

Humic substance-enhanced ultrafiltration for removal of cobalt

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Abstract

It is well known that the membrane separation process combined with surfactant micelle (micellar-enhanced ultrafiltration) or polyelectrolyte (polyelectrolyte-enhanced ultrafiltration) can remove heavy metal ions or radionuclides effectively. However, the complexing agent, surfactant or polyelectrolyte remained in effluent is a serious disadvantage of these methods. In this study, humic substances (HS) were used as complexing agents instead of synthetic chemicals. The HS are sorts of natural organic matters and their functional groups such as carboxyl and phenyl groups can bind with the cation and form complexes. The effects of HS concentration and pH on the removal of cobalt were investigated. At the HS concentration of 3 g/L and pH of 6, over 95% of cobalt was removed by regenerated cellulose membrane with molecular weight cut-off (MWCO) of 3000. As the HS concentration increased, the removal of cobalt was also enhanced because of the increase in binding sites (functional groups). The removal of cobalt increased from 72.5% to 97.5% as pH increased from 4 to 8 at the HS concentration of 3 g/L. It resulted from the more deprotonation of functional groups in humic acid at higher pH.

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1. Introduction

Once heavy metal ions are introduced to the environment, they are not biodegraded and transported to ecosystem via various pathways. Ultimately, heavy metal ions are transported and accumulated to human body along food chain. Accumulation of heavy metal in the body causes serious problems such as cancer or damage to brain and nerve system [1]. Therefore, contamination of water or groundwater with heavy metal ions is a serious problem. Precipitation, ion-exchange, and reverse osmosis are frequently used for heavy metal removal. However, precipitation cannot remove metal ions completely. But the cost of ion-exchange resin and the low permeate flux of reverse osmosis are the problems [2]. To obtain high removal efficiency and low operating cost, ultrafiltration process combined with surfactant

micelle (micellar-enhanced ultrafiltration, MEUF) or polyelectrolyte (polyelectrolyte-enhanced ultrafiltration, PEUF) was proposed. Many surfactants and complexing agents such as sodium dodecyl sulfate (SDS), poly acrylic acid (PAA), and polyethyleneimine (PEI) were investigated for removal of heavy metals, radionuclides, or anionic metals with ultrafiltration [3–17]. However, these synthesized chemicals are expensive and non-biodegradable, and the environmental hazard of them remained in effluent is a serious disadvantage of complexation-membrane separation methods [18].

In this study, the removal of cobalt from aqueous solution using humic acids was investigated. Humic acid is an organic matter in soil and it contains various kinds of functional groups such as carboxylic or phenyl groups. Researches on the interaction between heavy metals and the humic acids in soil were actively carried out [19–21]. However, the application of humic acids in the removal of heavy metals from aqueous solution was not widely investigated. Only several studies on the humic substances immobilized silica or algi-

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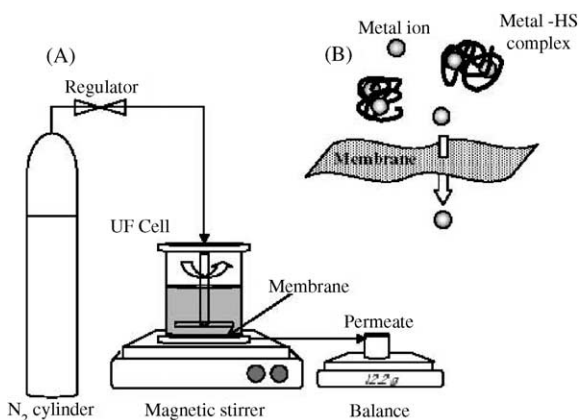


Fig. 1. Schematic diagram of (a) experimental apparatus and (b) humic substance-enhanced ultrafiltration.

nate was reported [22–25]. The purpose of the present work is to investigate the removal characteristics of cobalt at various concentrations of humic acid and different pH. The effects of electrolytes and cobalt salts were also investigated.

2. Materials and methods

Two kinds of cobalt salts, $\text{Co}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and CoCl_2 were purchased from Aldrich Chemical (USA). Technical grade of humic acid purchased from Aldrich Chemical (USA) was used in experiments without further purification. The pH of cobalt solution was adjusted by 1N HNO_3 , HCl and NaOH . The initial concentration of cobalt ion was 0.5 mM. The concentration of humic acid varied from 0.1 to 3 g/L. Solvent-resistant stirred cell (Millipore, USA) and regenerated cellulose membranes (Amicon, USA) with molecular weight cut-off (MWCO) of 3000 Da and 10,000 Da were used for ultrafiltration. Batch filtration was carried out at room temperature and 2 bar of transmembrane pressure using nitrogen (Fig. 1). Initial 100 mL of solution was filtered until it was reduced to 50 mL, where the volume reduction ($V_R = V_{\text{feed}}/V_{\text{retentate}}$) was 2. The permeate concentrations of cobalt and humic acid were measured by atomic absorption spectroscopy (AAS, Perkin-

Elmer 3300, USA) and COD kit (Humas, KOR), respectively. The species of metal ion was calculated by a computer program, MINEQL+ (Environmental Research Software, USA).

3. Results and discussion

3.1. Relative flux

The relative fluxes, the ratio of flux of solution to that of pure water, at various pH and the concentration of humic acid are shown in Fig. 2. As the retentate concentration of solute increases, the concentration polarization and plugging of membrane pores by humic molecule become severe. Thus, the relative flux decreased as the concentration of humic acid increased. The retained humic molecules were accumulated at the membrane surface, and there was more accumulation on a membrane with higher MWCO. As a result, the flux reduction was severer in a membrane with MWCO of 10,000 than that with MWCO of 3000. The actual flux of the 10,000 MWCO membrane was greater than that of the 3000 MWCO by two-folds. For example, at pH 3 and 3 g/L of humic acid, the relative flux of a 10,000 membrane was 0.42 and that of a 3000 MWCO membrane was 0.61. However, the actual flux of higher MWCO membrane ($13.3 \text{ L/m}^2 \text{ h}$) was still higher than that of lower MWCO membrane ($28.8 \text{ L/m}^2 \text{ h}$). Therefore, in this study, the higher MWCO membrane seems to be more advantageous in permeate flux. Even though there were some variations in flux depending on pH, the flux decline was mainly governed by the concentration of macromolecule (humic acid).

3.2. Removal of cobalt

3.2.1. Effect of humic acid concentration and pH

At a higher concentration of humic acid, there are more functional groups of humic acids in the solution. As a result, the removal of cobalt increased with humic acid concentration (Fig. 3). At pH 6 and 3 g/L of humic acid, cobalt was removed >95% with a 3000 MWCO membrane, and it was removed >90% with a 10,000 MWCO membrane. pH affected

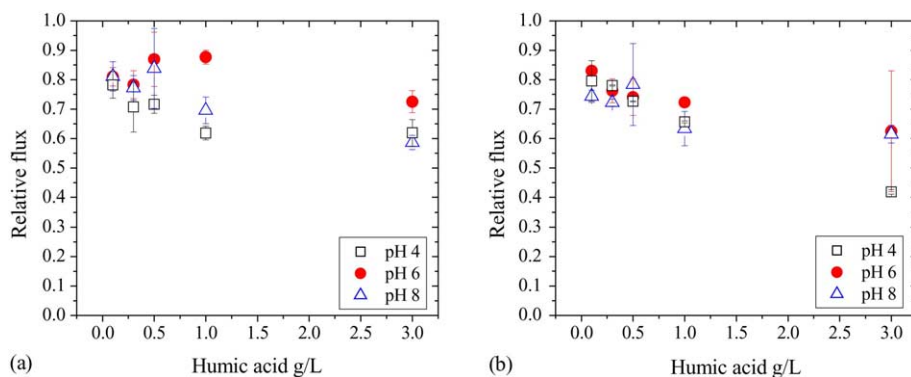


Fig. 2. Relative flux at different pH: (a) a membrane with MWCO of 3000 and (b) a membrane with MWCO of 10,000.

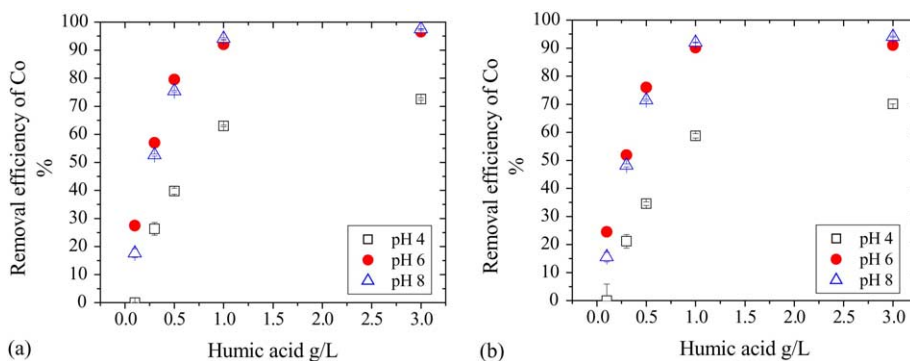


Fig. 3. Removal efficiency of cobalt at different pH: (a) a membrane with MWCO of 3000 and (b) a membrane with MWCO of 10,000.

the removal efficiency of cobalt. In a membrane with MWCO of 3000 and at 1 g/L of humic acid, the removal efficiency of cobalt increased from 63.0% to 94.1% as the pH increased from 4 to 8. At low pH, there are a lot of protons in solution, and it makes carboxylic or phenyl group protonated. On the contrary, at higher pH, H^+ bound with functional groups can be dissociated easily, and the deprotonated functional groups can bind with cobalt ions [26,27]. Furthermore, at higher concentration, more precipitation of cobalt is expected in the form of hydroxide [27]. Mynin and Terpuvov [7] reported that the selectivity of cobalt was 87–99.1% with humic acid and ceramic membrane, which are similar removal efficiency to the present study.

3.2.2. Effect of electrolyte

To investigate the effect of the electrolytes in wastewater, 1 g/L (=0.017 M) of sodium chloride was added into cobalt solutions. In the presence of electrolytes, the flux decline was similar but the permeate COD increased (data not shown). At pH 4 and 8, the removal efficiency of cobalt decreased slightly by the addition of 1 g/L of sodium chloride (Fig. 4). However, at pH 6, the removal efficiency decreased significantly. In a membrane with MWCO of 3000 and 0.5 g/L of humic acid, the cobalt removal decreased from 80% to 50% in the presence of 1 g/L of sodium chloride. According to Spark et al. [28], humic molecules were coiled up into rigid spherocolloids at high concentration of electrolyte. Only the

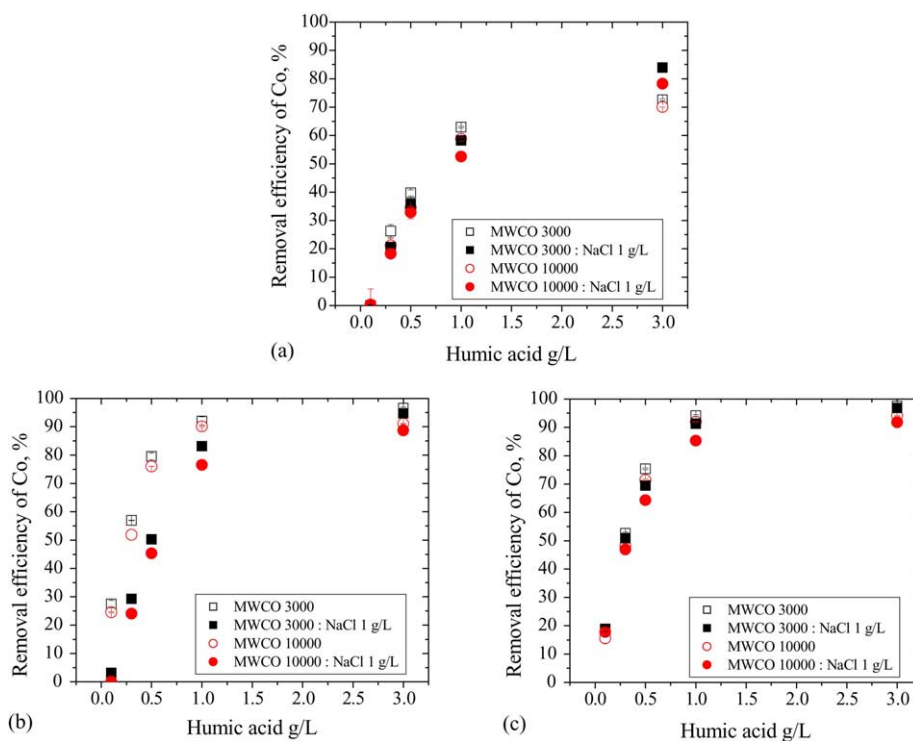


Fig. 4. Removal efficiency of cobalt in the absent or presence of 1 g/L of sodium chloride: (a) pH 4, (b) pH 6, and (c) pH 8.

surface of colloidal humic acid would interact with cobalt ions. It is considered that the decrease in the removal efficiency resulted from the reduced surface area of humic acid at a high electrolyte concentration. According to the calculation of cobalt species, the portion of Co^{2+} decreased from 100% to 89.8% by the addition of sodium chloride at both pH 4 and 6. By complexation of cobalt with chloride ion, the rest of cobalt existed as CoCl^+ . Since CoCl^+ has lower valence than Co^{2+} , the removal efficiency of cobalt was lowered. At pH 8, the distribution of cobalt species was not affected by sodium chloride. Therefore, the reduced complexation of cobalt ions with humic acid resulted in lower removal efficiency.

3.2.3. Effect of cobalt salt

Up to this point, cobalt nitrate was used as a source of Co(II) in all experiments. To investigate the effect of counter ion, cobalt chloride was used (Fig. 5). At high concentration of humic acid (>1 g/L), the effect of counter ion was negligible, while there were small differences in the removal efficiency at low concentration of humic acid. At pH 4, the removal of cobalt of nitrate salt ($\text{Co}(\text{NO}_3)_2$) was similar to that of chloride salt (CoCl_2). At pH 6, 0.5 g/L of humic acid, and a membrane with MWCO of 3000, the removal efficiency of nitrate and chloride salts was 80% and 69%, respectively. At pH 8 and the same conditions mentioned above, the removal efficiency of nitrate and chloride salts was 75% and 83%, respectively. At pH 6, the removal of cobalt of nitrate salt

was higher than that of chloride salt but it was vice versa at pH 8. As a result, it seemed that counter ion effect on cobalt removal with humic acid was negligible.

3.3. COD in the permeate

Not only the cobalt concentration in permeate but also permeate humic content is an important parameter of water or wastewater treatment process. If there are large amounts of humic acids in permeate, the chemical oxygen demand (COD) and turbidity will increase and another advanced treatment process would be necessary. The COD of initial solution was from 160 to 3160 ppm as humic concentration increased from 0.1 to 3 g/L. The COD in permeate is shown in Fig. 6 at various concentration of humic acid and pH. At a higher concentration of humic acid and a higher MWCO membrane, more humic acids pass through a membrane. As a result, the permeate COD increases. At a higher concentration of humic acid, the difference in the permeate COD was obvious. At 3 g/L of humic acid and a membrane with MWCO of 3000, the permeate COD was 133 ppm at pH 4 and 71 ppm at pH 8. Humic acid is the soluble part of humic substance at acidic condition, and the solubility of humic acid decreases as pH. Since the unsolubilized portion of humic acid could not pass through a membrane, the permeate concentration (or COD value) of humic acid was lowered at higher pH.

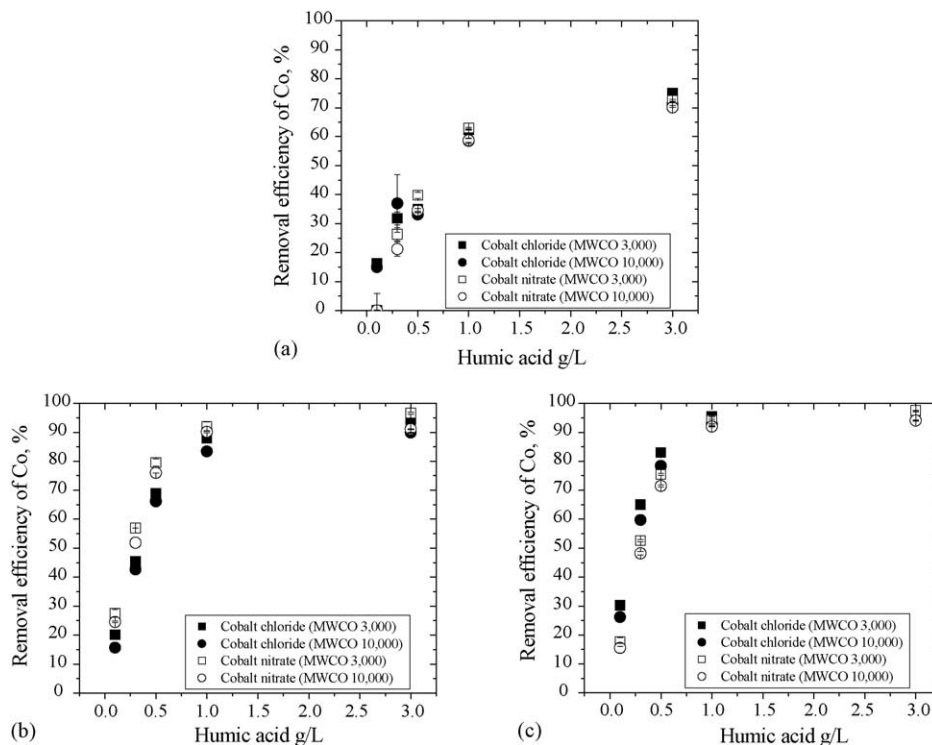


Fig. 5. Removal efficiency of cobalt nitrate and cobalt chloride: (a) pH 4, (b) pH 6, and (c) pH 8.

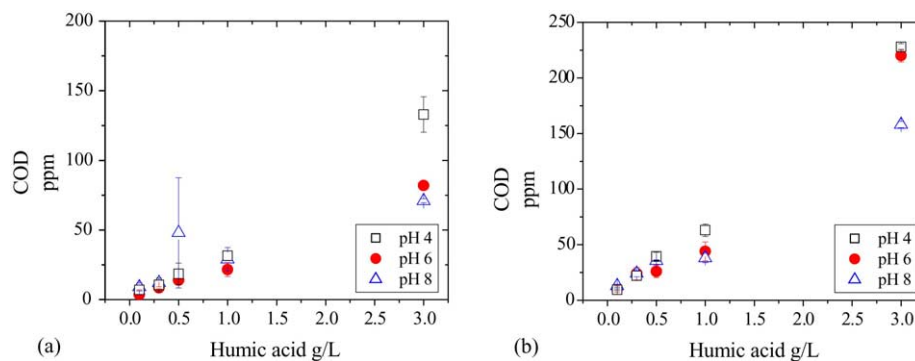


Fig. 6. Chemical oxygen demand of permeate at different pH: (a) a membrane with MWCO of 3000 and (b) a membrane with MWCO of 10,000.

4. Conclusions

When the concentration of humic acids was high enough (~ 3 g/L), cobalt was removed more than 95% in a 3000 MWCO membrane and more than 90% in a 10,000 MWCO membrane at pH 6. As the pH of solution increased, more functional groups of humic acid were deprotonated. As a result, the removal efficiency of cobalt increased at a higher pH. When electrolytes such as sodium chloride were added into the solution, the higher ionic strength reduced the complexation of cobalt ion with functional groups of humic acids and the removal of cobalt decreased. Regardless of counter ions – nitrate and chloride – the removal efficiency was not affected at high concentration of humic acid. At low concentration of humic acid, there was a slight difference in the removal efficiency between nitrate and chloride salts of cobalt, but the trend was not consistent. Because humic acid is natural material, it is considered that the ultrafiltration with humic acid is an economically and environmentally feasible process to remove cobalt.

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