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Interaction of Microelements at Coprecipitation with Humic Acids

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Abstract—Through the example of the sorption-coprecipitation data for microelements simulating the corrosion, activation, and fission products, the nature of the isotherms of sorption of cations (M) by natural humic acids (HAs) was discussed. The dependence of the microelement distribution coefficient (K_d) on the ratio of the mass to volume of the HA solution in the 10–990 mg/L concentration range was associated with the occurrence of two parallel processes in the sorption system: competitive sorption of the M and Ca(II) ions by the HA precipitate and the formation of nonsorbable ($K_d < 10$ mL/g) complex of the M ion with high-molecular-weight organic compounds remaining in solution after HA precipitation. Optical spectroscopic data for the HA solutions and solutions above the solid HA precipitate revealed the presence of high-molecular-weight organic compounds in solution, as indicated by a maximum at 220 ± 20 nm and a shoulder at 264 ± 30 nm, characteristic for fulvic acids (FAs). A probable scheme of the interaction of the sorbate cations with the precipitate of HAs and their accompanying fulvic acid molecules was proposed. For the first time, removal of tritium (THO) from aqueous solutions by HA precipitates via isotope exchange reaction was reported.

Keywords: microelements, radionuclides, tritium, humic acid, coprecipitation, fulvic acid, complexation, competitive sorption, model

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Humic acids (HAs) act as active organic carriers of microelements ions, microelements radionuclides in aqueous and soil solutions [1–4]. A feature specific of the chemical behavior of HAs in solutions is their “dualism” consisting in manifestation of both the properties of high-molecular-weight ionic complexes containing acidic sites of different strengths and redox groups and the properties of colloidal solutions prone to coagulation as a result of protonation primarily in acidic solutions [5–9]. Humic substances attract researchers’ attention not only due to importance of the knowledge of the physicochemical and geochemical behavior of the products of their binding to ions in solutions but also due to the possibility to control the mass transfer of radionuclides and spontaneous purification of natural objects on the basis of green chemistry principles and competitive sorption [2, 3, 10, 11] via creating sorption barriers to the transfer of radionuclides [12]. Migration of cesium-137, strontium-90, tritium, uranium isotopes, transuranium elements, and other long-lived radionuclides strongly contributes to global accumulation and transfer of long-lived man-made radionuclides. The latter originate from and are associated with nuclear fuel cycles and can enter the environment in the events of technogenic accidents, as a result of nuclear weapons testing, during process operations, and in storage. The radionuclide binding efficiency is determined by the acid-base properties of humic acids [9, 13–15]. Elucidation of the role of HAs in the transfer of the above-mentioned radionuclides and of those with similar chemical properties in the aquatic environment is an important independent task whose solution will allow more thoroughly evaluating the technological options for eliminating the consequences of radiation accidents and predicting the dispersion and disposition of radionuclides in the environment. For example, Sr(II) ions were found to form stable complexes

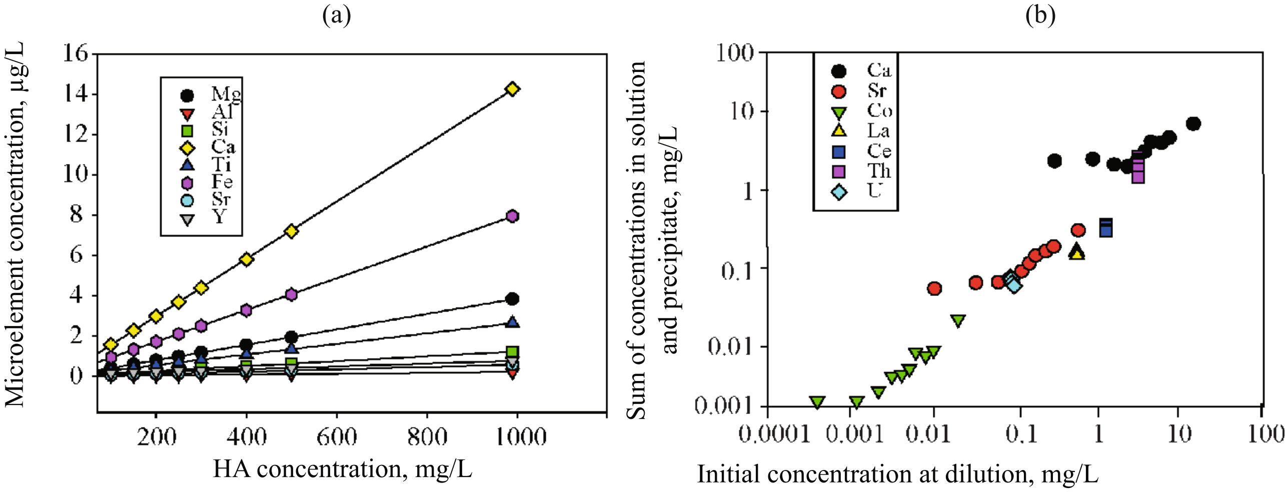

Fig. 1. (Color online) (a) Change in the composition of the HA solutions in terms of the contents of individual elements, caused by dilution, and (b) ratio of the concentrations of the elements in the starting HA solutions, with the microelement concentrations in phases estimated by different methods. (Abscissa) Concentration determined by calculating the degree of dilution of the starting HA solution with a known composition and (ordinate) concentration determined by summing the element contents in the filtrate and precipitate.

with humic acids in neutral and alkaline media [16]. Their equilibrium sorption characteristics depend on the degree of occupation of the HA exchange sites and on the concentration level of the Sr(II) carrier, analog ions in solution, and acidity of the medium. The dependence of the distribution coefficient of Sr(II) on the initial HA concentration at coprecipitation suggests the possibility of formation by strontium ions of a nonsorbable or a weakly sorbable complex with the products of acid hydrolysis of HAs [17, 18]. These facts and presumptions need to be refined through the example of a broad range of microelements with dissimilar physicochemical behavior [19, 20]. This study was aimed to obtain and analyze the sorption-coprecipitation isotherms of a representative group of multiply charged cations of elements, to establish the chemical nature of the products of complexation in HA solutions, and to formulate on this basis a sorption model of the interaction of the sorbate microelements at coprecipitation with HAs.

EXPERIMENTAL

The sorption experiments were carried out with the use of a solution of cations, prepared by dissolving a weighed portion of monazite in an aliquot of sulfuric acid [17]. Working solutions with a variable concentration of natural humic acid were prepared in glass tubes by introducing aliquots of the solution of cations into the medium of HA of different concentrations from a BIOHIT Proline Plus 1000 dosing device. We used humic acid of natural origin from the vicinity of Salekhard town (Tyumen oblast), characterized by the following concentrations of the main elements, wt %: C 62.0, H 4.3, N 1.4, O 32.5. Natural HA solutions of this type are hydrocarbonate-chloride-sodium weakly mineralized water containing 700–1050 mg/L humic acids, as well as neutral and acidic bitumens [21]. Table presents the composition of the main elements of the HA used in our experiments.

For the sorption experiments, the test solution with the HA concentration of 990 mg/L and distilled water were added in different proportions to 60-mL low-density polyethylene vessels so that the HA concentration was changed and the total volume was 49 mL after mixing. Next, an aliquot of the solution of microelements, obtained after the sulfuric acid treatment and dissolution of the weighed portion of monazite, was introduced into each vessel. The employed procedure of displacement of sulfuric and phosphoric acids by hydrochloric acid ensured the subsequent presence of <1–10 mg/L of free sulfate and phosphate anions. The solution volume V in each vessel was 50 mL; pH of the solutions was maintained at 1.5–2.0 at 23°C (measured on an Anion pH meter). The contents of both the microelements and HA in the starting solutions were changed by dilution (Fig. 1a). After acidification and formation of an HA suspension the stoppered vessels with the solutions were left to stand for 2 days with regular stirring. Next, the HA precipitate in each vessel was separated from solution by filtration through a blue band paper filter. The resultant filtrates were analyzed for the content of 30 microelements on a mass spectrometer with the results being checked in the TotalQuant mode. To determine the mass of the microelements sorbed by the HA precipitates, the filters with the HA were air-dried and burnt to ashes in platinum crucibles in air at 500°C. The residues were treated with 1 mL of ultrapure-grade concentrated HNO_3, and the volume of the test solution was brought to 50 mL with bidistilled water. In the prepared solutions the concentration of the elements was measured under conditions similar to those in determination of the composition of the starting solution and the filtrates. Mass spectrometric analysis was performed on an ELAN 9000 instrument; the initial (C_{in}) and final (C_{fin}) concentrations of each of the microelements in the solutions analyzed and their concentration in the HA precipitate (C_{HA}) were set without dilution. Based on these parameters recalculated for the mass of the microelement per unit volume of the starting test solution, the degree of sorption of the microelement (S) was calculated from the difference in the compositions of the solutions before and after coprecipitation with protonated humic acid [$S(1)$] and from the ratio of the microelement contents in the solid and liquid phases [$S(2)$]:

$$S(1) = (C_{\text{in}} - C_{\text{fin}});\ S(2) = C_{\text{HA}}/(C_{\text{fin}} + C_{\text{HA}}). \qquad (1)$$

The microelement concentration in the solution was determined accurately to within 5%. Comparison of the results of determining the degree of sorption by both methods (1) revealed the smallest preparative error for the calculation by the $S(2)$ method [22]. The error is caused by the fact that setting the initial concentration C_{in} in the solutions by diluting the HA solution (Fig. 1a) entails a systematic shift of the concentration level in the region of low concentrations of the microelements, associated with manifestation of the buffer properties by humic acids, when chemical elements were introduced with an aliquot of the microelement solution. Therefore, increase in the degree of dilution below a certain limit does not lead to a significant decrease in the microelement concentration in solution for individual elements (e.g., Ce, U, Th, and other; Fig. 1b).

The tritium concentration in the HA solutions was measured using a standard radioactive solution (SRS, All-Russian Scientific Research Institute for Physical-Engineering and Radiotechnical Metrology) of tritiated water THO with the radionuclide content of 10^6 Bq/g. The contents of a 10-mL glass ampule with tritium was diluted with 1 L of distilled water so that the resulting radionuclide activity was 966 Bq/mL, or 9500 cpm/mL, at the time of measurement. The working solution was prepared by 25-fold dilution of the SRS solution. It was poured into several 250-mL flat-bottomed glass flasks, from each of which 1 mL of tritium water was taken into potassium-free glass vials in order to set the initial tritium activity in each flask. Different HA amounts were added to the solutions; into one solution HA was not added (control). The prepared solutions had pH 7.5. The flasks were closed with ground stoppers and placed in a fume hood where they remained until the end of the experiment. To study the tritium sorption by humic acid, 10 mL of the solution was taken from each flask and poured into 50-mL glass beakers, and humic acid was precipitated by adding a 50-μL aliquot of 6 M HCl. After 30–40 min of settling the solution was filtered through a blue band filter. The same volume of HCl was also added to the control solution to account for the loss in the counting efficiency due to quenching caused by addition of the acid. The filtered solutions had pH 1.5–2.0 in all the experimental variants. Truplicate 1-mL samples of the solution were taken from the filtrate and placed into glass vials for β-activity measurements. For tritium activity measurements, 11 mL of ZhS-8 scintillation cocktail per vial was used. The measurements of the samples were performed on a DELTA-300 spectrometric setup. The samples were stabilized by keeping in the instrument for 2 h. The time of triplicate analysis of each sample was 10 min, whereby $a \leq 3\%$ relative error in the count rate measurement was provided. During count rate data processing, a correction was introduced to account for the change in the tritium concentration in the experimental solutions, caused by dilution with water, and for the change in acidity [23].

The optical transmission spectra of the neutral humate solutions of different dilution degrees, as well as of the filtrates obtained after acid precipitation and separation of the HA precipitates at pH 1.5–2.0, were recorded on a SpectraMax Plus 384 Absorbance Microplate Reader (Molecular Devices) spectrophotometer. The optical density of the solutions was determined relative to distilled water. To obtain filtrates, neutral HA solutions with different concentrations were acidified with 0.1 mL of 6 M HCl solution to pH 1.5–2, whereupon the resulting HA precipitates were filtered off, the filtrates were diluted

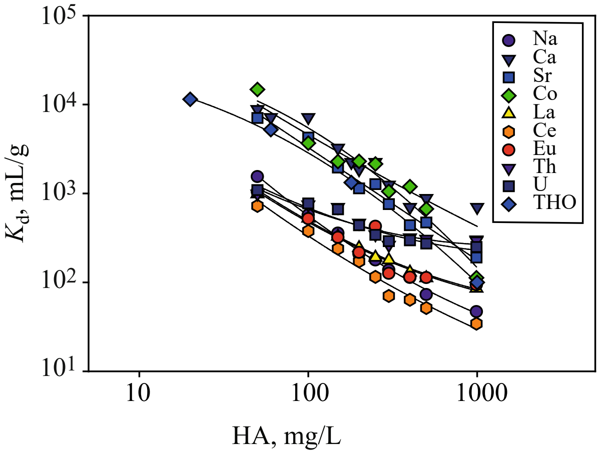

Fig. 2. Examples of the experimental isotherms of coprecipitation of the microelements with the HA precipitate, pH 1.8, 23°C (see text for explanations).

with distilled water, and measurements were performed. This allowed tracing the dependence of the optical density of the HA solutions on the concentration of the main component, humic acids, and to establish a relationship between the concentration and optical density of the neutral HA solutions and the relative concentration of acido-soluble organic carbon compounds remaining in the filtrates after separation of the HA precipitate (fulvic acids, FAs, and neutral and acidic bitumens). The size and charge of the colloidal HA particles were determined using a Zetasizer Nano ZS Particle Analyzer (Malvern Instruments) combining the measurement techniques of dynamic light scattering and electrophoresis.

RESULTS AND DISCUSSION

It is known that the HAs isolated from environmental samples (soil, bottom sediments, peat, and coal) can significantly differ in the mineral composition. This is due to the fact that acid and alkaline treatments of humic substances lead to removal from the HA fraction of inorganic cations and anions acting as stabilizers of the size, shape, and charge of molecular and colloidal HA particles [24]. Lack of noticeable amounts of fulvic acids in the composition of the source of humic acids selected by us allowed studying the HA behavior without additional chemical purification procedures. Like in the coprecipitation of microelements with hydroxides [25], the coefficient of distribution (K_d) of the humate complexes of microelements between the solution and precipitate of HAs is determined by pH at which they were coprecipitated with humic acid, as well as by the dissolved organic carbon concentration [18]. Figure 2 presents an example of the experimental dependences of K_d at coprecipitation of microelements on the total (initial, before precipitation) HA concentration in the starting solution of the mineral water. Since humic acids are practically insoluble at pH 1.5–2, the observed K_d–[HA] dependence may be associated with the existence in the solution of a nonsorbable or a weakly sorbable complex formed by microelements with those organic carbon compounds that remain in the filtrate after separation of the HA precipitate. Table shows that FAs, and to a lesser extent neutral and acid bitumens, are acido-soluble organic carbon compounds in the mineral water. Another factor that may be responsible for the observed K_d–[HA] dependences is competitive sorption of the cations, above all Ca(II) ions, occurring in the filtrate in macroconcentrations, by the precipitate (Fig. 1a).

The technique employed for studying the sorption equilibria provides the following description of the competitive reactions involving cation M and the competing cation Ca(II):

$$M_{aq} = \overline{M},\ K_1 = [\overline{M}]/[M_{aq}], \qquad (2)$$

$$M_{aq} + \overline{Ca} = Ca_{aq} + \overline{M},\ K_2 = [Ca_{aq}][\overline{M}]/[M_{aq}][\overline{Ca}],$$

$$M_{aq} + AF = M(FA)_{aq},\ \beta(M) = [M(FA)_{aq}]/[M_{aq}][FA], \qquad (3)$$

Here, the overline indicates the solid state of the sorbent, and subscript aq, the state of M in solution as aqua ion; K_1 is the concentration constant of sorption of the M ions by the reactive groups of humic acid, K_2, constant characterizing the competitive sorption of the microelement by the Ca-form of HAs in the concentration approximation, and β(M), concentration constant of formation of the $M(FA)_{aq}$ complex with the ligand represented by the FA molecules in the acidic solution above the HA precipitate. It is presumed that this complex is not sorbed by the solid phase of HAs. By combining Eqs. (2) and (3) it is possible to represent the expected reactions of competitive sorption of the M and Ca(II) ions by the reactive groups of HAs as follows

$$K_d(M) = [\overline{M}]/\{[M_{aq}] + M(FA)_{aq}]\}$$
$$= K_1(M)/\{1 + \beta(M)[(FA)\},$$
$$K_d(M, Ca) = K_1(M, Ca)(1 + \beta(Ca)[(FA)]/\{1 + \beta(M)[(FA)]\},$$
$$K_d(M, Ca) = K_d(M)/K_d(Ca),\ K_1(M,Ca) = K_1(M)/K_1(Ca). \qquad (4)$$

Table 1. Composition of the mineral water from 37RE well, Salekhard, pH 7.8 (for analytical techniques, see [21])

Ion, parameter	Concentration, mg/L	Notes
NH_4^+	0.05	
$(K,Na)^+$	0.18	
Mg^{2+}	0.01	
Ca^{2+}	0.02	
Cl^-	0.30	
Br^-	4.20	
HCO_3^-	0.14	
F^-	1.0	I^-, SO_4^{2-}, CO_3^{2-}, NO_2^-, NO_3^- were not detected
Eh, мВ	350	
Dry residue	2.10	
Neutral bitumens	2.1	Extraction into chloroform at pH 7, weighing the air-dry residue after distilling off the extractant
Acidic bitumens	1.5	Extraction into chloroform at pH 3, weighing the air-dry residue after distilling off the extractant
Humic acids	990.0	Precipitation by sulfuric acid at pH 2, weighing the air-dry residue after distilling off the extractant
COD of the mineral water, mg O/L	1040–1060	
COD of the solution after HA precipitation at pH 2, mg O/L	5.0	FA content estimated from COD is 4.0 mg/L

To identify the acido-soluble compounds of organic carbon in the natural water, we carried out spectrophotometric examination of the solutions of the mineral water, as well as of the products of its dilution with bidistilled water and the acidic filtrates after the HA separation from the natural water at pH 1.8. The optical spectra of the solutions showed that the natural solution used by us is a typical representative of humic acids whose colloidal chemical properties are enhanced with increasing HA concentration [26–30]. Figures 3 and 4 present the absorption spectra of the neutral HA solutions of different degrees of dilution and of the acidic filtrates isolated after HA precipitation from the mineral water at pH 1.8. Table 1 shows that the filtrates comprise FAs and, to a lesser extent, neutral and acidic bitumens. Figure 5 presents the dependences of the empirical absorption coefficients (E_2/E_3, E_4/E_6) calculated by us from the spectral characteristics of the HAs of the mineral water (pH 7.8) by the procedure described in [26] against those for the HAs isolated from soil [28]. The E_2/E_3 coefficient is the ratio of absorbance at 250 nm to that at 365 nm and characterizes the degree of humification and the molecular weight of HAs ([26] and references therein). Coefficient E_4/E_6, the humification index, is the ratio of absorbance at 465 nm to that at 665 nm, interpreted similarly to the coefficient E_2/E_3. The experimental dependences presented in Fig. 5 show that both absorption coefficients

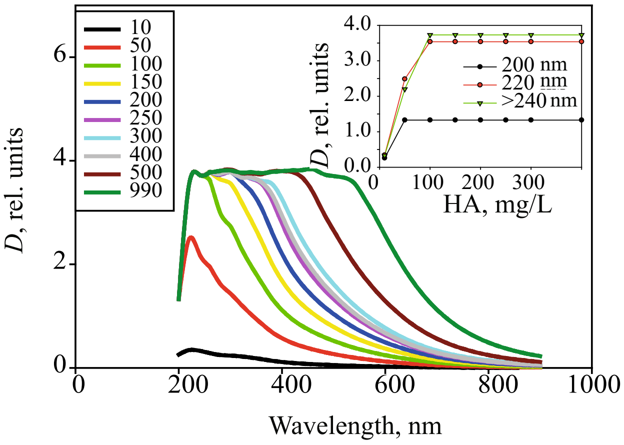

Fig. 3. (Color online) Spectra demonstrating the changes in the optical density (D) of the natural HA solutions of different concentrations, pH 7.8, 23°C. Numbers at points are the HA concentrations, mg/L.

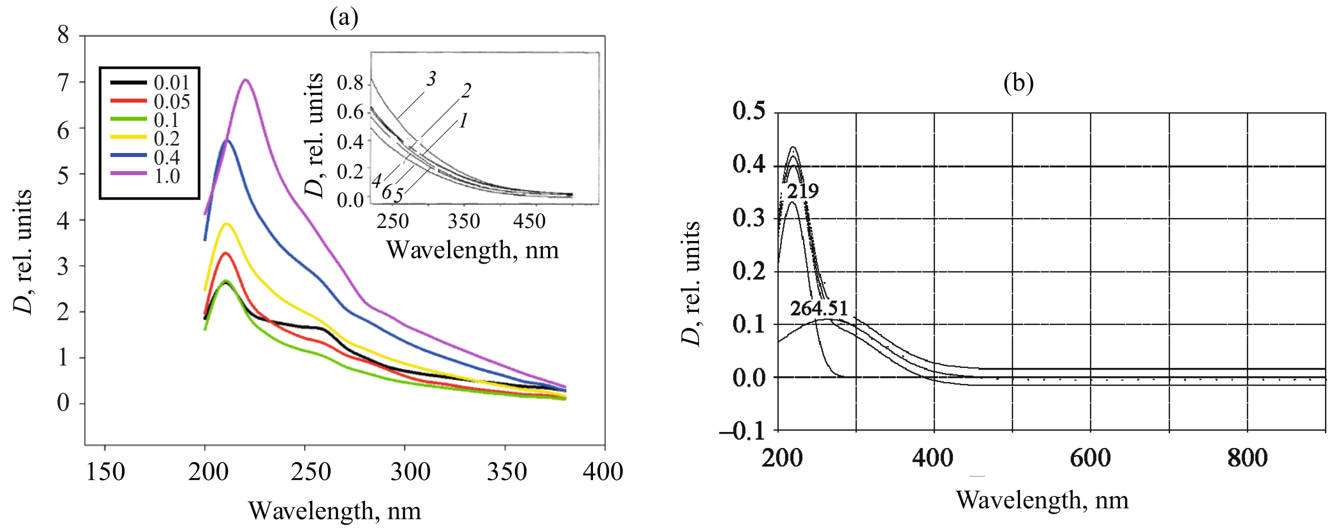

Fig. 4. (Color online) (a) Spectra demonstrating the changes in the optical density of the filtrates obtained after precipitation of HAs of different concentrations, pH 1.8, 23°C. Numbers in the plot are the degrees of dilution of the filtrate after precipitation of HA with the concentration of 990 mg/L, rel. units. Inset shows the optical absorption spectra of natural FAs of different origin with the concentration close to that in the filtrates [31]. (b) Optical spectrum of the filtrate with the degree of dilution of 0.4 and its decomposition into two components using PeakFit program. (Dots) Experimental spectrum, (lines) result of decomposition of the spectrum into two components; (R^2) coefficient of determination, (SE) standard linearization error, *F*-statistic ($R^2 = 0.994$; SE = 0.008; $F = 1048$). Numbers of curves in the inset indicate the source of FA [31]: (*1*) heavily used croplands, (*2*) heavily used meadows, (*3*) cropland to meadow transitional lands, (*4*) durable meadows, (*5*) meadow, and (*6*) alder swamp.

qualitatively characterize the same decreasing trend with increasing HA concentration. Such a change indicates an increase in the molecular weight of the macromolecules with increasing HA concentration. Similarity of the optical spectra of the compared HA types suggests that the humic acids used in this study are characterized by a relatively higher degree of polymerization, which tends to decrease with progressive dilution of the HA

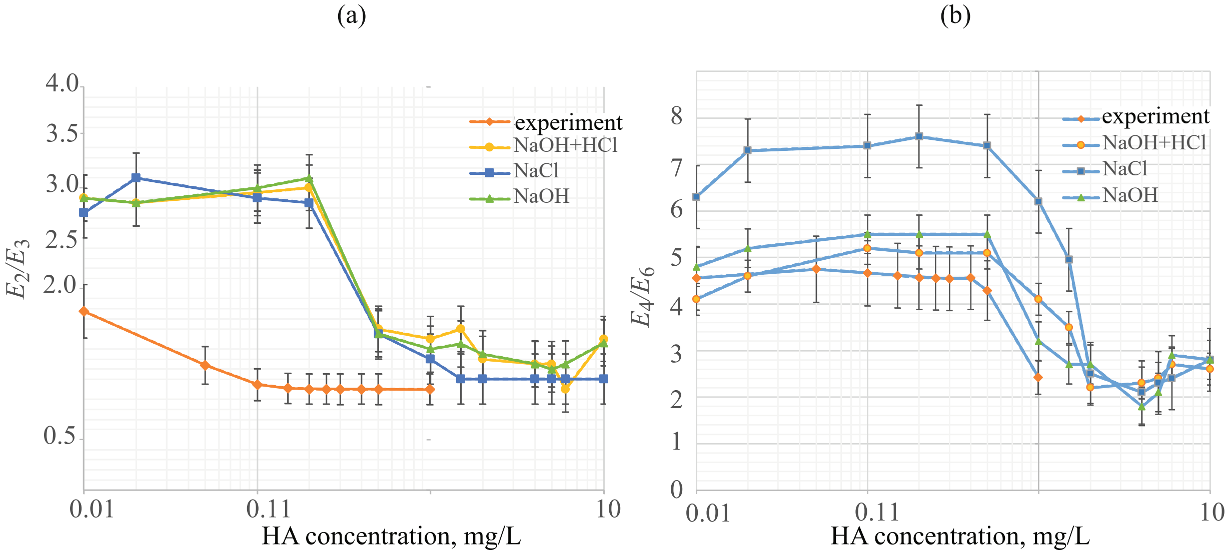

Fig. 5. (Color online) Comparison of the absorption coefficients (E_2/E_3, E_4/E_6) calculated from the spectral characteristics of the natural mineral water with HA at pH 7.8: (a) (E_2/E_3) ratio of absorbance at 250 nm to that at 365 nm and (b) (E_4/E_6) ratio of absorbance at 465 nm to that at 665 nm, determined in this study (experiment); symbols NaOH + HCl, NaCl, NaOH indicate the technique of isolation of fulvic acids from soils according to [26].

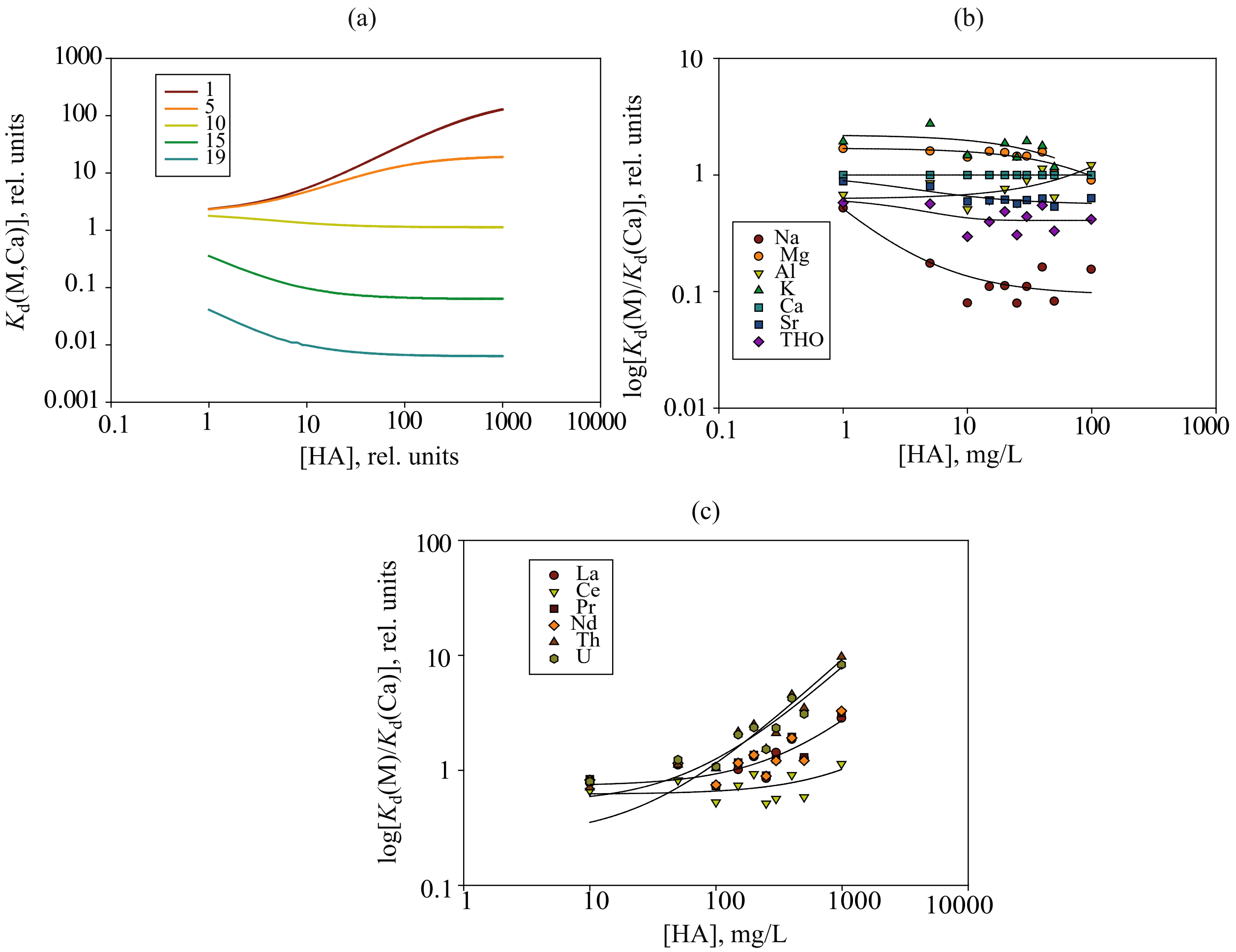

Fig. 6. (Color online) Examples of the isotherms of sorption-coprecipitation of the microelements with the HA based on the results of numerical analysis using model (2)–(4), (7) and based on the data in Fig. 2, processed in the coordinates of Eq. (7). Numbers at curves indicate the relative value of the K_1(M,Ca) coefficient in Eq. (7). (a) General view of the K_d(M,Ca) dependence on the HA concentration [HA] in solution according to (7). (b, c) Experimental isotherms with (b) derivative $P = d[K_d(\mathrm{M,Ca})]/d([\mathrm{HA}])<0$ or (c) $P>0$.

solutions (Fig. 5). As the HA concentration grows, the optical density of the solutions increases, with the entire optical range covered at HA concentrations of ≥900 mg/L (Fig. 3). Compliance with the Bouguer–Lambert–Beer law by both the neutral HA solutions and solutions of organic compounds remaining after acid precipitation of HAs (by definition, acido-soluble forms of humates are fulvic acids) indicates the closeness of the optical and colloidal chemical properties of the solutions studied by us to those of both true solutions of high-molecular-weight compounds (Figs. 3, 4, and 6) and of colloidal solutions. Attribution of high-molecular-weight compounds in the filtrate to FAs is validated by the closeness of their optical spectra to those of some types of FAs isolated from soils and groundwater (Fig. 5) [31, 32]. Data presented in Fig. 5a are consistent with the experimentally determined colloidal chemical properties of the mineral water with HAs. With concentration in the solution increasing in the 10–500 mg/L range the colloidal state of the HA particles changes insignificantly. Specifically, according to the light scattering data, their average size increases from 15 to 20 nm, and the ζ-potential remains at –30 mV. When the 500 mg/L HA concentration is reached, it increases stepwise to –10 mV for a part of the colloidal particles, probably due to simultaneous contact coagulation and aggregation (polymerization) [10].

Unlike dark brown natural HA solutions, the filtrates isolated after the HA precipitation at pH 1.5–2 are transparent and colorless in the visible spectral region, and their absorption spectrum is similar to those of some types of fulvic acids [26, 29]. At the same time, their optical spectra in the UV region exhibit an absorption band with

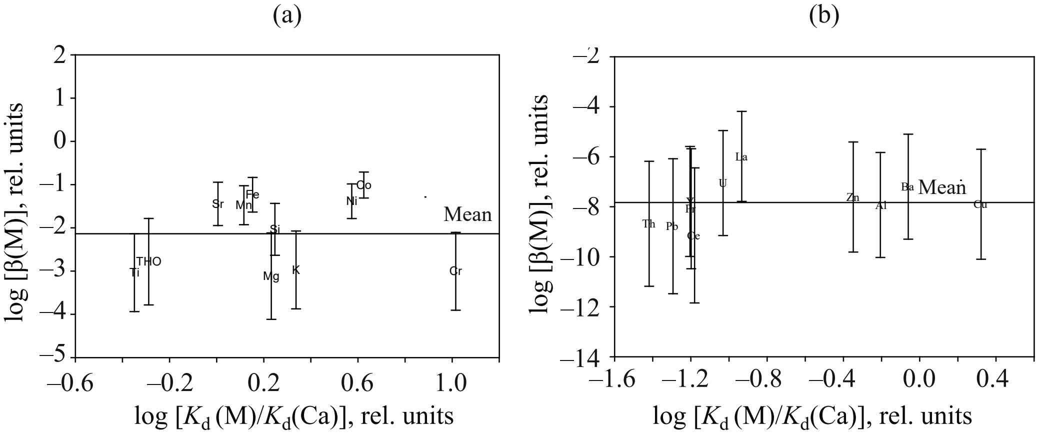

Fig. 7. Ratios of the distribution coefficients K_d(M)/K_d(Ca) and concentration constants of complexation of the microelements with the product of acid dissolution of HAs [β(M)], rel. units, in the filtrate above the HA precipitate, pH of the filtrate 1.8, 23°C, determined using the experimental data in the framework of model (2)–(4). (Mean) Mean value for the entire sample. (a) Group of cations with log β (M) = (–2 ± 1) and (b) group of cations with log β (M) = –(8 ± 3).

a maximum at 211 ± 20 and a shoulder at 264 ± 30 nm (Fig. 4). Interaction of macromolecules/colloidal particles with light is described by the Bouguer–Beer–Lambert-law. In particular, the linear correlation between the optical density at 220 nm, D(220 nm), of the filtrates and the relative concentration of the humate solution before HA precipitation, expressed as the $[\mathrm{HA}]/[\mathrm{HA}]_{\max}$ ratio, where $[\mathrm{HA}]_{\max}$ is the maximum HA concentration in the experiments, 990 mg/L, is described by the following equation:

$$D(220\ \mathrm{nm}) = (0.417 \pm 0.047) + (1.036 \pm 0.106)[\mathrm{HA}]/[\mathrm{HA}]_{\max}, \quad (5)$$

with the correlation coefficient $R = 0.950$ and linearization standard error 0.090. The error scattering obeys the normal distribution; the probability of making no type 1 error for the significance level $\alpha = 0.050$ is 0.980. With optical density taken to be proportional to the concentration of the fulvic acid macromolecules [FA]

$$D(220\ \mathrm{nm}) = \varepsilon(\mathrm{FA})[\mathrm{FA}], \quad (6)$$

where ε(FA) is the absorption coefficient of fulvic acids at 220 nm (rel. units), joint analysis of Eqs. (5) and (6) shows that the [FA]/[HA] ratio is a constant characterizing the FA content above the HA precipitate at pH 1.5–2. This allows using in Eq. (4), instead of the unknown FA concentration in the solution above the precipitate [FA], the initial HA concentration, [HA]:

$$K_d(\mathrm{M,Ca}) = K_1(\mathrm{M,Ca})[1 + \beta(\mathrm{Ca})][(\mathrm{HA})]/(1 + \beta(\mathrm{M})][(\mathrm{HA})]. \quad (7)$$

Model (2)–(4), (7) suggests three types of relationships between the humic acid concentration [HA] in the solution and the ratio of the distribution coefficients of the competing ions (Fig. 6a). Specifically, joint analysis of the numerical modeling results and the experimental sorption isotherms shows that, with increasing [HA], K_d(M,Ca) can decrease (Na, K, Mg, Sr, Al, Bi ions), increase (Pb, Th, U, La, REE), or remain unchanged (THO, Ca) (Figs. 6b and 6c). Processing the coprecipitation isotherms (Fig. 2) in the coordinates of Eq. (7) reveals all the possible types of relationships for the sorption isotherms obtained. Comparison of the distribution coefficients (Fig. 2) and the selectivity coefficients (7) (Fig. 6) suggests a high general sorption specificity of the HA precipitates for cations of analog radionuclides of corrosion, fission, and activation product, as well as the possibility of effective decontamination of solutions by coprecipitation with natural HAs.

Formation of the HA precipitate is associated with protonation of the acidic exchange sites, so it can be presumed that coprecipitation of the microelements will be accompanied by sorption of heavy hydrogen isotopes by the freshly formed precipitates via isotope exchange reaction. This presumption is confirmed by the sorption behavior of tritium (THO) in the form of tritiated water at its coprecipitation with HA (Figs. 2, 6). The formal K_d of tritium characterizes a high degree of heterogeneous tritium-protium isotope exchange. As seen from Fig. 2, tritium can be sorbed by the protonated form of HAs with a relatively high K_d, especially at low concentrations of the competing Ca(II) cation. Increase in the concentration of the latter, together with that of the concentration of HA itself, suppresses the sorption via isotope exchange reaction. The established fact of the tritium isotope enrichment of humic acids will obviously allow reevaluation of the effect of the salt composition of the freshwater reservoir water containing humic substances on seasonal variations of the tritium concentration therein [23, 33]. Along with the above-mentioned dependence of K_d on the HA concentration, tritium sorption is significantly affected by a number of other parameters of the state of the aquatic environment and by the degree of equilibrium of the entire isotope exchange sorption system, which will be the subject of further, more thorough, consideration.

Our results show that the concentration constant of the formation of the nonsorbable complex M(FA), β(M), is relatively small for almost all the cations considered. The molecular weight of the fulvic acids is unknown to us, but estimation of their mass concentration under presumption that both the HA and FA molecules have close absorption coefficients at 220 nm, ε(FA) = ε(HA), gives the range of observed FA concentrations [FA]~0.1–10 mg/L, close to the chemical analysis data (see table).

Based on their β(M) constanst, the elements of interest can be conditionally divided into two groups: elements that form relatively stable complexes, with –log β(M)~2 ± 1 (K, Mg, Sr, Mn, Fe, Ni, Co, T, Ti) and elements that do not form stable complexes, with –log β(M)~8 ± 3 (Al, Cu, Zn, Ba, La, REM, Bi, Pb, Th, U) (Fig. 7). For calcium(II) ions, logβ(Ca) was estimated at 1.30 ± 0.30 for both groups of cations. The modeling results are characterized by F-statistic in the 10–400 range, which allows model (2)–(4), (7) to be considered as satisfactorily describing the sorption behavior of cations at coprecipitation with HA.

Thus, examination of the sorption isotherms of the cations (M) by natural humic acids (HAs) showed that the dependence of distribution coefficient K_d on the ratio of the mass to volume of the HA solution in the HA concentration range of 10–990 mg/L is associated with proceeding of two parallel processes in the sorption system: competitive sorption of M and Ca(II) ions by the HA precipitate and formation of a nonsorbable ($K_\mathrm{d} < 10$ mL/g) complex between the M ion and ligands (presumably, fulvic acids). These ligands accompany the HA in the mineral water and remain in the solution with pH 1–3 after HA precipitation. This conclusion is confirmed by the optical spectroscopic data for the HA solutions and the solutions above the HA precipitate. Specifically, they show that the solution contains high-molecular-weight organic compounds comprising optically active groups, as suggested by the absorption maximum at 211 ± 20 nm and a shoulder at 269 ± 30 nm in their spectra, typical for some types of fulvic acids. A probable scheme of the interaction of the sorbate cations with the products of acid dissolution of HAs was proposed. For the first time, the possibility of isolation of tritium (THO) from aqueous solutions by HA precipitates via isotope exchange reaction was demonstrated.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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