,” *Korean J. Chem. Eng.*, **24**(2), 239-245 (2007).