COPPER MOBILITY IN SOILS AS AFFECTED BY SEWAGE SLUDGE AND LOW MOLECULAR WEIGHT ORGANIC ACIDS

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Copper is an essential micronutrient, but at increased concentrations, it quickly becomes toxic to plants, and remediation is needed. Because the land disposal of copper containing sewage sludge is increasing each year, there is a need to evaluate the mobility of copper in soil as affected by sewage sludge and low molecular weight organic acids (citric acid and oxalic acid). Copper mobility was studied in a Marvyn soil (fine-loamy, siliceous, subactive, thermic, Typic Kanhapludult) without or with 1 of 2 sewage sludges from the Birmingham, Alabama area. A total of 5 column experiments were performed. The columns were leached with solutions containing potassium sulfate (10^{-2} M/L) to maintain proper ionic strength, in addition to different combinations of copper, oxalic acid, and citric acid. The Cu^{2+} concentration in all applied solutions was 1000 mg Cu^{2+} per kg of solution. In the column experiments containing sewage sludge, the effluent copper concentration did not reach the influent concentration. In the column experiments without sewage sludge, the influent copper concentrations were easily reached in the effluent, independent of the addition of oxalic or citric acid. A batch equilibrium study showed that both sewage sludges could adsorb more than 50,000 mg of copper per kilogram of sewage sludge, compared with 1250 mg of copper per kilogram of Marvyn soil. This amount is so high that sewage sludges could possibly be used for copper detoxification in mine tailings or farm lands where copper pollution is a potential problem for vegetation. (Soil Science 2006;171:29–38)

Key words: Maximum adsorption, copper, breakthrough curves, HYDRUS-1D, Langmuir isotherms, sewage sludge, mine tailings.

UNLIKE for other heavy metals, minerals governing Cu^{2+} solubility in soils are not well known (Lindsay, 1979). Most of the Cu^{2+} minerals are more soluble than the soil Cu (copper adsorbed to soil) and will dissolve to form soil Cu (Lindsay, 1979; Alloway, 1995). Below pH 6.5, the ion Cu^{2+} will be the domi-

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nant copper species in soil solution, whereas $CuOH_2^0$ is the major solution species above pH 7. The hydrolysis species $Cu(OH)^+$ becomes significant between pH 6.5 and 7. Several Cu^{2+} complexes, inorganic and organic, also contribute to total copper in soil solution. Sulfate ($CuSO_4^0$) and carbonate ($CuCO_3^0$) complexes are important inorganic complexes, because, according to Lindsay (1979), at a concentration of $10^{-2.36}$ M SO_4^{2-}, activities of Cu^{2+} and $CuSO_4^0$ are equal, and at CO_2 pressure of 0.005 MPa, the activities of $CuCO_3^0$ and $Cu(OH)_2^0$ are equal. The contributions of the other inorganic complexes are negligible, and total inorganic copper in soil solution can be estimated by the following equation (Lindsay, 1979):

$$[Cu_{inorg}] = [Cu^{2+}] + [CuOH^+] + [CuSO_4^o] + [Cu(OH)_2^o] + [CuCO_3^o] \quad (1)$$

Reactions controlling Cu^{2+} in soil solution are similar to those controlling other micronutrients (Tisdale et al., 1993), such as precipitation-dissolution, plant absorption-exudation, and immobilization-mineralization. However, adsorption-desorption reactions are of the greatest interest because they most directly affect the levels of copper in the soil solution. Most organic complexes of copper are soluble in water and may not be subject to adsorption-desorption reactions. To determine if organic-copper complexes are adsorbed to the soil, concentrations of Cu^{2+} in solution are measured in the presence and the absence of an appropriate organic chelating agent (i.e., oxalic acid, citric acid, and sewage sludge), and the breakthrough curves are compared to establish which organic compound is retarding Cu^{2+} movement the most. McLaren et al. (1981) found that total solution copper concentrations were increased above equilibrium levels for Cu^{2+} by the presence of soluble organic complexes. McBride and Blasiak (1979) found that 99.9 % of total soluble Cu^{2+} was in complexed forms at pH 8. Hodgson et al. (1966) estimated that 99% of Cu^{2+} was organically complexed in calcareous soils. Stevenson and Fitch (1981) found that the amount of Cu^{2+} that can be bound to humic and fulvic acids is equal to the content of acidic groups. This corresponds to the sorption of from 48 to 160 mg of Cu^{2+} per gram of humic acid (Kabata-Pendias and Pendias, 1992). High sorption of Cu^{2+} by peat-muck soil and humic acid has been reported (McLaren et al., 1981). Besides humic and fulvic acids, soils contain low molecular weight organic acids such as aliphatic carboxylic, phenolic, and amino acids (Stevenson and Fitch, 1981). These acids are considered soluble, and their presence may maintain Cu^{2+} in the soil solution. Bloomfield et al. (1976) suggested that Cu^{2+} may form negatively charged organic complexes not retained by clay minerals. McBride (1981) found that the effects of organic compounds on Cu^{2+} depend on the nature of the adsorbing surface as well as the type of organic compound. For example, fulvic and glutamic acids were found to enhance Cu^{2+} adsorption at a given pH, whereas citric acid and EDTA prevented adsorption by maintaining Cu^{2+} in soil solution (McBride, 1981).

Adsorption and desorption of heavy metal cations are important processes in soils, because they determine the availability of the cations to plants. They also affect the mobility of cations in the soil profile. Excellent reviews have been published describing the adsorption-desorption behavior of heavy metal cations in soils in the presence of organic chelates (Ponizovsky et al., 1999; Temminghoff et al., 1999). Specific adsorption of copper in soils has been evaluated (McLaren and Crawford, 1973; Forbes et al., 1976; McLaren et al., 1981; McBride, 1981). The copper ion is specifically adsorbed by silicate clays, organic matter, iron, aluminum, or manganese oxides. Among all the divalent cations, it is the most strongly held by iron and aluminum oxides (Tisdale et al., 1993). The mechanism of this adsorption is a chemisorption process involving the formation of Cu-O-Al or Cu-O-Fe surface bonds, which is controlled by the quantity of surface OH^- groups (Kabata-Pendias and Pendias, 1992; Tisdale et al., 1993). These OH^- groups are pH-dependent, and therefore, the adsorption of Cu^{2+} is a function of pH (Kabata-Pendias and Pendias, 1992).

In most soils at pH 5.5, copper may be present as specifically adsorbed ions, which are considered to be part of the solid phase. These ions cannot be removed by cation exchange processes when large quantities of other cations are added to the soil (McLaren and Crawford, 1973; Baker and Senft, 1995). The amounts of copper ions which can be removed by exchange reactions will be definitely affected by the pH of the solution. McLaren et al. (1981) studied the adsorption of copper by individual soil components at equilibrium with copper concentrations normally found in natural soils and concluded that copper adsorption isotherms were essentially linear. They also found that oxides and organic materials adsorbed the greatest amounts of copper. They, however, found little effect on copper adsorption by changes in pH or background concentrations of cations within the ionic strength and pH range found in agricultural soils. On the other hand, Sauvé et al. (2000 and 2003) found that the partitioning coefficients of copper in organic and inorganic soils were largely predicted by the pH alone. Polo et al. (1999) studied the effects of sewage sludge on copper adsorption by soils and found that copper adsorption by soils was decreased. In other words, copper remaining in soil solutions was increased in sewage sludge–treated soils despite the low copper concentration in the sewage sludge.

The objectives of this study were to determine (1) the adsorption-desorption of copper in the presence of oxalic acid, citric acid, and

TABLE 1
Soil physicochemical characterization

Analysis	Unit	Values
pH		6.6
P (double acid)	mg/kg	46.0
Ca (double acid)	mg/kg	150.0
Mg (double acid)	mg/kg	11.5
K (double acid)	mg/kg	60.5
CEC	mmol (+)/kg	45
Organic matter	%	2.6
Particle size		
Sand	%	79
Silt	%	13
Clay	%	8

sewage sludge and (2) the effects of oxalic acid, citric acid, and sewage sludge on the transport parameters of copper using breakthrough curves. The results will improve our understanding of copper retention in biosolid-amended soils and the observed copper detoxification in mine tailings receiving sewage sludge.

MATERIALS AND METHODS

A Marvyn loamy sand soil (fine-loamy, siliceous, subactive, thermic, Typic Kanhapludult), Ap horizon, from the Auburn Cuellars Rotation experiment (plot 1) was used in this study. The soil pH was measured using a pH meter (Beckman Instrument Inc. Model 71) with a combination glass electrode. The measurements were taken 30 min after mixing 20 g of dry soil and 20 mL of deionized water to make a soil/solution ratio of 1:1 on a weight basis (McLean, 1982). The pH meter was calibrated with pH 4– and pH 7–certified buffers, and the soil samples and water were remixed immediately before a reading was obtained. Particle size analyses were carried out by the Bouyoucos hydrometer method as described by Gee and Or (2002). Exchangeable cations and CEC were determined using 1 N NH$_4$OAC at pH 7 as described by Thomas (1982). The ammonium concentrations (NH$_4^+$) were determined using the microplate method as described by Sims et al. (1995). The total NH$_4^+$ contents were used to estimate the CEC of the soil at pH 7. The soil chemical characterization is summarized in Table 1. Sewage sludges and soil were analyzed for total element composition using the method described by Baker and Amacher (1982). Two grams of soil or sewage sludge was transferred to a porcelain crucible and heated overnight at 450 °C to destroy organic matter. The ashes

were transferred into a 100-mL polypropylene beaker, and 10 mL of a 30% H$_2$O$_2$ solution was added to the beaker and evaporated to dryness at 90 °C. The treatment was repeated until the sample no longer effervesced on addition of H$_2$O$_2$. Three drops of concentrated H$_2$SO$_4$ and 10 mL of a 48% HF solution were added to the beaker and evaporated to dryness at 125 °C in a sand bath. The treatment was repeated twice, then additions of 15 mL of a concentrated HNO$_3$, 2 mL of concentrated H$_2$SO$_4$, and 5 mL of a 60% HClO$_4$ were made, and the heating continued until strong fumes of SO$_3$ were produced. After cooling the polypropylene beakers, 25 mL of deionized water was added to complete the extraction of all the elements. Total concentration of copper and other elements was determined by ICP-OES (inductively coupled argon plasma-optical emission spectrophotometry). The results are summarized in Table 2.

Column Experiments

Figure 1 represents the setup for the column experiments. The column was a Plexiglas cylinder, 30 cm long with a diameter of 5 cm. The column was filled with the Marvyn soil (columns 1, 2, and 3) at a bulk density of 1.5 g · cm^{-3}. When sewage sludge was used (columns 4 and 5), 200 g of soil was mixed with 20 g of sewage sludge, making a ratio of 10:1 soil/sewage sludge, and the mixture was placed in the bottom quarter of the cylinder (about 7.5 cm of height). The remaining part of the cylinder was packed with the Marvyn soil. Each column

TABLE 2
Soil and biosolids total elementary analysis

Analysis	Unit	Village Creek waste water plant	Trussville waste water plant	Soil
Ash	%	44.0	42.7	97.4
Total P	mg/kg	87434.4	69754.9	191.3
Total Ca	mg/kg	20799.1	18758.8	1223.7
Total Mg	mg/kg	4458.6	2800.3	374.1
Total K	mg/kg	2718.6	3710.9	1631.8
Total Cu	mg/kg	472.8	1413.4	2.4
Total Ba	mg/kg	75.5	24.1	0.2
Total Cd	mg/kg	4.0	2.9	0.3
Total Co	mg/kg	6.8	7.4	2.5
Total Cr	mg/kg	58.9	34.8	5.4
Total Na	mg/kg	1180.2	1200.4	83.8
Total Ni	mg/kg	26.3	25.6	1.9
Total Zn	mg/kg	1869.6	1146.3	8.6
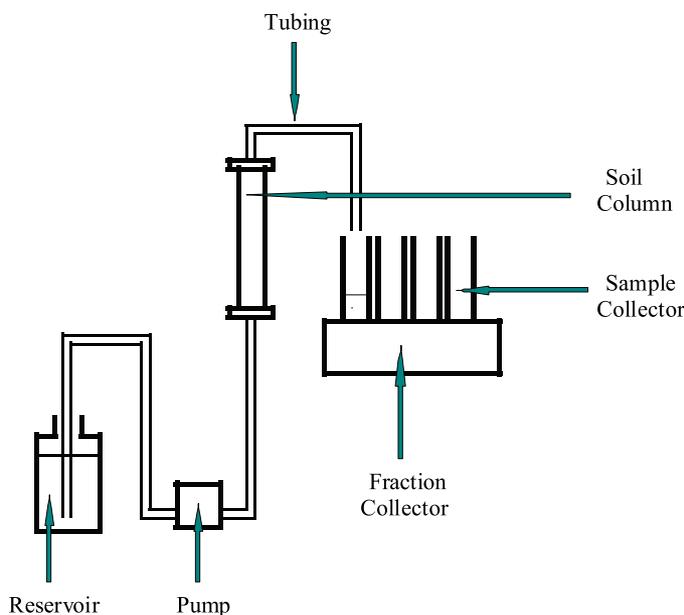
Fig. 1. Schematic representation of the column experiment apparatus.

medium was dry at the start of the experiment. The initial potassium content of the soil and soil/sewage sludge mixtures, as determined by the water extract method, was 29.6 (soil), 54.7 (mixture soil/sewage sludge 1), and 112.6 mg/kg (mixture soil/sewage sludge 2). Potassium content in the soil sample, as determined in the double-acid method, was 60.5 mg/kg (Table 1). No copper was detected in the soil sample or the mixtures by the water extract method or the double-acid method (Table 1). The column was leached with a copper solution containing 1000 mg of copper per kilogram of solution (1.57×10^{-2} M/L $CuSO_4$), and the effluent was collected in sample tubes every 10 min. Oxalic acid (10^{-3} M/L) or citric acid (10^{-3} M/L) was added to the solution only in case that low molecular weight organic acid was needed. Potassium sulfate (10^{-2} M/L K_2SO_4) served as background electrolyte to keep the ionic strength of the effluent solution constant. With

a flow rate of 1.2 mL/min maintained by a peristaltic pump, 12 mL of effluent was collected per sample tube and analyzed for pH, copper, and potassium concentrations. The pH of the effluent samples was determined immediately after the collection of the samples. Copper and potassium were determined using atomic adsorption (AA) and atomic emission using an atomic absorption spectrophotometer, respectively. A breakthrough curve was established for each column, and the retardation factor R, the distribution coefficient K_d, and the longitudinal dispersivity D were calculated using the HYDRUS-1D software package for simulating one-dimensional movement of water, heat, and multiple solutes in variably saturated media (Simunek et al., 1998). In this study, five column experiments (Table 3) were conducted: (1) the column was packed with Marvyn soil, and the influent solution contained only copper and potassium sulfate; (2) the column was

TABLE 3

Chemical composition of the eluent that was introduced into the medium for the five column experiments

Column no.	CuSO$_4$	K$_2$SO$_4$	Oxalic acid	Citric acid
1	1.57×10^{-2} M/L	10^{-2} M/L	NA	NA
2	1.57×10^{-2} M/L	10^{-2} M/L	10^{-3} M/L	NA
3	1.57×10^{-2} M/L	10^{-2} M/L	NA	10^{-3} M/L
4	1.57×10^{-2} M/L	10^{-2} M/L	NA	NA
5	1.57×10^{-2} M/L	10^{-2} M/L	NA	NA

packed with Marvyn soil, and the influent contained oxalic acid in addition to copper and potassium sulfate; (3) the column was packed with Marvyn soil, and the influent contained citric acid in addition to copper and potassium sulfate; (4) the bottom quarter of the column was packed with a mixture of the Marvyn soil and sewage sludge 1 (Village Creek waste water plant in Birmingham, AL); and (5) the bottom quarter of the column was packed with a mixture of the Marvyn soil and sewage sludge 2 (Trussville waste water plant in Trussville, AL). The influent solution in column experiments 4 and 5 contained only copper and potassium sulfate.

Sorption Isotherm

To determine how much copper can be adsorbed by the sewage sludges and by the Marvyn soil, a series of batch experiments was conducted. Triplicate 10-g samples were prepared of oven-dried (105 °C) sewage sludge 1, oven-dried sewage sludge 2, and oven-dried Marvyn soil for each of 9 copper concentrations, resulting in a total of 81 samples. Each sample was placed in a 125-mL Erlenmeyer flask, and copper was added to each replicate set in the following amounts: 0, 1, 2, 4, 8, 10, 20, 40, and 80 mg. Deionized water was then added to bring the total volume in each flask to 100 mL. The flasks were secured on a reciprocal mechanical shaker and shaken overnight for equilibration purpose. The contents of the flasks were filtrated through Whatman no. 42 filter paper, and the copper

concentration of the filtrates was determined by AA. Amounts of copper adsorbed on the soil or on the sewage sludge were calculated from the difference between the initial copper concentrations and the equilibrium aqueous phase concentrations of copper. Because sewage sludges adsorbed so much copper, 5 additional copper concentrations were added only to the sewage sludges, resulting in the following amounts of copper being added to triplicate 10-g samples of oven-dried sewage sludges: 100, 200, 400, 800, and 1000 mg. The same procedure was used to determine the amounts of copper adsorbed.

RESULTS AND DISCUSSIONS

The pH values of the samples collected during each column experiment were immediately determined and are presented in Fig. 2. Zero time for all column experiments is defined as the time at which the first drop of the effluent appeared (1 pore volume of effluent is equivalent to 200 min of leaching). Although initial pH values for all columns differed somewhat, they were close to the pH of the Marvyn soil pH (6.6). First, there was a slight increase in pH, suggesting that some H^+ ions were adsorbed by the column medium, followed by a steady decrease. This might be the result of the lack of equilibrium observed at the beginning of many column experiments, particularly when the medium in the column was not saturated by a background solution. At the end of each column experiment (10 pore volumes of effluent), the pH values of the collected effluent samples were
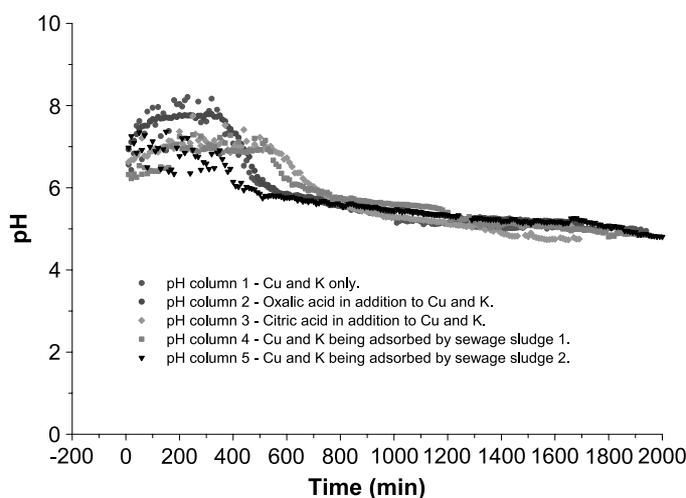
Fig. 2. Changes in pH value of the effluent as time (leaching volume) progresses.

TABLE 4

Values of the distribution coefficient (K_d), the retardation factor (R), the longitudinal dispersivity (D), and the regression coefficient (r^2) for copper (Cu) and potassium (K) as estimated by HYDRUS-1D

Column no.	K_d	R	D (cm)	r^2
Cu				
1 (100% Soil)	1.26	5.26	3.04	0.980
2 (100% Soil)	1.26	5.24	2.81	0.991
3 (100% Soil)	1.41	5.74	1.17	0.990
4 (75% Soil)	1.26[†]	5.26[†]	3.04[†]	NA
(25% Mixture)[‡]	5.85	16.95	13.06	0.992
5 (75% Soil)	1.26[†]	5.26[†]	3.04[†]	NA
(25% Mixture)	5.46	15.85	30.00[§]	0.992
K				
1 (100% Soil)	0.13	1.42	0.83	0.977
2 (100% Soil)	0.17	1.56	2.07	0.949
3 (100% Soil)	0.16	1.53	1.15	0.974
4 (75% Soil)	0.13[†]	1.42[†]	0.83[†]	NA
(25% Mixture)	0.63	2.72	30.00[§]	0.935
5 (7% Soil)	0.13[†]	1.42[†]	0.83[†]	NA
(25% Mixture)	0.56	2.52	30.00[§]	0.927

[†]These values were not optimized. They were fixed to values obtained by the optimization in column 1.

[‡]The mixture consisted of sewage sludge and the Mavyn soil in the ratio of 1:10.

[§]These values were constrained to the value of the length of the column.

very close to the pH value of the influent solution (pH 4.7).

Potassium, which was used to maintain a constant ionic strength, was hardly retarded by the soil or sewage sludge, and the maximum (influent) potassium concentration was quickly obtained (Table 4; Fig. 3). This was in part

attributed to the potassium already present in soil and in part to the lower valence of K^+ compared with Cu^{2+}. This may have been different if a Ca^{2+} or Al^{3+} solution had been used to maintain a constant ionic strength. According to Cavallaro and McBride (1978), Ca^{2+} greatly reduces the efficiency of heavy metal adsorption, suggesting a stronger Ca^{2+} than K^+ affinity for adsorption sites.

When the influent contained only copper and potassium sulfate (column 1), the breakthrough curve (Fig. 4) showed that copper detection in the effluent occurred 400 min after the start of the experiment (about 2 pore volumes of effluent). Maximum copper concentration was obtained 1600 min after the start of the experiment (about 8 pore volumes). When the eluent contained oxalic acid (column 2) in addition to copper and potassium sulfate, the breakthrough curve (Fig. 4) resembled the one obtained when copper and potassium sulfate alone were present in the eluent solution. Apparently, oxalic acid did not affect copper movement in the soil. When the eluent contained citric acid (column 3) in addition to copper and potassium sulfate, the breakthrough curve (Fig. 4) showed that copper detection in the effluent happened 600 min after the start of the experiment (about 3 pore volumes). Citric acid affected copper movement by increasing the retardation factor (Table 4). However, the maximum copper concentration was obtained 1600 min after the start of the column experiment (about 8 pore volumes), which was the same time observed for the maximum copper concentration when copper was alone or mixed
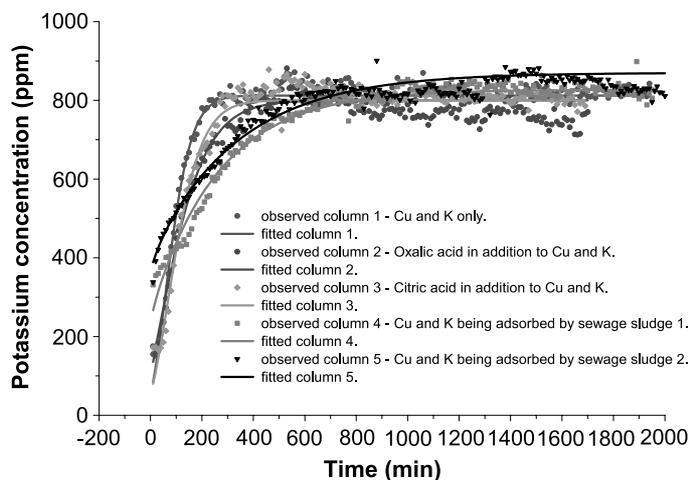
Fig. 3. Breakthrough curves for K+ in columns 1 to 5.
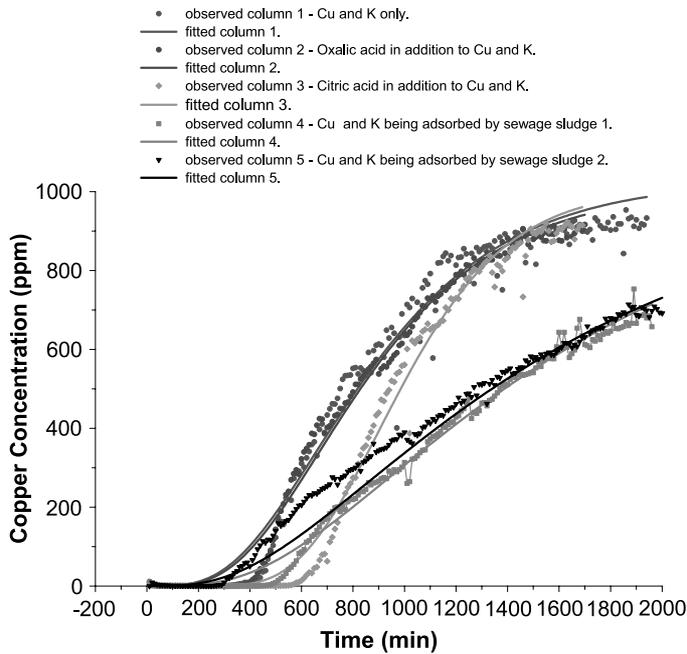
Fig. 4. Breakthrough curves for Cu^{2+} in columns 1 to 5.

with oxalic acid in the eluent solution. Bineyev et al. (1982) found that copper adsorption by soil or sewage sludge was 64% higher when copper was used alone in solution than when copper was added in a mixture of amino acids. This was the case when copper was used in a mixture with oxalic acid, but when copper was present in a mixture with citric acid, it was shown that citric acid formed stronger complexes with copper than oxalic acid or amino acids, and the retardation factor was higher than the ones obtained in the first two column experiments. The use of sewage sludge 1 (column 4) showed a threefold increase in R over the previous
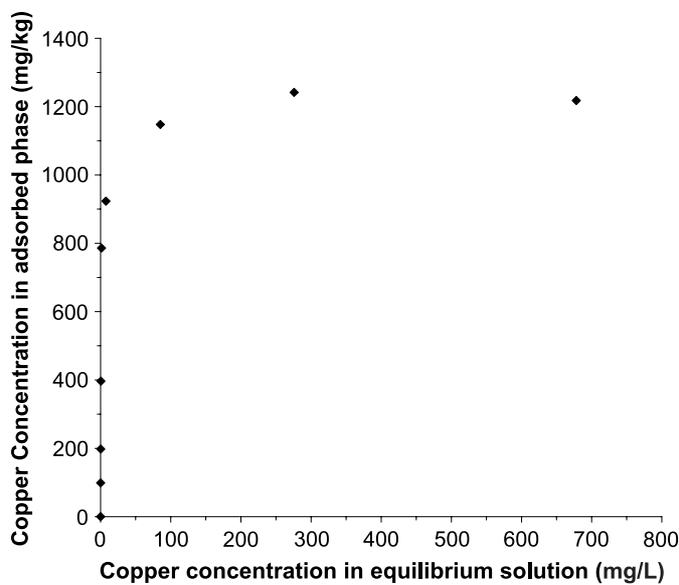
Fig. 5. Langmuir adsorption isotherm when Cu^{2+} is being adsorbed by the Marvyn soil.

3 column experiments (Table 4). Copper was first detected in the effluent 500 min (about 2.5 pore volumes) after the start of the experiment, the same time as when no sewage sludge was used, but the maximum copper concentration was not yet obtained 2000 min (about 10 pore volumes) after the start of the experiment (Fig. 4). In case of sewage sludge 2 (column 5), detection of copper in the effluent first happened 300 min after the start of the experiment (Fig. 4), which is 200 min earlier than with sewage sludge 1 (column 4). However, the retardation factor R (Table 4) was almost the same as for sewage sludge 1 (16.95 for sewage sludge 1 and 15.85 for sewage sludge 2). Like in case of sewage sludge 1, the maximum copper concentration was not obtained 2000 min after the start of the experiment (about 10 pore volumes).

Not reaching the maximum copper concentration for both sewage sludges is an indication that sewage sludges adsorb a large quantity of copper and potentially other heavy metals. Bergkvist and Jarvis (2004) found that soils amended with sewage sludge have a very high adsorption capacity with regard to cadmium. Liu and Wang (2004) studied *in situ* speciation of copper-humic substances in a contaminated soil during electrokinetic remediation and found that copper-humic substances were associated with 50% of the total copper contained in the soil. To check how much copper could be adsorbed by the sewage sludge, a Langmuir

adsorption isotherm was determined for the soil (Fig. 5) and the sewage sludges (Fig. 6). The maximum adsorption of copper for the soil was 1250 mg/kg. In case of the sewage sludges, the maximum copper adsorption was 50,000 mg/kg, which is 40 times higher than the soil maximum adsorption of copper. Both sewage sludges adsorbed the same amount of copper. This is an indication that these sewage sludges have the same amount of copper adsorption sites and could be used to detoxify copper from mine tailings because they adsorb so much copper. Over time, however, the decomposition of sewage sludge may be followed by copper desorption. Keeping the pH of the soil around pH 6.5 by liming would lower copper availability to plants and minimize the risk of leaching. Addition of organic matter would maintain copper in an organic form that would be less available to plants or leaching.

CONCLUSION

In general, copper adsorption by soils is affected by soil organic matter content. The presence of low molecular weight organic acids and sewage sludge in soils might prevent copper adsorption by forming soluble copper complexes. In this study, oxalic acid–copper complexes did not affect the mobility of copper in a Marvyn loamy sand. Citric acid–copper complexes, however, retarded the mobility of copper in the same
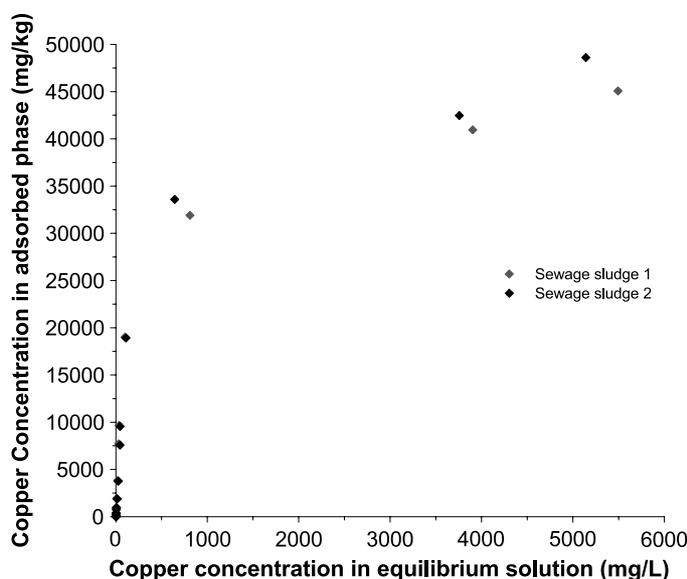
Fig. 6. Langmuir adsorption isotherm when Cu^{2+} is being adsorbed by the sewage sludges 1 and 2.

soil. Adding sewage sludge to the soil greatly slowed the mobility of copper in the column medium. The maximum (influent) copper concentration was not yet obtained 2000 min (about 10 pore volumes of the influent) after the start of the experiment. The maximum copper adsorption was determined to be 1250 mg/kg and 50,000 mg/kg for the soil and sewage sludges, respectively. With this amount being adsorbed, sewage sludges could be used to detoxify copper in soils and mine tailings.

Heavy metals such as Cu^{2+} are known to be adsorbed by soil organic matter in large amounts (Lehmann and Harter, 1984). Sewage sludge provides abundant organic matter, and its utilization as land applied amendment is limited mostly by the heavy metals content (Polo et al., 1999). The fact that sewage sludge adsorbs large amounts of heavy metals, as demonstrated by this study, should be one of the factors in favor of more use of sewage sludge as a heavy metal detoxifier. Unfortunately, because of the heavy metal load already present, the adsorption of heavy metals could be rendered ineffective by the release with time of excess heavy metals. The fear of sewage sludge releasing heavy metals considered toxic to the environment has caused the EPA to establish regulations for sewage sludge use in the environment.

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