

Adsorption of Heavy Metal Pollutants by Landfill Soils

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The leachate in landfill sites carries out highly concentrated inorganic and organic pollutants. Such pollutants can be intercepted by the adsorption of landfill soil and will proceed with a long-term stabilization-degradation reaction in the soil. Moreover, the possibility of groundwater pollution due to the leachate from landfill can be reduced through the intercepted adsorption by the soil. Simulated adsorption batch experiments were carried out in this study to investigate the adsorption removal of heavy metals by soils. The tested soils included red loam from the Taichung sanitary landfill site and six alluvial soils located over the most widespread area in Taiwan. The results indicated the following trend for the ability of heavy metal adsorption removal by such tested soils: Hsinying soil > Chungsin Village soil > Chung Hsing University soil \approx Hsuehchia soil > Taichung sanitary landfill soil > Mashan soil > Tunghsiao soil. The adsorption removal of heavy metals followed $Pb \approx Cu > Ni \approx Cd \approx Zn$. The adsorption removal by red loam increased with Cd concentration; however, part of the Cd removal in the high-pH region for high Cd concentration was due to precipitation. Thus, consideration of the speciation distribution was necessary to determine the maximum probable precipitated amount and the minimum probable adsorbed amount. In addition, in the presence of organic ligand [ethylenediamine tetraacetic acid (EDTA)], the adsorption effect of Cd by red loam was suppressed because of the complexation with EDTA, and the adsorption decreased with increasing EDTA concentration.

Sanitary landfill is the most common approach for the final disposal of solid wastes in Taiwan. The leachate produced from the landfill site usually carries out highly concentrated inorganic and organic components. Such a potential hazard to the environment has aroused concern and become a chief object of research in solid waste treatment (1). Because food wastes are a large proportion of solid wastes and the weather is humid and rainy in Taiwan, the composition and the quantity of leachate produced from landfill are quite different from those in foreign areas. The infiltration of waterborne pollutants always increases with increasing flow rate of leachate produced, thus increasing the possibility of groundwater pollution. In addition, the constitution and the equipment of many landfill sites in Taiwan are not so well appointed, and the management system of landfill sites exhibits certain defects. Therefore, some inorganic hazardous pollutants, such as heavy metals, from industrial solid wastes can commonly be found in the leachate. Since the soil itself possesses a good adsorption function to the pollutants in leachate (2,3), it is expected that optimal control of soil properties and environmental factors of the landfill site not only can improve the

water quality of leachate, reducing the loading and cost of treatment, but also prevent pollution of the groundwater (4,5). The main thrust of this work is to investigate the adsorbability of inorganic heavy metal pollutants in leachate by the soil in landfill sites. The results may have important implications for the determination of landfill sites according to the properties of soil and the optimum control parameters on the operation of landfill.

EXPERIMENTAL

Materials

The tested soils were obtained from seven locations in Taiwan. The samples represent soils with various texture and properties. The locations and notations of the tested soils are specified in Tables 1 and 2. After the drying process under sunlight, the soil samples were crushed and sieved (No. 10, 2 mm pore diameter) to remove impurities in the soil, such as stones and roots, before use. All heavy metal electrolyte solutions were prepared from perchlorate salts, and sodium perchlorate was used as the inert electrolyte for maintaining constant ionic strength (6,7). The organic chemical, ethylenediamine tetraacetic acid (EDTA), was selected as the complexing ligand with heavy metals. The pH was adjusted by the addition of 0.1 N $HClO_4$ or NaOH. All chemicals were of reagent grade, obtained from Lin-Chun, Japan, and used without further purification. Distilled, deionized water was used for all experimental operations.

Determination of Soil Properties

The size distribution of soil particles was determined by sieving each given amount of soil sample through a series of pore diameters from 0.002 to 1 mm. The average size of soil particles and the texture of soil samples were thus calculated and specified (8,9). The pH was measured by pH meter (Hanna, Model HI8417, Italy) after the mixture of 25 g of soil sample and 25 mL of distilled, deionized water settled quiescently for 1 hr (10). Organic matter in soil was determined by the Walkley-Black method, in which the consumption of potassium dichromate was determined to convert the amount of organic matter oxidized (10). Cation exchange capacity (CEC) was measured by replacing the unchangeable cations in the soil sample with ammonium ions through the addition of a concentrated solution of ammonium acetate into the soil sample (10).

TABLE 1 SIZE DISTRIBUTION AND TEXTURE OF TESTED SOILS

Soil (Location and Notation)	Composition (%) of the Soil Sample			Texture
	Sand 2-0.05mm	Silt 0.05-0.002mm	Clay <0.002mm	
Taichung Sanitary Landfill Red Loam Soil (Taichung, R)	42.04	33.80	24.16	Loam
Chunghsin Village Soil (Chunghsin Village, C)	34.04	53.80	12.16	Silty Loam
Chung Hsing University Soil (Taichung, U)	38.04	49.80	12.16	Loam
Tunghsiao Soil (Tunghsiao, T)	97.52	1.40	1.08	Sand
Hsinying Soil (Hsinying, E)	6.04	52.80	41.16	Silty Clay
Hsuehchia Soil (Hsuehchia, K)	40.04	51.80	8.16	Silty Loam
Mashan Soil (Mashan, M)	84.02	14.40	1.58	Loamy Sand

TABLE 2 pH, ORGANIC MATTER CONTENT, AND CEC OF TESTED SOILS

Soil (Location and Notation)	pH	Organic Matter Content (%)	CEC (meq/100g)
Taichung Sanitary Landfill Red Loam Soil (Taichung, R)	4.15	1.24	4.17
Chunghsin Village Soil (Chunghsin Village, C)	5.20	2.21	7.91
Chung Hsing University Soil (Taichung, U)	5.90	1.61	7.61
Tunghsiao Soil (Tunghsiao, T)	8.40	0.03	0.88
Hsinying Soil (Hsinying, E)	7.70	1.37	17.94
Hsuehchia Soil (Hsuehchia, K)	7.65	1.31	7.04
Mashan Soil (Mashan, M)	8.10	0.26	2.95

Adsorption of Heavy Metals

A 1-L solution of 0.5 M ionic strength with a certain amount of heavy metal ions was prepared in an Erlenmeyer flask. One hundred mL of each solution was transferred into a polyethylene plastic bottle, to which 10 g of the tested soil was added into each of the nine bottles, leaving the rest to be a blank, and a certain amount of acid or base was added in incremental amounts to obtain the final pH from 4 to 10 after the saturated adsorption at a period of 24 hr. The suspensions were filtered through 0.45- μ m pore size, 47-mm-diameter filter paper (Gelman, United States of America). The equilibrium pHs of the filtrates were determined and the residual heavy metals were measured by the atomic adsorption spectrophotometer (ZAA-8000, Hitachi).

RESULTS AND DISCUSSION

Analyses of the Tested Soils

The size distribution and the texture of the seven soil samples are indicated in Table 1. The sand contents of Tunghsiao (T) and Mashan (M) soils were 97.52 and 84.02 percent, respectively, and thus were labeled coarse-textured soil. Taichung sanitary landfill red loam soil (R), Chunghsin Village soil (C), Chung Hsing University soil (U), and Hsuehchia soil (K) showed close composition between sand and silt ratios and were classified as medium-textured soil. However, Hsinying soil (E) was thought to be fine-textured soil because of the high contents of both silt and clay.

Table 2 gives the pH, organic matter content, and CEC of the tested soils. Red loam soil (R) and Tunghsiao soil (T) presented the lowest and the highest pH values (4.15 and 8.40, respectively). The pH values of both of the two coarse-textured soils were greater than 8. The organic matter contents of all the soil samples were low, whereas the organic matter in sand was much less than that in loam and clay. Usually, the removal of heavy metal according to adsorption and complexation mechanisms was more significant when the organic matter content in soil was higher (11). CEC values of soils roughly increased with increasing organic matter content. Sands indicated the lower and loams the higher CEC values. Hsinying soil (E), which had the highest clay content, presented the largest CEC value, 17.94 meq/100 g.

Effect of Type of Soil

To compare the adsorbabilities of heavy metal ions by soil, a little inconsistency was observed among the tested soils. However, a general trend in the ability of heavy metal adsorption removal was still noted, and the order Hsinying soil (E) > Chunghsin Village soil (C) > Chung Hsing University soil (U) \approx Hsuehchia soil (K) > Taichung sanitary landfill red loam soil (R) > Mashan soil (M) > Tunghsiao soil (T)

was concluded. This order was compatible with the sequences of CEC values and organic matter contents of the tested soils. This implied that the adsorption removal of heavy metals exhibited a close relationship with the number of functional groups in the soil. The removal of heavy metals by the seven tested soils is represented by cadmium and is shown in Figure 1. There was a breakpoint between pH 6 and 8 at which all the removals increased sharply. At pHs greater than 9, the removals were always beyond 95 percent; however, there was a marked difference in the adsorbabilities of Cd among the soil samples at low pHs. The order $E > C > R > K > U > M > T$ was observed. Hsinying soil (E) was identified as the silty clay of fine-textured soil, which exhibits the largest specific surface area and the highest CEC value, and the best Cd removal situation was then indicated. On the other hand, Tunghsiao soil (T) and Mashan soil (M) presented more sand and less clay composition, higher pH, and the lowest organic matter content and CEC value. Therefore, the adsorbability of heavy metal was relatively weak.

Effect of Type of Heavy Metal

Although there was a little inconsistency in the sequences of adsorption removal by soils among the selected heavy metals, a general order of $Pb \approx Cu > Ni \approx Cd > Zn$ was concluded. The removal of heavy metals by the seven tested soils is represented by Taichung sanitary landfill red loam soil (R) and is shown in Figure 2. Such a removal sequence as a function of pH might have something to do with the solubility product constants of heavy metal hydroxides. At a concentration of 10^{-4} M, the removal of heavy metals from soil suspension partly resulted from the formation of hydroxide precipitates at high pHs. Comparing the solubility products of the selected heavy metals in this study, it was found that the formation

sequence of hydroxide precipitates followed the order $Cu > Zn > Ni > Pb > Cd$ with increasing pH. However, this order was not completely the same as that from the adsorption experiments, in particular, the sequence of Pb and Zn. The relatively high removal of Pb could be related to its large hydrolysis equilibrium constant. Pb showed the largest first hydrolysis equilibrium constant among the five heavy metals and enhanced adsorbability by soil. Zn might exhibit the specific affinity with red loam soil. Therefore, a significant and consistent removal percentage was observed for the whole pH region studied.

Effect of Concentration of Heavy Metal

Figure 3 shows the adsorption removals of Cd by Taichung sanitary landfill red loam soil (R) at various Cd concentrations. Although the results indicated that the removals of Cd were all less than 10 percent in the pH region studied at a Cd concentration of 10^{-5} M, and the removals were obviously enhanced at Cd concentrations of 10^{-4} M and 10^{-3} M, the speciation distribution of Cd should be considered because the mechanisms of Cd removal actually included both adsorption and precipitation at Cd concentrations greater than 10^{-4} M. This was cited by theoretical calculation at the presence of 10^{-4} M Cd in solution. To determine the minimum probable amount of Cd removal by adsorption, the maximum probable amount of removal by precipitation calculated on the basis of the hydrolysis equilibrium constants and the solubility product constant of Cd was subtracted from the actual removal by experiments, and the pH-dependent distribution curve of Cd removal by adsorption was then obtained. The results are shown in Figure 4. It was also found that removal by adsorption increased gradually when the pH of the solution increased. Up to a pH value of 8.43, the adsorption amount

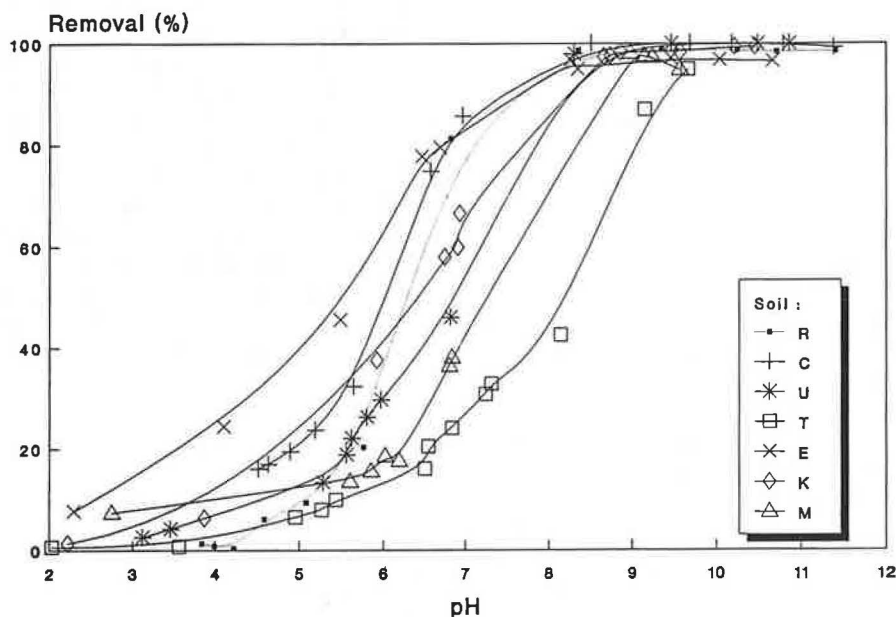


FIGURE 1 pH-dependent adsorption removals of Cd by the seven tested soils (10g/L soil, 0.5 M ionic strength, 10^{-4} M Cd).

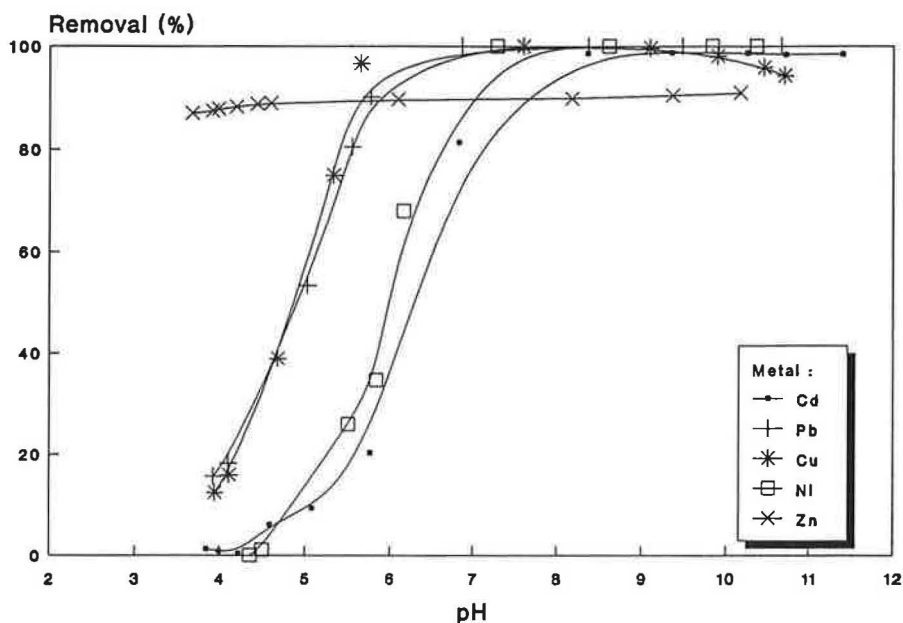


FIGURE 2 pH-dependent adsorption removals of various heavy metals by Taichung sanitary landfill red loam soil (10g/L soil, 0.5 M ionic strength, 10^{-4} M heavy metals).

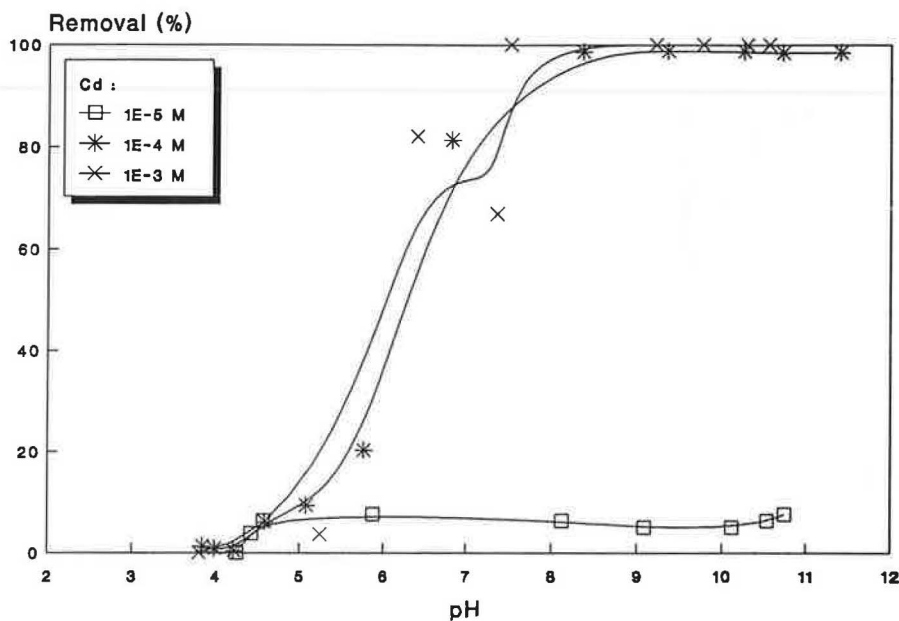


FIGURE 3 pH-dependent adsorption removals of Cd by red loam soil at various Cd concentrations (10g/L soil, 0.5 M ionic strength).

reduced significantly because of the formation of precipitates. That is, the adsorption should be the only mechanism for Cd removal at pHs less than 8.43. Moreover, the diminution of Cd removal by adsorption at pHs greater than 8.43 was considered on the basis of the maximum probable amount of precipitation. The actual Cd removal by adsorption might be more than that indicated in Figure 4 if the consecutive redissolution of $\text{Cd}(\text{OH})_2$ precipitates proceeded toward an equilibrium situation because of the reduction of Cd in aqueous phase by adsorption.

Effect of the Presence of EDTA

To simulate the influence on the adsorbability of heavy metal by soil in the presence of organic ligand in leachate, EDTA is commonly selected (12–16). When Cd and EDTA coexisted in the soil solution, the adsorption removal of Cd was markedly affected because of the strong complexation reaction. Figure 5 shows the pH-dependent Cd removals at various Cd:EDTA ratios (10:1, 1:1, and 1:10) based on a fixed Cd concentration of 10^{-4} M. The removal of Cd significantly

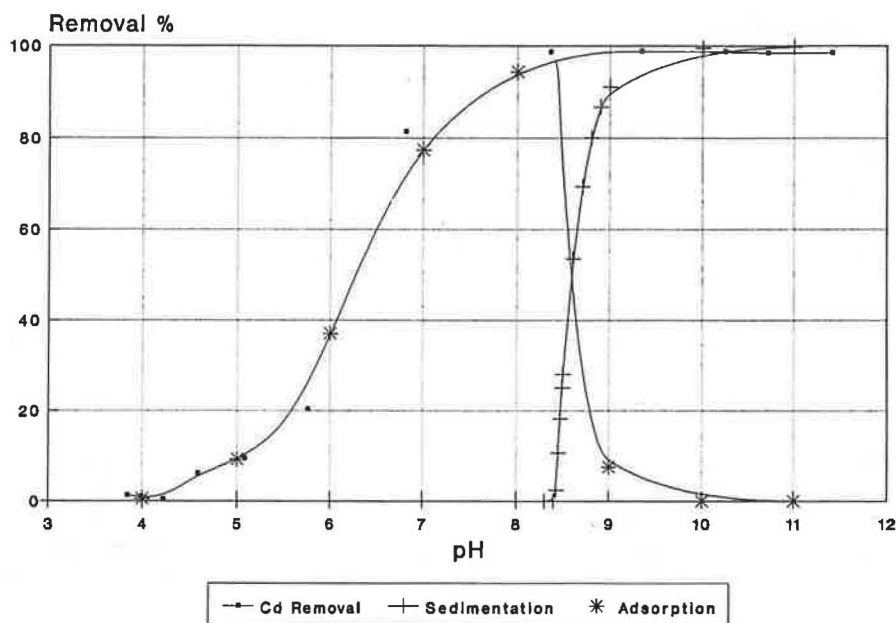


FIGURE 4 pH-dependent maximum probable removal of Cd by precipitation and minimum probable removal of Cd by adsorption on red loam soil (10g/L soil, 0.5 M ionic strength, 10^{-4} M Cd).

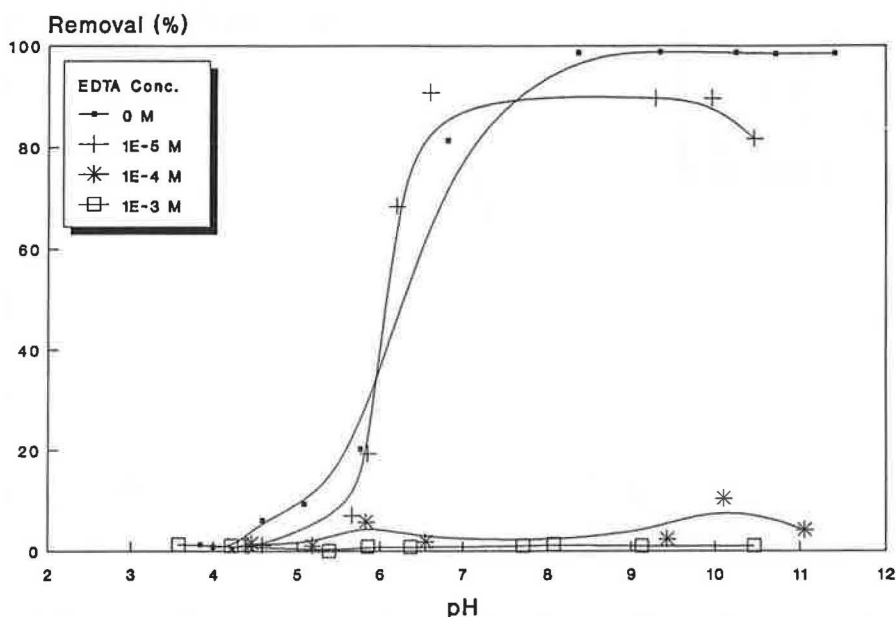


FIGURE 5 pH-dependent adsorption removals of Cd by red loam soil in the presence of EDTA with various concentrations (10g/L soil, 0.5 M ionic strength, 10^{-4} M Cd).

decreased with increasing concentration of EDTA, and the removals of Cd were extremely scarce in the whole pH range at a Cd:EDTA ratio of 1:10.

At a Cd:EDTA ratio of 10:1, the removals of Cd at pHs less than 9 were similar to those without EDTA in solution, and the removals reduced about 10 percent consistently at pHs greater than 9. This could be demonstrated by the spe-

ciation distribution diagram (Figure 6) established through the calculations of Cd-EDTA complex-formation constants. For the dissolved Cd species, 10 percent of Cd existed as the complexed CdEDTA^{2-} and 90 percent as the hydroxyl species at all the pHs. However, most were Cd^{2+} at pHs less than 9. The removals of Cd decreased by 10 percent in the presence of EDTA when the pH was raised to 8 or higher. This defi-

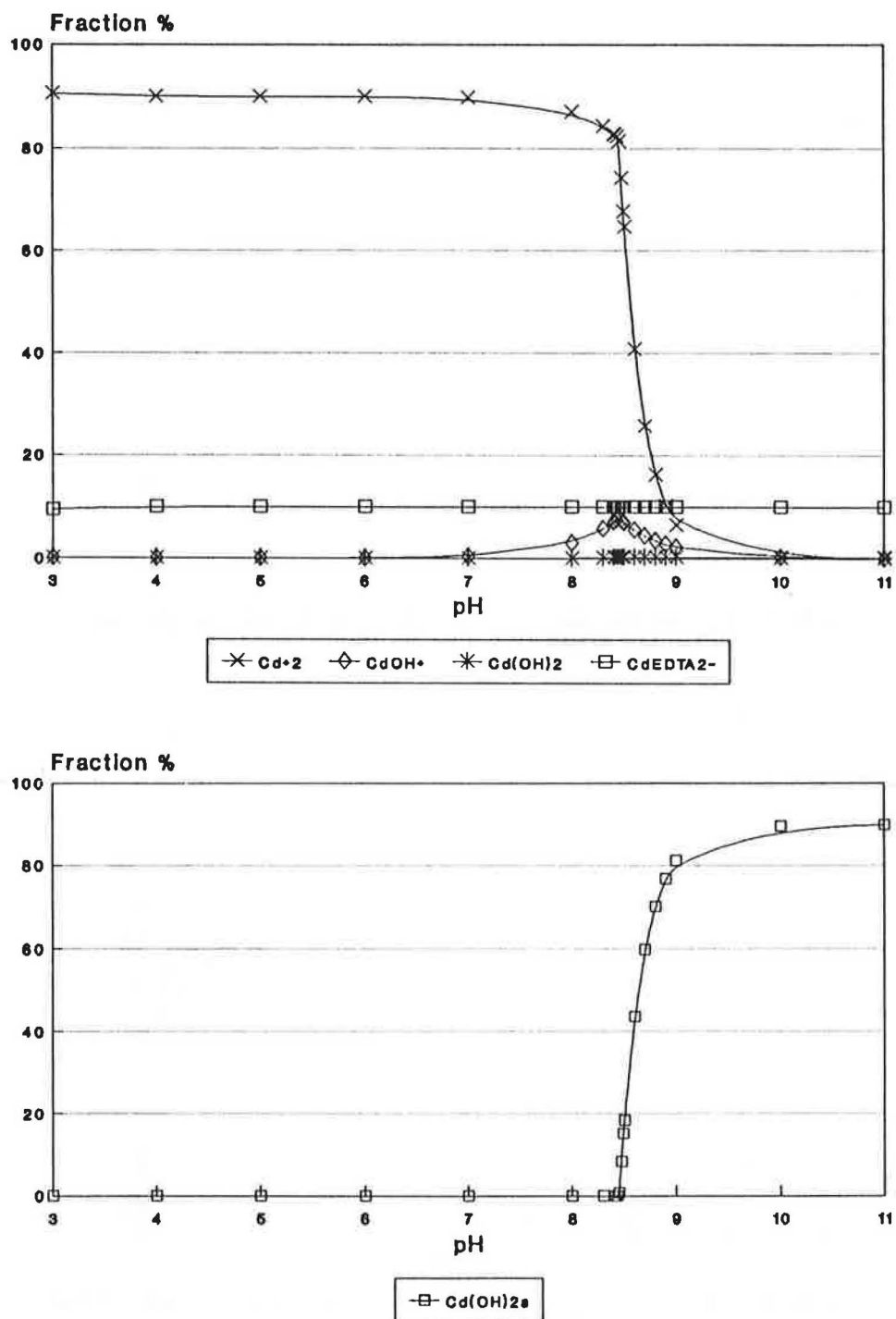


FIGURE 6 Speciation distribution of dissolved Cd (*top*) and Cd(OH)₂ precipitate (*bottom*) in Cd-EDTA aqueous solution (0.5 M ionic strength, 10⁻⁴ M Cd, 10⁻⁵ M EDTA).

nitely implied that the formation of the complexed Cd-EDTA²⁻ caused the depression of Cd removal, that is, CdEDTA²⁻ could not be adsorbed by the tested soil.

At a Cd:EDTA ratio of 1:1, the removals of Cd were largely diminished compared with those without EDTA in solution, and the removals were all within 10 percent in the whole pH

range studied. Since CdEDTA²⁻ was the predominant species (Figure 7), the removals of Cd were significantly reduced. At a Cd:EDTA ratio of 1:10, the removals of Cd were further depressed and were almost zero at all pHs. To look at the speciation distribution of Cd and EDTA in solution, all the Cd presented as the complexed CdEDTA²⁻. Ten percent of

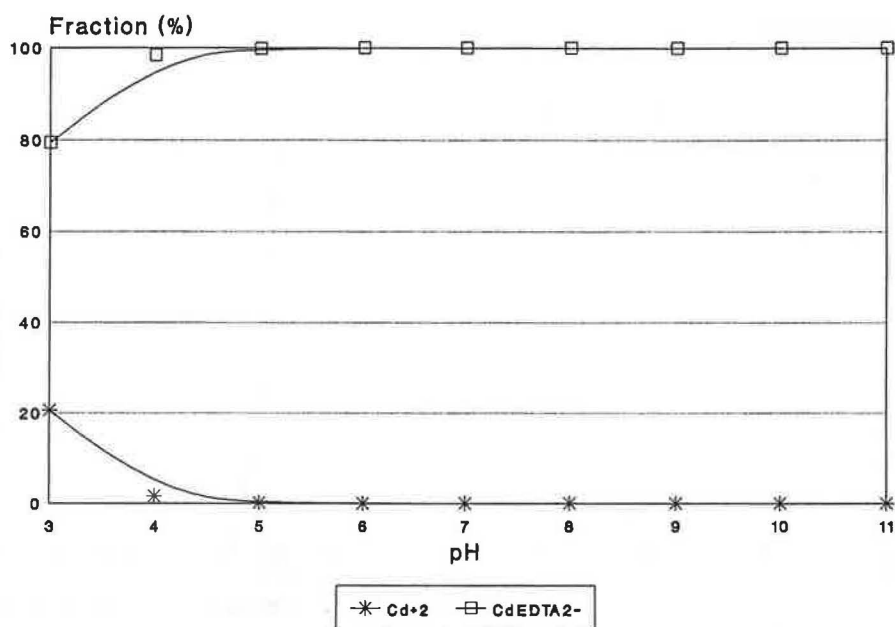


FIGURE 7 Speciation distribution of Cd in Cd-EDTA aqueous solution (0.5 M ionic strength, 10^{-4} M Cd, 10^{-4} M EDTA).

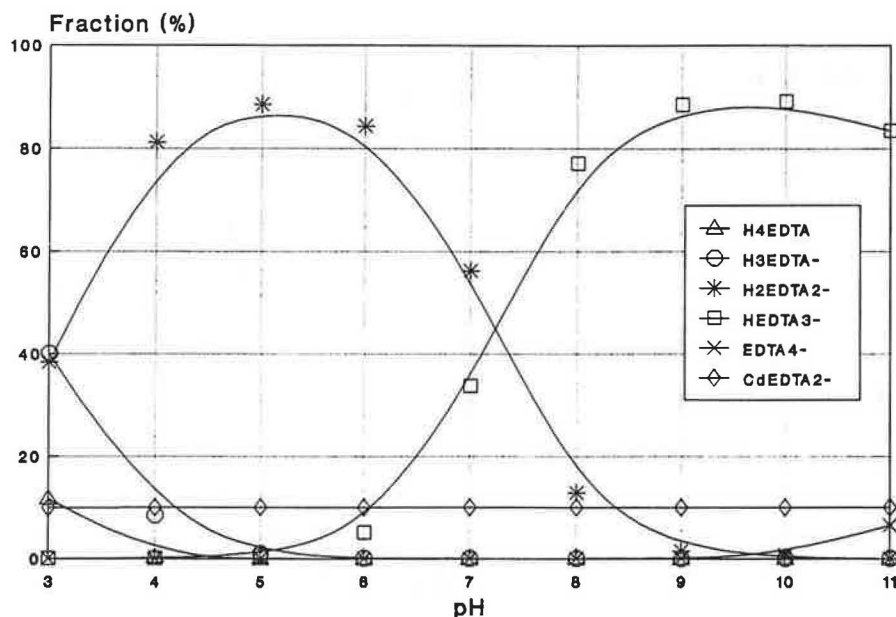


FIGURE 8 Speciation distribution of EDTA in Cd-EDTA aqueous solution (0.5 M ionic strength, 10^{-4} M Cd, 10^{-3} M EDTA).

EDTA existed as CdEDTA^{2-} . However, all other EDTA species were mostly $\text{H}_2\text{EDTA}^{2-}$ (predominated at pH 3 to 7) and HEDTA^{3-} (predominated at pH 7 to 11) (Figure 8). Because the 90 percent free EDTA (either $\text{H}_2\text{EDTA}^{2-}$ or HEDTA^{3-}) might compete with CdEDTA^{2-} for surface adsorption sites of the soil, the removals of Cd were much less

than those at a Cd:EDTA ratio of 1:1 in the whole pH range. Moreover, the surfaces of soil particles were negatively charged in the pH region studied, and the repulsion between the CdEDTA^{2-} and the surfaces also probably decreased the removals of Cd. At Cd:EDTA ratios of 1:1 and 1:10, no $\text{Cd}(\text{OH})_2$ precipitate formed in the whole pH range, according

to the calculations based on the hydrolysis equilibrium constants and the solubility product constant. This also contributed to the fact that the removals of Cd were so limited.

CONCLUSIONS

The adsorbability of heavy metal by various soils under the same operation conditions was affected by the texture and the properties of soil, including the pH, organic matter content, and CEC. Although a little inconsistency in the adsorabilities of heavy metal ions by soils was observed among the seven soils tested in this study, a general trend was still noted. The order Hsinying soil (E) > Chunghsin Village soil (C) > Chung Hsing University soil (U) \approx Hsuehchia soil (K) > Taichung sanitary landfill red loam soil (R) > Mashan soil (M) > Tunghsiao soil (T) was concluded. Moreover, a general order of $Pb \approx Cu > Ni \approx Cd > Zn$ was found for the sequence of adsorption removal by various soils. This result might have something to do with the hydrolysis equilibrium constants of heavy metal ion and the solubility product constant of heavy metal hydroxide.

When the Cd concentration was 10^{-5} M, the adsorption removals were not greater than 10 percent in the whole pH range, and the removal increased with increasing Cd concentration. However, the $M(OH)_2$ precipitates were formed and removed at high pHs and high Cd concentrations. Thus, the speciation distribution of heavy metal ions in aqueous solution should be evaluated when the adsorabilities of heavy metals by soils are compared. The adsorption removal of Cd by red loam soil (R) was suppressed in the presence of organic ligand, EDTA, because of the strong complexation reaction between Cd and EDTA. Such suppression was more obvious when the ratio of EDTA:Cd was increased. At an EDTA:Cd ratio of 10:1, the removals of Cd were almost zero at all the pHs studied.

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