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Cadmium Distribution within Model System Containing Kaolin and Humic Acids

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Abstract

Binding cadmium with humic acids (HA) taken from a sample of lake bottom sediment has been studied depending on the acid-base medium status parameter of the system (within the range of pH 3–10) and on the concentration of cadmium ions (5, 10 and 50 μmol/L). Ion-exchange separation of non-bound cadmium ions and its complexes with HA has been carried out using the method of ion exchange on sulphocationite with the subsequent analysis via the method of flame atomic absorption spectroscopy. Cadmium binding has been investigated for the system containing kaolin and HA, within the range of pH from 3 to 10. A comparative analysis has been performed for total cadmium binding in the systems containing kaolin and HA separately, as well as in the systems where they are present simultaneously with all other factors being constant. We took into account he fraction of metal bound with HA in the solution, in the sediment and on the surface of kaolin. It has been demonstrated that the additivity of the systems (the decrease of free metal concentration in a trinary system is equal to the sum of concentration decrease values in double systems under the same conditions) is observed within the pH range of 4.6–5.8. In other cases the binding of cadmium in a trinary system would be lower, than it is for the sum of double systems: first, due to HA deactivation owing to its adsorption onto the surface of kaolin (within acidic pH range), and then due to blocking the adsorption centres of kaolin (within neutral and alkaline pH ranges).

Key words: cadmium, kaolin, humic acids, sorption, complex formation

INTRODUCTION

Mineral components and naturally occurring organic matter in natural soil and water systems are most often presented by humic substances, are usually coexistent [1]. Humic substances represent anionic polyelectrolytes with high heterogeneity of physical and chemical properties those are capable to be strongly bound with mineral surfaces. In this case the main mechanism of binding is presented by specific adsorption and ligand exchange with protonated surface hydroxyl groups [2]. In the nature, as a rule, mineral surfaces are to a considerable extent covered with humic substances. At the same time, the influence of this covering upon the adsorption behaviour of pollutants such as heavy metal cations finally is not comprehensively established [2, 3].

It is customary to assume that the adsorption centres on a mineral surface exhibiting high affinity with respect to heavy metal cations, are involved in the specific adsorption of humic substances, such as humic acids and fulvo acids. As a consequence, the sorption of metals by mineral surfaces would be determined to a considerable extent by the adsorption of humic substances in naturally occurring environments [4, 5]. The studies on the influence humic substances upon the sorption of metals onto mineral surfaces carried out with various metals and sorbents has brought about rather different and sometimes inconsistent results [6–11]. Delivering additional adsorption centres for binding metals, adsorbed humic substances could increase the solid phase adsorption capacity with respect to metals. However, adsorbed humic substances can partly occupy adsorption centres, capable of binding metal ions, too, which could result in decreasing the sorption of metals by proper mineral surface. Moreover, the presence of dissolved humic substances can reduce the sorption of metals onto the solid phase due to the formation of soluble metal complexes [2, 3]. Taking into account the sorption behaviour of metals on mineral and organomineral surfaces, as well as the sorption of humic substances by mineral surfaces, the greatest influence of humic substances upon binding metal cations with the solid phase should be expected at low pH values. Just under these conditions, an organomineral surface is formed, whereas metal cations are weakly sorbed by a mineral surface [12, 13].

In order to adequately forecast the migration of metal cations in natural environments it is necessary to estimate quantitatively the influence humic substances upon the sorption of metals by solid phase. Till now, there is no unequivocal answer to the question whether adsorbed humic substance exhibit simply additional adsorption centres without blocking the mineral surface, according to the model of linear additivity [9], or the interaction between metal cations with humic substances on the mineral surface proceeds in a more complicated manner. There are hypotheses [5, 7] that metal cations demonstrate a higher affinity with respect to adsorbed humic substances, rather than with respect to dissolved ones. The author of [10] has found out that the sorption of copper in the goethite–humic system is highly non-additive. The non-addittivity value for copper binding to a considerable extent depends on acid-base medium status such as pH value, ionic strength, the ratio between goethite and humic acids (HA) as well as copper concentration. The authors of [11] also reported deviations from the additivity rule found out for cadmium–humic acids–haematite system. At low pH values the additivity approach results in the overestimation of the cadmium sorption level for humic–haematite complex, whereas at high pH values, on the contrary, there is underestimation observed. As the concentration of cadmium increased, the deviation from the additivity law exhibits an increase. However, the authors of [9] did not found out any specific interaction between HA and cobalt on the surface of various minerals, such as kaolinite, gibbsite and goethite.

The authors of [14] demonstrated that there is no difference observed between a combined system and the sum of two independent systems in a metal–HA–kaolin system at the initial stages of sorption at low concentration of metal cations. Within alkaline pH range, HA promote a decrease in the metal cation sorption level, and the character of this decrease (changing the sorption level with increasing the values of pH) is to a much greater extent corresponding to the character of metal–humate complex formation than to the character of HA desorption from a mineral surface. At the initial sorption stages, a moderate increase in cobalt and cadmium sorption level is observed at high values of metal cation concentration. A decrease in the sorption level is inherent in all the four metals (copper, zinc, cobalt, cadmium) at high values of pH, as well as in the case of low salt concentration.

In the present work, we have chosen the system containing kaolinite, humic acids taken from a sample of bottom sediment, and cadmium ions to be a model system.

EXPERIMENTAL

In this work we used an HA preparation isolated from a sample taken from lake bottom sediment (the Yamal-Nenets Autonomous Okrug, Russia). The ash level of the preparation amounted to 6.3 %; the total acidity determined with the use of the barite method, was equal to 2.47 mmol/g (as calculated for an ash-free weighed sample portion) [15]. The elemental composition was determined employing an EA-1108 CNHS-O analyzer (Carlo Erba Instruments, Italy); as recalculated for an ash-free weighed sample portion the composition was as it follows, %: C 50.5±4.6, H 7.1±0.8, N 1.9±0.2, O 38.8±4.8, S 1.7±0.1.

For the experiments we used KE-2 kaolin with the specific surface area (according to the adsorption of methylene blue) $S_{sp} = 15.4\ \mathrm{m}^2/\mathrm{g}$. The grain-size composition of kaolin was the following: 10–50 μm – 93.60 %, 5–10 μm – 2.04 %, 1–5 μm – 2.54 %; <1 μm – 1.82 %. The content of organic matter determined according to the Tyurin method, did not exceed 0.04 %.

The parent HA solution was prepared *via* dissolving a weighed sample portion of dry preparation in 20 mL of a 0.1 M NaOH solution using an ultrasonic bath and then the volume of the solution was brought to 1 L adding a background electrolyte solution (0.1 M $NaNO_3$).

We studied the distribution of cadmium between the species coexisting in the system depending on the acid-base medium status (pH value) of the system. For this purpose we prepared systems containing kaolin (25 g/L), HA (250 mg/L) and cadmium ions (5, 10 and 50 μmol/L) in various combinations, with pH value ranging within 3–10. The values of pH required were reached by the addition of little volumes of 0.1 M HNO_3 solution. The total volume of solutions amounted to 20 mL. All the investigations were carried out in the presence of 0.1 M $NaNO_3$ solution in order to maintain constant ionic strength.

The solutions were shaken during 24 h at a room temperature, then they were centrifuged during 30 min (the rotation frequency being of 3000 min^{-1}).

The separation of humate cadmium complexes of and free species of the metal was carried out employing a cation-exchange column [16]. The method is based on the fact that HA binding the metal ions into complex hinders its binding with a cation-exchange resin (cationite) [17]. The advantages of this technique of separation combined with the atomic absorption analysis consist in its rapidity and a low detection limit. A disadvantage of this technique consists in the fact that HA and humates are adsorbed onto a cationite [17]. We experimentally studied the sorption of HA onto such cationites as Lewatit S 1468 (Germany), KB-4 and KU-2-8 (Russia) in the Na-form. It has been established, that KU-2-8 resin almost does not bind HA. The height a cationite layer in the column was selected so that after flowing 10 mL of solution with the concentration of cadmium amounting to 50 μmol/L, through the column, a complete removal of cadmium was observed, whereas no HA sorption occurred. The height of the cation-exchange resin layer established this way has amounted to 30 cm. Under the conditions of the experiment, the sorption humate components within the column did not exceed 3 %. The determination of cadmium concentration was performed using the method of atomic absorption spectroscopy with flame atomization employing Shimadzu AA-6300 spectrometer (Germany). The determination of HA concentration in the solution after equilibration was carried out *via* a photometric method at the wavelength values amounting to 370, 400 and 430 nm employing KFK-3 photometer. At all the points, equilibrium pH values were measured.

RESULTS AND DISCUSSION

We have studied the binding of cadmium in the system containing 250 mg/L of HA, within the range of pH 3–10 at the initial concentration of cadmium equal to 5, 10 and 50 μmol/L.

It has been revealed that with increasing pH, the concentration of free cadmium decreases, whereas the concentration of cadmium bound with HA both in the form of dissolved species, and in the form of sediment, exhibits, on the contrary, an increase. The relative position of plot branches describing the change in the concentration of cadmium humates in the solution (Fig. 1) indicates that the limiting binding ability of humates is reached. Thus, with increasing the concentration of cadmium, the contribution of dissolved cadmium–humic complexes in the total concentration of cadmium exhibits a decrease. In this case the fraction of cadmium in the precipitate for all the concentration values under investigation appeared to be comparable. Figure 1 demonstrates two distinctly seen steps. The first step (pH 3.5–4) corresponds), in our opinion, to the deprotonation of carboxylic groups those are

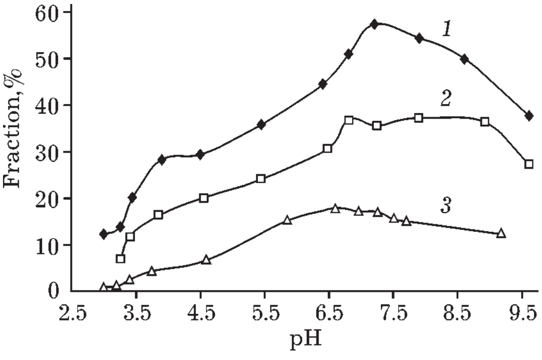

Fig. 1. HA complex-forming ability depending on pH value. Initial concentration of cadmium, μmol/L: 5 (*1*), 10 (*2*), 15 (*3*).

binding cadmium ions. Moreover, for this region one can observe the solubility of HA to be considerably increased, *i.e.* the concentration of potential ligands in the solution exhibits an increase. Further (at pH 4–5) a plateau is observed, since within this pH region the basic part of carboxylic groups is deprotonated, whereas phenolic groups remain non-dissociated. At pH 5–7.5 a gradual deprotonation of phenolic groups occurs, which corresponds to an increase in the complex-forming ability of humates. The further reduction of the concentration of cadmium–humic complexes could be caused by an increase in the hydrolysis level for cadmium ions as well as with precipitating the products of hydrolysis.

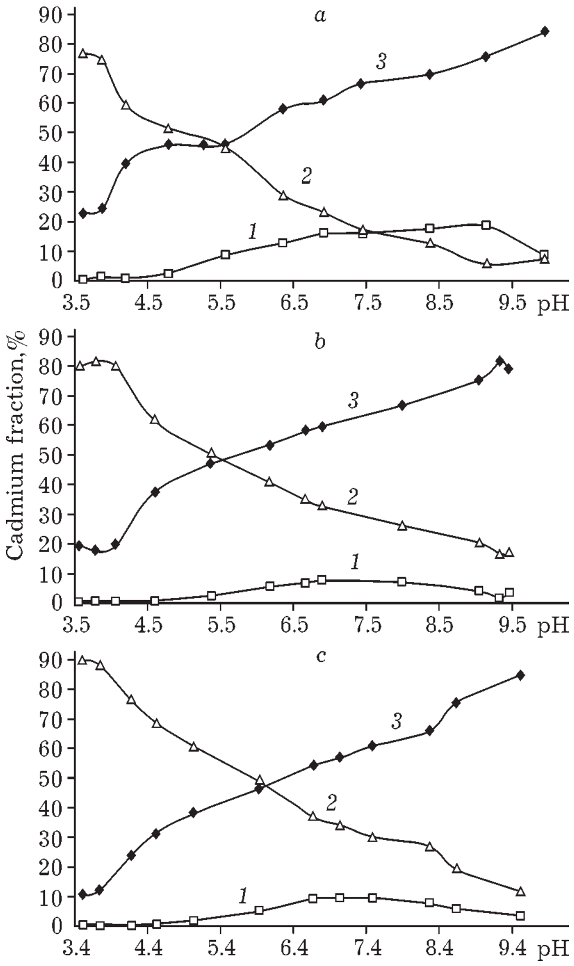

Fig. 2. Cadmium distribution diagrams in the presence of HA and kaolin at the initial concentration of cadmium 5 (*a*), 10 (*b*) and 50 μmol/L (*c*): *1* – soluble cadmium humates, *2* – unbound cadmium, *3* – insoluble cadmium humates and cadmium bound with kaolin.

As the initial concentration of cadmium increases, there is a shift the sorption level maximum observed toward lower pH values, which is in quite a good agreement with an approximate constancy of the distribution coefficient for cadmium.

We have also investigated the adsorption of HA and binding cadmium in HA–kaolin–cadmium trinary system, containing 250 mg/L HA, 25 g/L kaolin within the pH value range of 3–10 at the initial concentration of cadmium amounting to 5, 10 and 50 μmol/L.

It has been revealed that the concentration of cadmium in the system does not exert any considerable effect on the adsorption of HA onto kaolinite.

Figure 2 demonstrates the diagrams of cadmium distribution in the system at various cadmium concentration values. One can see that with increasing the values of pH, the concentration of free cadmium decreases at the same time the concentration of cadmium bound with kaolin and HA exhibits an increase. In this case, one can observe a maximum within the range of pH equal to 6–8 on the curve corresponding to cadmium humate concentration in the solution depending on the value of pH. The further increase in pH values results in strengthening the hydrolysis of cadmium ions and precipitating the products of hydrolysis. Exception for high acidity pH regions, cadmium is prevailing in e precipitated species: cadmium adsorbed by kaolin; cadmium humates sorbed from the solution; cadmium bound with HA preliminary adsorbed by the surface of kaolin; insoluble cadmium humates. The separation of these species seems to be almost impossible.

At pH 4–5 the fraction of cadmium humates in the solution (see Figure 2, curves *1*) appears insignificant, whereas a considerable decrease in the content of free cadmium ions in the solution (curves *2*) is corresponding to equally considerable increase in the content of cadmium in the precipitated species (curves *3*). Among the latter, to all appearance, kaolin-sorbed cadmium–humic complexes are prevailing irrespective of the mechanism of their formation.

The comparative analysis of cadmium binding in binary and trinary systems was carried out at the concentration of cadmium amounting to 10 μmol/L and HA content equal to 250 mg/L. The fraction was taken into account

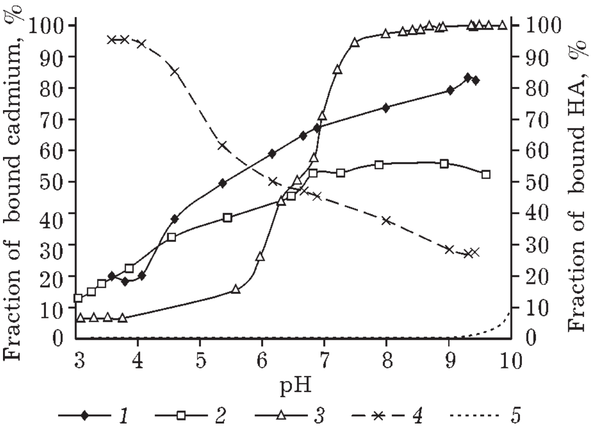

Fig. 3. Comparative characteristics for binding cadmium in binary and trinary systems: *1–4* – cadmium binding in the presence of: kaolin and HA (*1*), HA (*2*), kaolin (*3*), kaolin and cadmium (*4*, right axis), *5* – the fraction of $Cd(OH)_2$ in the system without HA and kaolin.

concerning the metal bound with HA in the solution, in the sediment and on the surface of kaolin. The curves obtained for the fraction of bound cadmium depending on pH value for various systems are demonstrated in Fig. 3 (left axis).

Within the acidic and neutral pH value region, cadmium binding with HA is prevailing, since in this case the surface of kaolin contains insignificant amount of deprotonated hydroxyl groups. At pH > 7, on can observe saturation of complex-forming centres of HA and an increase in the adsorption of cadmium by kaolin.

On the curve corresponding to the change in binding cadmium for trinary system, one can distinguish several regions. So, at pH 3.5–4.6 the binding of cadmium in the system containing kaolin and HA is lower in comparison with that for the system without kaolin. This could be caused by the fact that almost all HA units are located on the surface of kaolin (see Fig. 3, curve *4*), hence, a part of HA functional groups cannot be accessible with respect to cadmium. With increasing pH value, the adsorption of HA by kaolin decreases, and the fraction of cadmium bound in trinary system, represents a total cadmium binding level in double systems such as Cd–HA and Cd–kaolin. Such a law is observed up to pH values equal to 5.8. Further, the deviation from additivity begins again, *i.e.* the sum of bound cadmium fractions for double systems would exceed the fraction of bound cadmium in trinary system. This fact could be explained by that that HA would block the adsorption centres on the surface of kaolin, drawing the greatest contribution in the sorption of cadmium within this range of pH values. The formation of cadmium hydroxide precipitate would influence the concentration of free cadmium in the system only at pH > 9 (see Fig. 3, curve *5*).

CONCLUSION

Thus, it has been established that the acid-base medium status and total concentration of cadmium influence to a considerable extent the distribution of metal between different components of the system. The behaviour of humate complexes at various pH values is considered to be caused by the formation of mainly two types of the complexes such as carboxylic ones (within acidic pH region) and phenolate complexes (at elevated pH values). It has been demonstrated that for the conditions under investigation cadmium prevails in the adsorbed form and the form of insoluble humates.

The data obtained allow us to conclude that the description of system containing cadmium, HA and kaolin, as the sums of individual double systems is adequate only for narrow range of pH values (5.2±0.6). In the general case one should take into account mutual influence between clay and humic substances upon binding of metals in the system.

REFERENCES

1 G. Sposito, The Surface Chemistry of Soils, Oxford University Press, Oxford, 1984.
2 E. M. Murphy, J. M. Zachara, *Geoderma*, 67 (1995) 103.
3 R. D. Harter, R. Naidu, *Adv. Agron.*, 55 (1995) 210.
4 J. A. Davis, J. O. Leckie, *Environ. Sci. Technol.*, 12 (1978) 1309.
5 J. A. Davis, *Geochim. Cosmochim. Acta*, 48 (1984) 679.
6 F. Dalang, J. Buffle, W. Haerdl, *Environ. Sci. Technol.*, 18 (1984) 135.
7 D. P. H. Laxen, *Water Res.*, 19 (1985) 1229.
8 H. Xu *et al.*, *Sci. Total Environ.*, 81/82 (1989) 653.
9 J. M. Zachara, C. T. Resch, S. C. Smith, *Geochim. Cosmochim. Acta*, 58 (1994) 553.
10 A. P. Robertson, Goethite, Humic acid interactions and their effects on copper(II) binding (Dissertation), Stanford University, 1996.
11 A. W. P. Vermeer, J. K. McCulloch, W. H. van Riemsdijk and L. K. Koopal, *Environ. Sci. Technol.*, 33 (1999) 3892.
12 M. M. Benjamin, J. O. Leckie, *J. Colloid Interface Sci.*, 79 (1981) 209.
13 P. W. Schindler, P. Liechti, J. C. Westall, *Neth. J. Agr. Sci.*, 35 (1987) 219.

14 K. M. Spark, J. D. Wells, B. B. Johnson, *Austr. J. Soil Res*., 35 (1997) 113.

15 A. A. Kayugin, L. V. Cherkashina, G. N. Shigabaeva, *Vestn. TyumGU*, 3 (2008) 153.

16 C. M. G. Van den Berg, J. R. Kramer, *Anal. Chim. Acta*, 106 (1979) 113.

17 I. V. Perminova, Analiz i Kvalifikatsiya i Prognoz Svoystv Guminovykh Kislot (Doctoral Dissertation in Chemistry), Moscow, 2000.