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Characteristic of Cd sorption in the copper tailings wasteland soil by amended dissolved organic matter from fresh manure and manure compost

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The aim of this study was to investigate the effects of dissolved organic matter (DOM) from fresh manure and its compost on the sorption of Cd on copper tailings wasteland and normal farmland soils, in Tongling City, China. In the presence of DOM, Cd sorption capacity decreased markedly for both soils, especially for the copper tailings wasteland. The Cd sorption isotherms could be well described by the Freundlich equation ($r^2 = 0.98$), and the binding intensity parameter of soils in the presence of fresh manure DOM was lower than compost DOM. An increase in DOM concentration significantly reduced the sorption of Cd by both soils. Within the Cd and DOM concentration range studied, the decrease in Cd sorption caused by fresh manure DOM was consistently greater than that of compost DOM. Moreover, the reduction of Cd sorption caused by DOM was more obvious in the soil with higher pH. In addition, the sorption of Cd increased with an increase in pH for both soils without the addition of DOM, while Cd sorption in the presence of DOM was unexpectedly decreased with an increase in pH at a pH >6.6.

Key words: Cd Sorption, copper tailings wasteland soil, fresh manure, manure compost.

INTRODUCTION

In China, mining for metals is a large and important industry supporting economic development. The mining activities have brought not only economic prosperity, but also environmental problems. Abandoned mine tailings can result in severe pollution and have aesthetic impacts on the local environment. Mining and metal smelting have already become major sources of heavy metal contamination in soils and water bodies. Effective measures need to be taken to remediate the land occupied by tailings so that risks to the environment can be controlled. It was estimated that more than 20 million hm^2 of farmland (roughly 1/5 of the total farmland area) have been contaminated in China at present (Wei and Chen, 2001). Among them, the mining industry wasteland already accumulated to 2.0×10^6 hm^2. The contradiction raised up by the population increase and the farmland reduction made the work of recovering the wasteland particularly

important Usually, there is less organic material in this copper tailings wasteland (0.104 ~ 2.16 g kg^{-1}) (Tian et al., 2005) than in normal farm land (5 ~ 30 g kg^{-1}), which needs we have to supply enough organic material into the copper tailings wasteland soils when we try to remedy them. The organic matters to be used are some C-enriched organic wastes, such as agricultural organic solid wastes and their compost.

The mobility of dissolved organic compounds may significantly influence the mobility of heavy and transition metals in soil and subsurface environments. Organic complexes have long been recognized to have an impact on migration of metals (e.g. Pb, Cu, Zn, and Cd) in soil (McBride et al., 1997). Oden et al. (1993) reported that the soluble organic compounds from six different sources had varying abilities to influence Cu mobility in a porous medium. The molecular size, hydrophobicity, and chemical composition of natural organic compounds have been shown separately to affect their ability to complex metals (Tam and McColl, 1991; Guggenberger et al., 1994; Kinniburgh et al., 1996). Few studies have been considered to quantitatively compare the effect of dissolved organic

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matter (DOM) derived from agricultural organic solid wastes and their compost on the sorption of Cd in copper tailings wasteland soil and to investigate the effect of DOM concentration and pH on Cd sorption by the kind of soils.

Composting is a common practice before fresh agricultural organic solid wastes, such as fresh manure, is applied to soil to eliminate pathogens and achieve biological transformation of the organic matter. Research has shown that the composting process alters greatly the composition and characterization of DOM of organic waste (Liang et al., 1996; Chefetz et al., 1998). Undoubtedly, soils amended with fresh manure and manure compost display different physicochemical properties, especially in terms of DOM composition in soil, which will affect behavior of metals in soils.

Because of their potential impact on the fate of heavy metals (Davies et al., 2006; Okoronkwo et al., 2006), the chemical characteristics and metal-binding properties of bio-solids and bio-solids amended soils have been widely investigated for the last three decades. Some studies have attempted to identify individual organic compounds and metal-binding sites (Dudley et al., 1987). But organic materials derived from soil or from bio-solids are extremely heterogeneous, containing a myriad of individual compounds with a variety of functional groups. As a result, it has been difficult to isolate and positively identify more than a small fraction of the compounds or to fully characterize their functional groups.

On the other hand, dissolved organic compounds can be separated into pragmatically defined fractions that have similar molecular weight and hydrophobicity. Characterization of the metal-binding capacities of such fractions could offer valuable insight that is needed to improve predictions of the extent of metal transport in copper tailings wasteland soil amended with organic wastes. Specific knowledge of metal-binding characterisics of bio-solids derived dissolved organic matter could also be helpful in predicting the feasibility of remediating metal-contaminated soils by amending them with bio-solids.

Characteristics of dissolved organic matters that influence metal binding include the types of functional groups present, the arrangement of those groups with respect to one another, and the size of the "molecule" they are part of. Leenheer (1981) developed a fractionation and isolation scheme that uses XAD-8 resin chromatography to separate dissolved organic compounds into hydrophilic and hydrophobic components. Hydrophilic compounds in natural organic matter are likely to include simple organic acids, polyhydroxy phenols, carbohydrates, amino acids, and amino sugars. Examples of compounds that would be found in hydrophobic fractions include phenols, hydrocarbons, fats, nucleic acids, and quinones.

Using this approach, Guggenberger et al. (1994) reported that the Cr- and Cu- binding abilities of hydrophilic

acids collected from water percolated through a Spodosol exceeded those of hydrophobic acids by two to eight times. The molecular weight (MW) distribution of dissolved organic compounds may also be correlated with metal-binding behavior. But investigations of the metal-binding capacity of dissolved organic compounds with different MWs are few. In one study, Kuiters and Mulder (1992) observed that low-MW DOM was responsible for 50 to 99% of the Cu-binding in litter extracts of both deciduous and coniferous trees.

The binding capacities of various soil-derived organic compounds with trace metals (transition metals such as Cu and Ni and heavy metals such as Pb, Cd) have been studied by a variety of techniques, including metal-ion retention by cation-exchange resins (Crosser and Allen, 1977), dialysis (Zunino and Martin, 1977), gel permeation chromatography (Dudley et al., 1987; Kuiters and Mulder, 1992), and ISE, ion-selective electrode (ISE) (Breault et al., 1996). In the ISE technique, the metal-binding ability of DOM is assessed by adding a metal ion to a DOM solution and then measuring the concentration of free metal ions in the solution with an ISE. Fitch et al. (1986) reported that a Cu_2^+-ISE permits measurements at low concentrations of the metal ion (as low as pCu 8). The low determination limit of this method is important in the investigation of natural systems where metal concentrations in aqueous phase and the percentage saturation of organic ligands by metals can be very small.

Therefore, the purpose of this study was to quantitatively compare the effect of DOM derived from fresh manure and manure compost on the sorption of Cd on a copper tailings wasteland and a normal farmland soil and to investigate the effect of DOM concentration and pH on Cd sorption by the two soils. This would provide information for assessing the potential of fresh manure and its compost DOM in facilitating metal transport in copper tailings wasteland normal farmland soils.

MATERIALS AND METHODS

Soil sampling

Tongling city is located between 30° 45' 12" N and 31° 07' 56" N and 117° 42' 00" E and 118° 10' 06" E. The city is well known for its large number of copper mines, and has a very long history of mining activities. Ecological restoration of the tailings is in its infancy in this region.

The positions of the sampling sites were recorded using a Global Position System (GPS) and landscape and vegetation were recorded by digital camera (Fuji Finepix 6900 Zoom). A copper tailings wasteland (Typic Ustochrepts) and a local normal farmland soil samples (Typic Acrorthox) were taken from the top 20 cm soil. Three tailing samples were collected at each sampling site. After removing the plant cover (if there was any), the tailings were sampled using a stainless steel shovel. About 2 kg of tailings packed in a plastic bag comprised one sample of tailings.

Preparation of soil and soil samples for chemical analysis

The copper tailings wasteland and local normal farmland soils sam-

Table 1. The chemical properties of copper tailings wasteland soil and normal soil.

Sample	pH	Total N (g kg^{-1})	Total P (g kg^{-1})	Total K (g kg^{-1})	Organic matter C (g kg^{-1})	Cu (mg kg^{-1})	Cd (mg kg^{-1})	Zn (mg kg^{-1})	Pb (mg kg^{-1})
A	6.81	3.21	0.11	1.56	0.50	834.75	6.80	228.20	38.85
B	7.84	1.24	0.12	10.02	13.61	25.45	0.23	43.06	13.46

A: Soil samples were taken from copper tailings wasteland;
B: Soil samples from local normal farmland soil.

Table 2. The chemical properties of fresh manure and manure compost.]

Sample	pH	Total N (g kg^{-1})	Total P (g kg^{-1})	Total K (g kg^{-1})	Organic matter C (g kg^{-1})	Cu (mg kg^{-1})	Cd (mg kg^{-1})	Zn (mg kg^{-1})	Pb (mg kg^{-1})
A	6.84	15.2	120.11	25.21	556.64	76.21	2.31	222.21	28.11
B	7.92	9.1	129.12	30.24	430.12	89.24	2.72	243.24	30.12

A: Samples were taken from fresh manure;
B: Samples from manure compost.

Table 3. The characterization of dissolved organic matter (DOM) from fresh manure and compost.

DOM origin	pH	Cd g mg^{-1} DOC	Hydrophilic[#]			Hydrophobic[##]		
			HiA %	HiB %	HiN %	HoA %	HoB %	HoN %
A*	6.84	0.31	78.12a	59.43 b	12.26c	69.86a	4.82d	6.02d
B**	7.92	0.22	35.67b	19.81 c	7.79cd	50.21a	2.31d	23.14b

*Samples were taken from fresh manure.
**Samples from manure compost.
[#]HiA, hydrophilic acid; HiB, hydrophilic base; HiN, hydrophilic neutral.
[##]HoA, hydrophobic acid; HoB, hydrophobic base; HoN, hydrophobic neutral.
Means followed by the same letter within each column are not significantly different at P 0.05.

ples were taken to the laboratory and air dried. Large pieces of plant debris and other particles were removed. Soil samples were air-dried, ground to firstly pass through a 2 mm sieve, and sub-samples (200 g) were then grinded and passed through a 1 mm sieve and stored in plastic bottles for the determination of pH and bio- available nutrients; while sub- samples were passed through a 100 m sieve for determination of total nutrients and metals. Fresh manure and compost were collected from the Shantian Milch Cow Garden in Nanjing City, Jiangsu Province, PR China, and stored at 4°C until used.

The compost was mature compost produced from our previous composting experiments using the above fresh manure (Li and Huang, 2005). Selected physicochemical properties of the soils, fresh manure, and compost are given in Table 1 and 2. Soil Soil texture was determined by using the pipette method (Gee and Bauder, 1996). Sample pH was quantified, using a suspension of 1:1 (solid to water) for soil and 1:5 for organic waste, with an Orion (Beverly, MA) 902A Ionanalyzer. Total N was determined by the Kjeldahl digestion–distillation method (Bremner, 1996).Total P was determined by $H_2 SO_4$–$HClO_4$ digestion and analyzed by the molybdenum blue color method (Kuo, 1996). Total K was determined according to Black (1965). The organic carbonate content was calculated from the amount of CO_2 released by reaction with HCl (Loeppert and Suarez, 1996). Total metal contents were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a Perkin Elmer Optima 2000 DV following HNO_3-$HClO_4$ digestion.

Extraction and characterization of dissolved organic matter

Fresh manure and compost were extracted with double-distilled water using a solid to water ratio of 1:10 (w/v) on a dry weight basis on a reciprocal shaker at 200 rpm for 16 h at 20°C. After the suspension was centrifuged at 12000× g for 20 min, the supernatant was filtered through a 0.45 μm sterilized membrane (GN-6 Metrice; Gelman Sciences, Ann Arbor, MI). The filtrates were stored at 4°C and analyzed for pH (Orion 902A Ionanalyzer), total dissolved organic carbon (DOC) using a total organic carbon (TOC) autoanalyzer (TOC-5000A; Shimadzu, Kyoto, Japan) and Cd with a FAAS (Varian Spectra AA-20). The selected properties of the DOM are listed in Table 3.

Dissolved organic matter obtained from fresh manure and manure compost was characterized by fractionation into hydrophilic and hydrophobic fractions using the method developed by Leenheer (1981), with slight modification. Dissolved organic matter solution was first pumped through the first glass column (Column I, 20 x 230 mm) packed with XAD-8 resin (Fluka, Buchs, Switzerland) by a peristaltic pump at a flow rate of 2 mL min^{-1}. Hydrophobic base (HoB) of DOM sorbed on the XAD-8 resin was then backflush-eluted with 0.25 bed volume of 0.1mol L^{-1} HCl, followed by 1.5 bed volume of 0.01 mol L^{-1} HCl. The effluent from Column I was acidified to pH 2 with 6 mol L^{-1} HCl and then passed through the second XAD-8 resin-packed column (Column II) followed by a 0.01 M HCl rinse. Hydrophobic acid (HoA) retained in Column II was desorbed by backflush elution with 0.1 mol L^{-1} NaOH. The effluent
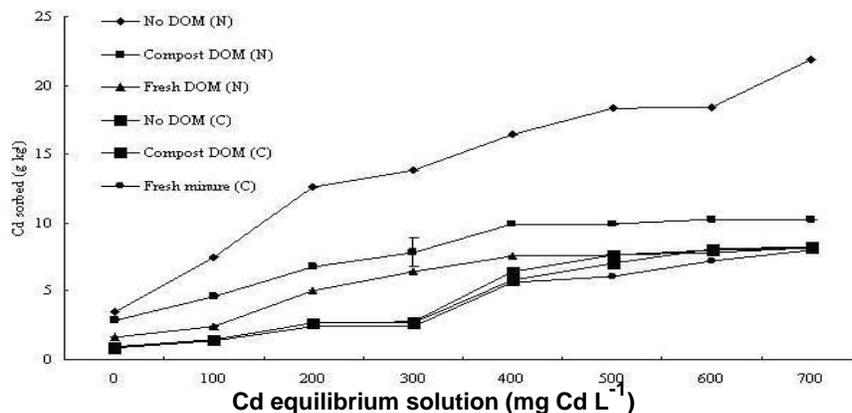
Figure 1. Cadmium sorption isotherm of the normal farmland soils (N) and copper tailings wasteland soils (C) with and without the addition of 400 mg C L^{-1} of the fresh manure or compost dissolved organic matter (DOM).

through Column II was considered the hydrophilic fraction. The hydrophobic neutral fraction sorbed on the XAD-8 resin was calculated by subtracting the sum of HoB, HoA, and hydrophilic fraction from the total input DOC of the extract. The effluent that contained only the hydrophilic fraction from Column II was pumped through a third column (Column III) containing a strongly acidic cation exchange resin, Dowex-50wx8 resin (Fluka).

Hydrophilic base (HiB) was desorbed by forward elution with 1.0 mol L^{-1} NaOH from Column III. The effluents from Column III containing hydrophilic acid (HiA) and neutral (HiN) were then passed through a weakly basic, polyamine anion exchange resin, Biorad (Hercules, CA) AG 3x4 (Column IV). The HiA fraction retained in this resin was eluted with 1 mol L^{-1} HNO₃. The HiN was obtained from the effluent of Column IV. Each fraction obtained was determined for DOC.

Cadmium sorption experiment

Preliminary experiments were performed to determine the time required to achieve equilibrium for Cd sorption by the soil samples, which could be reached after 1.5 h. Therefore, an equilibrium time of 2 h was chosen in the present study. A soil sample of 0.4 g was weighed into a 50 mL polyethylene centrifuge tube and shaken with 20 mL of 0.01 mol L^{-1} KCl solution (background electrolyte for maintaining stable ionic strength) at 200 rpm for the sorption experiment. The KCl solution consisted of 0, 12.5, 25, 50, 100, 200, 400, 600, and 800 mg Cd L^{-1} as CdCl₂ with or without the addition of 300 mg C L^{-1} of DOM derived from fresh manure and its compost. All treatments were done in triplicate. All suspensions were adjusted respectively to pH 7 for the copper tailings wasteland soil with HCl or NaOH to minimize the error caused by pH fluctuation. The soil suspensions were shaken on a reciprocal shaker at 200 rpm for 2 h. The tubes were then centrifuged at 3500× *g* and filtered through Whatman No. 2 filter paper.

Cadmium concentration in the filtrates was determined with an ICP-OES. The quantity of Cd sorbed was calculated by subtracting the Cd in the equilibrium solution from total initial Cd. Another series of experiments was performed to evaluate the effect of DOM concentration on Cd sorption and desorption. A soil sample of 0.4 g was shaken with 20 mL of solution containing 40 mg Cd L^{-1} and different DOM concentrations of 0, 50, 100, 150, 200, 300 and 400 mg C L^{-1} (a concentration range found in soils receiving slight to heavy application of organic waste) at a background ionic strength of 0.01 mol L^{-1} KCl. The rest of the procedure, including pH

adjustment and centrifugation, were the same as the above experiment. The residues obtained after sorption were washed three times using double-distilled water, then 20 mL of 1 M MgCl₂ (pH 7) was added into the tube and shaken for 2 h. After the suspension was centrifuged and filtered, Cd in the filtrate was determined to obtain desorption of Cd previously sorbed by soils.The effect of pH on Cd sorption in the presence and absence of DOM was also performed in this study.

A soil sample of 0.4 g was shaken with 20 mL of solution containing 0.01 M KCl and 40 mg L^{-1} of Cd in a centrifuge tube with or without the addition of 400 mg C L^{-1} DOM. The pH of all suspensions was adjusted to various levels ranging from pH 2 to 10. In this study, the concentration of DOM-born Cd was much lower than the Cd concentration added as CdCl₂, so that the effect of DOM-born Cd on the Cd sorption experiment was negligible.

RESULTS AND DISCUSSION

Cadmium sorption isotherm

Figure 1 gives the equilibrium isotherms of Cd sorption of the copper tailings wasteland soils with or without the addition of DOM derived from fresh manure or its compost. The amount of Cd sorbed increased with an increase in equilibrium Cd concentrations and eventually attained a plateau value at high equilibrium Cd concentrations. The sorption capacity of the normal farmland soil for Cd was much higher than that the copper tailings wasteland soil at same equilibrium concentration of Cd, which might be because of the higher pH, higher organic matter C (Table 1). More variable negative charges and sorption sites were formed in the soil of higher pH and higher organic matter C contents, which favor Cd sorption. In the presence of DOM, the Cd sorption capacity decreased markedly for both soils, but the effect on the copper tailings wasteland soil was greater than that on the normal soil. Dissolved organic matter derived from mature compost had a smaller effect in reducing the sorption capacity for Cd than that of fresh manure for both soil types. The Cd sorption data were plotted according to the

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Table 4. Parameters of the Freundlich equation for Cd sorption by soils in the presence and absence of 400 mg C L^{-1} of dissolved organic mater (DOM).

Parameter	Copper tailings wasteland soil			Normal farmland soil		
	No DOM	Compost DOM	Fresh manure DOM	No DOM	Compost DOM	Fresh manure DOM
K	52.1	32.1	10.7	2776	379	47.9
1/n	0.786	0.850	1.003	0.301	0.552	0.873
r^2 *	0.967	0.991	0.995	0.942	0.958	0.930

*Significant at p 0.01.
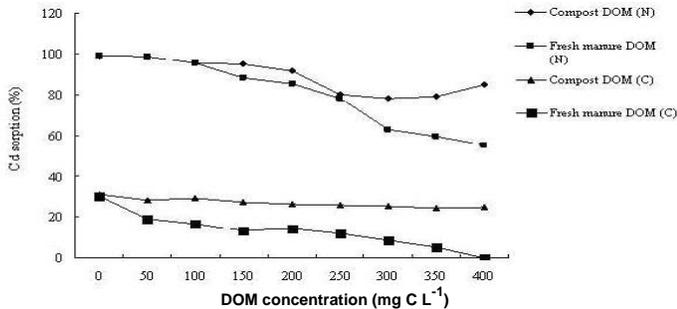
Figure 2. Effect of concentration of dissolved organic matter (DOM) from fresh manure and composted manure on the cadmium sorption onto the copper tailings wasteland soils (C) and normal farmland soils (N) with initial Cd concentration of 40 mg/L.

linear Freundlich equation:

$$Log(x/m) = \log K + 1/n \log C$$

Where x/m is the amount of Cd sorbed (mg kg^{-1}), C is the equilibrium Cd concentration (mg L^{-1}), K is the equilibrium partition coefficient, and 1/n is the sorption intensity.

The Cd sorption isotherms conformed better to the Freundlich equation than to the Langmuir equation (data not shown) as indicated by the high values for the correlation coefficient of determination (r^2 > 0.948). Other studies also reported that the Freundlich equation described Cd sorption for soils better than the Langmuir equation (Atanassova and Okazaki, 1996).The Cd sorption behavior of the copper tailings wasteland soil can be described better by the Freundlich model than that of the normal soil. The calculated parameters of the Freundlich sorption isotherms are listed in Table 4. Generally, the higher the sorption intensity parameter (1/n) is, the lower the binding affinity of soil with Cd. The equilibrium partition coefficient (k) is positively related to the Cd sorption capacity of soils. The Cd sorption capacity and the binding affinity of the normal farmland were higher than that of the copper tailings wasteland as indicated by the higher K but lower 1/n value. The Cd sorption capacity and binding energy calculated for the two soils with the DOM treatments decreased in the following order: no DOM > compost DOM > fresh manure

DOM. The role of DOM in reducing Cd sorption could be due to the formation of soluble Cd–organic complexes, because Cd can be strongly bound by organic matter (Stevenson and Ardakani, 1972).

Dissolved organic matter concentration effect

Increasing the DOM concentration caused a significant reduction on the sorption of Cd by both soils (Figure 2). A significant negative linear correlation between DOM concentration and Cd sorption was observed for these treatments at the DOM concentration range studied r = -0.948 and - 0.925 for fresh manure DOM and compost DOM in the copper tailings wasteland soil, respectively; r = - 0.990 and - 0.996 in the normal soil, respectively [p < 0.05]. Sorption was decreased by 7.3% and 12.4% with a DOM increment of 100 mg C L^{-1} for compost and fresh manure DOM, respectively, in normal soil, and correspondingly 1.5% and 6.8% in copper tailings wasteland soil, based on the linear regression equations obtained in (Figure 2).

When DOM concentration added was raised to 400 mg C L^{-1}, there was no Cd being sorbed by the copper tailings wasteland soil with fresh manure DOM treatment, while in normal soil Cd sorption was reduced by 47% and 28% for fresh and compost DOM treatments, respectively. Fresh manure DOM had a more significant effect in reducing Cd sorption than that of compost DOM and the effect was more pronounced for normal soil than copper tailings wasteland soil.

The origin and concentration of DOM affected not only the Cd sorption of the two soils, but the desorption of Cd sorbed previously in the sorption study (Figure 3). A relatively higher desorption was found for Cd sorbed in the presence of a higher concentration of DOM, especially for fresh DOM treatment. This might result from a stronger binding affinity of Cd with fresh DOM, and as a result it hinders partly the precipitation of Cd as CdSO$_4$ under such a high-pH condition, as compared with compost DOM. In addition, it was assumed that the higher affinity of the Cd–compost DOM to the soil matrix may also contribute to this phenomenon. This implied that Cd mobility might be facilitated greatly in the soil receiving DOM, especially for fresh manure DOM, because of the reduction of Cd sorption onto soil and the relatively ready

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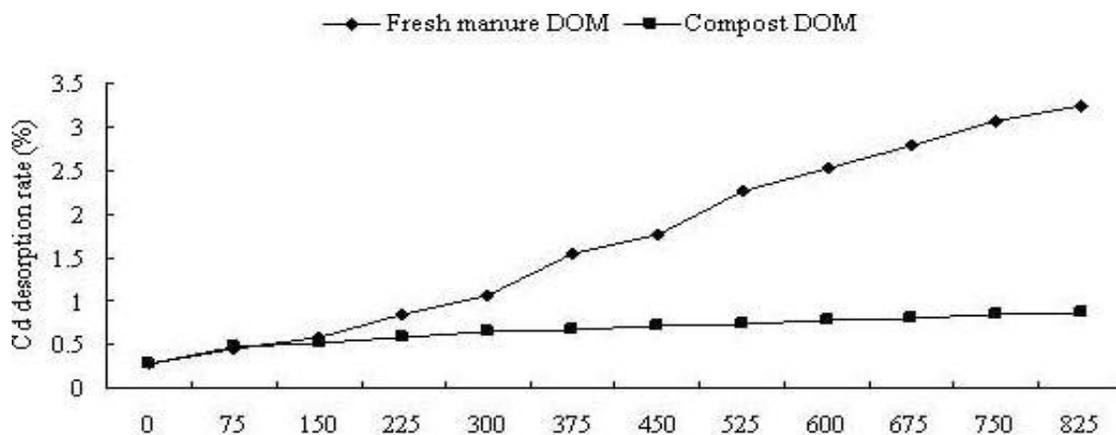
Figure 3. Desorption of Cd sobbed under the addition of various dissolved organic matter (DOM) concentration and with initial Cd concentration of 400 mg/l by copper tailings wasteland soil through 1 mol/l (pH = 7) extraction for 2 h.

desorption of Cd sorbed previously in the presence of DOM.

The differences in Cd sorption and desorption behavior caused by DOM of different original materials appeared to be closely related to the chemical components of DOM. Manure compost DOM contained a relatively greater amount of high molecular weight hydrophobic fractions, especially hydrophobic acid (HoA) and hydrophobic neutral (HoN), but fewer hydrophilic fractions, especially hydrophilic base (HiB) and hydrophilic acid (HiA), than that of sludge DOM (Table 3). The Fourier transform infrared (FT–IR) spectrum showed that the hydrophobic fraction had a considerably more aromatic acids or aromatic phenols, while the hydrophilic fraction was richer in carboxyl and polyhydroxyl groups (Wu, 2004). DOM of compost materials appeared to have more C–N and C–O groups of a chelating feature, possibly from organic acid, amino acid, and amines, than compost DOM, especially for the HiA, HiB, and HoA fractions (Zhou, 2000). Keefer et al. (1984) pointed out that the HiB fraction was mainly comprised of N-containing groups including most amino acids, amino sugars, low molecular weight amines, and pyridine, while the HiA fraction contained the components of the –COO functional group, such as uronic acids, simple organic acids, and polyfunctional acids, which resulted in the higher affinity of Cd with HiB. In addition, many researchers also revealed that hydrophobic fractions of DOM bind more strongly on soils and minerals than the hydrophilic fractions (Kaiser et al., 1997). Liang et al. (1996) found that increased sorption of the DOM extracted from the composted manure is probably due to an increase in molecular weight of the major DOM components. It is reasonable to presume that the reduction of mobile DOM in the soil receiving manure compost DOM was due either to sorption of greater amounts of compost DOM in comparison with fresh manure DOM by the soils, or the formation of a Cd–compost DOM complex. The Cd–compost DOM complex could be sorbed repeatedly by

the soils, although DOM sorption by soils was not measured in this study.

In contrast, fresh manure DOM contained more HiB fraction, which was not readily sorbed by soils but could strongly associate with Cd. Thus, fresh manure DOM had a stronger capability to reduce Cd sorption by soils than did compost DOM.

pH effect

As shown in Figure 4, the presence of fresh manure DOM could counteract partially the effects of pH change on Cd sorption by both normal farmland and copper tailings wasteland soils. Increasing pH from 2 to 8 caused a sharp rise in Cd sorption for both soils receiving no fresh manure DOM. A sharp change in Cd sorption was found between pH 4 and 5. Maximum Cd sorption was obtained at pH > 5.8, in which more than 99% of Cd could be sorbed by the two soils of different organic carbon content. This was caused mainly by the formation of $Cd(OH)_2$ at pH > 5.8, because in the present experiment, the pH at which $Cd(OH)_2$ precipitation occurred was calculated as 5.77 based on the $Cd(OH)_2$ solubility product of 2.2×10^{-20}. Addition of fresh manure DOM reduced the Cd sorption at each respective pH for both soils. The reduction was especially obvious with an increase in pH, which implied that DOM could bind with Cd more readily and strongly at a higher pH. However, at pH > 6.8, Cd sorption unexpectedly decreased with increases in pH in the presence of sludge DOM for both soils.

Hydroxyl groups bound with Cd could be easily ionized in high pH to yield a negative charge. Consequently, the Cd–DOM complex bearing a negative charge would be repelled by the soils of the same charge through which Cd sorption was reduced. Other workers have also reported different binding forms of Cd with organic ligands
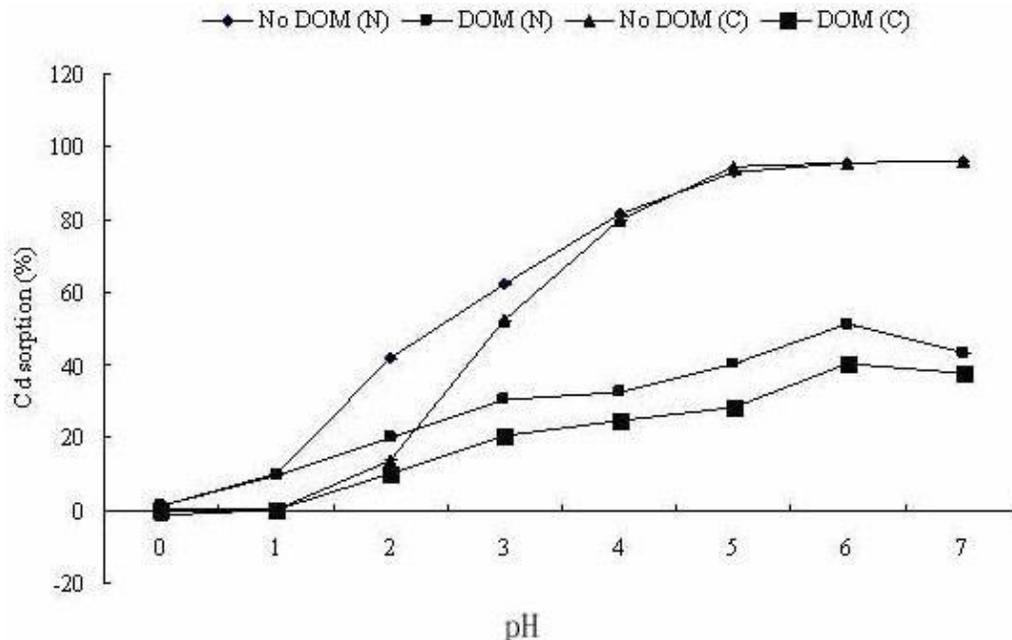
Figure 4. Effect of pH sorption onto the normal farmland soils (N) and copper tailing wasteland (C) with or without the addition of 300 mg Cl^{-1} of fresh manure dissolved organic matter (DOM).

in various pH levels (Messori et al., 1997). Besides, the dissolved macromolecules exhibited different structures in aqueous solution in various pH conditions, which could modify the exposed surface area and alter the functional group chemistry of DOM. It has been observed that organic molecules dispersed into aggregates of smaller size (<0.1 μm) at high pH and that such constituents exhibited a high affinity toward Cd (Myneni et al., 1999). Thus, it is clear that Cd sorption by soils was simultaneously affected by both pH and DOM concentration at a lower soil pH. At a high-pH condition (>6.8), however, Cd sorption was predominantly affected by DOM due to a strong binding affinity of DOM with Cd.

Conclusion

Our results confirmed that addition of DOM derived from fresh manure and manure compost reduced the sorption of Cd by both a normal farmland and a copper tailings wasteland soil. The Cd sorption isotherm in the presence of either fresh manure or compost DOM could be well described with the Freundlich equation. The values of *K* of the Freundlich equation of fresh manure DOM were less than those of compost DOM for both soils, indicating that fresh manure DOM had a greater effect on reducing soil Cd sorption capability than did compost DOM. This could be attributed to the higher hydrophobicity of compost DOM than fresh manure DOM.

There was less Cd being sorbed as DOM concentration increased. Unlike Cd sorption in soil without DOM addi-

tion, Cd sorption was unexpectedly decreased at pH > 6.8 with an increase in pH in the presence of fresh manure DOM. Therefore, application of fresh manure and com-post or C-rich organic waste on copper tailings wasteland soil and the liming of fresh manure-amended soil at pH > 6.8 should be approached cautiously, because this may facilitate formation of soluble DOM–metal complexes and the leaching loss of metals from surface soils, especially for Cd. In the same way, this means that the hyperaccu-mulator can remove much more heavy metal from the copper tailings wasteland soil in the phytoremediation by amended C-enriched organic wastes into soil.

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