ISSN 0016-7029, Geochemistry International, 2007, Vol. 45, No. 2, pp. 178–184. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © I.Ya. Koshcheeva, S.D. Khushvakhtova, V.V. Levinskii, V.N. Danilova, Yu.V. Kholin, published in Geokhimiya, 2007, No. 2, pp. 208–215.

Interaction of Cr(III) with the Humus Acids of Soil, Water, and Bottom Sediments

I. Ya. Koshcheeva[a], S. D. Khushvakhtova[a], V. V. Levinskii[b], V. N. Danilova[a], and Yu. V. Kholin[c]

[a] *Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, ul. Kosygina 19, Moscow, 119991 Russia*
e-mail: varshal@geokhi.ru
[b] *Tver State Technical University, nab. Nikitina 22, Tver, 170026 Russia*
[c] *Karazin Kharkov State University, pl. Svobody 4, Kharkov, 610077 Ukraine*

Received May 19, 2005

Abstract—The interaction of Cr(III) with humus acids [fulvic (FA) and humic (HA) acids] was studied in the systems Cr(III)–FA, Cr(III)–HA, and Cr(III)–FA–HA. Chromium(III) reacts with FA extracted from the headwaters of the Moscow River and from the Krapivenka River (a tributary of Lake Seliger) to form a highly soluble high-molecular-weight Cr(III)-hydroxofulvate complexes with $\bar{\beta}_{11} = 1.93 \times 10^6$ and 5.70×10^6, respectively. Humic acids extracted from peat in the Tver area and the sapropel of Lake Seliger behave as complexing sorbents with conditional affinity constants $\log\beta = 3.78$ and 3.23 for Cr(III) sorption at HA sites in the peat and sapropel, respectively. In the three-component system Cr(III)–FA–HA, the Cr(III) distribution coefficient between solution and precipitate is controlled by the pH value and FA content in the solution and decreases by 1–1.5 orders of magnitude with increasing fulvic acid content.

DOI: 10.1134/S0016702907020061

INTRODUCTION

The volumes of anthropogenic pollutants are now comparable with those of natural processes. In some regions, chromium is a strong pollutant. Chromium compounds exert significant effect on the ecological state of the environment, especially at areas with the steel industry, leather processing, dyeing industries, galvanic productions, and others [1].

Chromium varies in oxidation degree from +2 to +6 but occurs in natural environments only in tri– and hexavalent states, with the latter being the least stable. Cr(III) participates in biological processes, forming stable complexes with many organic ligands, while Cr(VI) easily passes through cell membranes and is a very toxic ion [2]. Cr behavior in natural waters and soils depends on the pH and redox potential of the environment [3]. Most soils and underlying rocks, acid and weakly acid soils, and anaerobic groundwaters (pH 4–6) contain Cr(III). Cr(VI) compounds were found in alkali soils (pH 8–9) in the presence of oxygen-rich water [4].

Mutual transitions of Cr(III) and Cr(VI) in waters, soils, and bottom sediments depend on the concentration conditions of these environments. In particular, Cr(VI) is readily reduced by Fe(II) ions, sulfides, organic compounds, including those of the humus family. By contrast, Cr(III) is rapidly oxidized at a significant MnO_2 excess or is slowly oxidized by water-contained oxygen in alkaline environments [1].

Hence, if fresh waters and bottom sediments contain organic ligands, including humus, Cr occurs mainly as hydrolytic and compexing Cr(III) species.

The very low Cr (III) content (from 0.5 to 40 μg/l) in unpolluted natural fresh waters is related to the low solubility of Cr minerals [1]. Chromium (III) hydroxides also have a low solubility, and up to 98.5% Cr in river waters occurs in suspended forms [5], varying from 0.5 to 3.4 mg/g in suspensions of the rivers of European Russia [6]. At the same time, significant amounts of Cr(III) occur in water as highly soluble complex compounds, which account for up to 88% of the total Cr content in the presence of high-molecular organic ligands with a molecular weight of more than 10000 Da [7]. For example, up to 92.1 wt % Cr occurs as high-molecular compounds in hard oligotrophic waters, with 40% contained in compounds with a molecular weight of 6000 Da, up to 20% in compounds with a molecular weight of 5100–5700 Da, and up to 5 % in compounds with a molecular weight of 650–850 Da [8].

Experimental results show that Cr(III) interacts with fulvic acids (FA) extracted from peat and forest soil to form strong complexes: the conditional stability constants of Cr fulvate complexes $\log\beta = 5.8$ for FA extracted from peat and 5.24 for FA extracted from forest soils [9]. With humic acids (HA), chromium (III) and its hydrolytic species also form stable complex compounds with the following conditional affinity constants $\log\beta$ at pH 3.2–4.3: 3.4–4.3 for the Cr^{3+}–HA

system and 4.9–5.3 for the $Cr(OH)^{2+}$–HA system [10]. Thus, natural and experimental studies of Cr(III) species in waters, soils, and bottom sediments reveal a significant role of FA and HA in the migration and accumulation of chromium.

The fact that FA and HA extracted from water, soil, peat, and bottom sediment have a high ash content is often not taken into account, causing contradictions between published quantitative characteristics of FA and HA. The high ash content makes it difficult to obtain reliable and comparable results on the molecular weight and protolytic characteristics of the compounds, and hence, on the stability constants of the metal complexes.

The interaction of metal ions with FA and HA proceeds by means of complexing with oxygen-bearing groups and brings about opposite processes because of different solubility of humic acids, the range of their molecular weight, degree of oxidation, and other properties. Complexation with FA drastically increases the migration ability of metals, whereas HA as a complexing adsorbent causes the accumulation of metals in soils and bottom sediments [11].

Therefore, the aim of our research was to study the interaction of Cr(III) with ash-free FA and HA specimens extracted from natural objects and its behavior in the three-component Cr(III)–FA–HA system.

EXPERIMENTAL

Ash-free specimens of FA were obtained from highly colored waters of the upper reaches of the Mosow River and the Krapivenka River, a tributary of Lake Seliger, which is polluted Cr(III) by the waste waters of a leather-processing plant. Fulvic acids were extracted from these waters using absorption chromatography on BAU active charcoal [12] after preliminary accumulation by freezing and subsequent transformation of FA into the H^+ form by filtration through KU-2 cationite. The specimens contain from 320 to 1200 μg/ml FA, which was determined on an SF-16 spectrophotometer at λ = 420 nm and pH 5.0. The results of the CHNS analysis of FA conducted on a Carlo Erba 1108 analyzer (Italy) and recalculated onto an anhydrous basis, were as follows (%): C = 41.9; H = 3.6; N = 0.9; O = 53.6. The ash content of FA (also calculated on an anhydrous basis) was 0.3%.

Low-ash specimens of humic acids were extracted from peat collected in the Tver area and from bottom sediments of Botov Bay of Lake Seliger by the conventional technique, which involves the extraction of HA by 0.1M NaOH, acidification of the solution to pH1–1.5, separation of HA by centrifuging, and subsequent desalination of HA by 2–5% HF [13]. After the treatment, the ash content was 0.22%. The CHNS analysis of HA showed 51.3 C, 5.2 H, 1.5 N, 0.2 S, and 41.8 O.

Data on the dissociation constants of fulvic acids are required to characterize FA as a natural ligand. For this purpose, FA solutions were analyzed by potentiometric titration on a pH-121 potentiometer cell with a glass electrode in a nitrogen flow, using 0.049M KOH purified from carbonates as the titrant [14]. The dissociation constants were calculated from the differential curves of potentiometric titration using the CAS computer program with adequate mathematical models describing equilibrium in the polyelectrolyte systems [15].

The interaction in the Cr(III)–FA system was studied by the solubility method. The equilibrium was attained for 35 days at pH 5.0. Then, the solubility of 20-mg portions of Cr(III) oxide was studied depending on the FA content, which were increased from 0 to 2.8×10^{-4} M in 30 ml of the solution.

A high-molecular nature of synthesized hydroxofulvic Cr(III) complexes was determined by studying the molecular weight distribution using gel filtration through a column packed with neutral Sephadex G-25, which was preliminarily calibrated against molecular weights from 5000 to 300 Da. The column had an adsorbent layer height h = 37 cm, a diameter d = 1.7cm, and a dry gel weight m = 18 g. The chromium content in the fractions was determined by electrothermal and flame atomic absorption spectrometry on a Perkin Elmer 2380.

The study of the Cr(III)–HA system was conducted to determine the sorption capacity of humic acids for chromium(III) at pH 5.0. For this purpose, 20-mg HA samples (with an ash content 0.22%) were mixed, under static conditions, with 30-ml portion of chromium(III) chloride with the Cr content increased from 5 to 500 μg/ml. Under equilibrium conditions (after three days), the samples were analyzed for Cr content. Sorption isotherms were processed with the CLINP 2.1 computer program [15] to calculate the affinity constants of chromium(III) for HA, thus estimating the strength of chemical interaction between sorbent and metal ions.

In addition, the sorption of Cr(III) ions on HA was studied within the pH range of 2.0–6.0.

Three-component Cr(III)–FA–HA system was studied in an experimental series that approached equilibrium from above [by the interaction of 20-mg samples of low-ash HA with a solution having a constant Cr(III) content (200 μg/ml) and a FA content increased from 0 to 300 μg/ml)] and from below [by the interaction of aliquots of Cr(III) humate and solutions with increased FA contents]. When equilibrium was attained, the solution was analyzed for total Cr content, including all species of this element (ionic, hydroxoforms, and hydroxofulvates), and the distribution coefficient (K_d) of Cr between sorbent and solution was calculated. Both interactions were considered at pH of 5.0 and 3.0.

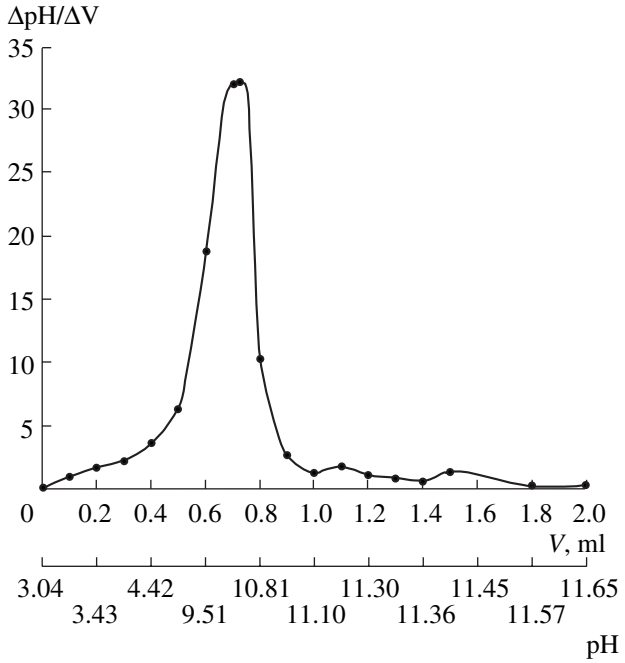

Fig. 1. Differential curve of the potentiometric titration of FA extracted from the Krapivenka River (a tributary of Lake Seliger): C_{FA} = 150 μg/ml; $C_{KOH} = 4.9 \times 10^{-2}$ M. Initial volume of the solution FA = 12 ml.

In all of the series, the solution was separated from the precipitate on Vladipor ultrafilters with pore sizes 350–400 nm.

RESULTS AND DISCUSSION

The study of the protolytic properties of FA, the predominant organic ligand of natural waters, is required to quantify its interaction with metal ions, in our research with Cr(III).

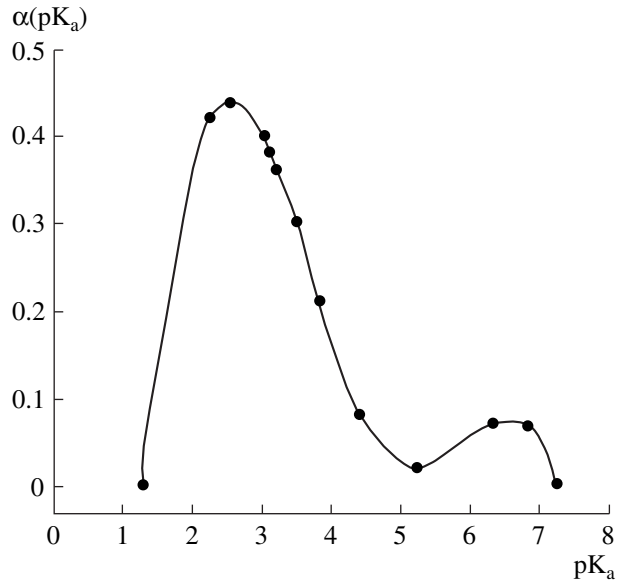

Fig. 2. Distribution of FA functional groups according to the dissociation constants.

A differential curve of potentiometric titration of the ash-free fulvic acid extracted from the Krapivenka River, a tributary of Lake Seliger, demonstrates at least two peaks: at pH 9.5 and 11.2 (Fig. 1). The protolytic characteristics of the oxygen-bearing functional groups of FA were obtained by processing our experimental data by quantitative physicochemical analysis (QPCA), using a model of a continuous distribution of equilibrium constants and CAS algorithm (constant affinity spectrum), which were developed at the Department of Analytical Chemistry at the Kharkov University [15].

Figure 2 demonstrates the distribution of FA functional groups over the dissociation constants. It is seen that acid groups, whose fraction α in the solution is higher than 0.3, have pK_a values from 1.8 to 3.6 with the most probable $\overline{pK_a} = 2.7$ (pK_1), while "weakly acid" groups have pK_a from 5.8 to 7.2 at the most probable value $\overline{pK_a} = 6.5$ (pK_2).

The average first and second dissociation constants for FA extracted from the waters of the Moscow River head with high color index were previously calculated to be $\overline{pK_1} = 2.7$ and $\overline{pK_2} = 4.3$, respectively [12].

It should be noted that the first dissociation constants for FA extracted from the Moscow River headwaters in various years from March to May, inclusive, vary from 0.6×10^{-3} to 5.7×10^{-3} at pK_a between 3.22 to 2.24, respectively; the second dissociation constants vary from 1.2×10^{-5} to 9.0×10^{-5} (with pK_a from 4.92 to 4.05, respectively) [14].

Thus, the dissociation constants for FA extracted from river waters of the same region (humid zone, Upper Volga Basin) could vary within one order of magnitude. The stability constants of fulvate complexes were calculated using the most probable dissociation constants of FA.

Interaction in the Cr(III)–FA System

The stability constants of Cr(III)–FA complexes were calculated from experimental data on chromium(III) oxide solubility depending on the FA concentration in the solution. It was demonstrated that the concentration of hydroxofulvate Cr(III) complexes increases by more than one order of magnitude with increasing FA content in the solution. These dependences are shown in Fig. 3 for FA extracted from the Moscow River head and in Table 1 for FA from the Krapivenka River.

The possible equilibrium in the heterogeneous CrO_3–FA system could be described by a set of equa-

tions, including equations for hydrolytic equilibria (1–2) and FA dissociation as the bidentate ligand (3–4),

$$Cr_2O_3 \cdot nH_2O(sol) \rightleftharpoons Cr(OH)_3^0 \text{ (solution)}, \quad (1)$$

$$Cr(OH)_3^0 \text{ (solution)} \rightleftharpoons Cr(OH)_2^+ + OH^-, \quad (2)$$

$$H_2FA \rightleftharpoons HFA^- + H^+, \quad (3)$$

$$HFA^- \rightleftharpoons FA^{2-} + H^+, \quad (4)$$

as well as an equation describing the formation of complex Cr(III) fulvates by interaction of Cr(III) dihydroxocomplex with fulvate ions (5):

$$[Cr(OH)_2]^+ + mFA^{2-} \rightleftharpoons [Cr(OH)_2FA_m]^{+1-2m}. \quad (5)$$

From these equations, we arrive at the equation for the stability constant of Cr(III) hydroxofulvate complex

$$\beta = \frac{[Cr(OH)_2FA_m]^{+1-2m}}{[Cr(OH)_2^+][FA^{2-}]^m}. \quad (6)$$

Solving Eq. (6) graphically, the m, the number of fulvate ions in the internal coordination sphere of Cr(III) ion, can be derived from the tangent of the $\log(C_{Cr_{tot}} - C_{Cr_0})$ versus $\log C_{FA}$ plot.

The FA extracted from the Moscow River head have $\log\alpha = 1.2$, while FA separated from the Krapivenka River (a tributary of Lake Seliger) show $\log\alpha = 0.7$, indicating the predominance of complexes of Cr(III)–FA = 1 : 1 in both cases. Then, final expression for conditional (for a certain pH) stability constant is as follows:

$$\bar{\beta}_{11} = \frac{[C_{Cr_{tot}} - C_{Cr_0}]}{\left(\frac{C_{Cr_0}}{1 + \frac{K_w}{k_3[H^+]}}\right)\left(\frac{C_{FA}\bar{K}_1\bar{K}_2}{1 + [H^+]^2 + [H^+]\bar{K}_1 + \bar{K}_1\bar{K}_2}\right)}. \quad (7)$$

The β_{11} was calculated assuming fulvate species with a weight-average molecular mass of $M_w = 2200$, which dominates at pH 5.0 [12] and $k_3 = 0.2 \times 10^{-5}$ [16]. The stability constants of Cr(III) fulvate complex are $\bar{\beta}_{11} = 1.93 \times 10^6$ for FA extracted from the Moscow River head and $\bar{\beta}_{11} = 5.70 \times 10^6$ for FA extracted from the Krapivenka River.

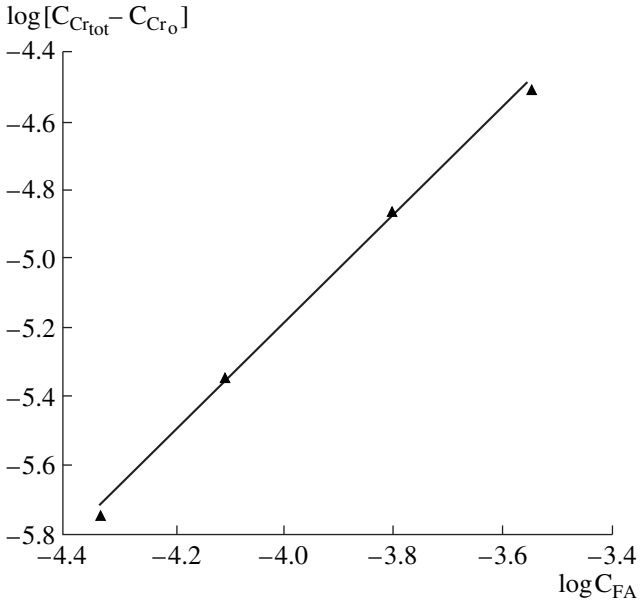

Fig. 3. Cr(III) solubility versus FA content.

The molecular-weight distribution of Cr(III) fulvate complexes was obtained by the fractionation of complexes synthesized in a previous experiment on neutral Sephadex G-25 column with a mass separation limit from 3000 to 180 Da. About 55% of the total Cr content is eluted in fractions whose elution volumes are typical of compounds with molecular weight from 3000 to 600 Da. This fact corroborates the formation of high-molecular weight Cr(III)–FA complexes, which significantly increases the migration ability of Cr(III) in nature.

Interaction in the Cr(III)–HA system

Interaction of Cr(III) with another group of humus compounds, humic acids, was studied by determining the HA sorption capacity for Cr(III) at pH 5.0. Figure 4 depicts the isotherms of metal sorption on HA extracted

Table 1. Solubility of chromium(III) hydroxofulvate complexes versus concentration of FA in the system (interaction time of 35 days; pH 5.0, μ = 0.1 (NaCl)). (for FA extracted from the Krapivenka River, a tributary of Lake Seliger)

FA			Cr (III) concentration in equilibrium solution, mol/l	$\log(C_{Cr_{tot}} - C_{Cr_0})$	β_{11}
μg/ml	mol/l	$\log C_{FA}$			
0	0	0	0.046×10^{-6}	–	–
70	3.18×10^{-5}	–4.50	0.354×10^{-6}	–6.45	7.9×10^{-6}
113	5.14×10^{-5}	–4.29	0.604×10^{-6}	–6.22	8.3×10^{-6}
272	1.24×10^{-4}	–3.91	0.714×10^{-6}	–6.14	4.0×10^{-6}
545	2.48×10^{-4}	–3.61	0.914×10^{-6}	–6.04	2.6×10^{-6}
				$\bar{\beta}_{11} = 5.7 \times 10^6$	$\log\bar{\beta}_{11} = 6.76$

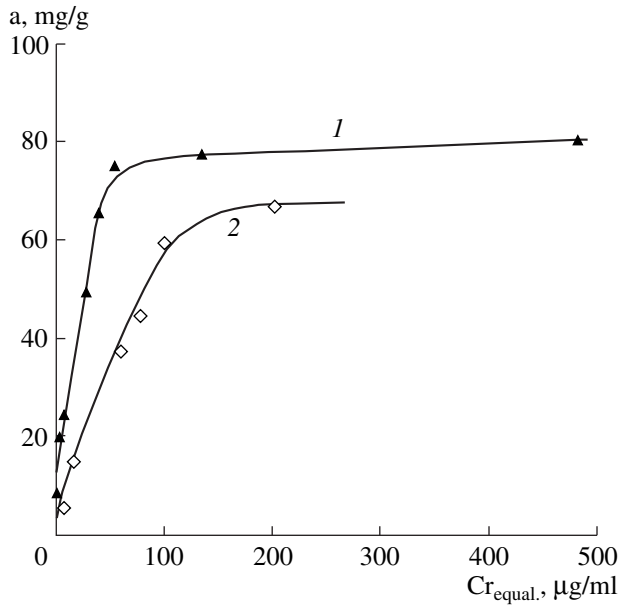

Fig. 4. Sorption isotherms of Cr(III) on HA extracted from peat from the Tver area (curve *1*) and sapropel from Lake Seliger (curve *2*). pH 5.0.

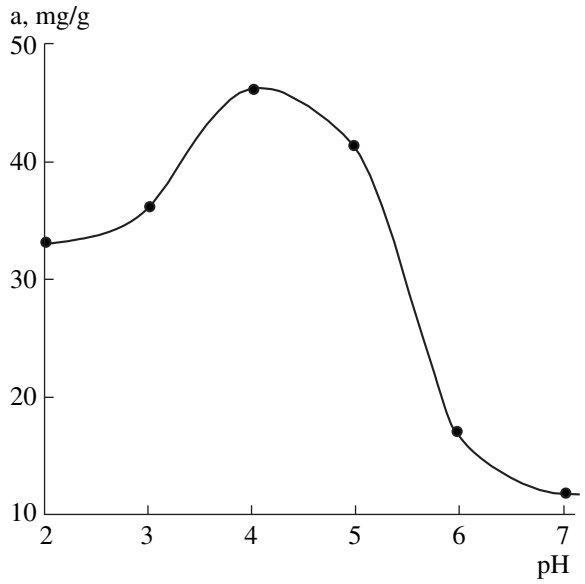

Fig. 5. Cr(III) sorption isotherms on HA extracted from peat versus pH.

from the peat of the Tver area (curve *1*) and from the sapropel of Lake Seliger (curve *2*). The shape of the isotherms indicates that the data of sorption experiment can be described by the Langmuir isotherm equation:

$$a_{Cr} = t\frac{\beta[Cr(III)]}{1 + \beta[Cr(III)]},$$

where a_{Cr} is the Cr(III) sorption on 1 g of the adsorbent, mol/g; t is the sorption capacity of the sample, mol/g; β is the conditional (at a constant pH) affinity constant of Cr(III) for HA sorption centers, l/mol (conditional equilibrium constant of the reaction Cr(III) + Q = CrQ, where Q is the sorption center); [Cr(III)] is the equilibrium content of Cr(III) in aqueous solution, mol/l. The isotherms were processed with nonlinear LSM (assuming the correctness of the Langmuir model) to determine t and $\log\beta$. Simultaneously, the experimental isotherms were approximated by the Langmuir nonlinear sorption isotherms and treated with linear LSM. The calculated sorption capacity of HA extracted from peat equals t = 82 mg/g and $\log\beta$ = 3.78; the sorption capacity of HA extracted from sapropel has the values t = 67 mg/g and $\log\beta$ = 3.23. These results testify to the complexing ability of Cr(III) with the oxygen-bearing functional groups of HA extracted from peat and sapropel. Thus, humic acids could serve as sorbents accumulating Cr(III) ions in natural conditions.

Using HA extracted from the peat of the Tver area as an example, we studied the dependence of Cr sorption on pH. Experimental data are shown in Fig. 5. It can be seen that this dependence is represented by a curve with a maximum at pH 4. At low pH values, the decrease in the sorption is related to the protonization of the carboxyl groups of HA. At pH > 4, the decrease in the Cr(III) sorption on humic acids is caused by an increase in hydroxo-species in the total balance of Cr(III) compounds.

Interaction in the Cr(III)–FA–HA

As was mentioned above, the migration behavior of Cr(III) in nature is controlled by concurrent interaction in the Cr(III)-FA–HA three-component system. In the model experiments at pH 3.0 and 5.0, equilibrium was approached from above, which could correspond, in natural basins, to Cr(III) distribution between two groups of humus compounds (FA and HA) at the simultaneous contact of Cr(III) ions with FA and HA. The consideration of this system (also with pH 3.0 and 5.0) when equilibrium is approached from below reflects the elution of Cr(III) ions from HA-bearing bottom sediments at increasing content of FA (Fig. 6). Data on Cr(III) distribution between solution and complexing adsorbent (for a system with approach of equilibrium from above) are shown in Table 2. It is seen in Fig. 6 and Table 2 that, in all cases (sorption at pH 3.0, 5.0, and desorption at pH 3.0 and 5.0) in the presence of fulvic acids, K_d drastically decreases by 1–1.5 orders of magnitude with an increase in the FA content or with an increase in the water color index. At lower pH, this decrease is more significant. In particular, the distribution coefficient for equilibrium approached from above (sorption) decreases from 9.0×10^3 to 8.5×10^2 (pH 5.0) and from 4.8×10^3 to 6.6×10^2 (pH 3.0), while that at equilibrium approached from below (desorption)

Table 2. Cr(III) distribution between solution (FA) and sediment (HA) in the system Cr(III)–FA–HA depending on FA content. m_{HA} = 20 mg; V_{sol} = 20 ml; $c_{Cr_{init}}$ = 10 μg/ml (equilibrium from top)

Ordinal No.	FA content, μg/ml	Cr(III) determined in the solution		Sorption of Cr(III) per 20 mg HA, μg	Sorption of Cr(III), μg/g HA	K_d
		μg/ml	in 20 ml solution, μg			
			pH = 5.0			
1	0	1.0	20	180	9.0×10^3	9.0×10^3
2	14	1.2	24	176	8.8×10^3	7.3×10^3
3	42	1.4	28	172	8.6×10^3	6.1×10^3
4	102	2.4	48	152	7.6×10^3	3.1×10^3
5	300	5.4	108	92	4.6×10^3	8.5×10^3
			pH = 3.0			
6	0	1.7	34	166	8.3×10^3	4.8×10^3
7	14	1.8	36	164	8.2×10^3	4.5×10^3
8	42	2.2	44	156	7.8×10^3	3.5×10^3
9	102	4.7	94	106	5.3×10^3	1.13×10^3
10	300	6.0	120	80	4.0×10^3	6.6×10^2

decreases from 2.1×10^5 to 0.6×10^4 (pH 5.) and from 2.0×10^5 to 0.3×10^4 (pH 3.0). It is seen in Fig. 6, illustrating the desorption of the Cr ion from HA in the Cr(III)–FA–HA three-component system, that even small contents of FA (20–50 μg/ml) are able to significantly increase the Cr solubility, thus retaining this ion in natural waters.

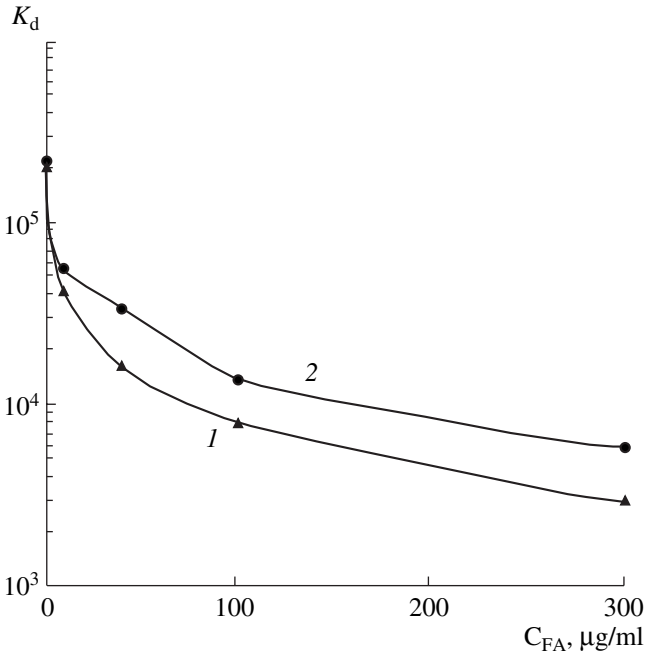

Fig. 6. Cr(III) distribution coefficient (K_d) versus FA concentration in the Cr(III) humate–FA system at pH 3.0 (curve *1*) and pH 5.0 (curve *2*) (equilibrium approached from below).

CONCLUSIONS

One of the most important interactions of metal ions with environmental components is their reactions with fulvic and humic acids, predominant organic compounds in waters and soils. Understanding the mechanism of the natural migration of elements (Cr, in this paper) significantly depends on the knowledge of interaction between metal ions and humus acids (FA and HA).

Our data indicate that FA retains Cr(III) in natural waters and causes its elution from bottom sediments owing to the formation of high-molecular soluble hydroxofulvate complexes, thus facilitating the natural migration of Cr(III). Humic acids are strong complexing adsorbents able to accumulate metal ions. Our results provide insight into Cr(III) behavior in natural environments: waters, solids, bottom sediments, and water suspensions.

REFERENCES

1. D. S. Orlov, L. K. Sadovnikova, and I. N. Lozanovskaya, *Ecology and Protection of the Biosphere during Chemical Pollution* (Vysshaya Shkola, Moscow, 2002) [in Russian].
2. T. M. Florence and G. E. Batley, "Chemical Speciation in Natural Waters," CRC Crit. Rev. Anal. Chem. **9** (3), 219–296 (1980).

3. R. E. Cranston and J. W. Murray, "Chromium Species in the Columbia River End Estuary," Limonol. Oceanogr. **25** (6), 274–278 (1980).
4. I. N. Lyubimova, "Content and Speciation of Mo, V, and Cr Compounds in Soils," in *Contents and Speciation of Trace Elements in Soils* (Mosk. Gos. Univ., Moscow, 1979), pp. 224–293 [in Russian].
5. V. V. Gordeev and A. P. Lisitsyn, "Microelements," in *Ocean Chemistry* (Nauka, Moscow, 1979), Vol. 1, pp. 337–375 [in Russian].
6. G. S. Konovalov, V. I. Koreneva, A. P. Korenev, and A. P. Garanzha, "Distribution of Mobile Species of Heavy Metals in River Suspension," Gidrokhim. Mater. **110**, 55–64 (1991).
7. P. Benes, E. T. Gessing, and E. Steinnes, "Interaction between Humus and Trace Elements in Fresh Water," Water Res. **10** (8), 711–716 (1976).
8. C. Stienberg, "Species of Dissolved Metals Derived Oligotrophic Hard Water," Water Res. **14** (9), 1239–1250 (1980).
9. M. Kragnic, J. Stupar, and S. Milicev, "Characterization of Chromium and Copper Complexes with Fulvic Acids Isolated from Soils in Slovenia," Sci. Tot. Environ. **159**, 23–30 (1995).
10. M. Fukushima, K. Nakayasu, Sh. Tanaka, and H. Nakamura, "Chromium (III) Binding Abilities of Humic Acids," Analitica Chimica Acta **317**, 195–206 (1995).
11. G. M. Varshal, A. A. Nesterov, S. D. Khushvakhtova, et al., " Lead (II) Complexation with Humic Acids and Effect of These Processes on the Lead Mobility in Waters and Soils," in *Applied Geochemistry. Ecological Geochemistry* (IMGRE, Moscow, 2001), Vyp. 2, pp. 459–473 [in Russian].
12. G. M. Varshal, T. K. Velyukhanova, and I. S. Sirotkina, "Fractionation, Quantitative Determination, and Study of Some Main Components Dissolved in the Organic Matter of Natural Waters," Gidorkhim. Materialy **59**, 143–151 (1973).
13. G. M. Varshal, T. K. Velyukhanova, D. N. Chkhetiya, et al., "Sorption on Humic Acids as a Basis for the Mechanism of Primary Accumulation of Gold and Platinum Group Elements in Black Shales," Litol. Polezn. Iskop., No. 6, 605–613 (2000) [Lithol. Miner. Resour. **35**, 538–545 (2000)].
14. A. Albert and E. P. Serjeant, *Ionization Constants of Acids and Bases* (Wiley, New York, 1962; Khimiya, Moscow, 1964).
15. Yu. V. Kholin, *Quantitative Physicochemical Analysis of Complexing in Solutions and on the Surface of Chemically Modifided Silica: Interesting Models, Mathematical Methods, and their Application* (FOLIO, Khar'kov, 2000) [in Russian].
16. Yu. Yu. Lur'e, *Handbook on Analytical Chemistry* (Khimiya, Moscow, 1989) [in Russian].