

Feasibility of micellar-enhanced ultrafiltration (MEUF) for the heavy metal removal in soil washing effluent

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Abstract

Heavy metals are the major pollutants in the soil and groundwater. They are not only toxic but also non-biodegradable. In field application of heavy metal remediation, soil washing is the most prevalent technology due to its low cost and wide applicability for various pollutants. However, a drawback of soil washing is the treatment of effluent which contains heavy metals and chelating agent used to enhance the extraction capacity. To treat soil washing effluent with conventional technologies such as precipitation are not appropriate. Because chelating agents disturb to extract or precipitate heavy metals from the wastewater. Therefore in this study micellar-enhanced ultrafiltration (MEUF) was suggested as an alternative technology to treat heavy metals from washing effluent. Through centrifugal MEUF and conventional dead-end MEUF tests, the conditions were optimized. When complexing agent and metal ratio was around 1, metal complexation reached the maximum at pH 8. In addition the value of surfactant over metals was 10, the removal efficiency showed 97% for all metals. The feasibility of MEUF for washing effluent was determined with removal efficiency, flux and COD reduction during the treatment of lab-scale soil washing effluent. In the effluent from soil washing, total metal concentration and complexing agent was 10.14 and 9.03 mM respectively and the pH was 6.34. When the optimized conditions were employed to treat washing effluent, the removal efficiency and COD reduction reached over 92% and 80%, respectively. However the flux decline was severe, but this can be improved by introducing cross-flow filtration.

Keywords: Cadmium; Copper; Lead; Micellar-enhanced ultrafiltration (MEUF); Mine contaminated soil; Soil washing; Zinc

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1. Introduction

As the concern about the health grows, contamination by heavy metals has been emerged in many fields. In other words, the concern of heavy metal contamination is getting heavier and threatening our everyday life. The most susceptible parts of heavy metal contamination are the soil and groundwater [1]. To restore the heavy metal contaminated soil, tremendous expenses and time are required for complete remediation. Heavy metal contamination is often reported in the mining places, smelters, military spots, automotive industries, etc. [2]. These heavy metals can naturally occur, however most of the harmful impacts come from the industries. Lead, zinc, mercury and cadmium are the most representative and notorious metals in the soil and groundwater. As the level and the area of heavy metal contamination increased, the technologies for the effective heavy metal removal have been extensively studied. Among many other remediation technologies, particularly soil washing is the one of the most prevalent technologies in the field due to its powerful metal extraction, relatively low costs, and as a pretreatment before the full-scale remediation steps [3]. The basic principle of soil washing is the transfer of the heavy metals which are bound to the soil, via desorption or solubilization. Chelating agents, acids, and surfactants are added on the washing solution to enhance the metal extraction efficiency. Despite of the advantages of the soil washing there is a serious problem that the washing effluent containing heavy metals should be released and treated for discharge. However there occurs a problem because conventional wastewater technology, chemical precipitation, does not work well in the presence of chelating agents. Chelating agents naturally inhibit the metal from precipitation due to their high binding affinity to metals. Micellar-enhanced ultrafiltration (MEUF) is the one of the alternatives of conventional metal removal technologies. This technique is based on the surfactant micelle formation which can be

retained on the ultrafiltration membrane by size [4]. MEUF has shown excellent performance to remove organic and inorganic contaminants from the groundwater and wastewater [5–10].

The objective of this study is to test the feasibility of MEUF for heavy metal removal from soil washing effluent. This is the extended application of MEUF to the more intricate contaminants and the circumstance.

2. Materials and methods

2.1. Chemicals

For optimization test, four heavy metal solutions were made by diluting metal-nitrate hydrate salts. Cadmium nitrate tetrahydrate was purchased from Aldrich chemical company Inc. (Milwaukee, USA). Copper nitrate hemipentahydrate, lead nitrate, and zinc nitrate hexahydrate were purchased from Sigma–Aldrich Chemical (St. Louis, MO, USA). To dilute these salts, the distilled water was used.

As a complexing agent, ethylenediaminetetraacetic acid (EDTA) was purchased from Sigma–Aldrich Chemical. Surfactant used in this study was cetylpyridinium chloride (CPC), which was purchased from Sigma–Aldrich Chemical. To measure EDTA concentration in the solution, 1 M of $\text{Cr}(\text{NO}_3)_3$ was used.

To adjust pH of the solutions standard 0.1 N, 1 N HNO_3 and NaOH were used (Daejung Chemicals & Metals, Korea). Heavy metal contaminated soil was collected from the mine area (Su-bok mine, Chung-Nam, Korea) to obtain the soil washing effluent.

2.2. Ultrafiltration

Centrifugal ultrafiltration was performed with Amicon ultra centrifugal filter devices (Millipore, USA). Centrifugal MEUF is the way employing centrifugal tubes with membrane apparatus which are widely used in biological experiment. The filter was regenerated cellulose membrane

with molecular weight cut-off (MWCO) of 10,000 and the effective area of 3 cm². On the filter, 3.5 mL of feed solution was filled for the centrifuge. After 15 min of centrifugation with 5000 rpm speed at 25°C, permeate was collected on the bottom and the volume of permeate was less than 1 mL. Conventional dead-end ultrafiltration was operated in the solvent-resistant stirred cell (Millipore, USA) at 23°C. The membrane had 7.6 cm diameter, 10,000 of MWCO and 45 cm² of the effective area. During MEUF, the solution was stirred at 150 rpm to minimize membrane fouling and the pressure was fixed at 2 bar. The initial volume was 100 mL and the MEUF was preceded until 20% of initial volume remained. The solution containing heavy metals was adjusted to pH 8, 1 mM of EDTA, 10 mM of CPC and 1 mM of metals concentration.

2.3. Soil washing

Lab-scale soil washing was done to obtain washing effluent which contained EDTA and heavy metals. Based on the preliminary test, EDTA concentration to perform soil washing was determined as 10 mM. 1 L of 10 mM EDTA solution was added to 200 g of mine soil then mixed thoroughly at 400 rpm for 8 h with mechanical stirrer of which diameter was 8 cm. After mixing, the washing effluent was filtered with GF/C filter (Whatman, England). Heavy metal concentrations in the effluent were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and atomic absorption spectroscopy (AAS) and shown in Table 1. The washing effluent of mine soil was composed of various heavy metals such as Zn, Cu, Pb, Fe and Mn. The total molar concentration of heavy metals was 10.14 mM and that of EDTA was 9.03 mM. The pH of the solution was 6.34.

2.4. Analysis

Four heavy metals which are dealt in this experiment were Cd, Cu, Pb and Zn. For analysis

Table 1

Metal concentration in the washing effluent of heavy metal contaminated soil

Metals	Concentration	
	mg/L	mmol/L
Mg	3.47	0.14
Cr	ND ^a	ND ^a
Mn	32.76	0.60
Fe	41.66	0.75
Co	ND ^a	ND ^a
Cu	22.71	0.36
Zn	33.45	0.51
Cd	1.45	0.13
Pb	44.68	0.21
Ca	298.0	7.44

^aNot detected.

of these metals, AAS and anodic stripping voltammetry (PDV 3000, MTI, Australia) were used. Before heavy metal detection, acid digestion was required to get rid of CPC, EDTA and other organics. Solution was mixed with 1 mL of HNO₃ and 0.5 mL of H₂O₂ and the distilled water was added up to 5 mL of total volume. This solution was heated for 2 h at 150°C [11].

Removal efficiency of the each metal was calculated by this equation

$$R(\%) = 100 \times \left(1 - \frac{c_p}{c_i} \right)$$

where c_p is the permeate concentration and c_i is initial feed concentration.

To determine the concentration of EDTA, spectrophotometric method was introduced. This method is based on the fact that chromium forms a strong complex with EDTA and the complex produces a distinctive color which is proportional to the EDTA concentration. The sample solution was filtered with 0.45 μm membrane, and 4 mL of filtrate was mixed with 1 mL of 1 M Cr(NO₃)₃ and then heated for 15 min at 110°C.

These samples were measured with UV/Vis spectrophotometer (HP 8452A, USA) at 555 nm wavelength [12]. CPC was detected with UV/Vis spectrophotometer at 258 nm wavelength.

3. Results and discussion

3.1. MEUF with synthetic wastewater

3.1.1. Effect of pH

Effect of pH was tested in the two systems. First one was performed in the single metal system, in which 1 mM of one single metal was contained and only pH was adjusted. In this single metal system, merely one metal complexation behavior was observed at the different pH (Fig. 1A). In contrast, mixed metal system contained four metals (Cd, Cu, Pb, Zn) and they were mixed with same molar concentration (0.25 mM). In this mixed metal system, competition among the metals was expected, however the removal efficiency by pH showed similar trends (Fig. 1B). In other words, no significant competition was observed from the results. This happened because EDTA formed complexes in a 1:1 molar ratio with all metals and the metal complexes had the same charges (-2).

In both systems at pH 12, Cu and Zn were removed around 95% while Cd and Pb were around 85%. The difference in removal efficiency can be explained by the stability constant. At pH 12, 100% of Cd and Pb were used to form $M\bullet EDTA^{2-}$. However, Cu and Zn devoted themselves to form not only $M\bullet EDTA^{2-}$ but also $MOH\bullet EDTA^{3-}$ which had higher affinity to CPC. Therefore Cu and Zn were removed around 10% more than Cd and Pb. Between pH 6 and 10, all the metals showed above 97% removal efficiency in single and mixed metal systems because all metals and EDTA took part in forming $M\bullet EDTA^{2-}$ this pH range. Consequently the range of pH 6–10 was the optimal condition to get the highest removal efficiency and these results were similar to Zhang et al.'s result [13].

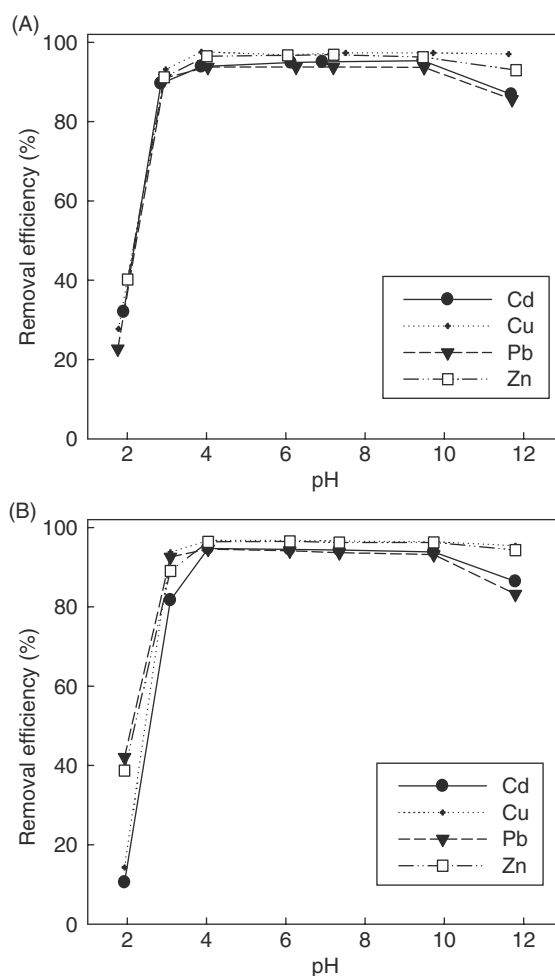


Fig. 1. Metal removal efficiency in (A) the single metal system and (B) the mixed metal system.

3.1.2. Effect of surfactant concentration

In general, as surfactant concentration increases, the removal efficiency boosts high up to a certain level. CPC concentration varied from 1, 2, 5, 10, 30 and 50 to remove 1 mM of mixed metal and 1 mM of EDTA in the solution. To reach the maximal complexation, pH was adjusted to 8.

As shown in the Fig. 2, above 10 mM of CPC concentration, no significant increase in removal

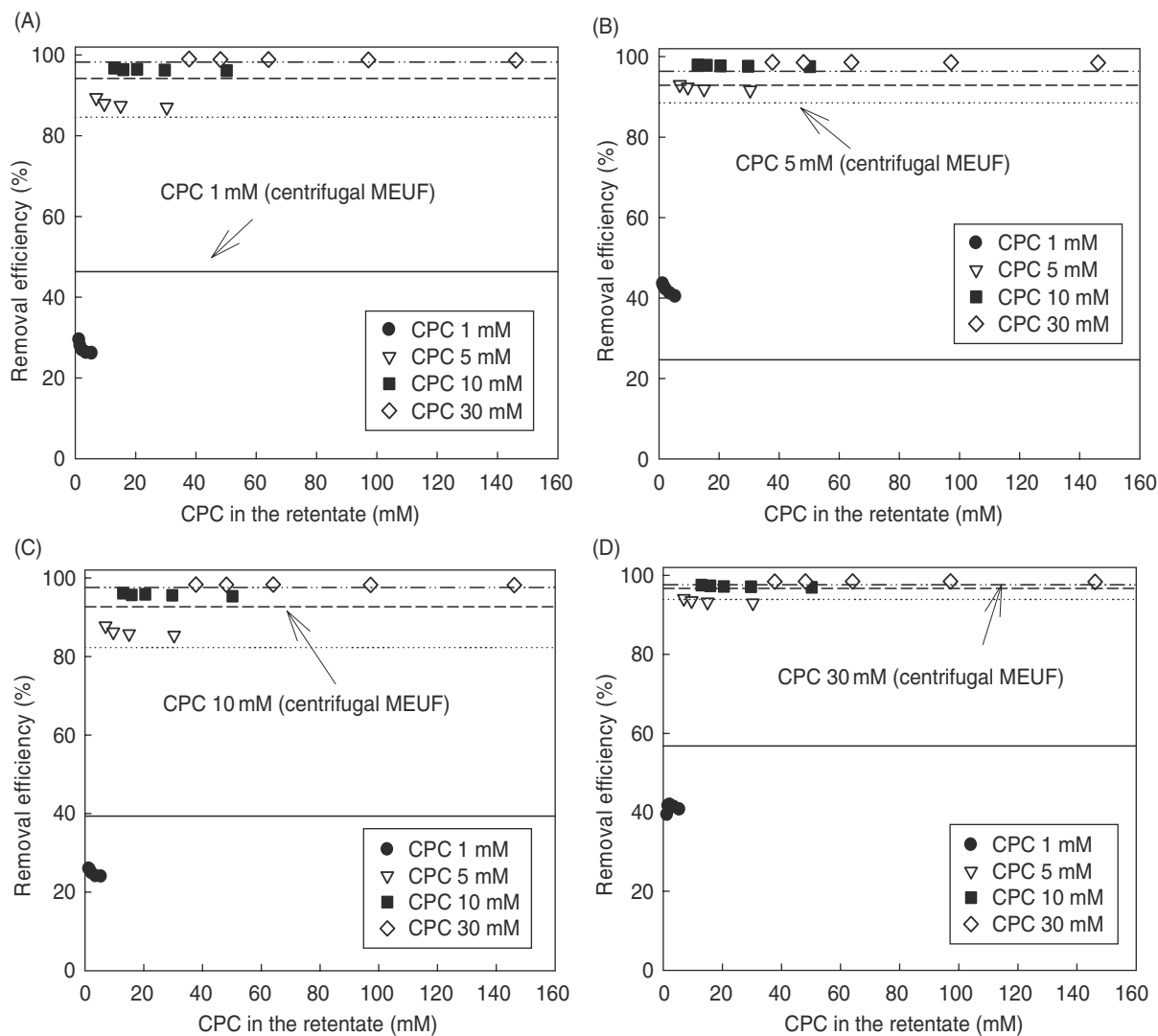


Fig. 2. Removal efficiency of (A) Cd, (B) Cu, (C) Pb and (D) Zn at different CPC concentration. Lines and dots indicate the centrifugal MEUF results and conventional dead-end MEUF results, respectively.

efficiency was observed. When 1 mM of CPC was used, all metals were removed less than 60% because only 1 mM of CPC was just higher than critical micelle concentration (CMC, 0.88 mM at 25°C). From the study of Yang and coworkers [14] the ratio of chromate and CPC was used at least 5 to reach over 90% removal. Here chromate had divalent negative charges like $M\bullet\text{EDTA}^{2-}$. Therefore, equivalent CPC usage was not sufficient

to remove metal complexes. Especially Fig. 2 showed the removal efficiency of each metal by centrifugal MEUF and conventional dead-end MEUF simultaneously. The values were similar to each other, hence centrifugal MEUF can be used to predict the optimal conditions. Moreover, effect of surfactant concentration on flux was done by conventional dead-end ultrafiltration. As the surfactant concentration was increased,

relative flux declined seriously due to the micelle formation and pile-up on the membrane (Fig. 4A). At 10 mM of CPC concentration, flux was declined to 60% and in 30 mM of CPC case, flux decline was even clearer by showing flux decrease to 40% of the water-based flux.

As a result, to get at least 80% of removal efficiency, the ratio between CPC and metals should be over 5 and the ratio of 10 was sufficient to obtain maximal removal.

3.1.3. Effect of ratio between EDTA and metal concentration

In this experiment, CPC concentration was fixed at 10 mM with 1 mM of mixed metals and pH was adjusted to 8 for the maximal complexation. At 0.5 mM of EDTA concentration, different removal efficiency was shown with the same sequence (Cu ≈ Pb > Zn > Cd, Fig. 3). Unlike Cd and Zn, Cu and Pb formed filterable solid tenorite (CuO) and lead hydroxide (Pb(OH)₂) respectively. In other words, the high removal efficiency of copper and lead was obtained not

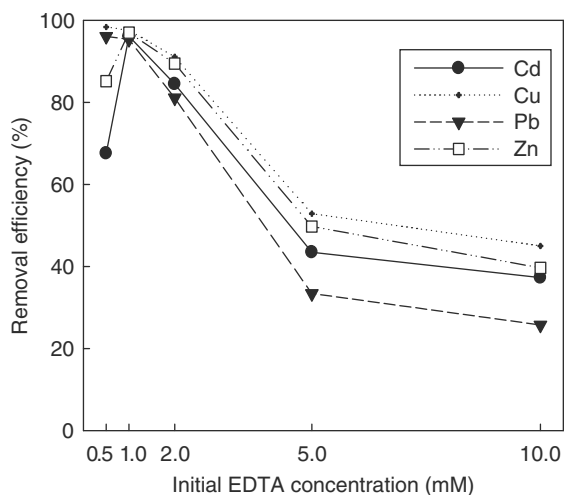


Fig. 3. Removal efficiency as a function of the EDTA/metal concentration ratio (experimental parameters: [Metal] = 1 mM, [CPC] = 30 mM and pH 8).

only with the complexation with EDTA but also with formation of impermeable solids. When the EDTA concentration was less than that of metals, all EDTA devote them to formation of M•EDTA²⁻.

As the EDTA concentration was over that of the metal, EDTA formed protonated species which had also negative charges such as HEDTA³⁻ or H₂EDTA²⁻. These protonated forms competed

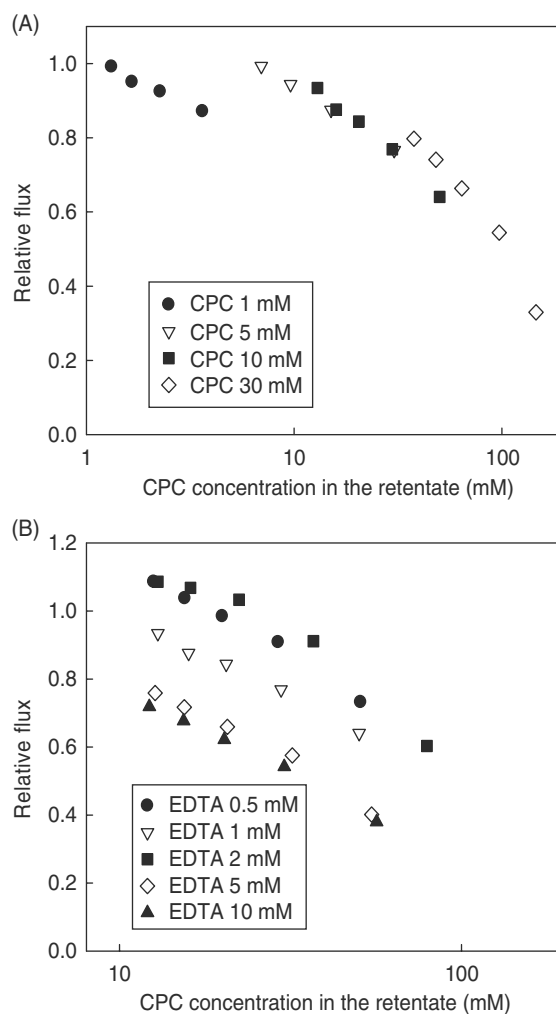


Fig. 4. Effects of (A) CPC and (B) EDTA on the flux of MEUF as a function of log scale CPC concentration in the retentate.

with metal complexes to bind with the surfactant electrostatically [15]. When 1 mM of mixed metals was used with 10 mM of surfactant, over 98% of each metal was eliminated. As the EDTA concentration was 10 mM, the removal efficiency for each metal decreased to below 60%. Simultaneously, the effect of EDTA concentration on flux was investigated because the counterion

occurred by added EDTA could influence micelle formation. Counterions can lower the CMC of micelles and this can influence like increased micelle formation. When EDTA concentration was 5 and 10 mM, around 20% of flux decline was observed (Fig. 4B). Consequently to obtain maximal removal efficiency the equimolar condition of metal and EDTA was required (Fig. 4).

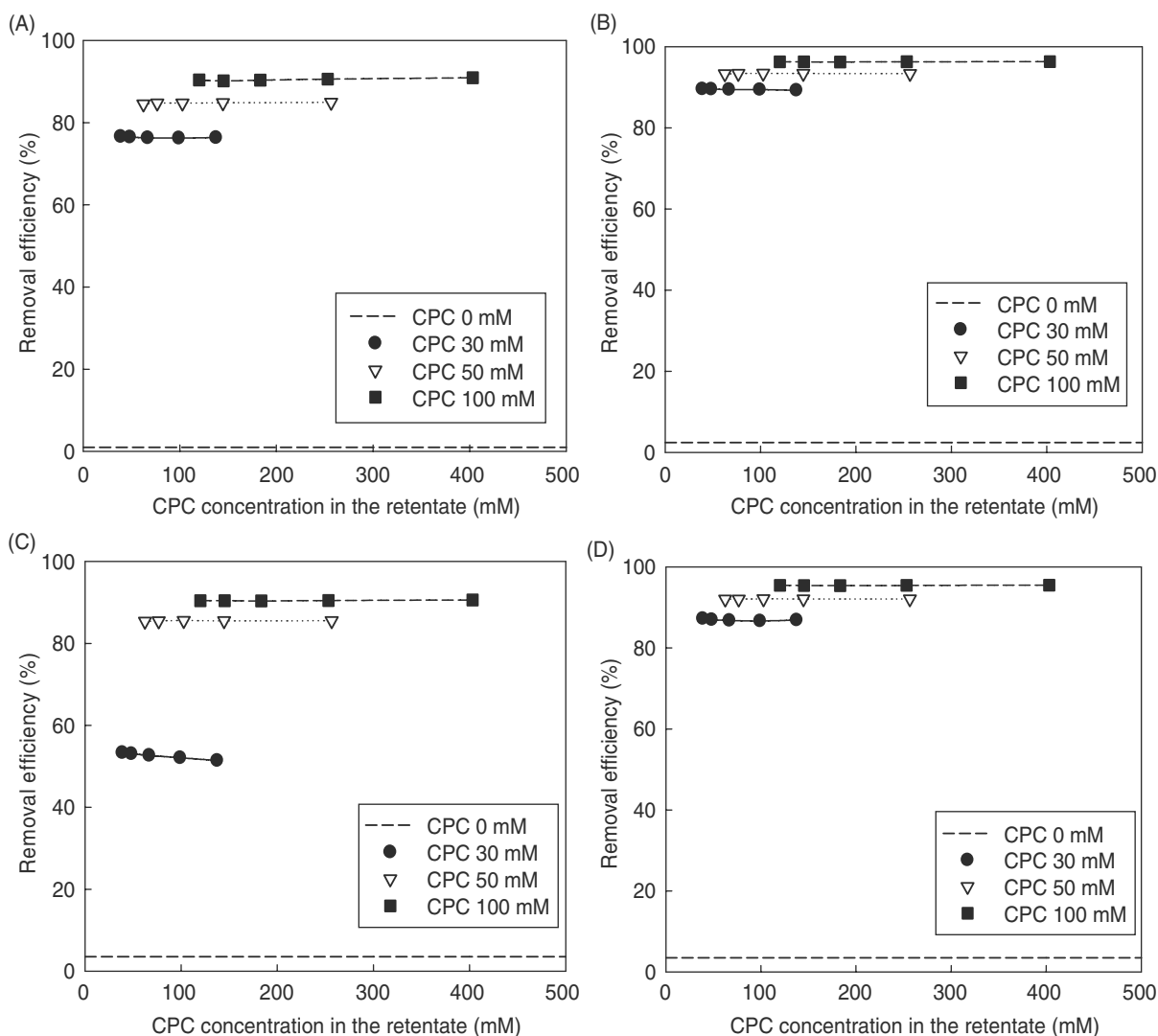


Fig. 5. Effect of CPC concentration on (A) Cd, (B) Cu, (C) Pb and (D) Zn removal efficiency by MEUF with the washing effluent of heavy metal contaminated soil.

3.2. MEUF with washing effluent of heavy metal contaminated soil

3.2.1. Effect of CPC concentration on metal removal efficiency

Based on the preliminary tests, surfactant concentration was the most critical factor which could affect operation of this washing effluent because the ratio between metal and EDTA concentration was 0.9 and pH was neutral as 6.34. Therefore pH adjustment or change of the ratio between EDTA and metal concentration were not necessary for the optimized conditions. The average metal concentration in feed solution was 1.15, 16.11, 38.39, 34.19 ppm for Cd, Cu, Pb and Zn, respectively.

Removal efficiency without surfactant was below 4% for each metal. Metals can be retained by the membrane due to the other organics naturally existing in the soil such as humic acids [16,17]. But the amount removed naturally was negligible.

To remove 9 mM of metals from the solution, at least 50 mM of CPC was required from the preliminary tests. As shown in Fig. 2, to reach at least 80% of removal efficiency, the ratio between the metal and surfactant concentration should be over 5. Consequently, 30, 50 and 100 mM of CPC was added to the washing effluent of heavy metal contaminated soil. At 30 mM of CPC concentration, only Cu and Zn were removed over 80% and Pb removal was the lowest. But when 50 mM of CPC was used, Pb removal restored the value similar to the level of other metals removal to 85%. It meant 30 mM of CPC was not sufficient for the total metal concentration. Moreover, at 50 mM of CPC Cu and Zn removal reached 92%. When the more CPC was added up to 100 mM, the removal efficiency of all metals went beyond 92%. The difference between each metal was not big, only 4% (92% of Cd, Pb and 96% of Cu, Zn).

3.2.2. Flux and chemical oxygen demand (COD)

As considerable amount of surfactant was used, flux decline became serious. Process was operated until 20% of retentate volume remained. When 50 mM of CPC was used, relative flux decreased to below 30% (Fig. 6). However, flux decline was inevitable in membrane process such as MEUF, poly electrolyte enhanced ultrafiltration (PEUF) with high surfactant or polyelectrolyte concentration [12,18,19]. Besides flux decline was generally more serious in the dead-end operation due to the cake formation. Thus cross-flow operation had an advantage that flux decline was not as serious as dead-end operation [20]. Therefore, in the field application of MEUF, cross-flow filtration may solve the problem of severe flux decline caused by the high surfactant concentration.

In case of COD, the soil washing effluent had high COD value around 2500 ppm. After MEUF, COD level dropped to around 500 ppm. By increasing the CPC concentration, the COD level got slightly lower but not significantly,

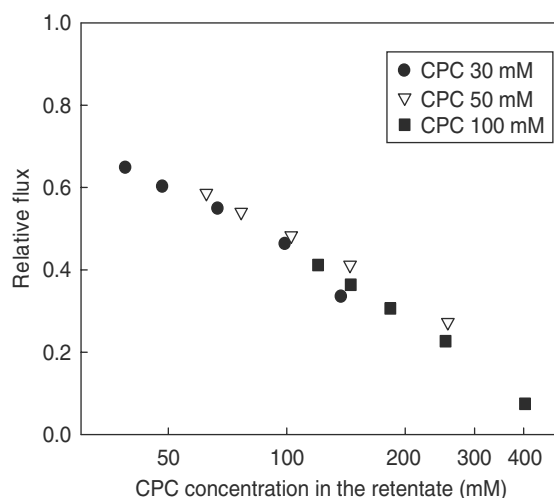


Fig. 6. Relative flux of MEUF with the washing effluent of heavy metal contaminated soil.

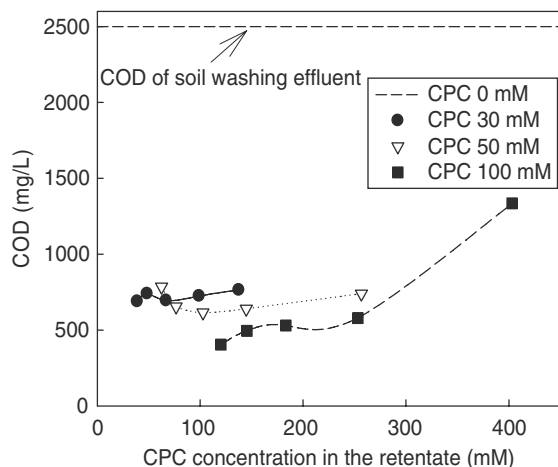


Fig. 7. COD in permeate of MEUF with the washing effluent of heavy metal contaminated soil.

around 80% of COD was eliminated from the first treatment (Fig. 7). This COD value came from the EDTA in the effluent by the calculated COD (2456 mg/L). Therefore the amount of other organics in the effluent was negligible, which was consistent to the result of little removal efficiency without CPC (Fig. 5). Following Fig. 8, the COD value mainly came from the CPC in

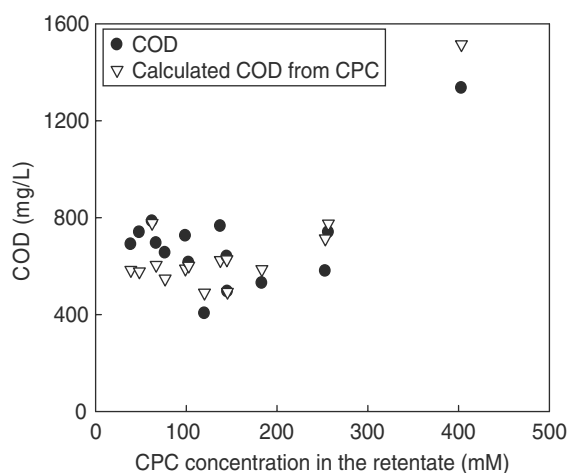


Fig. 8. COD value in permeate and the calculated COD from CPC concentration in permeate.

permeate. However, when 30 mM of CPC was used, the somewhat deviation of COD and the calculated value was shown because metal–EDTA complex which penetrated the membrane existed. Also when the solution was highly concentrated, COD value increased since the pile up surfactant cake leaked due to the pressure.

4. Conclusion

In this study, the feasibility of MEUF was investigated for the treatment of the washing effluent after soil washing. To get the washing effluent, lab scale soil washing of mine contaminated soil was carried out.

Prior to feasibility tests, the optimal conditions for metal removal were investigated by centrifugal MEUF and conventional dead-end MEUF tests. By centrifugal MEUF various conditions for metal removal were tested and the flux was observed by conventional dead-end MEUF test. At the same time, comparing centrifugal MEUF and conventional dead-end MEUF, it was found that centrifugal MEUF was fairly a good tool for condition optimization. Based on the result, the operational conditions were determined easily.

The feasibility for field application was determined by heavy metal removal efficiency, COD reduction, and flux. When the concentration ratio of metal and surfactant was 10, the removal efficiency for all tested metals reached above 92–95%. And the COD value remarkably decreased around 80% from 2500 to 500 ppm. While the removal efficiency and COD reduction had a good performance, flux decline was severe. When comparably high surfactant was used over 50 mM the flux decline was severe. However, if we consider this study was operated as a dead-end filtration, cross-flow filtration which is mostly used in field operation can improve the flux of the MEUF process. Consequently, MEUF was feasible to treat washing effluent of heavy metal contaminated soil with high removal efficiency and COD reduction. Operation as cross-flow

filtration can enhance flux hence MEUF will be applicable for field operation.

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