Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Humic-Substance-Enhanced Ultrafiltration for Removal of Heavy Metals

Kitae Baek[a]; Ji-Won Yang[b]
[a] Department of Environmental Engineering, Kumoh National Institute of Technology, Gumi, Gyungbuk, Republic of Korea [b] National Research Laboratory for Environmental Remediation, Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Yuseong-gu, Dajeon, Republic of Korea

To cite this Article Baek, Kitae and Yang, Ji-Won(2005) 'Humic-Substance-Enhanced Ultrafiltration for Removal of Heavy Metals', Separation Science and Technology, 40: 1, 699 — 708
To link to this Article: DOI: 10.1081/SS-200042665
URL: http://dx.doi.org/10.1081/SS-200042665

Separation Science and Technology, 40: 699–708, 2005
Copyright © Taylor & Francis, Inc.
ISSN 0149-6395 print/1520-5754 online
DOI: 10.1081/SS-200042665

Humic-Substance-Enhanced Ultrafiltration for Removal of Heavy Metals

Kitae Baek
Department of Environmental Engineering, Kumoh National Institute of
Technology, Yangho-dong, Gumi, Gyungbuk, Republic of Korea

Ji-Won Yang
National Research Laboratory for Environmental Remediation,
Department of Chemical and Biomolecular Engineering, Korea
Advanced Institute of Science and Technology, Yuseong-gu,
Dajeon, Republic of Korea

Abstract: The feasibility of a separation technique using ultrafiltration in connection with humic substances—humic-substance-enhanced ultrafiltration (HSEUF)—was investigated for the removal of the toxic heavy metals copper and cadmium. HSEUF is based on the high molecular weight of humic substances, as well as the binding of multivalent metals such as copper and cadmium to these materials. As the humic acid concentration increased, the removal of copper and cadmium was enhanced because of the increase in binding sites. As the pH of the solution increased, the removal of copper and cadmium was further improved because the solubility of the humic substances increased. In the simultaneous removal of copper and cadmium, the binding of cadmium to humic substances was inhibited significantly by the presence of copper at the low concentration of humic acid. However, copper binding was not affected by the presence of cadmium, because the affinity of copper to humic substances was greater than that of cadmium.

This work was supported by a grant (M1-0203-00-0001) of Korea Ministry of Science and Technology through National Research Laboratory program.

Address correspondence to 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, Dajeon 305-701, Republic of Korea. Fax: +82-42-869-3910; E-mail: jwyang@kaist.ac.kr

INTRODUCTION

Various industrial wastewaters produced by industries such as metal plating, metal finishing, mining, aerospace production, automotive manufacturing, and battery production, as well as by general chemical processes, contain toxic heavy metals. Conventional methods for the elimination, concentration, and/or recovery of these heavy metals are precipitation, ion exchange, electrodeposition, crystallization, evaporation, and liquid-liquid extraction. Some of the processes present great disadvantages, such as the use of heterogeneous reactions or distribution of substances among different phases. Such phenomena are controlled by diffusion and usually require long operating times. In other processes, final metal recovery requires additional treatments, which make the process more complicated and expensive (1).

It is well known that the membrane separation process combined with surfactant micelles (micellar-enhanced ultrafiltration) or polyelectrolytes (polyelectrolyte-enhanced ultrafiltration) can remove heavy metals effectively (1–13). Various surfactants and complexing agents such as sodium dodecyl sulfate, polyacrylic acid, and polyethyleneimine were investigated for the removal of heavy metals by ultrafiltration. However, the environmental hazard of complexing agents, surfactants, or polyelectrolytes that may remain in the effluent is a serous disadvantage of these methods.

Brown and black biopolymers associated with soil, sediment, and particulates suspended in water and consisting of material derived from the degradation of animals and plants are referred to as humic substances (14). Humic acid is one of the main components of organic carbon in natural aquatic environments (14, 15). These substances are a mixture of weak-acid polyelectrolytes and organic macromolecules exhibiting a large range of molar-mass distribution, substances, and functionalities. The main functional groups present in a sample of humic acid are carboxylic acids, alcohols, phenols, carbonyls, phosphates, sulfates, amides, and sulfides. All of these groups are capable of interacting with metal species in solution (16). It is therefore possible that the metal cations may interact with either the soluble fraction of the humic substance or the colloidal fraction of the humic substance, or both.

The present study investigates the feasibility of using humic-substance-enhanced ultrafiltration (HSEUF) to remove heavy metals in low concentrations from the aqueous phase using nontoxic humic substances instead of anionic surfactants or synthetic polyelectrolytes.

MATERIALS AND METHODS

Four types of salts—$Cu(NO_3)_2$, $Cd(NO_3)_2$, $CuCl_2$ and $CdCl_2$—were purchased from Aldrich Chemical (USA). A technical grade of humic acid purchased from Aldrich Chemical was used in the experiments without further purification. This humic acid was selected as a well-documented, representative commercial humic product that could easily be prepared in aqueous form. Based on the information provided by Aldrich Chemicals, this product, derived from lignite obtained via open-pit mining in Germany, contains approximately 9.4% Fe oxides, 3% S, 2% Na, 0.5% Ca, 0.4% Al, 0.05% Mg, and 0.04% K and has an average molecular weight of 20,000 to 50,000 Da (17). The concentrations of deprotonated ionizable sites were reported as 2.90, 3.03, and 3.23 mmol/g at pH 5.0, 5.5, and 6.0, respectively (18). Figure 1 shows the Fourier transform infrared (FTIR) spectrum of humic acid purchased from Aldrich. The contents of -COOH (910 cm^{-1} and 1680 cm^{-1}), aromatic groups (750 – 900cm^{-1}), tertiary alcohol groups (1120 cm^{-1}), amine groups (3420 cm^{-1}), and aldehydes/alkyl groups (1384 cm^{-1}) were observed. However, phenolic groups (1270 cm^{-1}) were not observed clearly. The pH of synthetic wastewater was adjusted by 1 N HNO_3, HCl, and NaOH. The initial concentration of metals was 10 mg/L. The concentration of humic acid varied from 0.05 to 1.0 g/L. Dead-end stirred-cell (Millipore, USA) and regenerated cellulose membranes with molecular weight cut-off (MWCO) values of 3000 and 10,000 Da were used for ultrafiltration. Batch filtration was carried out at room temperature and 2 bar of transmembrane pressure by nitrogen. The initial 50 mL of

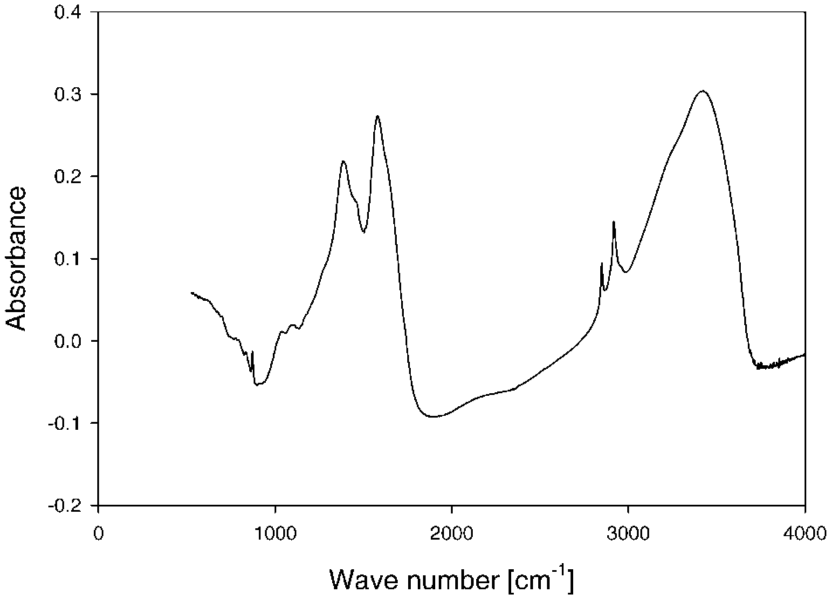

Figure 1. FTIR spectrum of Aldrich humic substance.

solution was filtered until it was reduced to 25 mL, where the volume reduction ($VR = V_{feed}/V_{retentate}$) was 2. The permeate concentrations of copper and cadmium were measured by atomic absorption spectroscopy (AAS, Perkin Elmer 3300, USA), and the humic acid concentration was measured by a chemical oxygen demand (COD) kit (Humas, Korea).

RESULTS AND DISCUSSION

Effect of Humic Acid Concentration

As the concentration of humic acid increased, the concentration of deprotonated ionizable groups, which are binding sites for heavy metals, increased also. As a result, the removal of copper and cadmium increased (Fig. 2). At pH 6 and >0.5 g/L of humic acid, >92% of the copper and cadmium were removed with a 3000-MWCO membrane, while >90% were removed with a 10,000-MWCO membrane.

The removal of copper and cadmium in the nitrate form as a counterion was slightly higher than the removal in the chloride form. The higher removal in the nitrate form, especially for cadmium, results from the higher concentration of metal ions with +2 as valence. Metal ions form various species or complexes in aqueous solution. The feasible complexes of copper and cadmium and their distributions were calculated by MINEQL+ (Environmental Research Software, USA) software (Table 1). In the presence of nitrate

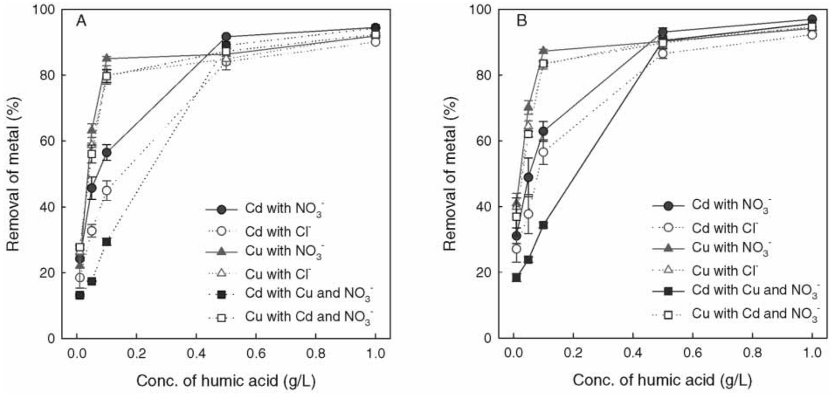

Figure 2. Removal characteristics of copper and cadmium with (A) 10,000-MWCO membrane and with (B) 3000-MWCO membrane. Initial concentration of metal: 10 mg/L of copper and/or 10 mg/L of cadmium, ionic strength: 0.05-mol/L $NaNO_3$ or NaCl, initial pH: 6.0, temperature: 25°C.

Table 1. Distribution of equilibrium concentration of copper and cadmium species in the presence of nitrate and chloride

Counterion	Metal	Me^{2+}(%)	$(Me(NO_3))^+$ or $(MeCl)^+$ (%)	$Me(NO_3)_2$ or $MeCl_2$ (%)
NO_3^-	Cd	99.4	0.6	—
	Cu	99.4	0.6	—
Cl^-	Cd	47.8	49.9	2.3
	Cu	97.6	2.3	—

or chloride, some of the metal ions form $(MeNO_3)^+$, $(MeCl)^+$, and $MeCl_2$(aq). In the case of cadmium, more than 50% exists as forms of $(CdCl)^+$ and $CdCl_2$(aq). The binding of Cd^{2+} to humic acid is preferred to $(CdCl)^+$ because ion binding to micelles or polyelectrolytes increased with the valence of the ion (2–9).

At the low concentration of humic acid, the copper removal was higher than the cadmium removal. This phenomenon was observed more clearly with simultaneous removal of copper and cadmium. At 0.1 g/L of humic acid, the removal percentages for cadmium and copper were 31 and 81%, respectively, with the 10,000-MWCO membrane and 34 and 84%, respectively, with the 3000-MWCO membrane (Fig. 2). These results are consistent with the micellar-enhanced ultrafiltration of copper and cadmium using sodium dodecyl sulfate (11). There have been research reports that the binding affinity of copper to polyelectrolytes or micelles was stronger than that of cadmium (11–13). In this study, however, valence change due to metal speciation was the major reason for higher levels of copper removal compared with those for cadmium.

To compare the flux carried out at various conditions, the concept of relative flux against flux of deionized water was introduced. Relative flux was defined as follows: (flux of sample)/(flux of deionized water), where the flux of deionized water was 23.4–27.5 l/m^2/hour for the 3000-MWCO membrane and 91.4–100.7 l/m^2/hour for the 10,000-MWCO membrane. The relative flux is shown in Fig. 3 as a function of humic acid concentration. Generally, flux is a function of retentate surfactant concentration in the micellar-enhanced ultrafiltration (2–9). As the concentration of humic acid in the feed increased, the relative flux decreased slightly because the concentration of membrane foulants increased. It is well known that a hydrophobic interaction between the membrane and the humic substances is a major mechanism in water treatment using a membrane process. However, in this study, fouling of the regenerated cellulose membrane by humic acid was not significant because of the hydrophilic characteristics of the regenerated membrane.

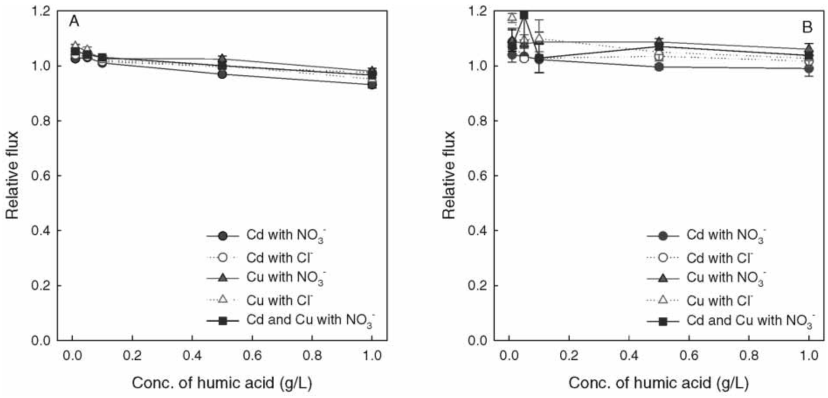

Figure 3. Relative flux with (A) 10,000-MWCO membrane and with (B) 3000-MWCO membrane. Initial concentration of metal: 10 mg/L of copper and/or 10 mg/L of cadmium, ionic strength: 0.05 mol/L $NaNO_3$ or NaCl, initial pH: 6.0, temperature: 25°C.

Not only the metal concentration but also the humic acid concentration in the permeate should be considered in wastewater treatment processes. Permeate humic acid results in COD and produces the brown color of treated water. Thus, higher levels of humic acid in the permeate require another advanced treatment process. COD in the permeate is shown in Fig. 4 as a function of humic acid concentration in the feed. At a higher concentration of humic acid and a higher-MWCO membrane, more humic acids

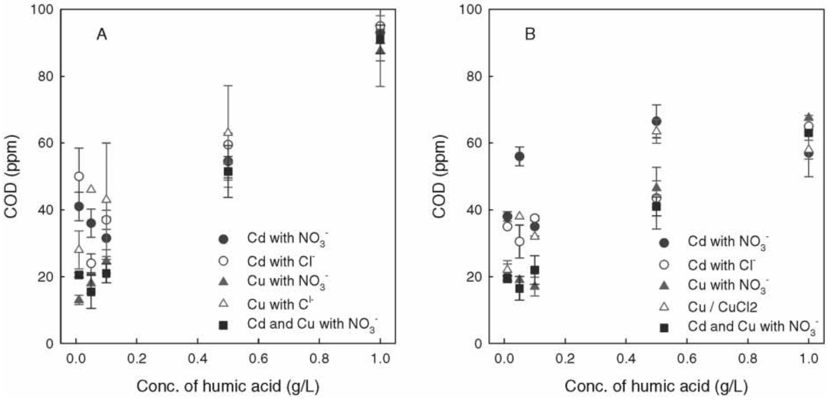

Figure 4. Permeate chemical oxygen demand with (A) 10,000-MWCO membrane and with (B) 3000-MWCO membrane. Initial concentration of metal: 10 mg/L of copper and/or 10 mg/L of cadmium, ionic strength: 0.05-mol/L $NaNO_3$ or NaCl, initial pH: 6.0, temperature: 25°C.

passed through the membrane; as a result, the permeate COD increased. Even though the concentration of humic acid increased from 0.5 to 1.0 g/L, the removal of heavy metals did not increase significantly and COD in the permeate increased from 55–60 to 90–95 (for a MWCO of 10,000). Considering the consumption of humic substances, recovery of heavy metals, and permeate water quality, the lower humic concentration (0.5 g/L) is superior to the higher concentration (1.0 g/L). The effects of counterion and metal on the permeate COD were negligible.

Effect of Ionic Strength

The metal removal with respect to the ionic strength for the simultaneous removal of copper and cadmium is shown in Fig. 5. As the ionic strength increased, the removal of copper and cadmium decreased gradually and the permeate COD decreased slightly. The flux was independent of ionic strength. According to Spark et al. (16), humic molecules were coiled into rigid spherocolloids at high ionic strength. Only the surface of colloidal humic acid would interact with metal ions. Therefore, the complexation of metal ions with humic acid decreased, resulting in lower levels of copper and cadmium removal.

Effect of pH

Figure 6 shows the simultaneous removal of copper and cadmium as a function of solution pH. In a membrane with a MWCO of 3000 and at

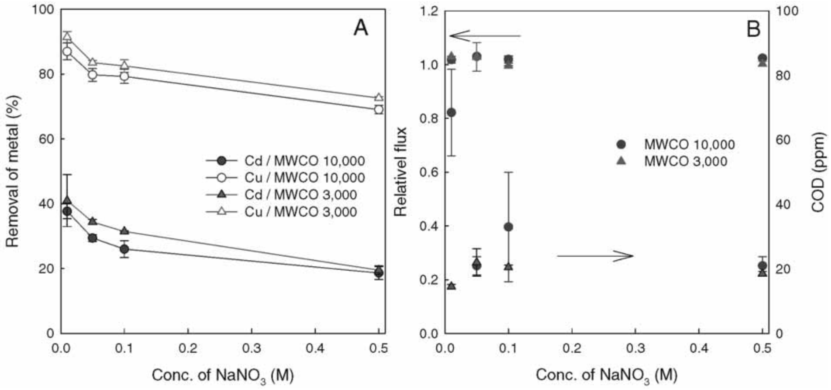

Figure 5. Effect of ionic strength on the simultaneous removal of copper and cadmium: (A) removal characteristics, (B) relative flux and permeate chemical oxygen demand. Initial concentration of metal: 10 mg/L of copper and 10 mg/L of cadmium, humic acid concentration: 0.1 g/L, initial pH: 6.0, temperature: 25°C.

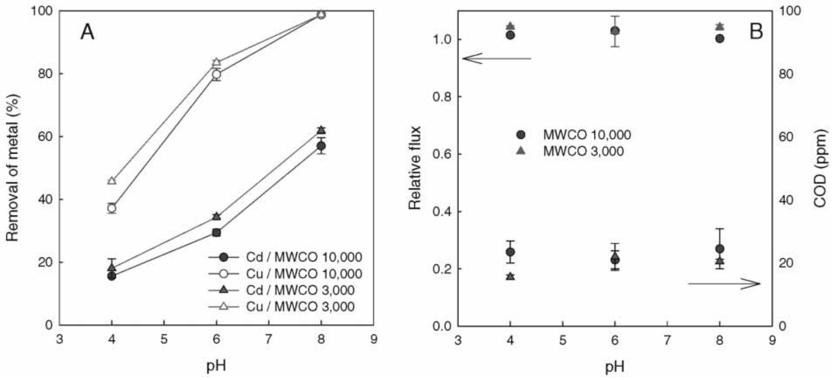

Figure 6. Effect of pH effect the simultaneous removal of copper and cadmium: (A) removal characteristics, (B) relative flux and permeate chemical oxygen demand. Initial concentration of metal: 10 mg/L of copper and 10 mg/L of cadmium, humic-acid concentration: 0.1 g/L, $NaNO_3$ concentration: 0.05 mol/L $NaNO_3$, 25°C.

0.1 g/L of humic acid, the removal of copper increased from 45 to 99% and that of cadmium increased from 18 to 62% as the solution pH increased from 4 to 8. At the low solution pH, a large quantity of protons in solution protonated carboxylic or phenyl groups of humic acid. At a higher solution pH, however, the proton bound with functional groups can be deprotonated and the deprotonated carboxylic and phenyl groups can bind copper and cadmium ions. Furthermore, at a higher concentration more precipitation of copper and cadmium is expected in the form of hydroxide. However, Spark et al. reported that the presence of the humic acid significantly reduced the precipitation of the metals at both low- and high-salt concentrations, probably due to the formation of soluble metal-humic species (16). This means that the quantity of heavy metals removed by HSEUF might be greater than those removed by precipitation.

CONCLUSIONS

At the humic-acid concentration of >0.5 g/L, 85–92% of copper and cadmium were removed by HSEUF in a single metal system and similar levels were observed in the simultaneous removal of copper and cadmium. At the concentration of <0.5 g/L humic acid in the simultaneous removal, the copper removal was much higher than that of cadmium because of higher affinity of copper to humic acid compared with that of cadmium. The removal of metal decreased as the ionic strength increased because of rigid spherocolloids of humic acid at high ionic strength. The removal of copper and cadmium increased as solution pH increased due to deprotonation of functional groups and hydroxide precipitation. Even though it is well known that the humic substances are major foulants in membrane process, the flux reduction was negligible in HSEUF. Thus, HSEUF is considered an economically and environmentally feasible process to remove low concentrations of heavy metals because humic acid is a natural biopolymer and selective to heavy metals.

REFERENCES

1. Canizares, P., Perez, A., and Camarillo, R. (2002) Recovery of Metals by Means of Ultrafiltration with Water-Soluble Polymers: Calculation of Design Parameters. *Desalination*, 144: 279–285.
2. Baek, K., Kim, B-K., Cho, H.-J., and Yang, J.-W. (2003) Removal Characteristics of Anionic Metals Using Micellar-Enhanced Ultrafiltration. *J. Hazard. Mater.*, 99: 303–311.
3. Baek, K., Kim, B.-K., and Yang, J.-W. (2003) Application of Micellar-Enhanced Ultrafiltration for Nutrients Removal. *Desalination*, 156: 137–144.
4. Baek, K., Kim, B.-K., and Yang, J.-W. (2004) Removal of Phosphorous Using Micellar-Enhanced Ultrafiltration with Cationic Surfactant: Effects of Surrounding pH. *Fresenius Environ. Bull.*, 13 (2): 105–111.
5. Baek, K., Lee, H.-H., and Yang, J.-W. (2003) Micellar-Enhanced Ultrafiltration for Simultaneous Removal of Ferricyanide and Nitrate. *Desalination*, 158: 157–166.
6. Baek, K. and Yang, J.-W. (2004) Cross-Flow Micellar-Enhanced Ultrafiltration for Removal of Nitrate and Chromate. *J. Hazard. Mater.* 108: 119–123.
7. Baek, K. and Yang, J.-W. (2004) Competitive Bind of Anionic Metals with Cetylpyridinium Chloride Micelle in Micellar-Enhanced Ultrafiltration. *Desalination*, 167: 101–110.
8. Baek, K. and Yang, J.-W. (2004) Micellar-Enhanced Ultrafiltration of Chromate and Nitrate: Binding Competition Between Chromate and Nitrate. *Desalination*, 167: 111–118.
9. Baek, K. and Yang, J.-W. (2004) Effect of Valences on Removal of Anionic Pollutants Using Micellar-Enhanced Ultrafiltration. *Desalination*, 167: 119–125.
10. Rivas, B.L., Pereira, E.D., and Moreno-Villoslada, I. (2003) Water-Soluble Polymer-Metal Ion Interactions. *Prog. Polym. Sci.*, 28: 173–208.
11. Scamehorn, J.F., Christian, S.D., El-Sayed, D.A., and Uchiyama, H. (1994) Removal of Metal Cations and Their Mixtures from Aqueous Streams Using Micellar-Enhanced Ultrafiltration. *Sep. Sci. Technol.*, 29: 809–830.
12. Huang, Y.C., Batchelor, B., and Koseoglu, S.S. (1994) Crossflow Surfactant-Based Ultrafiltration of Heavy Metals from Waste Streams. *Sep. Sci. Technol.*, 29: 1979–1998.
13. Ahmadi, S., Tseng, L.K., Batchelor, B., and Koseoglu, S.S. (1994) Micellar-Enhanced Ultrafiltration of Heavy Metals Using Lecithin. *Sep. Sci. Technol.*, 29: 2435–2450.
14. Prado, A.G.S. and Airoldi, C. (2003) Humic Acid-Divalent Cation Interactions. *Thermochim. Acta*, 405: 287–292.
15. Burba, P., Aster, B., Nifanteva, T., Shkinev, V., and Spivakov, B.Y. (1998) Membrane Filtration Studies of Aquatic Humic Substances and Their Metal

Species: A Concise Overview. Part 1. Analytical Fractionation by Means of Sequential-Stage Ultrafiltration. *Talanta*, 45: 977–988.

16. Spark, K.M., Wells, J.D., and Johnson, B.B. (1997) The Interactions of a Humic Acid with Heavy Metals. *Aust. J. Soil Res.*, 35: 89–102.
17. Van Stempvoort, D.R. and Lesage, S. (2002) Binding of Methylated Naphthalenes to Concentrated Aqueous Humic Acid. *Adv. Environ. Res.*, 6: 494–504.
18. Abate, G. and Masini, J.C. (2002) Complexation of Cd(II) and Pb(II) with Humic Acids Studied by Anodic Stripping Voltammetry Using Differential Equilibrium Functions and Discrete Site Models. *Org. Geochem.*, 33: 1171–1182.