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Research Note

Cations Adsorption on Goethite-Humic Acid Complex

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Studies were carried out on the effect of temperature on the adsorption of Cu^{2+}, Pb^{2+} and Mg^{2+} on synthetic goethite (a phase in soil). Humic acid was coated on the synthetic goethite and its effect on metal adsorption was also studied. The amount of humic acid added had varied effects on the adsorption of these cations. An increase in the amounts of humic acid resulted in an increased adsorption of Cu^{2+} and a decrease in the adsorption of Mg^{2+}. However, increasing amounts of humic acid coating on the goethite had no significant effect on the amount of Pb^{2+} adsorbed. An increase in temperature decreased the amount of Mg^{2+} sorbed by the goethite-humic acid complexes while the temperature effect on the adsorption of Pb^{2+} and Cu^{2+} varied according to the different levels of humic acid added.

INTRODUCTION

Several studies have been carried out on the chemistry of metals and heavy metals with respect to their adsorption by and desorption from soil and soil phases [1-4]. The results observed in the various studies indicated that metals are specifically adsorbed and their distribution between the solid and liquid phases is pH dependent [5-7].

Despite of the volume of literature available on the adsorption of these cations by soil and soil phases, little information is available on the effect of other phases in the soil on their adsorption. Taylor and Theng [8] looked at the sorption of Cd by complexes of kaolinite with humic acid (which are phases in soil). They reported that the amount of Cd sorbed is directly proportional to the humic acid content of the complexes, while Maiguire et al. [9] observed that sorption of Cs on clay is inversely proportional to the humic acid present.

Goethite has long been recognized as playing an important role in binding trace metals in soils and sediments. Since this phase does not exist in isolation, this work aims to look at the effect of humic acid on the adsorption of Cu, Pb and Mg by goethite.

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MATERIALS AND METHODS

Goethite was synthesized from reagent grade ferric chloride, sodium hydroxide and deionised distilled water. The goethite was then prepared by adding 2 M sodium hydroxide solution slowly to the solution of ferric chloride with constant stirring, until the pH of the suspension was 12. This was followed by ageing for 48 hours at 60°C in an oven. After ageing, the suspension was filtered using a suction pump and washed free of chloride with deionised distilled water. (Filtrate negative to silver nitrate test) [10].

The clean solid (goethite) was dispersed in 10^{-3} M $NaNO_3$ solution and wet sieved. The point of zero charge of the goethite prepared was 7.90 as determined by the method of Kinniburgh et al. [11].

Humic acid was extracted from a soil sample collected from a refuse dumping site in Ibadan (Nigeria). The method of Stevenson [12] was adopted for the extraction. A known mass of the soil was decalcificated using 0.1 M HCl and the decalcificated sample was treated with ethanol and benzene to remove non-humic substances. The filtrate, which contains the non-humic substances, was discarded, while the residue was dissolved in sodium hydroxide. The filtrate was mixed with 2 M HCl until the precipitate was seen and was further purified with ethanol and HF. The dark brown amorphous precipitate was washed free of chloride and dried.

Goethite-humic acid complex was prepared by

Table 1. Copper adsorption at 30°C and 50°C on goethite and goethite-humic acid complex.

30°C					50°C			
Amt Added	Goethite	0.05 g HA	0.25 g HA	0.50 g HA	Goethite	0.05 g HA	0.25 g HA	0.50 g HA
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6.10	1.13	2.26	2.04	2.24	2.26	1.70	2.36	2.36
12.20	2.03	4.24	4.02	4.56	4.56	3.40	4.40	4.70
18.30	2.64	5.78	5.68	6.58	6.40	5.10	5.70	6.80
24.40	3.10	7.22	6.96	8.14	8.08	6.80	6.54	8.46
30.50	3.41	8.50	8.24	9.50	9.45	8.50	7.22	9.84
36.60	3.71	9.48	9.52	10.68	10.21	10.20	7.89	11.06
42.70	3.95	10.27	10.69	11.78	10.61	11.90	8.55	11.86
48.80	4.14	11.05	11.81	12.87	11.03	13.60	9.25	12.55
54.90	4.29	11.71	12.91	13.83	11.22	15.30	9.95	13.19
61.00	4.43	12.17	14.05	14.77	11.41	17.00	10.61	13.77

Note: HA = humic acid

Table 2. Lead adsorption at 30°C and 50°C on goethite and goethite-humic acid complex.

30°C					50°C			
Amt Added	Goethite	0.05 g HA	0.25 g HA	0.50 g HA	Goethite	0.05 g HA	0.25 g HA	0.50 g HA
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5.95	1.47	2.37	2.38	2.38	1.65	2.34	2.38	2.38
11.90	2.79	4.73	4.74	4.75	3.30	4.66	4.74	4.76
17.85	4.00	7.07	7.07	7.12	4.80	6.98	7.07	7.12
23.80	5.06	9.39	9.39	9.48	5.87	9.30	9.39	9.47
29.75	6.06	11.71	11.71	11.82	6.57	11.61	11.71	11.80
35.70	6.98	14.02	14.03	14.16	6.98	13.91	14.03	14.11
41.65	7.86	16.33	16.33	16.49	7.13	16.23	16.34	16.42
47.60	8.38	18.64	18.64	18.79	7.04	18.54	18.68	18.73
53.55	8.78	20.93	20.96	21.06	6.51	20.86	20.96	21.04
59.50	9.04	23.22	23.27	23.30	4.94	23.18	23.28	23.34

Note: HA = humic acid

adding humic acid of varying masses to known volumes of goethite suspension (see Tables 1 to 3). The content in each of the flasks was made to mark in 500 mL standard flasks with sodium nitrate solution. The suspensions in the flasks were shaken vigorously and then left for 5 days to age before they were used.

ADSORPTION

A 5 mL portion of the goethite stock solution was measured out into eleven polyethylene bottles. To this, 0.30 mL of 0.0108 M of HCl and $0, 1, 2, 3, \cdots, 10$ mL of a known concentration of metal solution were added. These were adjusted to the 20 mL mark with 0.001 M $NaNO_3$. The containers were slightly shaken and kept at a controlled temperature for 24 hrs (at 30°C and 50°C). The pH of the different suspensions was recorded and the suspensions were later filtered, while the filtrate was stored for metal analysis using FAAS. The above procedure was repeated for the adsorption of metals on goethite-humic acid complexes.

All measurements were carried out in triplicate and blank runs were carried out in all cases. The results were also subjected to statistical analysis to determine the level of significance between the concentration of metals adsorbed on both the goethite and goethite-humic acid complex.

RESULTS AND DISCUSSION

The results of the adsorption of the various cations on goethite and on the goethite-humic acid complex are

Table 3. Magnesium adsorption at 30°C and 50°C on goethite and goethite-humic acid complex.

	30°C				50°C			
Amt Added	Goethite	0.05 g HA	0.25 g HA	0.50 g HA	Goethite	0.05 g HA	0.25 g HA	0.50 g HA
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6.05	2.00	0.78	0.95	0.84	2.00	0.72	1.04	0.92
12.10	4.05	2.08	1.91	1.64	4.00	1.43	2.10	1.62
18.15	6.10	3.68	3.44	3.44	6.02	2.48	3.01	2.62
24.20	8.13	5.74	5.42	5.58	8.01	4.32	4.38	4.02
30.25	10.13	7.92	7.62	7.80	10.01	6.45	6.28	6.04
36.30	12.13	10.18	9.84	10.06	12.04	8.66	8.47	8.30
42.35	14.14	12.54	12.08	12.35	14.08	10.94	10.73	10.60
48.40	16.18	14.94	14.39	14.68	16.08	13.26	13.04	12.96
54.45	18.25	17.34	16.74	16.96	18.12	15.61	15.38	15.28
60.50	20.35	19.74	19.09	19.24	20.01	17.92	17.78	17.60

Note: HA = humic acid

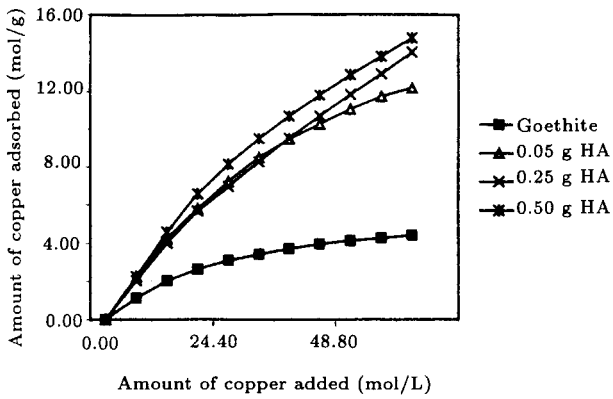

Figure 1a. Copper adsorbed at 30°C on goethite and goethite-humic acid complex.

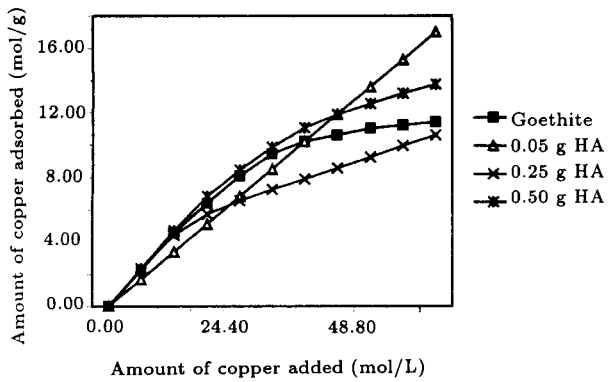

Figure 1b. Copper adsorbed at 50°C on goethite and goethite-humic acid complex.

shown in Figures 1 to 3. The amount of Pb^{2+} and Cu^{2+} sorbed on goethite (9.04 mole/g and 4.43 mole/g) was far less than that sorbed on the goethite-humic acid complex (23.22 mole/g and 12.17 mole/g), while more Mg^{2+} was sorbed on goethite than on the complex (see Tables 1 to 3).

As the amount of humic acid added increased, the amount of Cu adsorbed increased, while there was no remarkable increase in the amount of Pb adsorbed (apart from the initial increase) and a decrease in the Mg adsorbed (as shown in Figures 1 to 3). Similar results were obtained [13] for Cu^{2+}, Pb^{2+} and other trace metal cations on humic acid surfaces. The observed decrease in the adsorption of Mg on the goethite-humic acid complex was due to the fact that the adsorption sites for Mg on goethite have been blocked by humic acid, since the latter could be adsorbed on these sites [14,15]. It has also been proved that Mg is weakly coordinated to humic acid [16].

The amount of Cu^{2+} adsorbed on goethite (4.43 mole/g) was far less than that adsorbed on the goethite-humic acid complex (12.17 mole/g). This is in agreement with the observation made by earlier

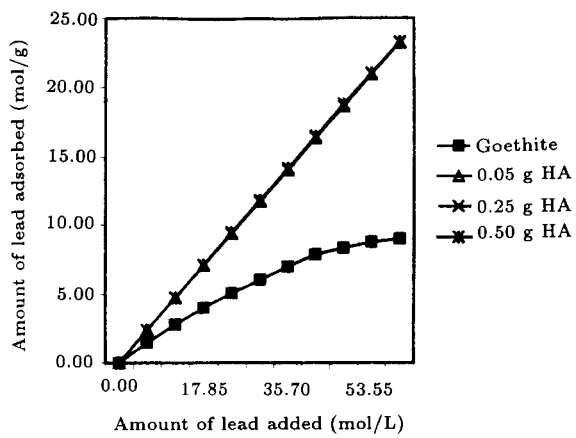

Figure 2a. Lead adsorbed at 30°C on goethite and goethite-humic acid complex.

authors that Cu forms an inner-sphere coordination complex with carbonyl groups of the humic acid, thereby increasing its adsorption capability [17,18]. The amount of Pb adsorbed on goethite (9.04 mole/g) was lower than that adsorbed on the complex (23.22 mole/g). The addition of humic acid resulted in a drastic increase in the adsorption of Pb^{2+}. This is due to the impartation of a negative charge to the surface of goethite by the addition of humic acid [19]. As the amount of humic acid added increased, there was no significant increase in the amount of Pb^{2+}. This also suggested that there is a limit to which the humic acid added could be increased.

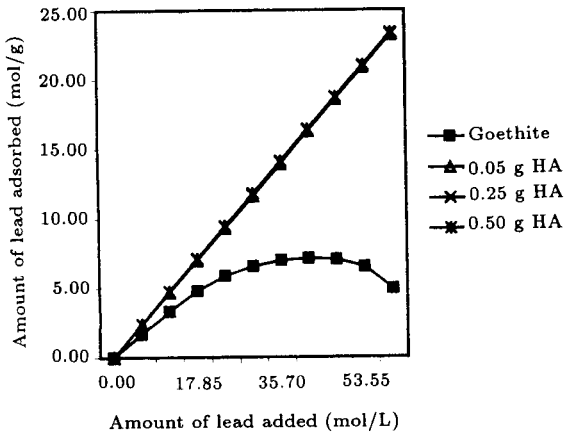

Figure 2b. Lead adsorbed at 50°C on goethite and goethite-humic acid complex.

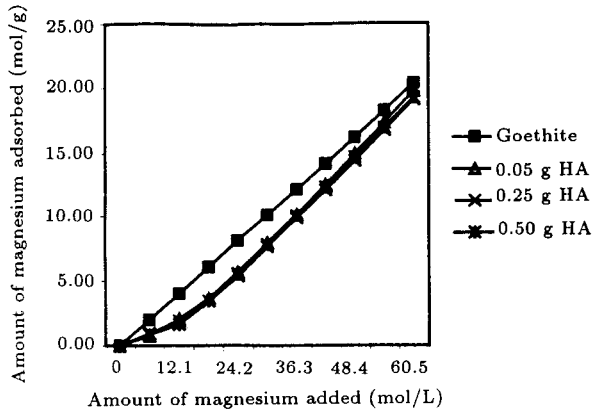

Figure 3a. Magnesium adsorbed at 30°C on goethite and goethite-humic acid complex.

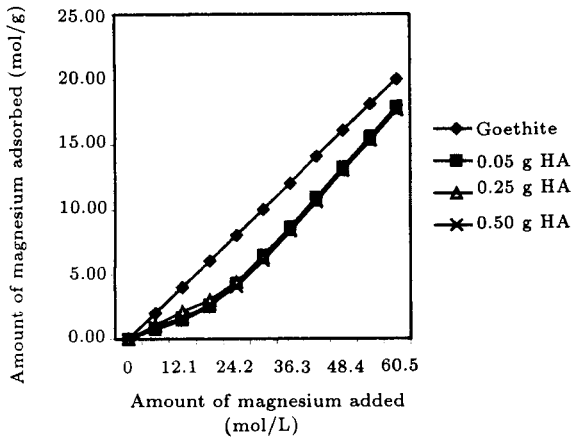

Figure 3b. Magnesium adsorbed at 50°C on goethite and goethite-humic acid complex.

Comparison between the amount of these cations adsorbed on goethite and that of the complex indicated that the humic acid added modified the structure of goethite. In addition, these two substrates reacted leaving the surface of the resultant substrate negatively charged. This made it possible for more of these cations to be adsorbed, except Mg, which has a decrease in adsorption. This implies that there are specific sites on the goethite which could sorb Mg^{2+} that have been occupied by humic acid. A similar observation was made by Maguire et al. [9] for the sorption of Cs on clay-humic acid complex. They reported that humic acid bonded to clay surfaces, potentially blocking the exchange sites which could sorb Cs; furthermore, the humic acid polymer adsorption sites are of low energy, which have no specificity for Cs, thereby decreasing its sorption.

The behaviour of these metals varied on these phases. Cu^{2+} and Pb^{2+} behaved in the same way on goethite and on the goethite-humic acid complex. These two ions are from the transition series and they have empty *d* orbitals that are available for complex formation. Mg^{2+} behaved differently on these phases because it is an alkaline earth metal with no empty *d*-orbitals for complex formation. The high affinity Mg^{2+} has for goethite might be due to the similar ionic radius it has with the ferric ion (0.65A and 0.64A, respectively). This implies that more Mg^{2+} ions can enter the goethite lattice, thereby increasing the adsorption.

At both temperatures and at all levels of humic acid added, it was clear that the addition of humic acid to goethite depressed the sorption of Mg by goethite. An increase in temperature has no effect on the amount of Pb adsorbed, while it has a varied effect on the amount of Cu adsorbed with different levels of humic acid added.

CONCLUSIONS

The surface reaction of goethite was modified by the addition of humic acid. The affinity of the metals for the complex followed this order: $Cu^{2+}>Pb^{2+}>Mg^{2+}$. This indicated that Cu^{2+} and Pb^{2+} had more affinity for the complex than Mg^{2+} which had an affinity for the solution. This could go a long way towards solving Mg deficiency in plants. The addition of humic acid to the soil would invariably release the inherent Mg in the

soil for plant uptake. Also, it would be advantageous in controlling the availability of the toxic Pb pollutant, since the addition of humic acid fixes Pb^{2+} ions in the soil. However, care should be taken to maintain the levels of soil organic matter.

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