

SOIL CHEMISTRY

The Influence of Aminopolycarboxylates on the Sorption of Copper (II) Cations by (Hydro)Oxides of Iron, Aluminum, and Manganese

T. N. Kropacheva, A. S. Antonova, and V. I. Kornev

Udmurt State University, Universitetskaya ul. 1, Izhevsk, 426000 Russia

e-mail: krop@uni.udm.ru

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Abstract—The influence of some complexing agents of (poly)aminopolycarboxylic acids (diethylenetriaminopentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and iminodiacetic acid (IDA)) on the sorption of Cu^{2+} by crystal and amorphous (hydr)oxides of Fe(III), Al(III), and Mn(IV) that are widespread mineral components of soils was studied. The obtained results are considered in terms of complex-formation in the solution and on the sorbent's surface. The effect of the complexing agents on the metal sorption (mobilization/immobilization) is determined by (1) the stability, structure, and sorption capability of complexonates formed in the solution; (2) the acidity, and (3) the nature of the sorbent. The desorption effect on Cu^{2+} cations was found to change in the following sequence of complexing agents: $\text{EDTA} > \text{DTPA} \gg \text{NTA} > \text{IDA}$. The high-dentate complexing agents (EDTA, DTPA) had the greatest impact on Cu^{2+} cations bound with crystalline (hydr)oxides of Fe, Al, and Mn. The low denticity of the complexing agents (IDA, NTA) and binding of Cu^{2+} with amorphous sorbents leads to the weakening of desorption. The decrease in acidity promoted the mobilization of the metal under the influence of complexing agents; the increase in acidity caused its immobilization. The growth in the mobility of heavy metals bound with soil (hydr)oxides of Fe, Al, and Mn due to the complexing agents entering the surface and ground water is considered a factor of ecological risk.

Keywords: soil, heavy metals, mobilization/immobilization, sorption/desorption, complexing agents, EDTA, DTPA, NTA, IDA

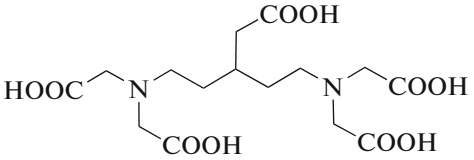
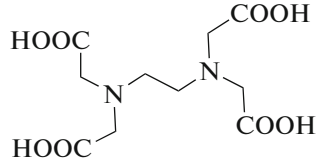
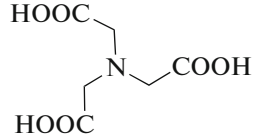
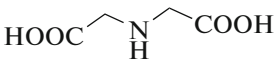
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INTRODUCTION

A set of physicochemical factors, including sorption with the participation of various organomineral phases—carriers, controls the migration of heavy metals (Hg, Pb, Cu, Zn, Cd, Ni, Co, Sn, Cr, Bi, and others) in the soils. Acidity, redox potential, and ionic strength of a soil solution with inorganic and organic ligands affect the distribution of heavy metals (HM) in the heterogeneous solution—solid soil phase system. In soil systems, different in the nature and concentration of ligands, the process of complex-formation in solution was found to lead to increasing (immobilization) or decreasing (remobilization) degree of sorption of metal cations [7, 11, 14, 17, 24]. The HM remobilization responsible for the contamination of soil—ground and surface waters is a factor of ecological risk. In particular, in the last ten years, the input of synthetic chelating agents—complexing agents—to the environment with industrial, communal, and agricultural wastes is a source of great concern. The most widespread complexing agents belong to (poly)aminopolycarboxylic acids—(poly)aminopolycarboxylic acids

(diethylenetriaminopentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and iminodiacetic acid (IDA) (Table 1)). At the total world production of about 200 000 t/year, these complexing agents are not removed by using traditional methods of wastewater purification. Many of them (EDTA, DTPA) do not decompose in the environment. All this results in exceeding the EDTA concentration in surface water ($2\text{--}1000\ \mu\text{g}/\text{dm}^3$) of many other organic pollutants of anthropogenic nature [22, 24]. In this connection, in many countries, some limitations on the use of EDTA and its analogues are accepted, and they are substituted for ecologically safe biodegradable complexing agents. Laboratory and field investigations confirm the strong remobilizing effect of EDTA on heavy metals in the soils, and this fact is a bases for using this complexing agent for the remediation of polluted soils by chemical extraction or phytoextraction [5, 7, 23]. However, as the soil solid phase is a polycomponent and polyfunctional system and it is responsible for the existence of HM in various forms [9, 10, 14, 15, 24, 29], experimental and theoret-

Table 1. Stability constants (complete) of Cu (II) complexonates

Complexing agent (H_nL)/denticity	$\log\beta$ (25°C, I = 0.1) [34, 35]	
Diethylenetriaminepentaacetic acid /8 (DTPA, H_5Dtpa)	CuL^{3-}	21.2
	$CuHL^{2-}$	26.0
	CuH_2L^-	28.9
	CuH_3L	32.7
	Cu_2L^-	27.9
Ethylenediaminetetraacetic acid /6 (EDTA, H_4Edta)	CuL^{2-}	18.8
	$CuHL^-$	21.9
	CuH_2L^-	23.9
	$Cu(OH)L^{3-}$	21.1
	Cu_2L	20.1
Nitrilotriacetic acid /4 (NTA, H_3Nta)	CuL^-	12.7
	$CuHL$	14.3
	CuL_2^{4-}	17.4
Iminodiacetic acid/3 (IDA, H_2Ida)	CuL	10.6
	$CuHL^+$	12.9
	CuL_2^{2-}	16.3

ical estimates of the remobilizing effect of EDTA (and other complexing agents) in simpler model systems with the participation of some phases-carriers imitating soil ones are necessary. For instance, of great interest as model HM sorbents are oxides, oxyhydroxides and hydroxides of Fe (II, III), Al (III) and Mn (III, IV) that are present in the soils in various forms: crystalline (goethite (α -FeOOH), hematite (α -Fe₂O₃), magnetite (Fe₃O₄), maghemite (γ -Fe₂O₃), gibbsite (α -Al(OH)₃), γ -boehmite (AlOOH), pyrolusite (β -MnO₂), manganite (γ -MnOOH), etc.), poorly crystalline (ferrihydrite (Fe₂O₃ · 2FeOOH · 2.5H₂O), ferrosityte (δ -FeOOH), birnessite ((Ca, Mg, Ni, K) (Mn⁴⁺, Mn²⁺) (O, OH)₂), vernadite (δ -MnO₂), etc.) and amorphous compounds [1–4, 10, 16, 19, 29, 30, 33]. Despite the thermodynamic instability, amorphous forms of hydroxides (as independent phases, films on the surface of other mineral particles, and as ingredients of organomineral complexes) are indispensable components of all soils. Owing to the small size of particles, great specific surface (100–800 m²/g), and high content of reactive surface centers, their sorption capacity is much greater than that of crystalline (hydr)oxides, which determines an important role of amorphous (hydr)oxides in the process of HM fixation.

Some works [8, 17–19, 21, 25, 26, 30] are devoted to studying the influence of (poly)aminopolycarboxylic acids on the HM sorption by Fe, Al, and Mn (hydr)oxides. However, because of the discrepant data obtained, the problems on the influence of the stability and structure of HM complexonates and of the hydroxide carrier nature on the desorption effect of complexing agents remains unclear. In this connection, the aim of this work is a systematic study of the influence of several (poly)aminopolycarboxylic acids (Table 1) on the HM sorption by some synthetic (hydr)oxides of Fe(III), Al(III), and Mn(IV) (Table 2) simulating soil minerals. (Hydr)oxides of Fe and Mn are strong HM concentrators [1–4, 10, 16, 29]. Therefore, in the soils with low humus content, a share of HM related to these hydroxides may be significant (10–50% of the total content) [9, 13, 24]. Cations of Cu²⁺ were chosen for the studies. These cations form normal, protonated, and hydroxyl complexonates of different molar (metal : ligand) compositions (1 : 1, 1 : 2, 2 : 1) related to specific conditions. Their stability regularly becomes higher with the increasing denticity of the complexing agent from 3 (IDA) to 8 (DTPA). The structure and stability of Cu²⁺ complexonates are close to those of Ni²⁺, Co²⁺, Cd²⁺, Zn²⁺, Pb²⁺ [6], which gives the results a more general character. The

Table 2. Some characteristics of the sorbents studied

Sorbents	S_{spec} , m ² /g (experimental data)	pH _{ZCP} (literature data)	pH ₅₀ of Cu ²⁺ sorption (experimental data)
Crystalline			
Hematite α -Fe ₂ O ₃	13 ± 1	7.5–9.5 [19]	5.6 ± 0.1
Goethite α -FeOOH	51 ± 2	7.5–9.5 [19]	5.6 ± 0.1
Aluminum oxide γ -Al ₂ O ₃	36 ± 3	8.1–9.8 [30]	5.7 ± 0.1
Pyrolusite β -MnO ₂	63 ± 3	4.4–5.9 [20]	5.2 ± 0.1
Amorphous (poorlycrystalline)			
Fe ₂ O ₃ · xH ₂ O (Ferrihydrite)	170 ± 6	7.5–8.5 [19]	5.8 ± 0.1
Fe ₂ O ₃ · 2FeOOH · 2.5H ₂ O			
Al ₂ O ₃ · xH ₂ O	112 ± 17	8.2–9.5 [30]	5.1 ± 0.1
MnO ₂ · xH ₂ O (Vernadite δ -MnO ₂)	142 ± 22	1.8–2.2 [32]	<2

existence of numerous sources of copper entering the soil (non-ferrous metals, galvanic production, and the use of microfertilizers and sewage sludge, etc.) causes an increase of the Cu content in the contaminated soils to 100–2000 mg/kg from its average concentration of 2–60 mg/kg. The results obtained create a good basis for evaluating the basic opportunity of remobilization/immobilization of HM cations under the influence of complexing agents in natural soil systems with the high content of Al, Fe, and Mn oxides and hydroxides.

OBJECTS AND METHODS

Commercially available preparations of complexing agents (CP) (Table 1) were used in the studies. Their solutions were prepared by the dissolution of the complexing agents in distilled water and standardized using pH-metric titration with KOH. The initial Cu²⁺ solution was made from Cu(NO₃)₂ · 3H₂O (AR), whose concentration was determined by complexometry using the traditional method (titration with EDTA in the ammonia buffer solution with murexide).

Commercial preparations of crystalline oxides (γ -Al₂O₃, hematite α -Fe₂O₃, pyrolusite β -MnO₂) and crystalline (goethite α -FeOOH) and weakly crystalline (amorphous) forms were obtained by synthesis (Table 2).

The synthesis of goethite was performed using the method [19] of mixing 250 cm³ of 0.1 mol/dm³ Fe(NO₃)₃ and 100 cm³ of 2 mol/dm³ KOH. The sediment obtained was kept in the mother solution at 70°C for 60 h. Then, it was washed with water to get pH close to 7, dried in the air and stored in a closed vessel at room temperature. For the synthesis of hydrogels (Fe(III), Al(III), and Mn(IV)), some described methods in literature were used to produce the X-ray amorphous or weakly crystalline particles. The Fe(III) hydrogel (ferrogel, Hydrous Ferric Oxide; due to the

ambiguity of its composition, the conditional Fe₂O₃ · xH₂O formula is used hereinafter) and Al(III) (alumogel, Hydrous Aluminum Oxide; the conventional formula is Al₂O₃ · xH₂O) were obtained using the method described in [12]—fast alkaline hydrolysis of the Fe(NO₃)₃ and Al₂(SO₄)₃ solutions. For this purpose, 20% NaOH was added to the solutions of these salts with the concentration of 0.05–0.10 mol/dm³ up to their pH 8.5 and 6.0, respectively. The preparations of ferrogel and alumogel obtained are easily dissolved by the Tamm reagent (oxalate buffer with pH 3.3) that satisfies the criterion of “amorphism,” which is used in soil science when characterizing the soil (hydr)oxides of Fe and Al. One can suggest that ferrogel is close to dycrystalline ferrihydrite (Fe₂O₃ · 2FeOOH · 2.5H₂O) in its properties; the same method is used for its synthesis [19]. Weakly crystalline hydroxide of Mn(IV) (Hydrous Manganese Oxide; the conventional formula is MnO₂ · xH₂O) was obtained using the method often used for the synthesis of vernadite (δ -MnO₂) [28]: 4.1 g of MnCl₂ · 4H₂O were dissolved in 900 cm³ of distilled water, and 100 cm³ of the solution, containing 2.2 g of KMnO₄, and 1.6 g KOH, were added there. The precipitate obtained was kept in the mother solution for an hour at continuous mixing; then it was left for 30 min. The X-ray amorphous state of the Mn(IV) hydroxide was verified using X-ray powder diffraction (a DRON-6 diffractometer, Fe-K α emission, Mn filter). It can be assumed that the properties of the Mn hydroxide obtained are close to those of vernadite having the poorly ordered pseudolayered structure [2, 3, 16, 23]. All the hydrogels obtained were washed many times with distilled water by decantation (to the neutral reaction and the absence of salt anions). Then, distilled water was added to the desired volume there, and the hydrogels were stored in the state of suspensions (the concentration of the hydrogels calculated on Fe₂O₃, Al₂O₃, and MnO₂ was 2–4 g/dm³). In the

sorption tests, fresh hydrogels were always used (the storage life in the closed vessel at room temperature did not exceed 2 days; in this period, as the control tests showed, the sorption characteristics of the hydrogels do not change). The contents of Fe(III) and Al(III) were determined by traditional EDTA titration after the dissolution of an aliquot of hydrogel in an acid. The Mn(IV) content in the hydrogel was measured by back titration based on the reduction of Mn(IV) with oxalic acid (heating to 80°C in the presence of H₂SO₄) and subsequent titration of its excess with the standard KMnO₄ solution.

The specific area of the sorbents' surface (Table 2) was determined based on the isotherms of low-temperature nitrogen sorption using the four-point BET method (a Sorbi-M[®] device). It should be taken into account that in the course of preparing the samples (drying at room temperature in the air and further dehydration in a nitrogen stream at 60 °C within 3–4 h), the specific area may decrease significantly.

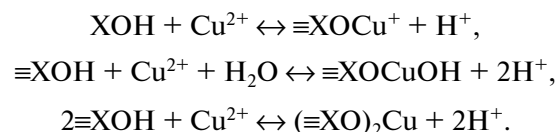
The Cu²⁺ sorption was studied in a static regime at continuous shaking for 30–60 min (the time of developing the equilibrium/quasi-equilibrium was determined in the preliminary kinetic experiments). The required acidity was made/supported by HNO₃ and KOH solutions.

The acidity was measured using an I-160MI ionomer (EC-10603/7 working electrode and ESr-10103 reference electrode). The constant ionic strength in the solutions was provided by the addition of the background electrolyte (0.1 mol/dm³ KNO₃). All the experiments were performed at 20 ± 2°C. The initial content of the reagents in the sorption tests was 10⁻⁴ mol/dm³ (Cu(II) and complexing agents) and 1 g/dm³ (sorbents). The crystalline oxides before sorption were hydrated at the required pH values for 15 min; in the case of amorphous hydroxides, suspensions of fresh preparations were used. After conducting the sorption, the (hydr)oxides were filtered through a paper filter (Blue ribbon), and pH of the equilibrium solution was measured. The residual Cu²⁺ concentration in the solutions after sorption was determined by photometry (SF-2000 spectrophotometer) according to the formation of a colored compound with sodium diethyldithiocarbamate. The presence of complexing agents in the solution (up to the ten times excess) does not prevent the determination of copper. The statistic processing of the results of parallel experiments showed that a relative error of the determination of Cu²⁺ sorption did not exceed 5%.

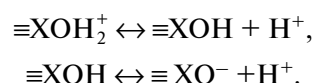
RESULTS AND DISCUSSION

The synthetic crystalline and amorphous (hydr)oxides of Fe, Al, and Mn studied as sorbents simulate the most important natural mineral phases—carriers participating in the fixation of heavy metals

and metalloids (Cr, Cu, Ni, Pb, As, Sb, and others) in the soils. From the standpoint of the theory of surface complexation (The Surface Complexation Theory) [15, 17, 19, 28–31], the sorption of cations of many d-metals, including Cu²⁺, on the surface of oxides, oxyhydroxides, and hydroxides of Fe, Al, and Mn (≡XOH, where X—Fe, Al, Mn), is formally described by heterogeneous reactions of the formation of intraspherical surface complexes according to the following schemes:



These reactions are influenced, apart from a purely chemical constituent (energy of the O–Cu chemical bond), by an electrostatic factor related to the presence of a variable charge on the surface due to the protonation/deprotonation of hydroxyl groups:



The zero point of surface charge (pH_{ZCP}) for (hydr)oxides of Fe and Al related to constants of protolytic equilibrium is in the range of weakly alkaline pH values; for Mn (hydr)oxides, it is in the range of acid values (Table 2).

The results of studying the effect of acidity on the Cu²⁺ sorption showed that in all the systems investigated, the degree of its sorption became higher with the increasing pH values (Fig. 1), which was naturally associated with a shift of the sorption equilibrium as above mentioned. To characterize the stability of the sorption state (at the fixed concentrations of a sorbent and sorbate), pH corresponding to the 50% degree of sorption (pH₅₀) can be used (the lower is the pH₅₀, the stronger is the sorption). The following sequence presents the sorption activity of the (hydr)oxides studied relative to Cu²⁺ based on the pH₅₀ values: MnO₂ · xH₂O ≫ Al₂O₃ · xH₂O > β-MnO₂ > Fe₂O₃ · xH₂O ≈ α-Fe₂O₃ ≈ α-FeOOH > γ-Al₂O₃. A larger specific surface of amorphous (hydr)oxides (compared to crystalline ones) promotes increasing their sorption capacity. The significantly stronger sorption of Cu²⁺ by amorphous Mn (hydr)oxides is related to the low values of pH_{ZCP} (Table 2), which determines a negative charge of the surface within the whole range of pH favoring the binding of cations. In addition, the high sorption capacity of weakly crystalline Mn(hydr)oxides (vernadite, birnessite) relative to various cations of metals is associated with the presence of cation vacancies in their layered/pseudolayered structure [2, 3, 16, 33].

The nature of the influence of chelating agents on sorption processes with the participation of metal cations depends on the stability and structure of metal complexing agents forming in the solution. When a

metal complexonate is not sorbed on the surface, the complex-formation in solution competes with the sorption and leads to a decrease in the sorption of metals (desorption, remobilization of metals). In this case, the desorption effect of chelating agents should increase as the stability constants of the complexonates forming in the solution become higher (Table 1). However, if a complexonate forming in the solution is sorbed on the surface, to predict its influence on the metal sorption becomes more difficult. Two mechanisms for the formation of triple surface complexes are possible: 1—complexes of the type A (surface—metal—ligand (complexing agent)) are formed due to the interaction with the surface of metal cation bound with the $\equiv\text{XOH} + \text{CuL}^{2-n} \leftrightarrow \equiv\text{XOCuL}^{1-n} + \text{H}^+$ ligand; 2—complexes of the type B (surface—ligand—metal) are formed resulting from the binding with the surface of the ligand retaining a metal cation: $\equiv\text{XOH} + \text{CuL}^{2-n} \leftrightarrow \equiv\text{XLCu}^{3-n} + \text{OH}^-$. The formation of surface complexes of the type A is possible if the ligand is not capable of saturating the coordination metal sphere, i.e. the decrease in the denticity of a ligand—complexing agent favors their formation. On the contrary, complexes of the type B are formed if a ligand has functional groups free from the coordination with a metal, i.e. the increase in the denticity of a complexing agent (Table 1) increases the probability of their formation. Surface complexes of the type A are better formed when the acidity is reduced (as the sorption of free metal cations), and complexes of the type B are better formed when the acidity increases (as the sorption of ligands).

Let us analyze the obtained results on the influence of different complexing agents on the Cu^{2+} sorption as related to acidity. In the presence of EDTA, a significant decrease in the degree of Cu^{2+} sorption on all crystalline (hydr)oxides of Fe, Al, and Mn was observed within a wide range of pH ($4 < \text{pH} < 10$) (Figs. 1 and 2). This phenomenon is related to the formation of the stable medium CuEdta^{2-} complexonate, in which the Cu^{2+} coordination sphere is completely saturated (the coordination number coincides with the EDTA denticity (6)), and the complexing agent itself does not have free functional groups for the formation of links with the sorbent's surface. As a result, the intraspheric sorption of the complexonate becomes impossible according to any sorption mechanism. The inhibition of Cu^{2+} sorption on amorphous/weakly crystalline Fe, Al, and Mn (hydr)oxides under the influence of EDTA is less and observed predominantly in the alkaline range of pH (Figs. 1, 2). In the acid conditions ($\text{pH} < 5$), the Cu^{2+} sorption (immobilization of the metal) on amorphous Fe (hydr)oxide even increased under the influence of EDTA. A reason for the weak desorption effect of EDTA on the amorphous sorbents is a successful sorption of the complexing agent itself on them (especially in acid medium), which makes the formation of surface complexes of the B type possible in the presence of metal cations. In

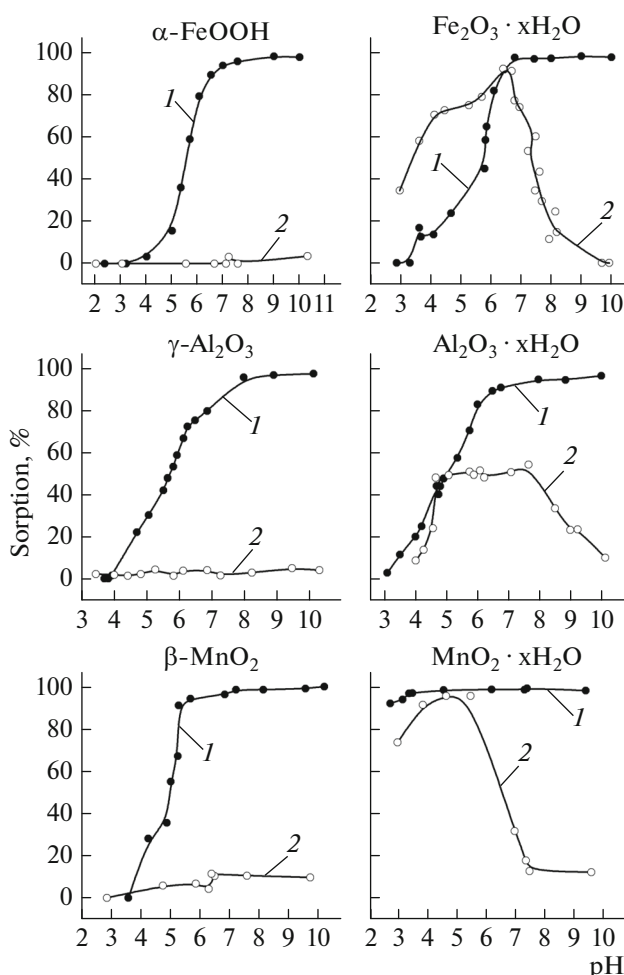


Fig. 1. The dependence of the Cu^{2+} sorption by different (hydr)oxides on the medium acidity: 1—in the absence of EDTA, 2—in the presence of EDTA. $C_{\text{Cu(II)}} = C_{\text{EDTA}} = 10^{-4} \text{ mol/dm}^3$, $C_{\text{sorbent}} = 1 \text{ g/dm}^3$.

the triple complexes (surface—ligand—metal), an EDTA molecule serves as a “bridge” ligand by binding simultaneously with Cu^{2+} and Fe^{3+} on the surface, while a free $-\text{COOH}$ group that resulted from breaking the glycinate cycle of the complexonate participates in the formation of this bond (Fig. 3). The formation of surface complexes of the B type was observed earlier in different metal cation—ligand (including complexing agents) systems with the participation of synthetic (hydr)oxides of Fe, Al, and soil as sorbents [11, 18, 24].

When passing to lower-dentate than EDTA complexing agents ($\text{EDTA} \gg \text{NTA} > \text{IDA}$), their remobilizing capability for Cu^{2+} decreases first of all due to the decrease in the stability of the complexonates forming in the solution (Fig. 2). The coordination unsaturation of Cu^{2+} in complexes with low-dentate ligands may be another reason for this phenomenon, which is responsible for the possibility of the intra-

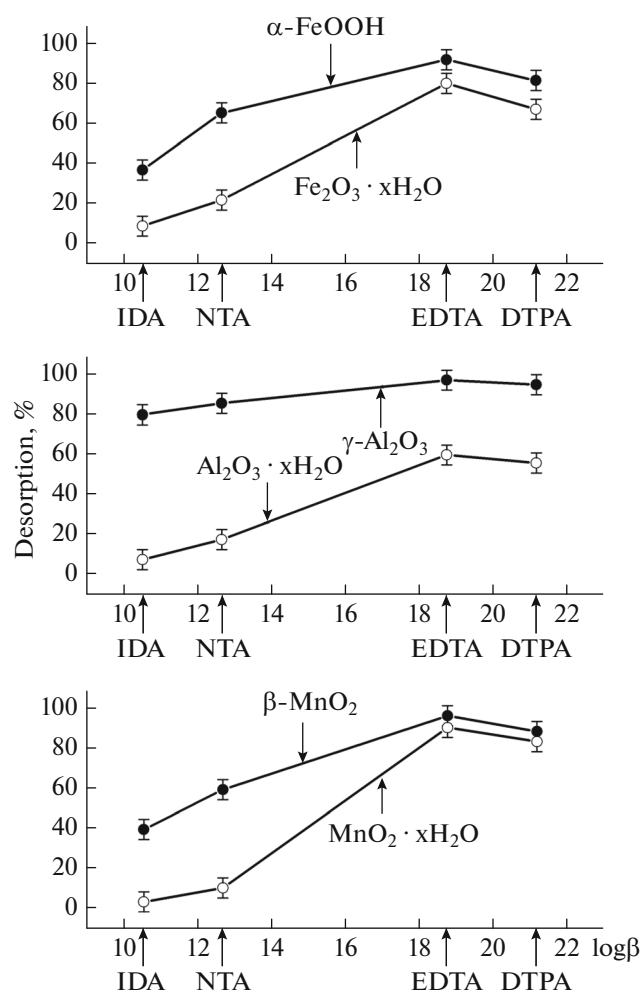


Fig. 2. The dependence of the Cu^{2+} desorption from the surface of (hydr)oxides on the stability of CuL^{2-n} complexonate formed in the solution $C_{\text{Cu(II)}} = C_{\text{EDTA}} = 10^{-4} \text{ mol/dm}^3$, $C_{\text{sorbent}} = 1 \text{ g/dm}^3$, $\text{pH} = 8.0 \pm 0.3$.

spheric sorption of complexonates with the formation of triple surface complexes of the A type (Fig. 3). In the presence of the highest-dentate DTPA complexing agent (Table 1), the degree of the Cu^{2+} desorption from the surface of all (hydr)oxides is reduced to some extent (compared to EDTA), despite the higher stability of the medium DTPA complexonate formed in the solution (Fig. 2). Probably, this is associated with the higher capability of DTPA to form surface complexes of the B type due to the DTPA denticity (8) exceeding the coordination number of Cu^{2+} . The latter permits DTPA groups that do not participate in the coordination to bind to the surface. In the surface complex with the participation of DTPA as a bridge ligand, the coordination of Fe^{3+} and Cu^{2+} becomes identical when each cation has its own half of the complexing agent molecule (Fig. 3), as it happens in the solutions of binuclear DTPA complexes [6]. Thus, if the increase in the stabil-

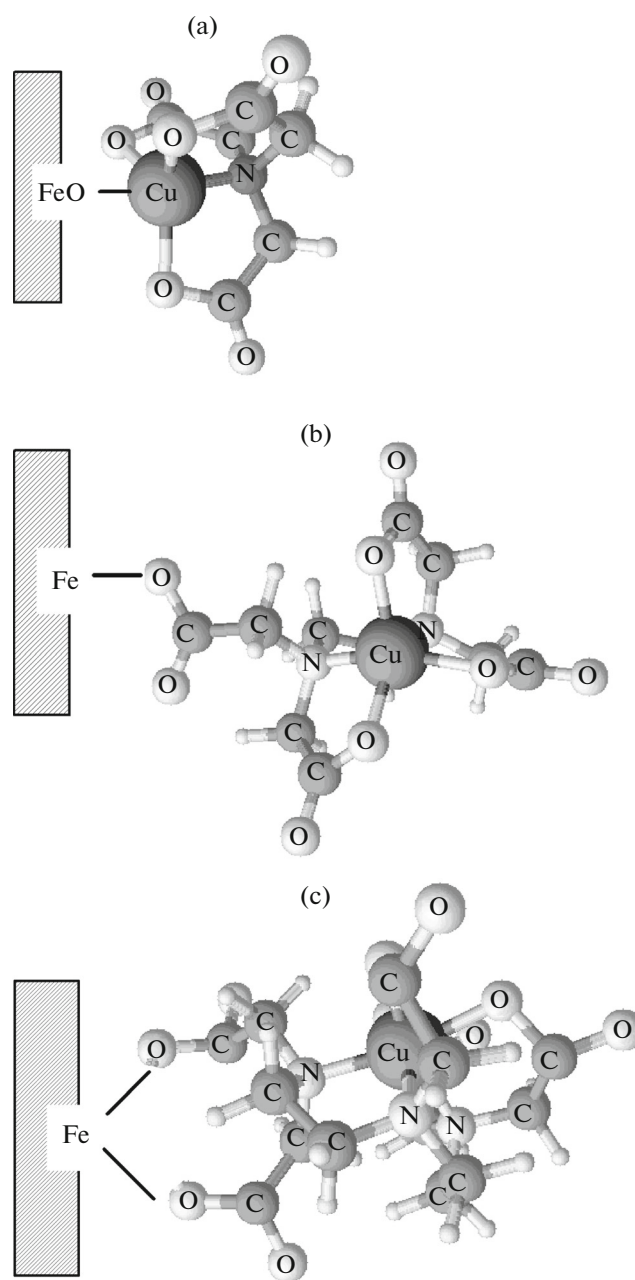


Fig. 3. An expected structure of the surface complexes: a—complex of the type A: Cu^{2+} —NTA—sorbent; b—complex of the type B: Cu^{2+} —EDTA—sorbent; c—complex of the type C: Cu^{2+} —DTPA—sorbent.

ity of the complexonate is accompanied by an increase in its sorption ability, the desorbing action of this complexing agent on a metal may be weakened.

The comparison of the influence of complexing agents on cations of Cu^{2+} that are sorption-bound to different (hydr)oxides (Figs. 1 and 2) showed that among the crystalline oxides, the desorption efficiency of all the complexing agents was somewhat higher in γ -Al₂O₃ compared to that in α -Fe₂O₃, α -FeOOH, and β -MnO₂. In amorphous (weakly crys-

talline) (hydr)oxides, the Cu^{2+} desorption under the influence of complexing agents, especially of low-dentate (IDA, NTA) ones, becomes lower due to a stronger sorption of metal cations by amorphous sorbents and the possibility to form surface triple complexing agents of the B type.

CONCLUSIONS

The results of the study show that in soil systems containing various oxides, oxyhydroxides, and hydroxides of Fe(III), Al(III), and Mn(IV), the remobilization of Cu^{2+} (and other HMs with the similar sorption and complex-forming properties— Ni^{2+} , Co^{2+} , Cd^{2+} , Zn^{2+} , and Pb^{2+}) becomes possible under the action of complexing agents from (poly)aminopolycarboxylates. This is related to the formation of metal complexonates that are stable and weakly sorbed in solutions. The remobilizing effect of complexing agents increases in the sequence $\text{EDTA} > \text{DTPA} \gg \text{NTA} > \text{IDA}$. Metal cations bound with crystalline (hydr)oxides of Al, Fe, and Mn are desorbed especially readily. In the case of amorphous forms of these (hydr)oxides, the HM desorption under the influence of complexing agents is mostly weakened for low-dentate complexing agents (NTA, IDA). The increase in the HM mobility and biological availability in the neutral and weakly alkaline media due to high-dentate complexing agents is somewhat stronger than the effect of organic ligands of natural origin (acetic, oxalic, citric, tartaric acids, glycine, and others). The transition of heavy metals from the bound state to the more dangerous mobile state due to complexing agents increases the risk of HM pollution of soil and ground and surface waters. Under certain conditions (amorphous sorbents, acid medium), the high-dentate (poly)aminopolycarboxylates can affect the HM sorption oppositely—stabilizing their sorption state. However, the immobilizing effect of the complexing agents is much lower than that of traditional ameliorators (lime materials, phosphates, organic substances, and others). Thus, the input of complexing agents (especially EDTA and DTPA) to the environment that are not practically decomposed (unlike NTA and IDA) and are capable to desorb HM successfully from the surface of natural sediments, including the soil, is a factor of ecological risk. To decrease the adverse effect of these complexing agents on water–soil systems, the development of new technologies for the purification of sewage (for instance, using specialized EDTA/DTPA-decomposing microorganisms) and the substitution of these traditional (poly)aminopolycarboxylates for new biologically decomposable “green” complexing agents are promising.

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