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Leaching of Copper from an Industrial Sludge Applied on a Soil Column

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With the development of industry, more and more industrial wastes are generated during production processes. One of the most serious related problems is the generation of industrial sludge that contains various toxic metals. Unsuitable disposal of the industrial sludge may lead to the environmental risk of heavy metals leaching to surface and ground water. Therefore, the leaching tests, which allow the determination of the leaching behavior of pollutants, play a major role in assessing the environmental impact of land application of industrial sludge to groundwater quality and ecosystem health. The study of leaching behaviors of metals is an important way to obtain valuable information about the chemical speciation of contaminants and their potential environmental risks (Li et al., 2001).

Leaching is the process by which contaminants are transferred from a stabilized matrix to liquid medium, such as water or other solutions. Generally, batch experiment and column experiment are the two methods in common use to study leaching processes. The release of heavy metal cations to the water phase depends on their affinity to bind to reactive surfaces in the soil matrix and pore water. Evidence is accumulating that free ion activity in soil pore water is one of the key factors controlling metal bioavailability to soil microorganisms and plants (McGrath et al., 1999), although it usually accounts for only 0.5 to 7% of the total amount of soil-borne heavy and transition metals (Lake et al, 1984). For heavy metals leaching, different fractions have different leachability. The composition of the industrial sludge importantly governs the release of heavy metals (Kuo et al., 2005; Li et al., 2001). Sequential extraction methods have often been used to study the speciation and possible associations between metals and soil or sediment components because they can help to characterize the leaching behavior by dividing all the metal into fractions. At present, a number of schemes have been proposed to fractionate metals on the basis of extractability in various chemical reagents either discretely or sequentially (Roy and Cartledge, 1997; Tack and Verloo, 1995). Of these methods, the sequential extraction presented by Tessier et al. (1979) has been widely used in soil and sediment studies.

Tianjin Copper Electrolytic Factory manufactures copper for many years. The sludge generated from copper production and wastewater treatment processes, which contains high level of copper, is piled up at an open place near the factory. In order to

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find out the environmental impact of this sludge disposal to soil and groundwater, we tested three solutions, i.e. DIW (deionized water), DOC (dissolved organic carbon) solution, and AR (simulated acid rain) on Cu leaching from the sludge using column experiment. The main objectives of the present study were to (i) investigate the downward movement behavior of copper from the industrial sludge; and (ii) characterize the difference of Cu chemical forms before and after leaching test, and determine which form mainly accounted for the release of Cu from the sludge.

MATERIALS AND METHODS

Sludge sample was obtained in October of 2004 from Tianjin Copper Electrolytic Factory, China. Dewatered sludge was sampled from the landfill place. The sample was air dried and passed through a 60 mesh sieve. Soils used in the column experiments were taken from the garden in Nankai University, Tianjin, China. Some properties of the sludge and soil are summarized in Table 1.

Table 1. Some characteristics of sludge and soil.

property	pH	OC[a], %	Cu mg/kg	Zn mg/kg	Mn mg/kg	Pb mg/kg	Cr mg/kg	Cd mg/kg
sludge	8.10	13.48	68500	2310	844	335	465	112
soil	7.11	2.48	56	nd	nd	nd	nd	Nd

a: organic carbon content. nd: not detected.

Polyvinyl chloride (PVC) tube with an inner diameter of 75 mm and a length of 1.0 m was selected as the experiment device. The tube was packed uniformly with air-dried soil to an 80-cm height and 137 g sludge (about 10-cm height) was incorporated on the top of the soil column. A layer of glass wool was placed at the bottom of the column, minimizing the dead end volume and preventing outflow of sludge particles. Each column was leached with one of the three leachants. The selected three solutions were DIW (Millipore Ultra-pure Water System), DOC (Humic acid, Fluka, Switzerland) solution with 10 mgC/L, and AR (simulated acid rain, concentrated H_2SO_4: concentrated HNO_3= 4:1 (v/v), adjust pH to 3.90±0.02). 200 mL of solution was added to the top of each treated column every day. Each treatment has three duplicates. Three columns packed only with about 90-cm height soil served as the control, which was eluted with DIW.

For the 100-d experiment, leachant was added to each column every day, and leachate was collected every day for Cu analysis (this continuous watering 100-d experiment is called Experiment I in this paper). In another set of 100-d experiment, from day 51 to day 80, no solution was added to the soil columns (this period was called "un-watered period", and this discontinuous watering experiment is called Experiment II). Solution application resumed from day 81 to 100. A 1 L cone bottle collected leachates every day and the volume of leachate was measured .The leachate was filtered through 0.45μm cellulose filter and acidified with two drops (0.1 mL) concentrated HNO_3 before copper analysis.

After leaching experiment, the soil column was dissected. The sludge was sliced from the top of the soil column, and the remaining soil column was sliced from the top to bottom into 9 layers, the thickness of which were 5, 5, 5, 10, 10, 10, 10, 10, and 15 cm, respectively. The sludge and soil were air-dried, crushed. The speciation of copper in the sludge was analyzed by sequential extraction procedure (Tessier et al., 1979). In soil samples copper was extracted by DTPA solution, which consisted of 0.05 M DTPA, 0.1 M triethonalamine (TEA) and 0.01M $CaCl_2$, and the pH of the solution was adjusted to 7.3 with 6 N HCl. The dry soil to liquid ratio was 1: 5, and the mixture was shaken for 2 h at room temperature. After centrifugation, the supernatant was filtered through 0.45 μm membrane for Cu analysis. Copper and other heavy metals in this study were measured by ICP-AES (IRIS Intrepid II XSP, Thermo Electron Corporation).

RESULTS AND DISCUSSION

Variation of copper concentration in leachate of soil columns for 100-d continuous leaching experiment was presented in Figure 1. It showed that, variation curves of three leachants were similar. That is, there were two peak values of Cu concentration during 100-d leaching experiment. The first one appeared after about 10-day continuous leaching, and the second one appeared on day 75. Concentration of Cu in leachate increased with the leaching time in the first 10 days. The peak values of Cu concentration in the leachates were 61.5, 86.8 and 157.9 μg/L for DIW, DOC and AR leachants, respectively. After that, Cu concentrations declined from day 13 to day 50. From day 51 Cu concentration in the leachates increased again, and the second peak values in the leachates were 369.2, 573.4 and 632.3 μg/L for DIW, DOC and AR leachants, respectively.

It suggested that the release of Cu from the sludge occurred in two stages. In the first leaching stage, leached Cu was mainly the copper existed as exchangeable fraction and free ion species. After being leached out, these mobile Cu began to adsorb and desorb in the soil column with the downward movement of leachate, and on day 10 Cu concentration in the leachate reached the first peak value. During the second stage, Cu was released from different fractions such as carbonates-bound, Fe/Mn oxides-bound, organically-bound and residual copper. Kuo et al. (2005) found the proportion of copper in the organic matter and residual fractions increased markedly whereas those in the Fe/Mn oxides, exchangeable and carbonate fractions declined considerably after the sludge was extracted with sulfuric acid. Chang and Liu (1998) used ammonia solution to leach copper from an industrial sludge and found copper was mainly leached from both the organic-bound and residual fractions. A comparable amount of copper was shifted from those fractions so that the second peak values appeared on day 75. Compared with other fractions of soil-borne heavy metals, fractions in exchangeable and free ion species usually account for only 0.5 to 7% of the total amount (Lake et al, 1984), which could explain why the second peak values were higher than the first ones. A 70-day leaching was favorable for the formation of mobile copper from those fractions.

Copper concentrations in different-depth soil layers after 100-d experiment are shown in Figure2. It shows that AR could release more Cu from the sludge and make much more Cu migrate downward. After release from the sludge by the three leachants, most Cu existed in upper layers in soil columns.

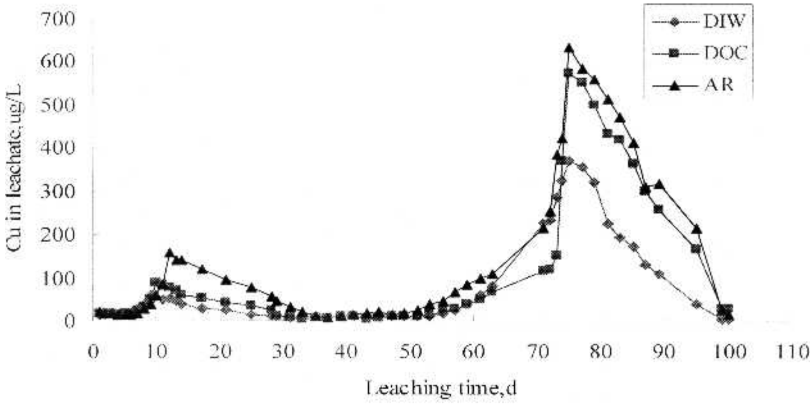

Figure 1. Cu concentration in the leachates in 100-d experiment (Experiment I)

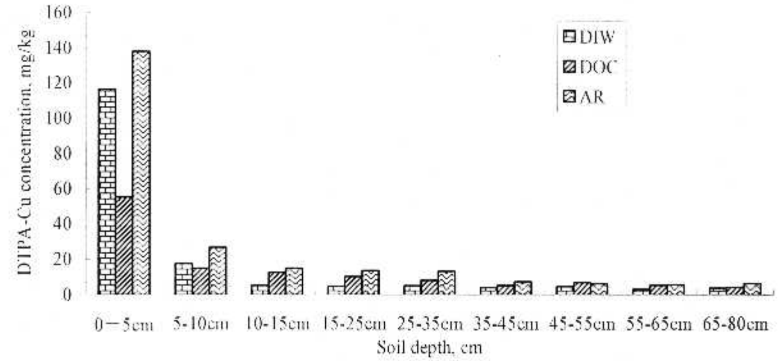

Figure 2. DTPA extractable Cu in soil layers in Experiment I.

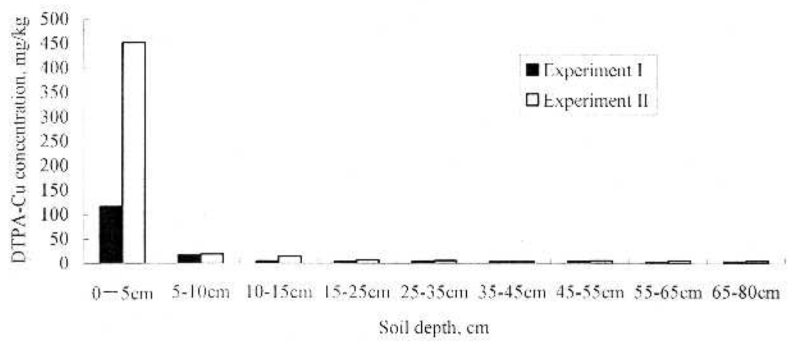

Figure 3. Comparison of Cu content in soil layers leached by DIW.

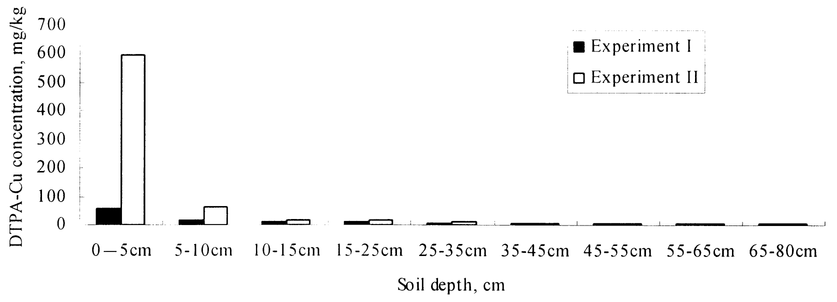

Figure 4. Comparison of Cu content in soil layers leached by DOC.

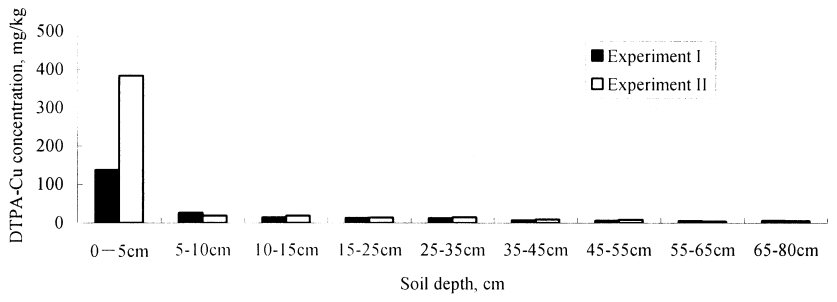

Figure 5. Comparison of Cu content in soil layers leached by AR.

Generally, heavy metals in the soil are rapidly retained as insoluble compounds and adsorbed to soil surface (Loganathan and Hedley 1997). In our previous works, downward movement of cupric ion in soil column was determined (Xu et al., 2005). Concentration of exchangeable copper decreased drastically from the top layer to the bottom, suggesting that soluble copper was adsorbed to soil significantly when it entered into soil. This is consistent with the results in this study. Most released soluble copper existed in the top layer of the column (Figure 2). Tam and Wong (1996) also reported copper could be more strongly adsorbed in soils than other heavy metals such as zinc, manganese and cadmium.

In order to find out the effect of 30-d un-watered period on the copper release from the sludge, we compared DTPA extractable Cu concentrations in soil layers in Experiment I and Experiment II. Figure 3~ Figure 5 gave the DTPA-Cu concentrations in different soil layers eluted with the three leachants. From these figures we can see that, significant difference of copper concentrations in soil layers between Experiment I and Experiment II presented only in the top 0-5 cm soil layers, while in other layers there were no difference. This indicated that, a 30-d un-watered period could obviously enhance copper concentration in the top layers of soil column, which suggesting the increase of copper release from the sludge.

Chen et al. (2003) investigated the phosphorus and copper leaching from dredged sediment with soil column experiment. They found that a 15-d un-watered period may promote the production of available phosphorus and the formation of mobile copper in the sediment layer. They assumed un-watered conditions may accelerate the decomposition of organic matter. Altaher (2001) also reported that peaks of copper in the leachate were observed after rain events, especially after an extended dry period. Drying the soil will increase the copper and TOC mobility possibly due to change in the structure of the organic substances present in the soil. As a result copper concentration increased in the top soil layers.

Copper concentrations in the leachates in Experiment I and Experiment II from day 81 to day 100 were compared, as shown in Figure 6~Figure 8. It showed that in the last 20 days, Cu concentration in the leachates varied slightly, which ranged from 1.3 to 32.7 μg/L. From the results above it can be concluded that after an "un-watered period", Cu release could be enhanced from the sludge. However, most released Cu was retained in the upper soil layers, which resulted in the increasing Cu content in the top 0-5 cm soil, but no significant difference in the leachate in the last 20 days between Experiment I and Experiment II.

Most studies dealing with sludge containing heavy metals discuss total metal concentration without attempt to evaluate various chemical forms in which metals exist. The chemical forms of Cu in the solid phase can greatly influence its fate in terms of leaching and subsequent transport (Clevenger 1990). Copper concentrations in different chemical forms in the sludge before and after leaching were shown in Table 2. It was founded that Fe/Mn oxides-bound copper was the main fraction in the unleached sludge which occupied 67.3% of the total Cu. Both residual fraction (25.4%) and organic matter-bound Cu (6.9%) constituted the other fractions; while exchangeable and carbonates-bound Cu only accounted for 0.005% and 0.41% of total Cu concentrations, respectively. After leaching by different solutions, the fractionation changed.

Table 2 gives changes of chemical forms of Cu before and after leaching. It showed that carbonates-bound Cu is unstable and easily transferred to soluble phase. In the unleached sludge its content was 272.0 mg/kg, while after leaching its content ranged from 8.6 to 15.8 mg/kg. Transfer of Fe/Mn oxides-bound Cu to mobile phase contributed to the most amount of Cu release from the sludge, which content varied from 44793 mg/kg in the unleached sludge to a range of 30074 to 31884 mg/kg after

Table 2. Comparison of copper chemical forms in the sludge before and after leaching, mg/kg.

	Total	Exchange-able	Carbonates	Fe/Mn oxides	Organic	Residual
Unleached sludge	66600	3.1	272.0	44793	4615	16917
DIW (Exp I)	51544	6.9	15.8	30783	3921	16817
DIW (Exp II)	50265	7.6	9.3	30074	3719	16455
DOC (Exp I)	52513	8.3	11.5	31884	4026	16583
DOC (Exp II)	51890	8.0	8.6	31536	4235	16103
AR (Exp I)	51086	7.0	14.3	31121	3512	16432
AR (Exp II)	50145	6.8	13.2	31079	3227	15819

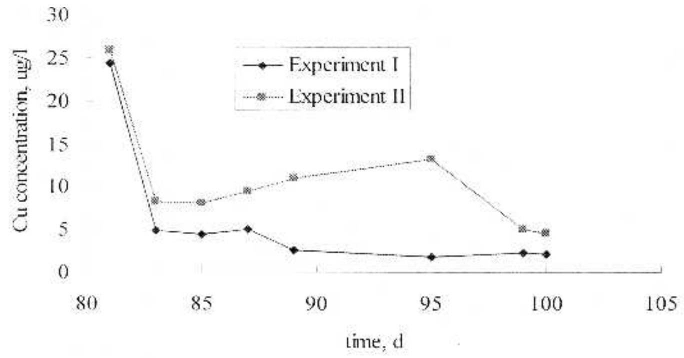

Figure 6. Copper in the leachate in the last 20d leached by DIW.

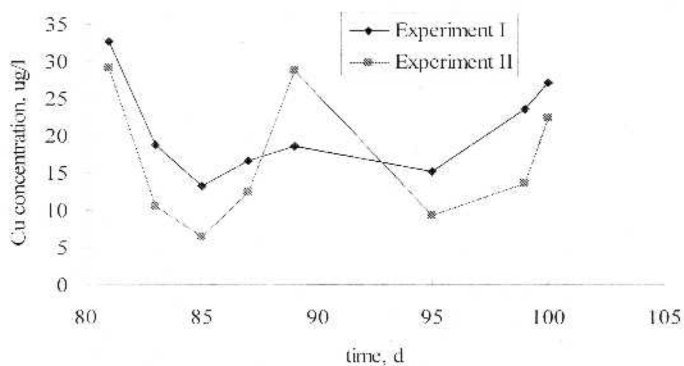

Figure 7. Copper in the leachate in the last 20d leached by DOC.

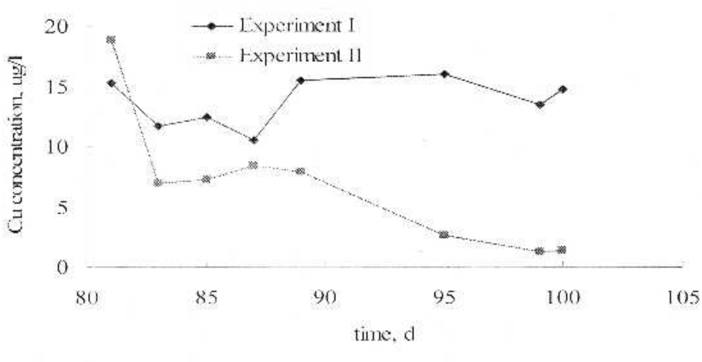

Figure 8. Copper in the leachate in the last 20d leached by AR.

leaching. Compared with continuous leaching (Experiment I), "un-watered period" (Experiment II) could enhance organic matter-bound and residual Cu release from the sludge, which resulted in the increasing Cu concentration in the top soil layers.

Leaching behaviors of copper from the industrial sludge showed that AR had higher

Cu concentrations in the leachates compared with DIW and DOC solutions. The 30-d un-watered period significantly increased DTPA-Cu concentration in the top 5 cm of soil columns, but had no significant effect in the subjacent soil layers. This also can be seen by the Cu concentrations in the leachates from day 81 to day 100 between Experiment I and Experiment II. Un-watered period has not significantly affected Cu concentrations in the leachates. Results from sequential extraction of the sludge indicated that, transfer of Fe/Mn oxides-bound fraction into mobile phase contributed to most amounts of Cu in the soil layers and leachates. Un-watered period could promote Cu release from organic matter-bound and residual fraction in the sludge.

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