

Adsorption Characteristics of Heavy Metals by Various Forest Humic Substances*¹

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ABSTRACT

Various forest humic substances were collected at different climate regions with different forest types, and adsorption of heavy metals such as Cu(II), Zn(II), Cd(II) and Cr(III) were characteristically conducted to obtain optimal adsorption conditions and to evaluate the removal efficiency of heavy metals by each forest humic substance. The adsorption isotherms for Cu(II), Zn(II), Cd(II) and Cr(III) conformed to Langmuir's equation. In the stirred reactor, the removal efficiencies of Cu(II), Zn(II) and Cd(II) by forest humic substances were more than 90% but that of Cr(III) was less than 60%. The adsorption capacities of heavy metals in the stirred reactor were considerably varied depending on the type of forest humic substances. Among humic substances, the one from deciduous forest at subtropical region showed the highest removal efficiency for Cu(II). There was no significant difference in removal efficiency by each heavy metal depending on reaction temperature ranged from 20 to 50°C except for Cr(III), and the adsorptions of Cu(II), Zn(II) and Cd(II) were occurred rapidly in the incipient stage within 10 min, while Cr(III) needed more reaction time to be adsorbed. The stirred and packed bed column reactors showed similar adsorption characteristics of heavy metals by humic substances, but the removal efficiency was considerably higher in the packed bed column reactor than in the stirred reactor. Therefore, in actual operation process, a continuous packed bed column reactor was more economical.

Keywords : humic substances, heavy metals, adsorption, forest soil, stirred reactor

1. INTRODUCTION

Heavy metals which were contained in industrial effluents or mining wastewater have been gradually caused soil and water contamination as well as exerted negative impacts to organisms. The frequently used methods for removing heavy metals from industrial and mining wastewaters involved physicochemical processes

such as cohesion, neutralization and adsorption, and these still revealed many problems in the aspects of processing efficiency or costs (Yang *et al.*, 1993; Pandey *et al.*, 2002). Therefore, methods of treatment have been continually developed, modified, and currently still required for more efficiency.

Forest humic substances are inexpensive and available in a great quantity in nature. Since the

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Table 1. Classification of samples

Temp. zone	Sites	Forest species	pH	Soil color
Subtropical	Kyungnam Namhae	Conifer: <i>Pinus thunbergil</i>	4.15	red and yellow
		Deciduous: <i>Quercus serrata</i> , <i>Acer spp.</i>	4.79	
		Mixed: <i>P. densiflora</i> , <i>Betula costata</i> , <i>Acer spp.</i> , <i>Q. acutissima</i>	4.79	
Southern Temperate	Chunbuk Imsil	Conifer: <i>P. rigida</i>	4.32	brown
		Deciduous: <i>Castanea crenata</i> Sieb, <i>Populus X alba glandulosa</i> <i>Q. aliena</i>	4.96	
		Mixed: <i>Robinia pseudoaccacia</i> , <i>Q. aliena</i> , <i>P. rigida</i>	5.10	
Middle Temperate	Chungbuk Danyang	Conifer: <i>P. densiflora</i>	5.09	brown
		Deciduous: <i>Robinia pseudoaccacia</i> , <i>Q. acutissima</i> , <i>Q. variabilis</i> Bl.	7.10	
		Mixed: <i>Q. acutissima</i> , <i>Robinia pseudoaccacia</i> , <i>Q. aliena</i> , <i>P. densiflora</i>	5.47	
Northern Temperate	Kangwon Hoengsung	Conifer: <i>P. densiflora</i>	4.73	brown
		Deciduous: <i>Q. mongolica</i> Fisch.	4.97	
		Mixed: <i>P. densiflora</i> , <i>Larix leptolepis</i> , <i>Q. aliena</i> , <i>Q. mongolica</i> Fisch <i>Q. dentata</i> Thumb.	4.81	

late 1970s, many researchers have reported that heavy metals could possibly be removed or adsorbed by humic substances. Forest humic substances have ability for chelating organic heavy metal complexes with heavy metals, oxidative heavy metals, hydroxyl heavy metals and light metals which produced from soil erosion. They contain various chemical functional groups such as carboxyl, hydroxyl and phenol groups which can provide active sites for heavy metal binding (Rate *et al.*, 1993; Oden *et al.*, 1993; Nederlof *et al.*, 1993; Jones *et al.*, 1993; Arias *et al.*, 2002). Humic substances with high cation exchange capacity (CEC) have been utilized for removing heavy metals, and so have drawn considerable attentions from those who are engaged in environmental studies (Schnitzer, 1969; Lee *et al.*, 1995).

Forest humic substances can adsorb heavy metals by ligand linkage, and the removal efficiency of heavy metals is significantly influenced by surface property of adsorbent (Wershaw, 1993; Baker, 1975; Lee *et al.*, 1995, Yang *et al.*, 1993). Specially, CEC, specific surface and electric charge density can affect the adsorption capacity of heavy metals. Also, the chemical characteristics of humic substances, size of particle, reaction time, pH, concentration of heavy

metals and correlation or competition between heavy metals are important factors for influencing adsorption of heavy metals by forest humic substances (Yang *et al.*, 1993; Witterbrodt & Palmer, 1996; Sunda & Huntsman, 1998; Sung, 1995; Arias *et al.*, 2002). Also, the type of reactor can make a difference in adsorption characteristics of heavy metals.

Therefore, in this work, the adsorption characteristics of heavy metals depending on various forest humic substances were evaluated, and those characteristics according to reactor types were also determined in order to apply for the pilot plant treatment system of waste water in the future.

2. MATERIALS and METHODS

2.1. Collection of Forest Humic Substances

Twelve kinds of forest humic substances were collected according to climate regions such as subtropical, southern temperate, middle temperate and northern temperate regions with three kinds of deciduous, coniferous and mixed forests as shown in Table 1. Five kilograms of each forest humic substance were collected.

Coniferous forests were mainly consisted of *Pinus thunbergii*, *P. rigida* and *P. densiflora*. Deciduous forests were *Acer spp.* in subtropical region, and *Quercus serrata* in other regions. Mixed forests were consisted of mixed species of coniferous and deciduous forests. According to soil type, red-yellow soil appeared in subtropical region, and brown forest soil, representative of Korean forest soil, appeared in other regions.

Collected forest humic substances were ground by Wiley's mill after drying at 50°C for 72 hrs. Ground forest humic substances were filtered through a sieve of 40 to 60 mesh, and stored in polyethylene sample bottle. The pH of forest humic substances from all climate regions was ranged from 4.15 to 5.47, indicating of significant acidified soil. Unusually the pH of forest humic substance from deciduous forest in middle temperate region showed 7.1 due to the accumulation of calcium carbonate from rock zone to the surface of sample.

2.2. Adsorption Isotherms of Heavy Metals by Forest Humic Substances

Heavy metals (200 ml) in various concentrations were contacted with humic substances from subtropical region at 25°C. The pH of Cr(III), Cu(II), Cd(II) and Zn(II) was adjusted to 6.0, 3.5, 3.5 and 3.5, respectively. The final concentration of heavy metals was quantified by ICP (Inductively Coupled Plasma). The equation for adsorbed amount(g) of each heavy metal by forest humic substances was calculated by the following equation; $g(\text{mg/g}) = V \times (C_i - C_f) / (1000 \times M)$ (V, volume of heavy metals; M, amount of humic substance; C_i , initial concentration of heavy metal; C_f , final concentration of heavy metal)

2.3. Adsorption Characteristics of Forest Humic Substances According to Reactor Types and Reaction Conditions

In order to determine adsorption characteristics of heavy metals by forest humic substances in stirred reactor, 1g of forest humic substances was reacted at 30°C for 1 hr at 120 rpm of shaking speed with each 100 ml of Cr(III), Zn(II), Cu(II), and Cd(II) in initial concentration of 10 ppm. The pH of heavy metal solution was adjusted to 3.5. And the filtrates were obtained by filtering with Whatman #2 filter paper, and determined by ICP. Also, the adsorption characteristics depending on reaction time, reaction temperature, particle size of humic substances and kinds of heavy metals were investigated by using forest humic substance from subtropical deciduous forest.

The reaction conditions for determining the removal efficiency of heavy metals depending on reaction time were as follows; concentration of each heavy metal 10 ppm, temperature 30°C and shaking speed 120 rpm for 5 hrs. The removal efficiency according to reaction temperature was measured at 20, 30, 40 and 50°C after 1 hr of reaction time at 10 ppm of concentration at 120 rpm of shaking speed. The particle size was differentiated to 4 groups such as 20 to 40, 40 to 60, 60 to 100 and less than 100 mesh. The different concentrations on 10, 20, 40 and 50 ppm were used to determine the effect of removal efficiency depending on various concentrations of heavy metals.

The packed bed column (11 mm of diameter) was packed with 3 g of forest humic substances, and was loaded with 10 ppm of initial concentration of each heavy metal at a flow rate of 2 ml/min, and the filtrates were collected in mess cylinder for measuring the final concentration of heavy metals by ICP.

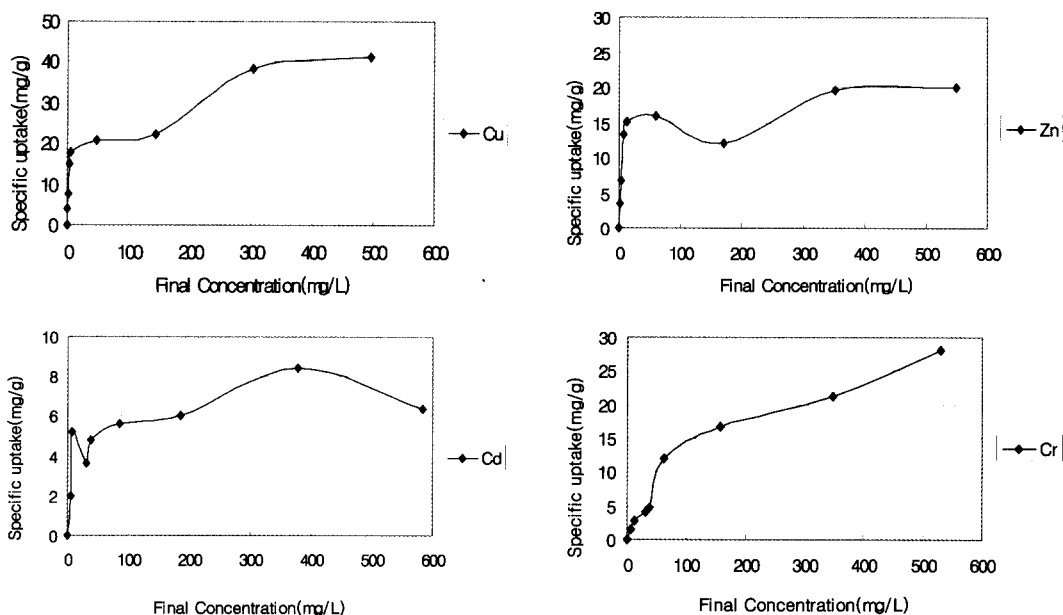


Fig. 1. Adsorption isotherms of heavy metals by forest humic substance collected from subtropical deciduous forest.

2.4. Determination of Heavy Metals

The used heavy metals were Cu(II), Zn(II), Cd(II) and Cr(III), which were purchased from Kanto Chemical Co., and the concentration of all these metals were 1,000 ppm for atomic adsorption analysis. Determination of heavy metals was conducted using ICP · AES (Inductively coupled plasma · Atomic emission spectrophotometer) - Liberty series II, and the conditions were as follows. The wavelength(nm) of Cr(III), Zn(II), Cu(II) and Cd(II) were 228.802, 267.716, 213.856, 327.396 and 228.802, respectively. The integration time was 1.00 sec, power 1.00 kw, viewing height 10, PMT voltage 650 V, plasma flow rate 15.0 ℓ /min., and auxiliary flow rate 1.50 ℓ /min. The above conditions except for wavelength were applied to all the heavy metals.

3. RESULTS and DISCUSSION

3.1. Adsorption Isotherms of Heavy Metals by Humic Substances

The adsorption isotherms of heavy metals at 25°C by forest humic substances collected from subtropical deciduous forest were Langmuir type (Fig. 1) even though there was a difference in the maximal adsorption ratio of each heavy metal (Schiewer & Volesky, 1995). The maximal adsorption ratios of Cr(III), Zn(II), Cu(II) and Cd(II) by forest humic substances from subtropical deciduous forest were 28, 20, 41 and 8 mg/g, respectively. In case of Cd(II), it had very low adsorption ratio, which resulted from the difference of binding energy by adsorption affinity between humic substance and heavy metal. Therefore, the maximal adsorption ratio was in the order of Cu(II)>Cr(III)>Zn(II)>Cd(II). In case of Cr(III), since the major factor

Adsorption Characteristics of Heavy Metals by Various Forest Humic Substances

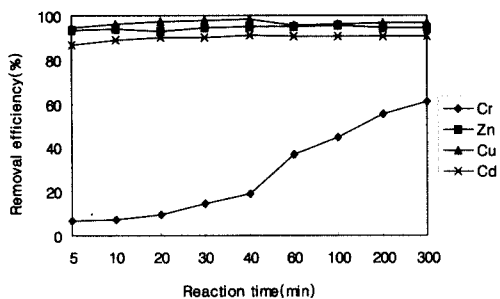


Fig. 2. Removal efficiencies of heavy metals on different reaction time by forest humic substance collected from subtropical deciduous forest in a stirred reactor.

for adsorbing heavy metal was electrostatic attraction, the adsorption ratio was lower in the low concentration, while increased as the concentration increased. The maximal adsorption ratio of each heavy metal by humic substances was higher than by tree barks, but lower than by active carbons and carbonized barks (Paik *et al.*, 1996). Arias *et al.* (2002) reported that the addition of humic acid to minerals such as kaolin could enhance the metal adsorption capacity of mineral surfaces.

3.2. Removal Efficiency of Heavy metals Depending on Reaction Conditions

3.2.1. Reaction Time

The removal efficiency of heavy metals by forest humic substance depending on reaction time were shown in Fig. 2. Cu(II) and Zn(II) were very quickly removed in solution by humic substance within 5 min by more than 90%. Barabra *et al.* (1995) also reported that Cu(II) was adsorbed in the incipient stage. In addition, Cd(II) was reached to the maximal adsorption by humic substance in 10 min. Generally, it has been known by the studies of adsorption reaction mechanism that the divalent ions were rapidly adsorbed to ligand in incipient

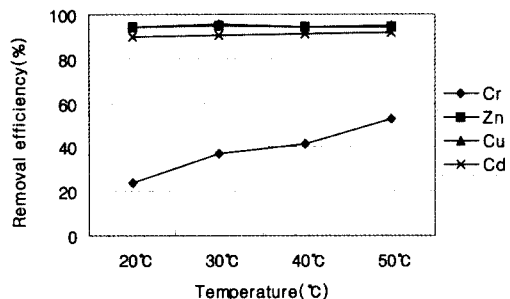


Fig. 3. Removal efficiencies of heavy metals on different reaction temperatures by forest humic substance collected from subtropical deciduous forest in a stirred reactor.

stage, and then the reaction rate was reduced. Compared with other metals, however, Cr(III) showed that the removal efficiency was very low in incipient stage, but gradually increased to 60% as reaction time increased, suggesting that it may be necessary for Cr(III) to be retained more in reactor for more efficient adsorption. Depending on forest type, the trend of adsorption characteristics in coniferous and mixed forests was very similar to that in deciduous forest, but the removal efficiency of Cd(II) was relatively lower in coniferous and mixed forests.

3.2.2. Reaction Temperature

The removal efficiencies of heavy metals depending on reaction temperature were shown in Fig. 3. The removal efficiencies of Zn(II), Cu(II) and Cd(II) were not affected depending on reaction temperature, whereas that of Cr(III) increased with increasing temperature. In case of Cu(II), Zn(II) and Cd(II), the removal efficiencies reached to more than 90% at all tested temperatures regardless of forest humic substances from various forest types, while the removal efficiency of Cr(III) was increased with increasing temperature. According to these results, the adsorption of divalent ions was not affected by seasonal and indoor or outdoor environments except for Cr(III).

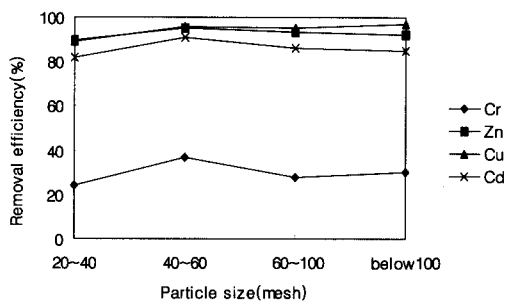


Fig. 4. Removal efficiencies of heavy metals depending on particle size by forest humic substance collected from subtropical deciduous forest in a stirred reactor.

3.2.3. Particle Size of Humic Substances

The particle size of humic substances did not influence the removal efficiency of heavy metals, and the kinds of humic substances also did not as shown in Fig. 4. Generally, it has been reported that the removal efficiency was increased in smaller particle size of ligand because there was more surface area and higher cation exchange capacity. In this study, there was no significant difference in removal efficiency of heavy metals by particles less than 40 mesh, while little reduced at particles ranged from 20 to 40 mesh, meaning that the particles larger than 20 mesh would affect the removal efficiency.

3.2.4. Concentration of Heavy Metals

The removal efficiencies of heavy metals according to various concentrations of heavy metals were shown in Fig. 5. The Cu(II) showed more than 90% of removal efficiency up to 50 ppm of concentration regardless of the type of humic substances. The Zn(II) was adsorbed by more than 90% at less than 20 ppm concentration, but the removal efficiency was gradually reduced at more than 40 ppm. In addition, at higher concentration of heavy metal, the removal efficiency has been differentiated according to the

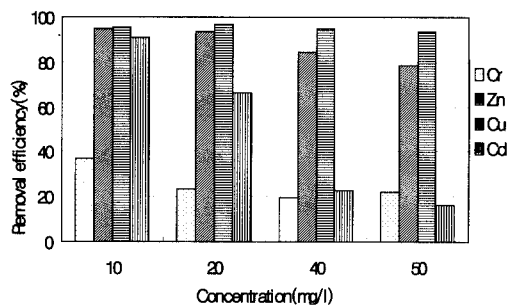


Fig. 5. Removal efficiencies of heavy metals depending on different concentrations by forest humic substance collected from subtropical deciduous forest in stirred reactor.

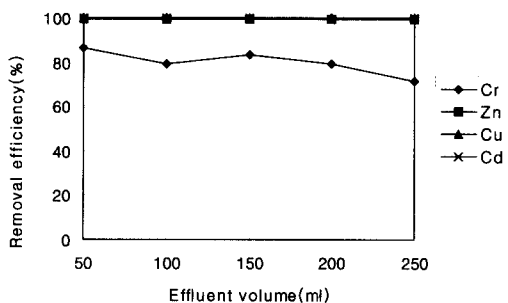


Fig. 6. Removal efficiencies of heavy metals by humic substances collected from subtropical deciduous forest in a packed bed column reactor.

type of humic substances, suggesting that the selection of humic substances should be important for adsorbing Zn(II). These result indicated that it was necessary for each heavy metal to be used at less than 20 ppm because the concentration of heavy metal affected the removal efficiency.

The Cd(II) showed 90% of removal efficiency at 10 ppm, but the efficiency rapidly decreased to 20% as the concentration was increased to 50 ppm. There was very low adsorption in case of Cr(III), and the change in concentration did not significantly affect the adsorption of Cr(III).

Table 2. Comparison of removal efficiencies of heavy metals by various forest humic substances in a stirred reactor (T=subtropical, S=southern temperate, M=middle temperate, and N=northern temperate zones ; C=coniferous, D=deciduous, and M=mixed forest)

Temp. Zone	Forest type	Removal efficiency (%)			
		Cr	Zn	Cu	Cd
Subtropical	Deciduous	37	95	96	91
	Coniferous	36	92	97	67
	Mixed	34	90	94	76
Northern Temp.	Deciduous	28	85	95	65
	Coniferous	45	81	93	41
	Mixed	35	81	92	57
Middle Temp.	Deciduous	29	92	94	89
	Coniferous	36	79	91	46
	Mixed	50	46	92	81
Southern Temp.	Deciduous	40	90	96	80
	Coniferous	52	77	90	44
	Mixed	40	87	92	76

3.3. Adsorption Characteristics of Humic Substances According to Reactor Type

3.3.1. Stirred Reactor

The removal efficiencies of heavy metals by various humic substances collected from different forest types and different climate regions in stirred reactor were shown in Table 2. The removal efficiencies of heavy metals by various humic substances was the highest in Cu(II), and followed by Zn(II), Cd(II), and Cr(III) in the order. There was a significant difference in removal efficiency according to forest type and climate region.

The Cu(II) indicated high removal efficiency, more than 90%, regardless of forest type and climate region, and these could be due to the high content of carboxyl groups in all the humic substances. Generally the deciduous humic substances contained more carboxyl group with low aromaticity than phenolic hydroxyl group, and

these could cause efficient binding with Cu(II) at low pH range. The highest removal efficiency was obtained in coniferous humic substances from subtropical region. However, the removal efficiency of Cr(III) by humic substances was ranged from 28 to 52%, and more than 50% of maximal efficiency was obtained by humic substances from coniferous forest at southern region and from mixed forest at middle temperate region. The humic substances from coniferous forest removed Cr(III) more efficiently by 7 to 10% than those from deciduous forest. The low removal efficiency of Cr(III) was due to high pH region in humic substances. Wittbrodt & Palmer (1996) reported that Cr(III) was adsorbed highly in very low pH region.

More than 80% of Zn(II) was removed by all the humic substances, and those from deciduous forest type showed more than 90% of removal efficiency. The humic substances from subtropical region indicated more than 90% of removal efficiency regardless of forest types. There was significant difference in removal

efficiency of Cd(II), which ranged from 40 to 90%. The humic substance from deciduous forest at subtropical region showed more than 90% of removal efficiency of Cd(II), while that was very low in humic substances from coniferous forest at all climate regions.

Therefore, it might be concluded that the removal efficiencies of heavy metals were higher by humic substances from subtropical region than by those from temperate regions. This may be resulted from that the humic substances from subtropical region are more decayed or decomposed and contain more functional groups which can be useful for adsorbing heavy metals. Halim *et al.* (2003) indicated that the formation of humic acid-metal complexes depended on the amount of humic acids, their aging and structural changes. In addition, three heavy metals except for Cr(III) showed higher removal efficiency by humic substances from deciduous forest.

3.3.2. Packedbed Column

In this study, the packed bed column makes it possible to conduct a continuous adsorption of heavy metals by humic substances. Fig. 6 showed the removal efficiency of 10 ppm concentration of heavy metals in a packed bed column filled with humic substances collected from subtropical deciduous forest.

The removal efficiencies of heavy metals were higher in packed bed column reactor than in stirred reactor, and those of Zn(II), Cu(II) and Cd(II) were reached to 100%. Pandey *et al.* (2002) also reported that the calcium alginate beads containing humic acids packed in column indicated more efficient in removal of all heavy metals. The Cd(II) was more efficiently adsorbed by 10 to 40% in packed bed column reactor than in stirred reactor. In stirred reactor, this low efficiency was caused by that the binding stability of Cd(II) with adsorbent was lower

than other heavy metals, and the bound Cd(II) was temporarily detached from ligand. Arias *et al.* (2002) reported the competitive adsorption of Cu(II) and Cd(II), that is, the presence of Cd(II) had not an important effect on Cu(II) adsorption, whereas a dramatic decrease was observed on the adsorption of Cd(II) in the presence of Cu(II). The Cr(III) was also improved in the removal efficiency by 30 to 40% in packed bed column reactor, compared with stirred reactor. In stirred reactor, the particle of humic substances with low density were suspended in the surface of water, and so caused inefficient contact with the Cr(III). However, in packed bed column reactor, the efficient contact of humic substances with solution of Cr(III) enhanced the adsorption (Crist *et al.*, 1995).

In packed bed column reactor, the Zn(II), Cu(II) and Cd(II) were almost completely adsorbed by all the humic substances regardless of forest type and climate region. However, in case of Cr(III), the removal efficiency was relatively low, but the humic substances from subtropical region showed superior removal efficiency of Cr(III) compared with those from other regions. And the humic substances from coniferous forest indicated higher removal efficiency than those from deciduous and mixed forests. The trend of Cr(III) removal in packed bed column reactor was very similar in stirred reactor. However, it was characterized that the removal efficiency of Cr(III) was almost constant at initial stage, but gradually decreased as the reaction time increased. According to these results, the efficient removal of Cr(III) were dependent on the selection of appropriate humic substances and reactor type.

4. CONCLUSIONS

The adsorption isothermal equation of each heavy metal by humic substances was a Lang-

muir type even though there were differences in maximal adsorption ratios according to kinds of heavy metals. The maximal adsorption ratios of Cr(III), Zn(II), Cu(II) and Cd(II) by humic substance from deciduous forest from subtropical region were 28, 20, 41 and 8 mg/g, respectively. In the removal efficiencies of heavy metals, Cu(II) and Zn(II) were rapidly adsorbed by more than 90% within 5 min of reaction time, and Cd(II) within 10 min, whereas Cr(III) needed to be retained in the reactor more time. According to reaction temperature, Cu(II), Zn(II) and Cd(II) were not affected, while the removal efficiency of Cr(III) increased with increasing reaction temperature. Also, the particle size of humic substances did not affect the adsorption of heavy metals. The removal efficiency of Cu(II) was more than 90% regardless of its concentration, but there was difference in removal efficiency of other heavy metals according to changes in their concentration. In stirred reactor, the Cu(II) showed the highest removal efficiency, and the Zn(II), Cd(II) and Cr(III) were followed in the order. Among humic substances, those from deciduous forest at subtropical region made the highest removal efficiency of heavy metals. Packed bed column reactor was more efficient for adsorbing Zn(II), Cu(II) and Cd(II) with 100% than stirred reactor.

REFERENCES

1. Arias, M., M. T. Barral, and J. C. Mejuto. 2002. Enhancement of copper and cadmium adsorption on kaolin by the presence of humic acids. *Chemosphere* Vol. 48: 1081~1088.
2. Barbara, R. C. and A. T. Stone. 1995. Nonreversible Adsorption of Divalent Metal Ions (Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Pb^{2+}) onto Goethite : Effects of Acidification, Fe^{II} Addition, and Piclinic Acid Addition. *Environ. Sci. Technol.* Vol. 29, No. 9: 2445~2455.
3. Baker, D. E. and L. Chesnin. 1975. Chemical monitoring of soils for environmental quality and animal and human health. *Adv. Agron.* 27: 305~374.
4. Crist, R. H., J. R. Martin, and J. Chonko. 1995. Uptake of Metals on Peat Moss: An Ion-Exchange Process. *Environ. Sci. Technol.* Vol. 30: 2456~2461.
5. Halim, M., P. Conte, and A. Piccolo. 2003. Potential availability of heavy metals to phytoextraction from contaminated soils induced by exogenous humic substances. *Chemosphere* Vol. 52: 265~275.
6. Jones, R. I., P. J. Shaw, and H. D. Haan. 1993. Effects of Dissolved Humic Substances On the Speciation of Iron and Phosphate at Different pH and Ionic Strength. *Environ. Sci. Technol.* Vol. 27: 1052~1059.
7. Lee, J. J., S. M. Chang, and J. Choi. 1995. Mechanisms of Humic Acid-Heavy Metal Complexation. *Korean J. of Soil Sci. & Fert.* Vol. 28(2): 114~122.
8. Nederlof, M. M., Johannes C. M. De Wit, Willem H. Van Riemsdijk, and Luuk K. Koopal. 1993. Determination of Proton Affinity Distributions for Humic Substances. *Environ. Sci. Technol.* Vol. 27: 846~856.
9. Oden, W. I., G. L. Amy, and M. Conklin. 1993. Subsurface Interactions of Humic Substances with Cu(II) in Saturated Media. *Environ. Sci. Technol.* Vol. 27: 1045~1051.
10. Paik, K. H., I. G. Choi, and K. Shin. 1996. Adsorption of Heavy Metal Ions by Constituents of Bark. *Mokchae Konghak* Vol. 24(3) : 51~56.
11. Pandey, A. K., S. D. Pandey, and V. Misra. 2002. Removal of toxic metals from leachates from hazardous solid wastes and reduction of toxicity to microtox by the use of calcium alginate beads containing humic acid. *Ecotox. and Environ. Safety* Vol. 52: 92~96.
12. Rate, A. W., R. G. McLaren, and R. S. Swift. 1993. Response of Copper(II)-Humic Acid Dissociation Kinetics to Factors Influencing Complex Stability and Macromolecular Conformation. *Environ. Sci. Technol.* Vol. 27: 1408-1414.
13. Schnitzer, M. 1969. Reaction between fulvic acid a soil humic compound and inorganic soil constituents. *Soil Sci. Soc. Am. Proc.* 33: 75~

- 81.
14. Schiewer, S. and B. Volesky. 1995. Modeling of the Proton-Metal Ion Exchange in Biosorption. *Environ. Sci. Technol.* Vol. 29, No. 12: 3049~3058.
15. Sung, W. 1995. Some Observation on Surface Partitioning of Cd, Cu, and Zn in Estuaries. *Environ. Sci. Technol.* Vol. 29: 1303~1312.
16. Sunda, W. G. and S. A. Huntsman. 1998. Control of Concentrations in a coastal Diatom by Interactions among Free Ionic Cd, Zn, and Mn in Seawater. *Environ. Sci. Technol.* Vol. 32: 2961~2968.
17. Wershaw, R. L. 1993. Model for Humus in Soils and Sediments. *Environ. Sci. Technol.* Vol. 27, No. 5: 814~816.
18. Wittbrodt, P. R. and C. D. Palmer. Effect of Temperature, Ionic Strength, Background Electrolytes, and Fe(III) on the Reduction of Hexavalent Chromium by Soil Humic Substances. *Environ. Sci. Technol.* Vol. 30: 2470~2477.
19. Yang, J. E., Y. K. Shin, and J. J. Kim. 1993. Application of Principles in Metal-Ligand Complexation to Remove Heavy Metals : Effects of Metal Concentration, pH and Temperature. *Korean J. of Soil Sci. & Fert.* Vol. 26(1): 37~42.