

Sorptive interactions of Cu on soil, clay and humic acid

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Abstract : Sorption and desorption of Cu on soils from four different locations of West Bengal have been studied. Sorption on humic acid and clays of the soils has also been measured. Measurements have been made at a pH of 6.0 without any back ground electrolyte. Comparison of sorption behavior of the soils have been made on the basis of the Langmuir parameters. One of the soils is very rich in organic matter and others are progressively poorer in it though richer in clay content. This enables us to make some guess on the role of each of the constituents on overall adsorption. Humic acids and clays isolated from each soil have also been tested for adsorption efficiency. Adsorption maxima for all these constituents fall far below their individual CEC. Experiments have been done on soil residues after removal of mobile organic matter by alkali extraction. A drop in adsorption maxima has been observed although the decrease will not up to the theoretically calculated amount betraying a more complicated combined existence of humus and clay in native soil. Desorption experiments have been carried out in solutions of NaCl, KCl, MgCl₂ and CaCl₂. The desorbing efficiency of the ions was found to be in the decreasing order of Ca²⁺ > Mg²⁺ >> K⁺ > Na⁺. This result suggests predominantly an ion-exchange reaction.

Keywords : Sorption, desorption, Cu, soils.

Introduction

Copper like other microelements is essential to plants, animals and microorganisms but is toxic when its concentration exceeds a certain critical level¹. Copper enters soil systems through applications of Cu-containing fungicides, stable manures (e.g. pig slurry), and liquid or solid wastes from Cu related mining and manufacturing. Investigation on the adsorption of heavy metals in soils has piled up in recent years²⁻¹³. Influence of pH, ionic strength, contact time, bioavailability of Cu to plants, its behavior at contaminated levels etc. have been studied.

There are two types of minerals that are involved in the adsorption-desorption of Cu²⁺ in soils : Permanent charge and variable charge. Permanent charge minerals such as montmorillonite carry a negative charge as a result of ion substitution during the formation of minerals. Variable charge minerals such as Fe, Mn and Al oxides carry charges varying from negative to positive, depending on pH. Adsorption and desorption of Cu²⁺ in soil are affected by the proportion of these two types of minerals. Moreover the Fe, Al and Mn oxides have a relatively strong affinity (pH dependent) for Cu²⁺ and other heavy metal cations and the adsorption of Cu²⁺ on these oxides is considered to be inner-sphere complex through a chemi-

sorption process¹⁴. Therefore, adsorption of Cu²⁺ in the variable charge soils is generally pH dependent^{10,11,15,16}. On the other hand, the ideas of specific (non-electro static) and non specific adsorption was conceived. It has been suggested that adsorption data at very low equilibrium concentration were of more relevance to soil studies⁸. Adsorption-desorption of Cu on some Indian soils was also carried out¹⁷⁻²¹. They explained the data with the help of Langmuir constants, selectivity coefficients etc. and soil properties by correlation analysis. Desorption by different extracting reagents were also studied.

The present paper presents adsorption and desorption data on soils from four different locations in West Bengal and also on their humic acids and clay contents. The current practice of measuring adsorption in presence of an indifferent electrolyte has not been adhered to. Hence the adsorption data reflects the overall adsorption including both the so called specific and non-specific adsorption. Desorption of added Cu from soils and clays have been determined in presence of neutral electrolytes such as NaCl, KCl, MgCl₂ and CaCl₂.

Results and discussion

Adsorption data of Cu on soils and their components

Table 1. Soil properties

Properties ^a	Soil locations			
	Pedong	Gonpur	Katwa	Bakkhali
Taxonomic classification	Typic Lithic Udorthents	Typic Ochraqualfs	Typic Ustifluvents	Typic Haplaquepts
pH (1 : 2)	4.23	6.0	6.5	6.5
CEC [cmol (p ⁺) kg ⁻¹]	9.7	10.0	6.55	15.27
CEC of clay [cmol (p ⁺) kg ⁻¹]	21.78	32.27	20.78	31.64
CEC of humic acid [cmol (p ⁺) kg ⁻¹]	276.0	420.0	403.0	374.0
CaCO ₃ (%)	0.45	1.75	2.10	2.0
Organic matter (%)	6.23	0.74	1.25	1.77
Clay (%)	20.0	32.5	16.0	22.0
Silt (%)	17.0	8.0	3.0	16.0
Fine sand (%)	40.0	26.0	40.0	33.0
Coarse sand (%)	23.0	34.5	41.0	29.0
Mineral phase present	Illite (Tr.), Micaceous minerals	Illite (M), Kaolinite	Illite (VS), Kaolinite	Illite (S), Kaolinite (MS)

Tr. - Trace; M - Medium; MS - Medium Strong; S - Strong; VS - Very Strong.

^aSoil parameters are expressed as average of five replicates.

were found to fit the Langmuir isotherm. Contrary to linear isotherms reported earlier⁸ at low solution concentration (0.06 µg/cm³), L type isotherms obtained in the present case (not shown in this paper). The initial portion of these isotherms were however linear at low concentration. The Langmuir constants x_m and b in the equation $x = (bx_m c)/(1 + bc)$, where c is the equilibrium concentration and x is the amount adsorbed (meq/100 g) were evaluated by least square method. The constant x_m , denotes adsorption maximum and b , the energy constant is related to binding energy (Table 2).

Adsorption maxima for Cu on the soils decreases in the order : Pedong > Bakkhali > Gonpur > Katwa. Highest adsorption by Pedong soil can be attributed to its high organic matter content. The latter has been claimed to possess a strong tendency for complexing copper²⁶⁻²⁸. For Bakkhali soil the adsorption is mainly due to clays, a mixture of illite and kaolinite. Adsorption by Gonpur soil, which is poorest in organic matter but richest in clay content, can be explained likewise though the dominant clay is kaolinite in this case. The Katwa soil, low in both organic matter and clays, returns the lowest figure. Soils having higher CEC sorbed the more Cu. Similar result was also reported earlier²⁹. The extent of adsorption for

Table 2. Langmuir constants^a

Soils	Cu	
	x_m (cmol kg ⁻¹)	b (L mol ⁻¹)
Pedong :		
Whole soil	8.34	4.7888 × 10 ³
Humus-free soil	1.39	1.0986 × 10 ⁴
Clay	15.02	6.2809 × 10 ³
Humic acid	123.46	1.1894 × 10 ⁴
Gonpur :		
Whole soil	3.51	3.3435 × 10 ⁴
Humus-free soil	1.07	2.8316 × 10 ⁴
Clay	18.45	9.4227 × 10 ³
Humic acid	86.90	2.4283 × 10 ³
Katwa :		
Whole soil	2.97	5.5332 × 10 ⁴
Humus-free soil	1.24	5.0000 × 10 ⁴
Clay	16.81	1.6650 × 10 ⁴
Humic acid	42.24	3.2876 × 10 ³
Bakkhali :		
Whole soil	5.23	2.7510 × 10 ⁴
Humus-free soil	2.56	2.9557 × 10 ³
Clay	15.74	4.9180 × 10 ⁴
Humic acid	32.0	6.250 × 10 ³

^aAverage of five replicates in each soil adsorbent.

Cu is below the CEC by all the soils. Sequence of energy constant values for Cu adsorption is Katwa > Gonpur > Bakkhali > Pedong which shows higher bonding energy for clay than organic matter.

Adsorption on humus-free soil residue exhibits exactly the same pattern as on whole soil. Adsorption of Cu is reduced considerably for all the soils but expectedly to different extent after removal of organic matter. In case of Pedong soil richest in organic matter content, reduction in adsorption maxima varied between 73 to 83% for the metals. Gonpur soil is poorest in organic matter content and reduction is 69% for Cu. It appears that removal of organic matter exposes some of the adsorption sites on the inorganic minerals originally masked by the organic components.

In spite of some marginal difference, adsorption maxima values for Cu adsorption for the four clays are very close to each other. Appreciably higher cation exchange capacity of Gonpur clay fraction is responsible for higher adsorption of Cu by Gonpur clay. It was reported earlier that Cu adsorption by clays was dominated by cation exchange³⁰. It appears that the value of energy constant is higher in case of illite rich clay.

Adsorption of Cu by the soil humic acids follows the same pattern. CEC of humic acids of different soil origin

was found to have wide difference and the adsorption maxima have been found to fall much below the CEC. Though the humic acids are known to possess the same basic structural characteristics they differ in the functional group distribution³¹. In respect of adsorption or complexation efficiency the adsorption sequence of humic acids by the soils is Pedong > Gonpur > Katwa > Bakkhali for Cu adsorption. The values of the energy constants *b*, are more or less the same except for Pedong humic acid.

Desorption was measured in presence of electrolytes such as NaCl, KCl, MgCl₂ and CaCl₂ in solutions. The cations in the electrolytes have been considered as desorbing agents. The desorption data of soils and clays are presented in Tables 3 and 4.

The table shows the respective desorption efficiency of the electrolyte cations which is generally Ca²⁺ > Mg²⁺ > K⁺ > Na⁺ for all the soils and clays. Desorption percentages of sorbed cations are invariably much higher than that reported earlier.

A maximum of 38% of Cu is released from Pedong soil. For the remaining three soils the desorption percentage is still higher, some times reaching 90%. Pedong soil is rich in organic matter and the heavy metal cations are likely to be complexed and tightly held to the solid phase.

Table 3. Desorption data of soil

Desorbed ion	Electrolyte concentration (N)	Amount of metal ion desorbed (cmol kg ⁻¹) by				Percentage of sorbed cation desorbed by			
		Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Cu ²⁺ from Pedong soil	6.4 × 10 ⁻³	1.42	2.76	2.87	3.15	17.02	33.09	34.41	37.77
Cu ²⁺ from Gonpur soil	„	0.85	2.20	2.98	3.07	24.20	62.70	85.00	87.00
Cu ²⁺ from Katwa soil	„	0.63	1.41	2.28	2.44	21.20	47.50	76.80	82.10
Cu ²⁺ from Bakkhali soil	„	1.18	3.86	5.04	5.14	22.60	73.80	96.30	98.20

Data against highest electrolyte concentration are shown only.

Table 4. Desorption data of clay

Desorbed ion	Electrolyte concentration (N)	Amount of metal ion desorbed (cmol kg ⁻¹) by				Percentage of sorbed cation desorbed by			
		Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Cu ²⁺ from Pedong clay	8.0 × 10 ⁻⁴	1.73	3.46	5.67	6.30	11.52	23.30	37.75	41.94
Cu ²⁺ from Gonpur clay	„	1.26	4.72	8.82	11.34	6.90	25.60	47.80	61.50
Cu ²⁺ from Katwa clay	„	1.89	4.40	12.28	12.91	11.20	26.20	73.00	76.80
Cu ²⁺ from Bakkhali clay	„	1.57	5.35	11.34	13.70	10.00	34.00	72.00	87.00

Data against highest electrolyte concentration are shown only.

Remaining soils are low in organic matter but high in clay. Ca^{2+} was found to be the strongest desorbing agent. The fact that almost to removal of the Cu could be accomplished in electrolyte solutions betrays ion-exchange reactions on the clay surface. This is further highlighted by the order of desorbing efficiency of the desorbing cations such as Ca^{2+} , Mg^{2+} , K^+ and Na^+ .

The desorption percentage was comparable among the clays. In this case also an almost 1 : 1 exchange of the ions was observed except in Pedong soil-clay. Soils other than Pedong contain kaolinite and illite in various relative proportions. Only Pedong clay fraction contains micaeous residues. The two sets of results confirms the desorption reaction was by and large ion-exchange occurring on the clay phases.

It may also indicate that adsorption too was controlled by non-specific factors or electrostatic forces.

Experimental

Four surface soil (0–0.2 m) samples from four different locations of West Bengal were used. Of these Pedong belongs to Darjeeling Himalayan region at an altitude of 1938 m. Gonpur is from lateritic zone developed under forest vegetation. Katwa is an entisol from gangetic alluvium. The fourth viz. Bakkhali belongs to deltaic saline tract. The samples were air-dried and ground to pass a 2 mm sieve before use. The taxonomic classification of the soils and their properties are presented in Table 1. The important aluminosilicates in the four soils were identified by X-ray diffraction analysis. X-Ray diffraction pattern was recorded in Philips PW-1730 X-ray crystallographic unit provided with a proportional counter, PW-1050/70 goniometer, PW-1390 electronic using $\text{CuK}\alpha$ radiation with Ni filter. Slit assemble is $1^\circ > 0.2 > 1^\circ$. These XRD data were described in Table 1.

Adsorption experiments were carried out on (a) soils washed with 0.1 (N) HCl followed by 0.5 (N) CaCl_2 solution and finally washed free of chlorides. Soil thus prepared has been described as whole soil, (b) soil treated with 0.5 (N) NaOH solution in nitrogen atmosphere for 24 h with intermittent shaking and centrifugation. The operation was repeated thrice. Soil residue left after alkali extraction was washed with acid and treated with CaCl_2 solution repeatedly and finally made chloride free as before. This soil residue contains about 25% of the original organic matter. The resulting soil was dried un-

der vacuum. These have been generally referred to as humus free soil, (c) humic acid was separated from the alkali extract by acidification²². It was then treated with 1% HF-HCl solution in teflon tubes and dialysed after repeated centrifugation. This humic acid was dried finally in vacuum followed by air-drying for one week.

Organic matter was destroyed by 30% H_2O_2 treatment overnight. Clay was dispersed by shaking with 0.5 (N) NaOH at pH 8.5. The clay fractions were collected from top 10 cm and precipitated by acidification. It was then converted to Ca-form by treatment with CaCl_2 solution. Finally it was made chloride free by repeated washing followed by dialysis.

In separate sets of experiments gradually increasing concentrations of the adsorbate solutions e.g. CuCl_2 were equilibrated in airtight stoppered pyrex bottles at 30 ± 0.5 °C for 24 h at a pH of 6.0 with intermittent shaking. 2.0 g each of soil and humus free soil, 50 mg of clay and 20 mg of humic acid were used for adsorption experiment. In adsorption experiments the metal ion concentrations in solution were maintained around 10^{-4} (N). After the required equilibration period of 24 h. the supernatants were centrifuged and aliquots were analysed for respective metals spectrophotometrically. The adsorption time of 24 h was found adequate by trial experiments. The amounts of metal ions adsorbed were calculated from the difference in initial and final concentrations of metal ions.

Cu was determined by zincon 1-(2-hydroxy-5-sulphophenyl)-3-phenyl-5-(2-carboxyphenyl)formazan] method²³. Experimental details were presented earlier²⁴.

Desorption experiments were carried out only on whole soils and clays. Metal-soil and metal-clay complexes were first prepared by equilibrating the soil and clay samples with CuCl_2 at a pH of 6.0 for 24 h. They were centrifuged and washed free of adherent electrolytes as far as possible. Dialysing the samples did complete removal of such electrolytes. It was then centrifuged and air-dried. These complexes were equilibrated with 10^{-4} to 10^{-3} (N) solutions of NaCl, KCl, MgCl_2 and CaCl_2 for 24 h and the released Cu ions were measured as in the case of adsorption.

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Bhattacharya *et al.* : Sorptive interactions of Cu on soil, clay and humic acid

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