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Physicochemical Aspects of the Contamination of Soil and Hydrosphere with Heavy Metals

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Abstract

Perspective directions and results of the investigations of physicochemical transformations undergone by mineral and organic components of soil and natural water in the presence of heavy metal ions, which are among the most widespread pollutants of the biosphere, are considered. The mechanism of the indicated processes is discussed along with the effect of various factors on their kinetics (nature of heavy metals and substrate, pH of the medium, action of solar radiation, *etc*.).

Content

INTRODUCTION

The processes of the interaction of heavy metal (HM) ions with mineral and organic components of soils and natural waters play an important part in the genesis of the latter and to a substantial extent determine their properties. The efficiency of these processes varies substantially depending on the nature of a toxicant and physicochemical parameters of the environment in which these processes take place [1–3]. Investigation of the kinetics and mechanism of chemical transformation of organic substances in the cultivated soil layer and in surface water taking into account synergistic and antagonistic effects gives the information which is important from the ecological viewpoint.

SOURCES OF POLLUTION OF THE ENVIRONMENT WITH HEAVY METALS

Heavy metals enter the environment with direct discharge of waste water, its leakage and (or) dripping, with river flows, by passing through various boundaries between the media: air – water, water – soil, soil – air, *etc.* The sources of heavy metals in surface waters are also dissolution and destruction (erosion) of rocks and minerals, wastes from metallurgic, metal-working, oil processing and chemical plants, concentrating mills, mines, *etc.* With the development of engineering, transport and industry, the relative ecological importance of each of these sources changes at all times. The application of waste water and wood wastes in agrotechnics also brings about the threat of biospheric pollution since the concentrations of HM in these wastes are rather high, mg/l: Pb 0.30, Zn 0.8, Cr 0.4, Cu 0.35, Cd 0.15 [4].

The level of soil and surface water basin contamination is substantially affected by industry-caused acidification [5]. Acid precipitation accelerates desorption of HM ions from the surface of soil-forming clay minerals, their substitution by hydrogen ions in humate complexes and thus the shift of ion exchange equilibrium toward an increase in the concentration of HM in the contacting aqueous phase, which finally leads to a decrease in the protective properties of soil. An increase in hydrogen ion content of the soil helps dissolving the oxides of HM present in the soil and promotes their migration into the surface waters and plant nutrition routes. At a substantially high acidification degree, also destruction of soil-forming minerals occurs, accompanied by the release of structural ions Al and Fe into the contacting medium [5]. With a high excess of acid, their complete destruction is possible, with the formation of Al, Fe, Mg salts and silicic acid.

Metal sesquialteral oxides entering the soil and hydrosphere from industry-related sources also take an active part in the formation of soil acidity. This process is participated not only by the surface groups of oxides but also by coordination-bound water molecules, the dissociation of which results in the formation of protons having a substantial effect on the ion exchange processes and on the coordination interaction of HM ions with soil components. Additional pollution of natural water with HM is provided through the atmosphere.

Metals in the hydrosphere are concentrated mainly in the surface film, in sediments and in the biota, while their concentration in water column remains rather small. The levels of environmental pollution with HM and chemical forms in which they are present are essential for ecology of the environment. The HM content of surface fresh water varies from several units to several hundred micrograms per litre.

The extent of surface water pollution in the Dnepr region is to a high extent determined by the variations of integral atmospheric pollution index; among HM, prevailing role is played by cadmium and manganese. Depending on the properties of media, they are present in different oxidation degrees as truly soluble and colloid dispersed substances or are present as the components of mineral and organic suspensions thus determining the migration ability of pollutants in the aqueous ecosystem. With an exception of open sea where impurities are present mainly as dissolved substances, the presence of suspended particles is characteristic of the major part of water systems.

The most widespread HM pollutants of soil and natural water are iron, copper, manganese, cobalt, which are also biogenic elements in view of their participation in the synthesis of proteins, enzymes, in photosynthesis, *etc.*

The oxidation degree of iron is +2 and +3, depending on the oxidation-reduction potential of the medium (Eh). The compounds of Fe(III), which are thermodynamically more stable, occur more frequently that the compounds of Fe(II). Zinc occupies the second place in surface water concentration coming after manganese. Its migration occurs mainly in the suspended state. Nickel, which is characterized by medium complex-forming ability, is transported by river water also in the form of suspensions. Approximately half of Co(II) dissolved in surface water is not bound in complexes.

Metals with high oxidation degree occur in natural water mainly in the form of oxygen-containing anions distinguished by poor complex-forming ability. Migration in river water in the form of suspensions is characteristic of these HM. Exceptions are chromium and molybdenum, which are mainly (>60 %) transported in dissolved state. Cationic forms of vanadium and chromium are well absorbed by suspended particles. Cobalt, molybdenum, vanadium and chromium are rather strongly bound by the bottom sediments of natural water reservoirs, which provides their low mobility.

The prevailing form of cadmium (II) is metal ion (up to 50 %). Due to weak bonding of this toxicant by the suspended particles, its migration in natural water occurs mainly in the dissolved state. Mercury (II) migrates in river water mainly in the form of soluble complex compounds. The predominant part of Pb(II) is present in surface water in suspensions (90–98 %). For the soluble forms of Pb(II), complexing extent is often as high as 98 %.

Among various physicochemical transformations occurring in soil and in natural water under the action of industry-related factors (adsorption, ion exchange, chemical and photochemical, oxidation-reduction, catalytic reactions and so on), migration of HM and their relations with the mineral and organic components of the ecosystem are important. The major role in HM migration processes and in their physiological activity in natural waters is played by organic admixtures, the main part of which is comprised by humic (HA) and fulvic (FA) acids. The latter are dominating in river water; their content is 20–40 times higher than that of HA. In particular, the FA content of the water of Kiev water storage pool varies within 14–54 mg/dm^3, the HA within 0.3–2.0 mg/dm^3 [8]. The mobility of HM ions is substantially dependent on the amount of organic substance in water, its nature, pH redox potential of the medium, *etc.* Fulvic acids and HA possess good complex-forming properties. The complex compounds of HM at definite concentrations are toxic for hydrobionts, while their complexes with organic substances do not possess toxic properties even at high concentrations, with an exception of some metals. Due to the polydentate character, HM complexes with natural organic substances are characterized by rather high stability. Humic compounds in the systems under consideration form bi-, tri- and even hexadentate coordination bonds. Not only the presence of complex-forming groups in the substrate molecule but also their nature and spatial configuration affect the strength of complexes. In order to predict the behaviour of HM during changes in the conditions of the aqueous medium and in anthropogenic action, important data are provided by the results of investigation of the kinetics and mechanism of complex-forming processes under consideration.

As a rule, the high-molecular complexes of Fe(III), Hg(II), Cr(III), Pb(II), Cu(II) account for 95–100 % of the total content of dissolved HM forms; for the case of Zn(II), Cd(II), Co(II), Ni(II), Mn(II), high-molecular complexes account for less than 70 %. For Fe(III) and Pb(II) ions, the formation of complexes with higher molecular mass (>10 thousand) is characteristic. A clearly exhibited trend is observed for the Co(II), Zn(II) and Cu(II) cations to form complexes with molecular mass 1 to 10 thousand, for the anions of Ni(II) and Cd(II) <1000. The metals can be placed in a row according to their ability to form complexes with FA [7]: Mn(II) < Fe(II) ~ Cd(II) < Co(II) < Zn(II) < Pb(II) < Ni(II) ~ Fe(III) < Cu(II) < Hg(II).

Within the recent decade, pollution of soil with HM has got the global character. The major sources of soil pollution with HM are aerosol industrial emissions of oxides and sulphides of elements, automobile emissions, solid industrial wastes, cattle breeding farms, overflow of rivers polluted with waste water, *etc.* [4]. The sediments of waste water from the city waste disposal plants contain elements, mg/kg: Zn 50–8000, Cu 150–4000, Pb 52–600, Cd 3–165, Cr 225–4200, Ni 3–1400 [9].

Under the conditions of anomalously high amount of HM arriving with atmospheric precipitation, an overwhelming part of HM is retained mainly in the upper humus layers of soil.

A widespread form of HM migration in black soil is the truly soluble form. In the gray forest soil, metals are transported in suspensions. The presence of HM causes changes in the status of humic substances, structure, pH and biological properties of the soil, which results in partial (or complete in some cases) loss of the soil fertility.

As a result of anthropogenic pollution, HM enter soil in the form of oxides and various salts, both water-soluble and almost insoluble ones (sulphides, sulphates, arsenates, *etc.*). Some HM are rather widely spread in nature (iron, titanium, manganese, *etc.*). The majority of HM belong to microelements because of their low content in the environment (<10 %). Nevertheless, the role of many HM is rather high in the soil genesis, especially for its organic constituent.

Lead, cadmium and mercury are among the most dangerous metal pollutants of soil. The background concentrations of these elements in the ground are: 0.5–1.7 mg/kg for Cd and Pb, and 0.02–0.50 mg/kg for Hg [4].

The migration of lead in soil occurs in various chelate forms with organic components, and as a result of the action of the ground fauna along the rootage. In this process, horizontal migration of lead along the drainage channels is possible. An insignificant part of lead is transported by the wind with soil particles. The concentration of lead in soil is small in comparison with its amount in the atmosphere [10]. Relative availability of cadmium for plants is due to its presence in the soil in ion-exchange form. Its migration is strongly affected by pH of the medium [11]. Nickel easily migrates into the soil layer; however, the rootage of most plants usually creates a barrier providing safety with respect to this metal.

The stability of complex compounds, which are formed in the systems HM – surface of soil-forming component and HM – metabolic centre, plays the major role in providing buffer properties of soil. The HM are placed in the following row according to the degree of inhibition of soil respiration: Ag > Hg > Zn > Sn > Sb > Tl > Ni > Pb > Cu > Co > Cd > Bi [12]. For rather high levels of soil pollution with HM, their inactivation occurs as a result of saturation of active centres in metabolites and in soil-forming components.

The content of metal pollutants in large rivers of Ukraine is ten times higher than the MPC; these rivers relate to polluted and heavily polluted ones according to the international standards. Only in the town near the Dnieper river, the amount of the accumulated industrial wastes with high HM content is, mln t: ash and slag – 28.2, metallurgical slag – 119, wastes of nonferrous metallurgy – 331, wastes of chemical industry – 5.4 [13].

In comparison with the 50-ies of the 20th century, the content of manganese in the Zaporozhye water reservoir increased by a factor of about 1.7, copper 1.1, zinc 7.8, cobalt nearly 70. The concentration of chromium reached 100 mg/l, cadmium 0.3 mg/l. The concentration of manganese in separate regions of the water reservoir is 5–370 mg/l, zinc 49–157, copper 2–12, lead 40–59 and iron 44–75 mg/l.

The bottom sediments of the Zaporozhye water reservoir turned into a gigantic store of HM, mg/kg of the dry substance: 131.6 Cr, 12.5 Cu, 348.6 Mn, 672.6 Fe. Total content of the indicated elements in the sediment layer 0–2 cm thick exceeds hundreds tons. In the deep layers of bottom sediments of some rivers the concentration of Zn, Cu and Fe is 2.49, 0.077 and 9.36 g/kg of silt, respectively.

As a result of the application of copper compounds as fertilizers, the level of pollution in the layer 0–20 cm of the black soils of Southern Ukraine is 5–7 mg/kg, up to 70 % of this amount being present in the mobile form.

The correlation coefficients characterizing the dependencies of the response of biotic constituent of natural ecosystems to the industry-related contamination with HM have rather large values (>70 %) in the region under consideration.

INTERACTION IN THE SYSTEM: SOIL-FORMING MINERAL – HEAVY METAL

Soil is a slow-moving medium, and the pollutants migrate in it slower than they do in water or in air; because of this, the concentrations of toxicants increase gradually. The HM are accumulated in soils mainly in the form of insoluble and weakly soluble compounds and undergo various physicochemical transformations: hydrolysis, sorption, transformation as a result of oxidative-reductive and photocatalytic reactions, *etc*. The rate and depth of the indicated transformations depend on the properties of HM and their compounds (sizes of atoms and ions, density, molecular mass, redox potential, concentration of anions, *etc*.). The interaction of the latter with the HM ions in some cases helps transferring them into difficultly soluble compounds (phosphates, carbonates, sulphates) or chelate complexes (HA, organic acids, amino acids, *etc*.), which affects the protective action of the biota. From the ecological viewpoint, the distribution of toxicants between the liquid and solid phases of soil is an important parameter on which the availability of toxicants for plants and their accumulation in the latter depend. In order to estimate toxicity of HM, one should have the data on the mechanism of fixation of HM ions in different components of the soil.

In revealing the regularity of HM distribution in the environment, sorption processes are important in the soil composed of the organic and mineral components with relatively large specific surface. The mineral component is represented mainly by layered silicates and metal hydroxides. According to the ability to enter the exchange complex of soil-forming minerals, which is characterized quantitatively by the value of *b* constant in Langmuir equation, the investigated cations form the following row: Cu > Ni > Mn > Cd (Table 1) [6].

The character of binding the HM cations and the efficiency of their adsorption on the basal and side faces of minerals were investigated by means of EPR. Binding of the adsorbate with the basal face of a mineral is preferably of electrostatic character, while at the side faces of aluminosilicate the decisive role is played by coordination interaction of HM ions with active centres of the adsorbate [14].

The EPR spectrum of Cu(II) ions adsorbed on the basal surface of the mineral was interpreted on the basis of the flat-square coordination of $Cu(H_2O)_6^{2+}$ with additional oxygen atoms of the surface bearing negative charge (Fig. 1, *a*). The parameters of the EPR spectra ($g_\parallel = 2.083$ and $g_\perp = 2.306$) correspond to the values for Cu(II) complexes in which the character of surroundings and the symmetry of polyhedron for the coordination sphere of the central ion are similar [15].

The EPR spectrum of Cu(II) ions adsorbed on the side faces of the mineral is a sum of the considered and auxiliary spectra of lower intensity with the parameters: $g_\parallel = 2.05$ and $g_\perp = 2.099$ (see Fig. 1, *b*). The obtained data provide the evidence of two different states of copper ions; the symmetry of one of them is higher than that of the other, which agrees with the results of sorption studies of the nature of montmorillonite surface. Sorption of Cu(II) ions is provided by the excessive negative charge of the apical oxygen atoms in one of the states of the adsorbate with distorted octahedral coordination. In another state, octahedral complexes of copper (II) are formed; with a decrease in the humidity of the mineral, they are transformed into the complexes with flat square configuration with partial substitution of water by negatively charges oxygen atoms. With complete dehydration of the sample, a broad signal is observed in the EPR spectra, which corresponds to tetrahedral surrounding of copper ions by apical oxygen atoms of the side faces of the mineral.

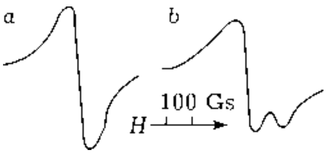


Fig. 1. EPR spectra of Cu (II) ions adsorbed on the basal surface of montmorillonite (*a*) and on the side faces (*b*): *a*, *b* – humidity: 20 and 1.5 %, respectively.

The kinetics of HM migration in soils is to a great extent dependent on relative content of the soil-forming aluminosilicate minerals and their ion exchange properties. In the case when the predominant role in adsorption processes is played by the basal faces of minerals, the binding of adsorbate to their active centres has electrostatic character. This promotes mi-

TABLE 1

Constants of Langmuir's equation characterizing adsorption of HM cations on Ca forms of minerals (numerator: *b*, ml/μeq, denominator: *a*, μeq/g)

Mineral	Cu^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}	Cd^{2+}
Kaolinite	0.70/55	0.65/52	0.60/55	0.53/53	0.77/52
Montmorillonite	0.65/10 000	0.60/980	0.50/980	0.45/990	0.42/970
Vermiculite	0.50/1350	0.50/1330	0.45/1360	0.40/1400	0.33/1300
Hydromica	0.65/250	0.65/250	0.55/260	0.53/260	0.50/230
Palygorskite	0.75/150	0.70/145	0.70/150	0.60/145	0.50/140

gration of HM, especially in the case of sufficient wetting of the soil. Migration occurs as a result of the gradient of HM ion concentration and as a consequence of their ion exchange displacement by potassium, magnesium and calcium ions into the contacting phase, which causes accumulation of HM along the routes of plant nutrition and worsening of the ecological parameters of soil. In the case of sorption of HM ions *via* coordination mechanism, which takes place under the conditions of selective sorption on the side faces of soil-forming minerals, the negative influence decreases substantially as a result of a decrease in migration ability of the cations under consideration.

PHYSICOCHEMICAL PROCESSES IN THE SYSTEM: HUMIC ACID – HEAVY METAL ION

In spite of low content of natural organic substances in soil in comparison with mineral ones, they determine the major physicochemical and biological properties of the soil and play an important part in humification, finally affecting the fertility of soil. In the complicated composition of the organic substances of soil humus, the central place from the viewpoint of importance in soil genesis is occupied by HA and FA, which are weakly dissociated polybasic organic acids.

The processes of sorption and complex formation in the HM – HA system are important for ecology of soil and hydrosphere, because they not only determine migration properties of toxicants but also are initial stages of many chemical and photochemical transformations which are underwent by mineral and organic components of the indicated objects of the biosphere.

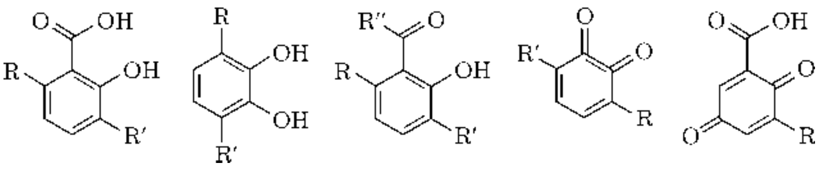
The interaction of HM cations with the organic components of soil occurs in more complicated manner than with the soil-forming minerals, mainly due to the features of chemical structure of natural organic substances. Since the nitrogen content of HA is about an order of magnitude lower than the oxygen content, the major donor centres providing HM binding on the surface of the sorbent are carboxylic and phenol groups in the oxygen-containing fragments of HA (Scheme 1).

The pK_a values for carboxylic groups are 4–5, and for phenol hydroxyls they are 9–10 [5]. For pH 3, the pK_a of complexes formed by Fe(III) and Al(III) ions with fulvinic acids are 0.1 and 3.7, respectively. For Mg(II), Mn(II), Zn(II), Cd(II), Pb(II), Ni(II) and Cu(II), pK_a for the same pH vary within the range 1.9–3.3 and increase up to 2.1–4.2 with pH increased to 5 [16].

The divalent cations can be arranged in the following row according to their ability to form complexes with FA: Cu(II) = Pb(II) > Hg(II) > Zn(II) = Ni(II) = Co(II) = Mn(II) = Cd(II).

In addition to carboxylic and hydroxyl groups, complex formation is participated also by the fragments of HA containing amino-carboxyl, imine and other groups [19]. As a result of the interaction of nitrogen atoms of the indicated groups with HM ions, partial displacement of oxygen-containing ligands from the internal coordination sphere of cation occurs. The influence of nitrogen-containing functional groups of HA on the sorption of Cu(II) ions increases with a decrease in the metal to HA mass ratio. In the case of high HM content, carboxylic and phenol groups play predominant role in sorption. Amino acid fragments possess low sorbing ability in comparison with other nitrogen-containing groups [20].

The interaction of HM with HA was investigated with the help of sorption equilibrium method, IR and EPR [21–23]. The stability constants of HM complexes decrease in phase with the limiting values of sorption determined from



Scheme 1.

isotherms, giving the sequence: Fe > Cu > Pb > Co > Ni > Cd = Mn (Table 2). This row correlates with the coordinating ability of HM ions. The ability of cations to be sorbed increases with an increase in pH, decrease in the concentration of adsorbate and increase in HA content of the equilibrium solution. The highest sorbtion ability is exhibited by Hg(II), Fe(III), Pb(II) and Cu(II), while in the case of Zn(II), Ni(II), Cd(II), Co(II) and Mn(II) ions it is much lower.

In the ability to be sorbed, the latter cations are comparable with the cations of alkaline metals and alkaline earths. The binding of adsorbate with the adsorbent surface in this case is due mainly to electrostatic forces. The established correlation between the radius of cation and its ability to be sorbed is exhibited less strictly for the metals of the main subgroups of I and II groups of the Periodic Table. Rather high relative stability constants of humate compounds of some metals (Fe, Cu, Pb) evidence in favour of the coordination character of bonding with active centres of the surface of HA.

The determined sorption parameters agree with the results of investigation of IR spectra of HA in their interaction with HM ions (Fig. 2). The absorption band corresponding to the vibrations of C=O carboxylic groups (1710 cm^{-1}) in the spectra of K forms of HA disappears completely with the appearance of the band at 1400 cm^{-1} related to antisymmetric vibrations of COO^{-} groups. The appearance of the band at 1400 cm^{-1} is also observed in the spectra of HA with adsorbed double-charged cations of Mn(II), Co(II), Cd(II) and Ni(II), but the band at 1710 cm^{-1} does not disappear because of incomplete binding of carboxylic groups of HA into ion associates. In the case of humates of Fe(III), Pb(II) and Cu(II), the IR spectrum within the region of vibrations of ionized carboxylic groups (1400 cm^{-1}) remains almost unchanged, in spite of high saturation of the exchange capacity of HA with these cations (see Table 2). This is an evidence of substantial contribution from coordination interaction into the sorption of the indicated ions.

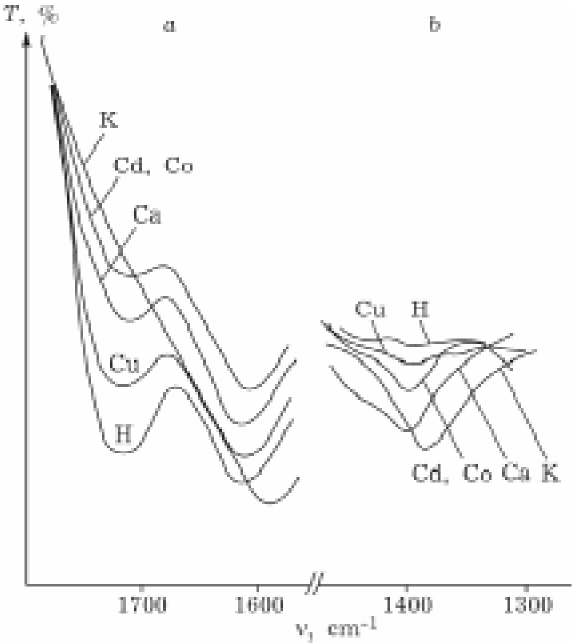


Fig. 2. IR spectra of the initial (*a*) and cation-substituted (*b*) forms of HA.

TABLE 2

Stability constants K_{stab}, limiting sorption *a* and the degree of saturation of the exchange capacity φ of HA with HM ions

Adsorbate	K_{stab}	*a*, μmol/g	φ, %
Mn^{2+}	2.2 I0^{6}	182	7.74
Cd^{2+}	2.2 I0^{6}	190	8.09
Ni^{2+}	2.4 I0^{6}	205	8.72
Co^{2+}	2.5 I0^{6}	220	9.36
Pb^{2+}	4.0 I0^{8}	410	17.45
Cu^{2+}	4.3 I0^{8}	420	17.87
Fe^{+3}	I.2 I0^{15}	635	40.53

Stoichiometric composition and structure of the complexes of HM with HA were studied using EPR [23]. The EPR spectrum of the HA sample containing sorbed ions of iron (III) exhibit the signals with *g* equal to 4.13 and 2.06, related to the complexes with distorted tetra- and octahedral coordinations, which can be represented correspondingly by formulas I and II (Fig. 3). The form II dominates in the initial samples. Drying of the samples causes an increase in the content of form I and in the intensity of the EPR signal with *g* = 4.13. Hydrogen ions have destructive action on the octahedral complexes. The content of hydrogen ions increases in the system with an increase in sorption of iron (III), which leads to a decrease in the intensity of the signal with *g* = 2.06.

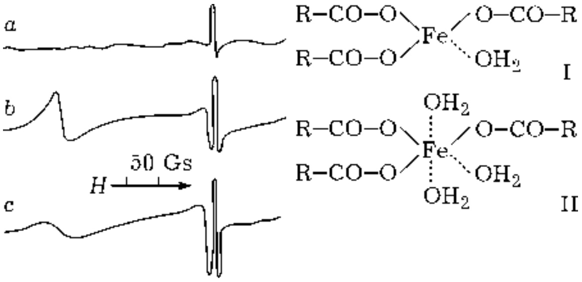


Fig. 3. EPR spectra of HA with the sorbed Fe(III) ions: *a* – initial HA, *b* – HA sample containing 90 μmol/g Fe(III) and exposed to vacuum at 375 K for 3 h; c – air-dry sample containing 90 μmol/g Fe(III), 5 % H_2O.

The EPR spectra of HA samples with small content of sorbed copper (II) (<20 % of the amount of –COOH groups) contain a signal described by spin Hamiltonian for the axial symmetry ($g_{\|}$ = 2.332; $g_{\perp}$= 2.049; $A_{\|}$ = 11.6 kA/m, $A_{\perp}$= 1.5 kA/m) which corresponds to the octahedral complex with two carboxylic groups of HA and four water molecules in the coordination sphere (Fig. 4, III). When the content of sorbed copper (II) exceeds ion exchange capacity of HA, the EPR spectrum becomes more complicated due to superposition of the line corresponding to form IV. The ions of copper (II) are easily displaced from form IV into the contacting solution, even by alkaline metals or alkaline earths, while form III is destroyed only under strong acidification (pH < 1). The data obtained are in accordance with the results of investigations carried out using the sorption equilibrium method [21].

Unlike the ions of iron (III) and copper (II), manganese (II) cations are weaker sorbed on HA. Independently of the amount of sorbed cations, only one line is observed in the EPR spectrum; it has hyperfine structure with g = 2.06 and a_0 = 7.164 kA/m and corresponds to octahedral aqua complexes of manganese (II) interacting with the carboxylic groups of HA *via* the electrostatic mechanism. Dehydration of manganese humate is accompanied by a decrease in a_0 to 6.2 kA/m, which indicates changes in the composition of the coordination sphere of Mn(II) ion due to partial substitution of water molecules by carboxylic groups. After wetting the sample its EPR parameters recover.

The coordination interaction of HM ions with the sorption centres of HA leads to a decrease in the concentration of free radicals and biradicals – products of humification of organic substances in soil, unlike the cations of the first and second groups which have only slight effect on paramagnetic properties of HA. With an increase in the content of many HM cations, the intensity of the main signal (g = 2.003) decreases linearly and almost disappears when its exchange capacity is saturated completely. The coordination interaction of HM ions with paramagnetic centres (PMC) of HA leads to deactivation of free radicals in them and to the inhibition of redox processes playing the predominant role in the soil genesis.

A special group of chemical reactions proceeding in soil includes the interaction of clayish minerals and humic substances with HM oxides and sulphides resulting in the destruction of soil components and in an increase in the level of pollution of biospheric objects with HM ions.

In the investigations of the kinetics and mechanism of dissolution of copper (II) oxide and sulphide in contact with the soil-forming components, we used natural montmorillonite, its H and Ca forms, and HA isolated from brown coal. Similarly to the interaction of the soil-forming components with Cu(II) ions in the dissolved state, in the case under consideration we also observed the formation of complexes with octahedral and tetrahedral configurations; their relative content in the system varied with

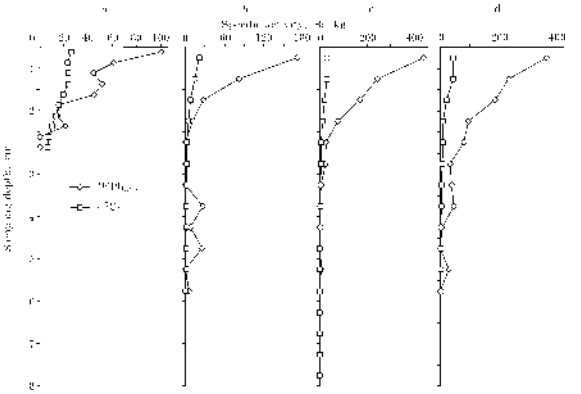


Fig. 4. EPR spectra of HA with the sorbed Cu(II) ions: *a*, *b* – Cu-humate containing 150 and 420 μmol/g of copper, respectively.

an increase in contact time and in the extent of dissolution of copper (II) oxide and sulphide.

The EPR spectrum of Al-montmorillonite samples after contact with CuO in water is a superposition of two signals. The signal observed in a weaker magnetic field corresponds in its parameters to the hydrated copper ions $Cu(H_2O)_6^{2+}$ connected with the mineral surface by electrostatic forces. The second signal relates to heteroligand aqua complexes in which some positions of the coordination sphere are occupied by donor atoms of the mineral surface. With an increase in contact time, redistribution of the ions between the indicated forms occurs; the fraction of aqua-surface complexes increases (Fig. 5). The observed process is reversible: almost complete transformation of copper ions into $Cu(H_2O)_6^{2+}$ occurs with an increase in humidity. The dissolution of copper oxides proceeds extremely slowly in neutral samples of Ca-montmorillonite. The signal corresponding to the aqua-surface complex was observed only after 12 months.

The intensity of EPR signal corresponding to the aqua complexes of Cu(II) is substantially lower in the case of sulphide than for oxide, for similar time of contact with the surface of Al-montmorillonite (see Fig. 5). Since the number of active centres on the mineral surface is sufficient for complete binding with copper ions formed during dissolution of sulphide, they are not detected in the contacting solution.

In comparison with the aluminium-containing form, Ca-montmorillonite helps dissolving copper sulphide rather than oxide. In this case, pH of the medium is higher than in the samples with Al-montmorillonite, which is favourable for the oxidation of sulphide sulphur with simultaneous release of copper ions into the contacting medium.

Almost complete dissolution of copper oxide is observed also during the formation of aqua humate complexes (Fig. 6). The EPR spectra do not change with time. With the saturation of the system with water vapour, redistribution of copper (II) forms occurs, resulting in an increase in $Cu(H_2O)_6^{2+}$ ion content. The intensity of EPR signal in the weak magnetic field increases substantially (see Fig. 6, *b*) in comparison with the air-dry sample (see Fig. 6, *a*). The indicated process is also accompanied by a decrease in the intensity of the signal of paramagnetic centres of HA due to spin exchange during their coordination interaction with copper (II) ions.

INFLUENCE OF HEAVY METALS ON THE TRANSFORMATIONS OF CHEMICAL SUBSTANCES IN THE ENVIRONMENT

The HM compounds possessing reductive-oxidative and catalytic properties play an important part in the processes of chemical transformations of substances in soil and in natural water bodies [24, 25]. Catalytic activity of HM in soil and in natural water is investigated insufficiently. When HM get into soil, they are fixed on the surface of natural minerals. In the adsorbed state, they catalyze many chem-

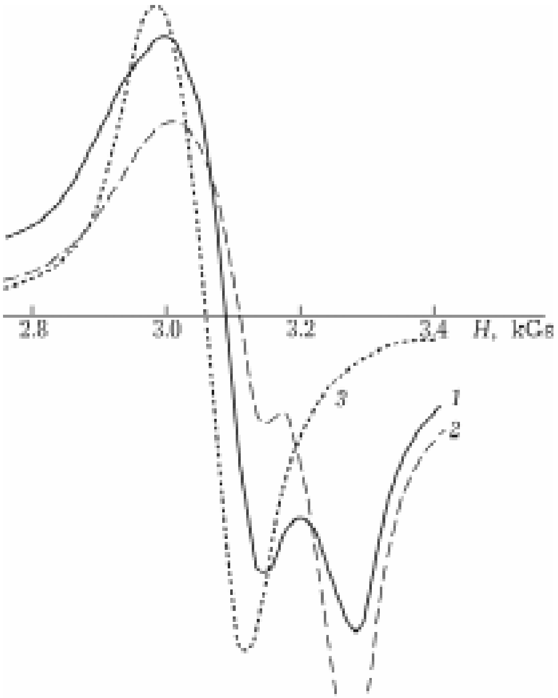


Fig. 5. EPR spectra of air-dry samples of Al-montmorillonite after contact with copper (II) oxide in water for 3 (*1*), 12 months (*2*) and additional moistening in saturated water vapour (*3*).

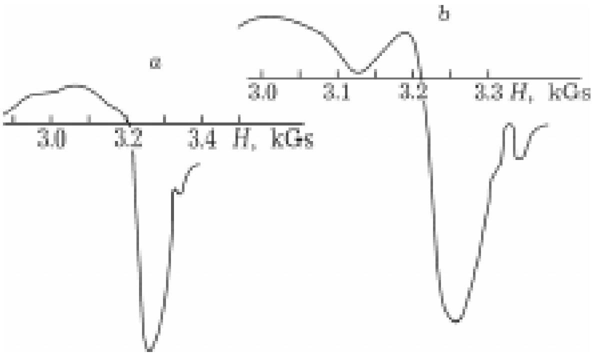


Fig. 6. EPR spectrum of air-dry HA sample after contact with copper (II) oxide in water for 12 months (*a*) and after additional moistening in saturated water vapour (*b*).

ical reactions in soil or in soil solution, in particular destruction processes [26, 27].

The exchange interaction of HM ions with natural minerals causes substantial enhancement of their catalytic activity toward the oxidation of sulphide sulphur in water. The rate of the catalytic reaction on natural aluminosilicates (kaolinite, palygorskite, clinoptilolite, *etc.*) the exchange complex of which contains ions: Ni(II), Co(II), Fe(III), Mn(II) and Cr(III), is 1–3 orders of magnitude higher than the rate of non-catalytic oxidation [28, 29].

Specific catalytic activity of a catalyst depends on the nature of the exchange cation. In the case of kaolinite and meta-kaolinite, Ni form is the most active one, while the activity of other forms is 1–2 orders of magnitude lower. The investigated exchange cations on the surface of the indicated catalysts can be placed in the following row according to their catalytic activity: Ni(II) > Fe(III) > Co(II) > Mn(II). For crystalline kaolinite, a large difference is observed between the activity of Ni form and other cation forms, while for meta-kaolinite this difference is insignificant. This is explained by changes in the structure of meta-kaolinite under thermal treatment and by stronger fixation of the exchange ions Fe(III), Co(II), Mn(II) on meta-kaolinite matrix in comparison with Ni(II). In the case of clinoptilolite, the activity of the exchange centres decreases in the row: Ni(II) > Cu(II) > Fe(III) > Cr(III) > Co(II) > Mn(II) > Zn(II). Catalytic activity of one and the same type of the exchange complex on the matrices of different nature decreases in the row: crystalline kaolinite > palygorskite > meta-kaolinite > clinoptilolite.

Differences in the process rate for the crystalline kaolinite and palygorskite in comparison with meta-kaolinite are explained by smaller exchange capacity of the latter. With large difference in the exchange capacity between clinoptilolite and meta-kaolinite (about 2 orders of magnitude), specific reaction rate values are comparable for the indicated minerals. This is explained by the fact that not all the Ni(II) ions in the catalyst are catalytically active. The values of specific catalytic activity for meta-kaolinite, crystalline kaolinite and palygorskite are of the same order of magnitude; however, the value for the crystalline sample is about two times higher. The latter is explained by changes in the chemical properties of the surface during the formation of meta-kaolinite from crystalline kaolinite. The exchange ions in meta-kaolinite go irreversibly deeper into the pseudo-hexagonal wells of the basal surface and become non-exchangeable. Exchangeable ions are only those at the side face, while in the crystalline kaolinite both the ions on the basal surface and the ions of the side space are exchangeable. Less rigidly fixed ions on crystalline kaolinite can pass into the contacting medium; as a result, they participate to some extent also in the homogenous catalytic oxidation of the substrate.

Changes in the catalytic activity are substantially affected by the non-equilibrium energy state of ions fixed on side faces and the basal surface of aluminosilicates. The catalytic activity of clinoptilolite is 2 orders of magnitude lower than that of kaolinite and palygorskite, while the exchange capacity of the former is 1–2 orders of magnitude higher.

The kinetics of the oxidation of S^{2-} ions on the indicated aluminosilicates is described by the equation

$$w = k[HS^-][O_2]^{0.2}[Cat]^n \qquad (1)$$

where n depends on the nature of the catalyst (Cat).

For the cation-substituted Ni forms of meta-kaolinite and clinoptilolite n = 0.5; for Ni-palygorskite n = 0.9, which is connected with different dispersed state of the catalysts. The mechanism of oxidation of sulphide sulphur in the presence of dispersed aluminosilicates with a transition metal ion in the exchange complex includes the formation of a sulphide of transition metal, active complex of oxygen with the latter, and adsorption of sulphide sulphur on the active centre of the mineral surface:

$$\begin{tikzcd} & \begin{array}{l} S + H_2O + Me_xS_yM \quad (2) \\ pH \approx 7 \end{array} \\ Me_xS_yO_2HS^-M \arrow[ur] \arrow[dr] & \\ & \begin{array}{l} S_2O_3^{2-} + H_2O + Me_xS_yM \quad (3) \\ pH \geq 8 \end{array} \end{tikzcd}$$

where Me is the transition metal ion, M is the catalyst matrix.

In case of definite levels of pollution, HM play the role of initiators of many photochemical reactions proceeding in the biosphere under the action of sunlight [30–33]. Among a wide range of physicochemical transformations proceeding in soil and natural water polluted with HM, of high ecological importance are the processes of photooxidative decomposition of organic compounds both those of industry-related origin (pesticides, surfactants, industrial and household wastes, *etc*.) and humic compounds, which are important components of the fertile layer of the ground [34–41]. The most important functions of soil include redistribution of the energy of absorbed sunlight between separate components, which provides substantial influence on the rate and depth of many reductive-oxidative, destructive, isomerization reactions, *etc*. As a result of the latter, the soil undergoes substantial physicochemical, morphological and biological changes. The direction and efficiency of these processes depend on chemical composition and concentrations of HM compounds present in the soil, since they possess high photochemical activity. The importance of these processes increases gradually because of annual growth of ozone holes in the Earth's atmosphere and consequent increase in the intensity of the UV component of solar radiation reaching the Earth's surface.

The molecules of organic substances, HM ions and complex compounds which can be formed in their interactions can participate as photoactive components in the processes under consideration. In the case of sufficiently high content of organic matter in the system, when the organic matter accounts for the main fraction of the absorbed light, the primary stage of the photochemical transformation is direct photolysis. The interaction of thus formed radicals with oxygen and HM ions causes deeper destruction of the organic substance.

In the second case, the primary stages of photochemical reaction result in the formation of highly active hydroxyl radicals *via* the photoreduction of hydrated HM cation. Hydroxyl radicals generated in this process interact with the substrate, which leads to the accumulation of various organic radicals in the solution. Under the action of atmospheric oxygen, the initial form of HM is recovered, with simultaneous formation of superoxide ions, organic peroxide radicals, along with the oxidation of radical fragments, which are the products of substrate destruction.

The primary photochemical process can also occur with the complex compounds of HM with HA and other organics. Phototransfer of electron occurs in this case between the metal ion and the functional group oh HA included in the coordination sphere of the cation. The reduced form of metal, organic radicals and ion radicals formed at the first stages participate in further thermal reactions [44–46].

General and specific features of these processes can be described considering the mechanism of photooxidative destruction of HA under the action of molecular oxygen in the presence of iron ions (Fig. 7). Depending on the nature of photoactive component, three main routes of photoreaction progress in this system can be distinguished. The primary stage of the photoreaction can be direct photolysis of HA under the action of the shorter-wavelength component of sunlight, resulting in the formation of radical fragments. The latter interact with iron ions generating organic cations and anions, or with molecular oxygen transforming into the corresponding peroxide compounds. Intermediates formed in the system participate in various thermal reactions with the components of the ecosystem giving rise to stable products of the substrate transformation. The efficiency of these processes, which compete with the recombination of the primary radicals, is determined by the concentrations of iron ions and oxygen, as well as by physicochemical parameters of the medium, pH,

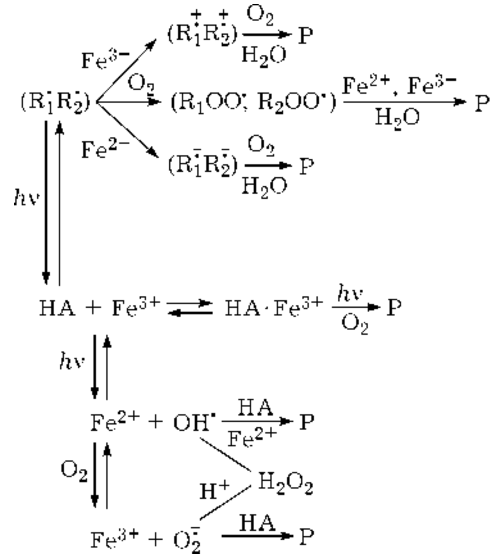


Fig. 7. Scheme of the mechanism of HA photooxidation in aqueous media containing Fe(II) ions.

reductive-oxidative potential, nature and concentration of the background electrolyte, *etc.*

Initiation of the photochemical process can occur also as a result of the generation of hydroxyl radicals, which are the products of photooxidation of water. Radical fragments formed in the interaction of hydroxyl radicals with HA molecules participate in the above-considered reductive-oxidative processes with oxygen and iron ions.

Along with the indicated routes of photooxidative degradation of HA, the system also provides photochemical transformation of the substrate in complex compounds which the substrate forms with iron ions. In this case, photoreaction is initiated due to the intra-complex electron transfer between the coordinating ion and a functional group of the HA ligand.

Iron ions form complexes with many organic compounds of natural and industry-related origin [46]. As a result of the formation of Fe(II) complexes with a number of natural organic substances (tannic acid, gallic acid, pyrogallol, *etc.*), the stability of the latter toward the action of atmospheric oxygen increases. Complex formation and increase in the stability of the substrate are promoted by an increase in pH of the medium and in the organic substance to Fe(II) ratio. The stability of ferrous ions to oxidation increases, too.

The rate of photoreduction of Fe(III) ions under the action of light (>300 nm) in the inert atmosphere increases noticeably with the introduction of HA into the solution (Fig. 8). With the mass ratios Fe : HA (1 : 1.5) used in the experiments, the active light was absorbed almost completely by humate complexes and free hydroxo complexes of iron (III).

The efficiency of photooxidation of the substrate in the form of complex is substantially higher than in the free state.

Independently of which of the indicated iron complexes play the role of photoactive component of the system, an increase in HA content of the solution under irradiation should lead to an increase in the quantum effect of photoreaction. Really, not only the degree of complex-binding of ferric ions increases, but so does also the rate of deactivation of hydroxyl radicals formed at the initial stage of the photochemical process, when the role of photoactive component is played by hydroxo-complex Fe(III) ions [44].

It follows from the comparison between the obtained kinetic data that the rate of photooxidative process in solutions containing the ions of Fe(III) and HA exceeds the sum of the rates of iron ion photoreduction and substrate photodecomposition for the process carried out in the corresponding single-component systems. This is explained not only by the participation of Fe(III) ions in the reactions with radical products of the direct and auto-oxidative photolysis of HA, but also by the interaction of the substrate with the primary hydroxyl radicals.

Due to the effect of atmospheric oxygen, the efficiency of photooxidation of HA by Fe(III) ions in soil and in the upper layers of the surface waters is rather high. The rate of oxygen absorption is proportional to the concentration of humic substance and nonlinearly depends on the intensity of light and on pH. Preliminary esterification of carboxylic groups decreases the consumption of oxygen as a result of photoreaction by 50 %, which indicates that the oxidation of HA proceeds through the primary stage of charge transfer from carboxylic groups on ferric ions bound with them through coordination [47].

In the presence of oxygen, also the accumulation of hydrogen peroxide occurs through the intermediate formation of superoxide anion radicals. Hydrogen peroxide decomposes as

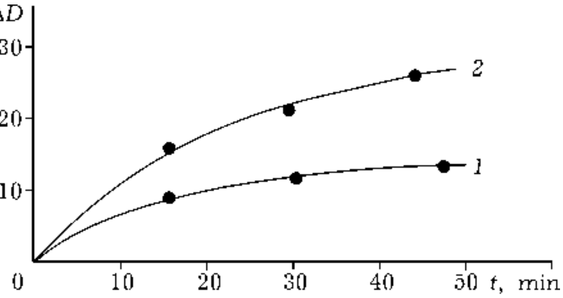


Fig. 8. Kinetics of a decrease in the optical density D of aqueous solutions of $FeCl_3$ without HA (*1*) and with HA added (*2*) (d = 1 cm).

a result of interaction with iron ions to generate hydroxyl radicals in the system under consideration (Fenton's reaction). In spite of low concentration of hydrogen peroxide formed in soil and in natural water under the action of sunlight, its role in the production of hydroxyl radicals in biosphere is rather substantial [47–49].

So, photooxidative destruction of HA in aqueous solutions containing Fe(III) ions proceeds *via* two main routes of the generation of hydroxyl radicals: as a result of Phototransfer of electron in hydroxo-complexes of iron, and due to thermal interaction of Fe(II) ions with hydrogen peroxide.

The interaction of HM with peroxide intermediates formed in photooxidation of organic substances is the basis of humification process and plays a substantial role in soil genesis.

Photooxidation of pyridinecarboxylic acids in Fenton's system proceeds according to the photocatalytic mechanism; under the action of sunlight, Fe(II) ions are regenerated by photoreduction of Fe(III) ions and, as a consequence, a definite ratio of these valence forms is maintained in the catalytic decomposition of H_2O_2. The participation of chelate compounds of Fe(II) and Fe(III) with the indicated acids in photochemical generation of the active form of the catalyst is assumed [50].

The processes of photochemical transformation of pesticides in soil and in hydrosphere are strongly affected by HM [31–33], which is important under the gradual increase in their amount present in the biosphere. As a model system for investigating the mechanism of the processes under consideration, we studied the system Cu – PKM (2.3.5-trichloro-4-aminopicolinic acid).

Spectrophotometric studies showed that rather stable complexes are formed in this system (K_{stab} = (196 ± 8) l/mol), and complex formation is limited to the first step:

$$Cu + P^- = CuP$$

where P^- is the piclorame anion.

This process involves broadening of the range of spectral sensitivity to longer wavelengths, which during photochemical process under natural conditions results in an increase in the fraction of acting light in the total flux of solar radiation reaching the soil surface. Photolysis of piclorame under the action of UV light in the presence of Cu(II) ions proceeds much slower than in their absence; photolysis results in more stable products than the direct photolysis of the substrate.

Under the addition of Cu(II) ions to the HA solutions, the optical density in the region 220–350 nm increases due to the formation of complexes between the components of the system under consideration (Fig. 9). The UV irradiation of HA solutions causes a noticeable decrease in the optical density in the indicated spectral region.

Photodestruction of HA in aqueous solutions of HM is accompanied by the accumulation of FA in them. The efficiency of this process increases in phase with an increase in the coordinating ability of HM ions. The highest yield of FA is observed in the presence of Hg and Cu ions.

Irradiation of the system with UV light leads to a decrease in the optical density not only in the region 330–250 nm but also in shorter wavelength region of the spectrum; the spectrum of the system becomes more characteristic.

CONCLUSION

In addition to the direct toxic effect on the conditions of human life, the HM of natural and industry-related origin which are present in soils and in hydrosphere affect the kinetics and directions of physicochemical processes that go in the biosphere with the participation of HM. Among diverse factors governing the efficiency of these transformations, predominant are: ion exchange and coordinating ability of HM ions, donor-acceptor properties of the sub-

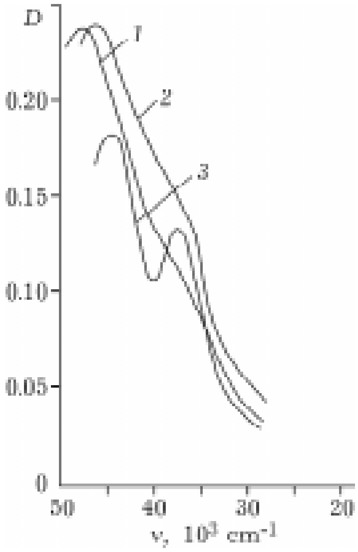


Fig. 9. Influence of Cu(II) ions on the electronic spectrum of HA in water: *1* – the spectrum of the aqueous solution of HA (12 mg/l); *2* – the same with $Cu(ClO_4)_2$ (5 10^{-3} mol/l); *3* – the same after irradiation for 1.5 h with the UV light.

strate, pH, reductive-oxidative potential of the medium, action of solar radiation, *etc*. The coordination interaction of HM ions is of special importance for photochemical processes of the transformation of organic compounds in soils and in surface water under the action of UV light. As a rule, in these processes the photochemically active spectral region of solar radiation reaching the earth's surface is observed to broaden toward longer wavelengths. The rate of photodecomposition of organic toxicants in soils and in the hydrosphere, the composition and stability of the formed products are substantially dependent on the level of contamination of the biospheric objects under consideration with HM.

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