Bull. Environ. Contam. Toxicol. (2001) 67:913–920

DOI: 10.1007/s00128-001-0208-6

Bulletin of Environmental Contamination and Toxicology

Adsorption of Copper on Polluted River Sediment

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Received: 26 February 2001/Accepted: 2 August 2001

Adsorption/desorption plays a dominant role in the transformation process and in the fate of heavy metals in natural waters. It also affects the amount of heavy metals that is bioavailable (Yin et al. 1997; Allen and Hansen 1996). Many works have been done regarding adsorption processes of heavy metals to oxide or hydroxides (Davis and Leckie 1978; Stumm and Hole 1976), clay minerals (Farah et al. 1980; Hirsch et al. 1989), river sediments (Fu and Allen 1996, Wen et al. 1998), soil (Yin et al. 1997) and other surfaces (Hering and Morel 1990). However, most of those researches were relied on pure materials or unpolluted samples. Study of natural materials is difficult but is important (Davis et al. 1998). Study of polluted samples is even more difficult due to their complex properties.

The concept of surface complexation put forward by Stumm and Shindler (Stumm et al. 1970; Hohl and Stumm 1976; Schindler and Gamsjäger 1972) has been widely used in describing the adsorption of ions on a variety of mineral phases in well-controlled laboratory experiments. This concept was used to describe the adsorption of ions onto soil and sediment (Davis et al. 1998; Wen et al. 1998). However, it is still an open issue that whether this concept can be used to explain the adsorption/desorption of polluted sediment. It is meaningful to work out a way to use the concept for polluted sediment. The purpose of this study is to analyze the adsorption/desorption behavior of Cu on polluted sediments taken from the Le An river using the concept of surface complexation and to find out if the polluted sediment could be sink for pollutants. Le An river, Jiangxi Province, flows into the biggest fresh water lake of China — Boyang Lake. As described by previous studies (Tang et al. 1994; Wen and Allen 1999; Liu et al. 1999), the river water and sediment have been polluted by heavy metals discharged from the largest open cast copper mine of China — Dexing copper mine located in the upstream portion of the river.

MATERIALS AND METHODS

The sediment samples were collected from Zhongzhou, Daicun, Hushan and Caijiawan, representing four polluted positions with different geochemical and hydraulic conditions along the Le An River (Tang et al. 1994; Liu et al. 1999; Wen and Allen 1999). To maintain a condition similar to the natural status, all samples were air-dried and sieved through a 240 mesh nylon screen right after

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collection. All experiments were conducted using the sieved sediment fraction. Stock sediment solution with a concentration of 10 g/L was made for each of the samples two weeks before conducting the titration and adsorption/desorption experiments.

Generally, it is thought that the polluted samples should be pretreated by washing off the pollutants on the surface prior to an adsorption experiment. But this will cause changes of the surface properties of the samples, i.e., using the pretreated samples may lead to results that do not reflect the real conditions. In this study, the sediments were not pre-washed prior to the experiments to avoid changing the surface properties of the sediment.

Potentiometric titration was done in a 100 ml Erlenmeyer flask. A 10 ml stock sediment suspension was added to the flask to make a sediment concentration of 1 g/L. $NaNO_3$ was added to achieve ionic strengths of 0.1, 0.01, and 0.001 mol/L. Triple distilled water was added to give a final volume of the suspension of 100 ml, and HNO_3 was added to keep a suspension pH value less than 3. The sample was stirred for 1 hour with a magnetic stirrer and was equilibrated for 30 min to achieve a stable pH. Then, NaOH was added until the suspension pH exceeded 10, which was monitored by using a Metrohm 682 automatic titrator. During the titration process, the suspension was kept bubbling with N_2 to extract CO_2, and the temperature was held at 25°C. The reference blank was also prepared in the same manner except that no HNO_3 was added and only the supernatant of the suspension was titrated. A duplicate experiment was performed in parallel to ensure the quality of the experiment. The surface charges of the sample at different pH and with different ionic strengths were calculated based on Eq. 1 (Stumm and Hohl 1976; Davis and Leckie 1978; Fu and Allen 1992). The data sets of pH value versus surface charge (σ_H) were obtained through this experiment.

$$\sigma_H = \left[\left(V_{HNO_3} N_{HNO_3} - V_{NaOH} N_{NaOH} \right)_{Sample} - \left(V_{HNO_3} N_{HNO_3} - V_{NaOH} N_{NaOH} \right)_{Blank} \right] \Big/ W \qquad (1)$$

where: σ_H = surface charge (mmol/g);
V = volume of acid or base added (L);
N = concentration of acid or base added (mmol/L);
W = weight of sediment sample (g).

Copper was selected as the absorbate because it was the main pollutant in the river. Two types of adsorption/desorption experiments were conducted. One was keeping a fixed pH with a set of metal concentrations as variables, from which the adsorption isotherms were obtained. The other one was using an array of pH values with fixed metal concentrations, from which the adsorption edge curves were obtained. In the experiments, a set of plastic bottles with 100 ml volume was used. Inside each bottle, 10 ml of sediment stock suspension were added to make the solid concentration as 1 mg/L. The pH of the suspension was adjusted by adding HNO_3 or NaOH. The suspension ionic strength was adjusted by adding $NaNO_3$ to 0.01 mol/L that is close to that of natural waters. The Cu concentration of the suspension was adjusted to be at the expected value using standard Cu solutions. Then the samples were shaken for 3 hours in a reciprocating shaker and were equilibrated for 24 hours at 25°C. Part of the supernatant was used for pH measurement, and part of the supernatant was filtrated through a 0.45 μm membrane for metal concentration measurement.

Surface areas of the samples were measured by standard BET adsorption method (ASAP-2000, Micromeritics, USA). Element compositions of the samples were determined by X-ray fluorescence spectrometry (3080E3, RIGAKU Industrial Co., Japan). Organic content was measured by using the potassium dichromate oxidation method (Nanjing Soil Institute 1977). Active Fe, Mn oxides contents were measured by using citrate-bicarbonate-dithionite method and amorphous Fe, Mn oxides contents were measured by the oxalic acid-ammonium oxalate method (Nanjing Soil Institute 1977). Cation exchange capacity was measured by using the ammonium acetate method (Nanjing Soil Institute 1977). Cu concentration was measured by using the atomic adsorption spectrometry (PE-3100, USA).

RESULTS AND DISCUSSION

The element compositions of the four samples measured by X-ray fluorescence spectrometry are listed in Table 1. The four samples have similar amount of Fe, Si, Al and Ca but different amount of other elements. The Cu concentrations in the four samples are 1134, 1906, 1055 and 571 mg/kg respectively, all of which are much higher than the average Cu concentration in sediment of Chinese rivers (42.5 mg/kg). This is because the sediments were polluted by Cu from the copper mine. Table 2 gives the measurement results of Fe, Mn, organic matter (OM), cation exchange capacity (CEC) and surface area of the samples. The organic contents and the surface areas of the four samples decline along the down stream of the river. Zhongzhou sample has the highest Fe and Mn oxide concentration.

Table 1. Element composition of the samples

Sample	Cu[1]	Pb[1]	Zn[1]	As[1]	Mn[1]	S[1]	Fe	Si	Al	Ca
Zhongzhou	1134	59	161	43	953	2418	5.55	29.6	8.84	0.36
Daicun	1906	326	1127	399	996	566	6.77	30.2	8.01	0.32
Hushan	1055	103	680	42	137	455	5.42	29.8	8.81	0.33
Caijiawan	571	78	531	37	1216	318	5.21	30.2	8.50	0.29
in revers[2]	42.5	34.5	164	-	750	-		-	-	-

1. Unit mg/kg, other items' unit % 2. Chinese rivers (Wang 1995)

Table 2 Some characteristics of the samples

Sample	OM (%)	Fe[1] (%)	Fe[2] (%)	Mn[1] (%)	Mn[2] (%)	CEC (meq/100g)	Surface area (m^2/g)
Zhongzhou	3.02	2.52	4.17	0.04	0.04	19.38	19.71
Daicun	3.85	1.54	2.28	0.10	0.08	13.62	18.32
Hushan	2.91	1.55	2.62	0.12	0.10	10.25	15.45
Caijiawan	2.61	1.20	3.22	0.11	0.13	18.50	14.94

1. amorphous oxide, 2. active oxide

According to the theory of surface complexation, solid surface is composed of specific functional groups that react with dissolved solutes to form surface species. Surface property that affects adsorption the most is the surface charge which varies in acidity reactions (Eq.2, Eq.3). Surface charge is determined by potentiometric titration experiments. pH of zero charge (pH_{pzc}) is a basic parameter. The solid surface in solution is negatively charged under the condition of $pH > pH_{pzc}$ and positively charged while $pH < pH_{pzc}$. The components of sediment that greatly affect pH_{pzc} value include Fe, Mn oxide that may drive pH_{pzc} toward high value, as well as kaolinite and organic matter that may lower the pH_{pzc} value. But for polluted sediment samples, the adsorption of metal ions may influence their surface charge properties and the pH_{pzc} value too.

$$SOH_2^+ = SOH + H^+ \qquad K_{a1}^{int} \tag{2}$$

$$SOH = SO^- + H^+ \qquad K_{a2}^{int} \tag{3}$$

Where, S = Surface

The sample potentiometric titration results are shown in Figure 1. It can be seen that the surface charge versus pH variation curves of the four polluted samples are different from that of the pure oxide (Park and Huang 1987) and that of the unpolluted sediment of the same river (Wen et al. 1998). The titration curves of σ_H vs. pH of a pure oxide or unpolluted sediment in inert electrolyte such as $NaNO_3$ or $NaClO_4$ at different concentrations cross at the pH_{pzc} point. However, the three σ_H vs. pH curves for the ionic strengths of 0.1, 0.01 and 0.001 for each of the Zhongzhou, Daicun and Caijiawan samples do not have a cross point. Only the two σ_H vs. pH curves for the lower ionic strengths of 0.01 and 0.001 have a cross point. The corresponding pH values are 6.3, 4.0 and 4.05 respectively for the three samples. If we take these pH values as the pH_{pzc} of the three samples, the pH_{pzc} values of Daicun and Caijiawan are close to that of the unpolluted Huanglongmiao sample (pH_{pzc}=4.20, Wen et al. 1998). But Zhongzhou sample has a high value of pH_{pzc}. That may be a result of its high Fe, Mn oxide content. The reasons that the σ_H vs. pH curve of ionic strength of 0.1 is apart from the other two curves are complicated. Nevertheless, it should be an important reason that the sample had been polluted by Cu. The patterns of the titration curves of Hushan sample appear quite differently from that of the others. The corresponding pH to the cross point of σ_H vs. pH curves for three different ionic strengths is 2.67 which is the lowest among the four samples. It means that the pH_{pzc} of this sample is very low and this sample is negatively charged in most cases. That is a plus for cation adsorption.

The titration curves give a macro-picture of the polluted sediment. But the information is not sufficient enough to explain the unusual types of Hushan titration curves, or separation of the titration curves of high ion strengths in three other three. However, the result clearly demonstrates that the surface characteristics of polluted samples are changed and are different from those of the unpolluted ones.

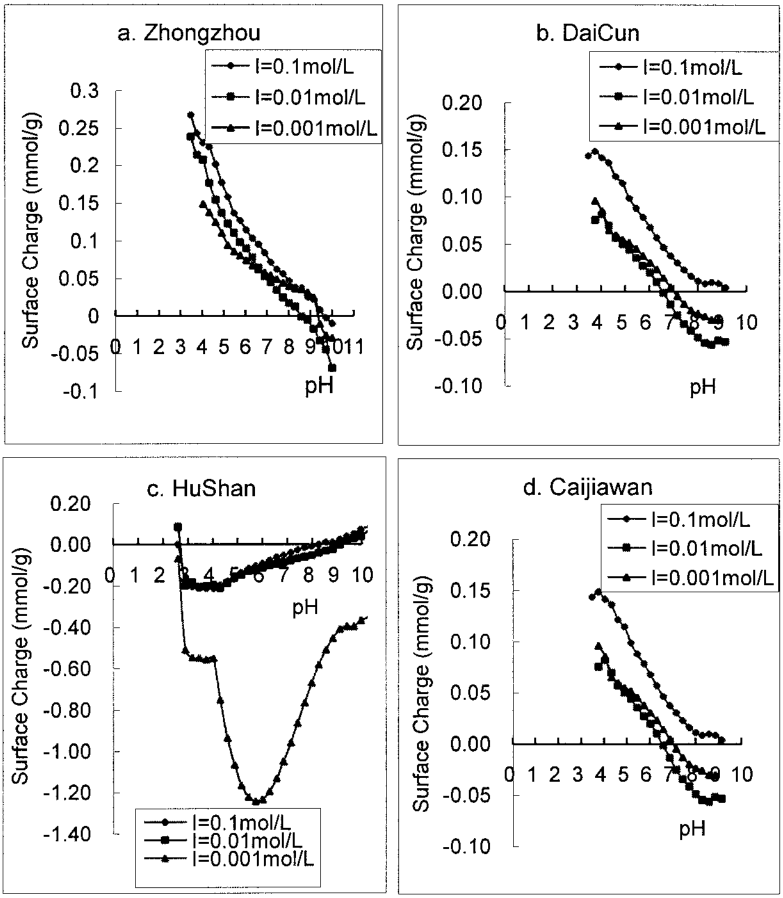

Figure 1. Surface charge of sediment vs. pH of solution

The adsorption/desorption reaction can be expressed as Eq.4 under the concept of surface complexation. This is a two way reaction. If the sediment surface is polluted by Cu, i.e., $(SO)_2Cu$ concentration is high, while pH is low, or, H^+ concentration is high, the reaction proceeds towards left-side, which means Cu^{2+} generation. The equilibrium of the reaction is depending on (1)the free surface concentration (SOH), (2)the Cu concentrations on surface ($(SO)_2Cu$) and in solution (Cu^{2+}) and (3)H^+ concentration in solution.

$$2SOH + Cu^{2+} = (SO)_2Cu + 2H^+ \qquad (4)$$

The pH edges of the four samples are shown in Figure 2. It shows that at the pH of natural water (6.5-8.0) the sediment can adsorb some Cu. However, a noticeable phenomenon is that for each of the samples, the adsorption fraction increases from about -100% to 100% at around pH 5-6 when Cu concentration is lower ($Cu^{2+}=1.56*10^{-6}$ mol/L). It means that all the samples have the potential of release and adsorption of Cu. With the increase of the Cu concentration in

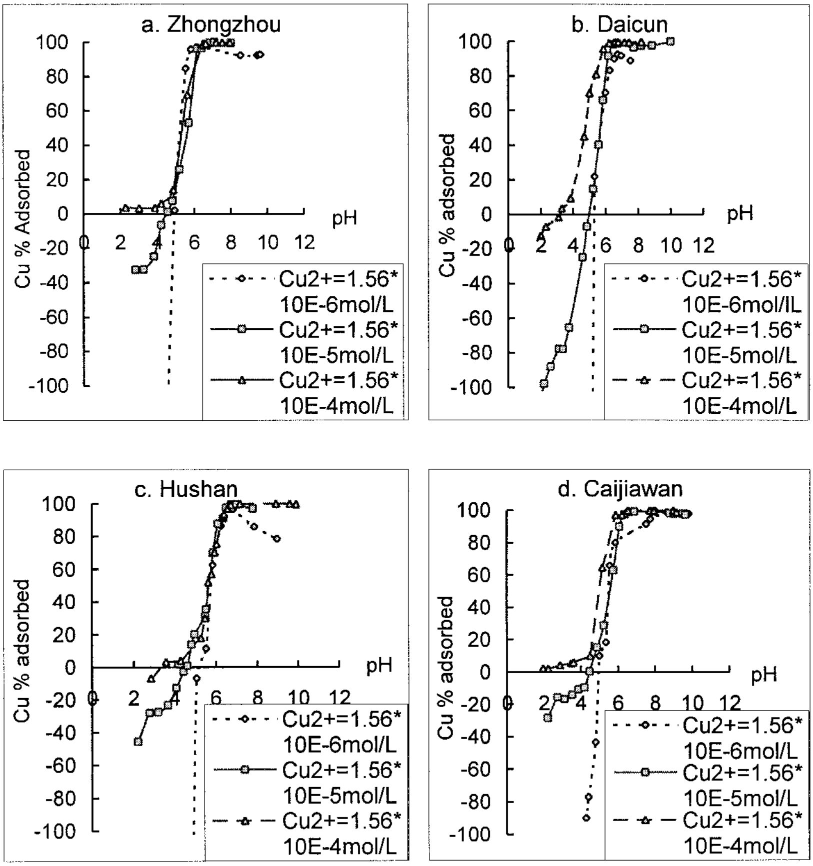

Figure 2. Cu adsorption edge curves

solution, the release of Cu from the samples decreases. For Zhongzhou and Caijiawan samples, Cu was not released when Cu concentration was $1.56*10^{-4}$ mol/L while pH is as low as about 2.0, which means that higher absorbate Cu concentration in liquid can stop the Cu release from the surface. See Equation 4, it indicates that elevation of Cu^{2+} concentration in solution promotes the production of $(SO)_2Cu$ and stops its release, which explains the results discussed above. The release of Cu from the Daicun sample can reach -100% at pH about 2.0 when the Cu concentration is $1.56*10^{-5}$mol/l. It means that the Daicun sample has greater Cu release potential than the others. Taking a look at Table 1 again, we see that the Daicun sample has the highest Cu concentration. Equation 4 can give a good explanation of this experimental result. The high degree of Cu pollution of the sample, i.e. more $(SO)_2Cu$ present, drives the reaction to left, which results in Cu^{2+} release. It also explains the influence of H^+, i.e., pH on the Cu adsorption.

To identify the adsorption capacities of the samples, the adsorption as a function of various Cu concentrations is tested and the results are shown in Figure 3. The amount of Cu adsorbed by each of the samples increase with the elevation of Cu

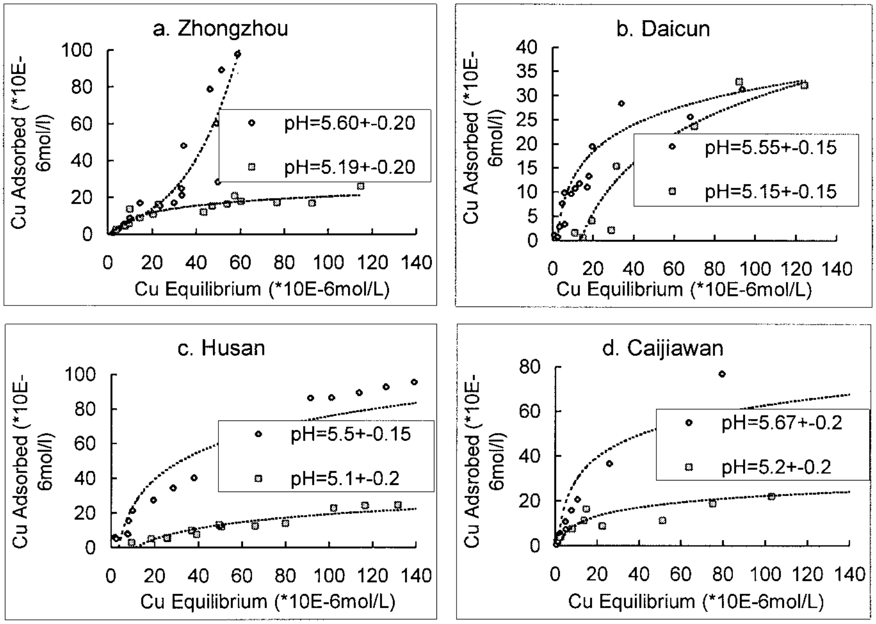

Figure 3. Cu adsorption isotherms

equilibrium concentration. Most of the adsorption curves appear to be Langmuir type as described in Equation 5. There are two exceptions. The adsorption on the Zhongzhou sample at pH 5.6 does not have a saturation adsorption point, which is hard to explain. The adsorption curve of Daicun sample at pH 5.15 has distinct negative adsorption at lower Cu equilibrium concentration.

$$G = G_0C/(K+C) \qquad (5)$$

Where, G is the adsorption amount (mol/g); G_0 is the maximum adsorption amount (mol/g); K is half saturation constant (mol/L); C is absorbate concentration (mol/L).

A calculation was conducted to match the experimental data with Equation 5. The results are listed in Table 3. It indicates that the adsorption of Cu on the polluted sediment sample can be formulated well via Langmuir equation. By comparing the G_0 values, it can be seen that the Hushan sample has the highest adsorption capacity, which corresponds to its surface charge characteristics as discussed earlier. The Daicun sample has the lowest adsorption capacity, which corresponds to its pH adsorption edges. These results support the conclusions of the titration and adsorption edge experiments. It also shows that the adsorption behavior of the polluted samples is dependent on pH, polluted ion concentration in liquid and the polluted degrees of the samples, but dependent not on surface areas (Table 2). Surface charge characteristics are most important in controlling the adsorption behavior of samples.

Table 3. Langmuir equation parameters

Samples	pH	G_0	K	R^2
Zhongzhou	5.19±0.20	33.784	44.084	0.917
Daicun	5.55±0.15	25.253	17.732	0.941
Hushan	5.55±0.15	81.967	420..8	0.877
	5.10±0.2	35.970	114.237	0.958
Caijiawan	5.67±0.2	39.216	12.220	0.975
	5.20±0.2	19.268	10.655	0.906

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