

PHYSICOCHEMICAL PROCESSES
AT THE INTERFACES

Modification of the Surface of Magnetic Iron Oxides
with Phosphonic Complexones

T. N. Kropacheva^{a, *}, A. S. Antonova^a, and A. Yu. Zhuravleva^a

^aUdmurt State University, Izhevsk, 426034 Russia

*e-mail: krop@uni.udm.ru

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Abstract—The conditions of chemical modification of the surface of synthetic magnetic iron oxides (magnetite Fe_3O_4 , maghemite $\gamma\text{-Fe}_2\text{O}_3$) by phosphonic complexones (PBTC, HEDP, HEIDPH, NTMP, EDTMP) are studied. It is shown that the maximum concentration of grafted groups is observed upon treating iron oxides with aqueous solutions of complexones containing two or three phosphonic groups at pH 2–3 and temperature of 50–60°C for 2–6 h. To characterize the grafted layer, various physicochemical research methods (XRD, FTIR spectroscopy, the BET method, thermal analysis, acid–base titration, sorption from solutions) were used. It is found that the modifying coating significantly increases the sorption ability of magnetic iron oxides towards metal cations (Cu(II), Cd(II)). A mechanism for binding of metal ions by modified sorbents is proposed.

Keywords: magnetic iron oxides, chemical surface modification, phosphonic complexones

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INTRODUCTION

Among many inorganic carrier sorbents, magnetic iron oxides (MIOs), i.e., magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), are of particular interest at present. In addition to the fact that MIOs are widely distributed in the environment and nontoxic, they have such a unique property as ferrimagnetism, which facilitates their extraction/regeneration during concentrating and separating organic and inorganic substances, upon using as a substrate in heterogeneous catalysis, upon immobilizing biological molecules to create magnetic markers, etc. For more effective retention of the target components, the surface of MIOs often needs to be chemically modified by fixing additional compounds bearing different functional groups that define the properties of the resulting surface-modified carrier [1–4]. One new approach to the surface functionalization of various oxides, including iron oxides, is the use of compounds containing a phosphonic group $-\text{PO}(\text{OH})_2$ as modifiers, which has high affinity for the surface of oxides and can act as a good “anchor” for the modifier [5–7]. In particular, when it comes to the use of MIOs for separation, extraction, concentration of ions of various metals—including heavy (Hg(II), Pb(II), Cu(II), Cd(II), Ni(II), Zn(II)), noble (Ag(I), Au(III), Pt(II)), and radioactive [2, 8–10] ones—phosphonic complexones [11], which along with $-\text{PO}(\text{OH})_2$ groups, contain other functionally active centers with simultaneous coordination of them with a metal ion, stable chelate

rings are formed. Such complexing magnetic sorbents may have advantages over widely known chelating sorbents based on modified silicon dioxide (ethylenediamine– SiO_2 , amino acid– SiO_2 , iminodiacetic acid– SiO_2 [6]) or complexing polymer resins [12]. There is information in the literature on the modification of iron oxides, including magnetic ones, with phosphonic derivatives (alkylphosphonic acids, amino/hydroxy/carboxyphosphonic acids, etc.) [5–7]; however, phosphonic complexones are absent among the used modifiers. In this regard, in this work the optimal conditions were studied for modifying the surface of magnetite and maghemite with several phosphonic complexones (PCs) and physicochemical properties of the resulting carriers, including sorption ones, are studied.

EXPERIMENTAL

The MIO preparations used in this work were obtained according to the methods described in the literature [13]. Magnetite was synthesized by incomplete oxidation of the Fe(II) salt in alkaline medium at 90°C ($3\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{KNO}_3 + 6\text{KOH} = \text{Fe}_3\text{O}_4 + \text{KNO}_2 + 24\text{H}_2\text{O} + 3\text{K}_2\text{SO}_4$). The resulting black Fe_3O_4 precipitate, after repeated washing with distilled water, was dried in air at 75°C. Maghemite was obtained from magnetite by oxidation in air at 250°C for 2 h ($4\text{Fe}_3\text{O}_4 + \text{O}_2 = 6\gamma\text{-Fe}_2\text{O}_3$), while the oxide color changed from black to brown. The resulting sorbents (in the form of

Table 1. Organophosphorus complexones used to modify the surface of magnetic iron oxides

Complexone	Formula
1-Hydroxyethane-1,1-diphosphonic acid	$\begin{array}{c} \text{PO(OH)}_2 \\ \\ \text{H}_3\text{C}-\text{C}-\text{OH} \\ \\ \text{PO(OH)}_2 \end{array}$
N-Hydroxyethylimino-N,N-di(methylenephosphonic) acid HEIDPH	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_2 \\ \\ \text{N} \\ \quad \\ \text{CH}_2 \quad \text{CH}_2 \quad \text{PO(OH)}_2 \\ \\ \text{(OH)}_2\text{OP} \end{array}$
Nitritotri(methylenephosphonic) acid NTPM	$\begin{array}{c} \text{(HO)}_2\text{OP} \\ \\ \text{CH}_2 \\ \\ \text{N} \\ \quad \\ \text{CH}_2 \quad \text{CH}_2 \quad \text{PO(OH)}_2 \\ \\ \text{(OH)}_2\text{OP} \end{array}$
Ethylenediamine-N,N,N',N'-tetra(methylenephosphonic) acid, EDTMP	$\begin{array}{c} \text{(OH)}_2\text{OP} \quad \quad \quad \text{PO(OH)}_2 \\ \quad \quad \quad \\ \text{CH}_2 \quad \quad \quad \text{CH}_2 \\ \quad \quad \quad \\ \text{N} \quad \quad \quad \text{N} \\ \quad \quad \quad \\ \text{CH}_2 \quad \quad \quad \text{CH}_2 \\ \quad \quad \quad \\ \text{(HO)}_2\text{OP} \quad \quad \quad \text{PO(OH)}_2 \end{array}$
2-Phosphonobutane-1,2,4-tricarboxylic acid PBTC	$\begin{array}{c} \text{PO(OH)}_2 \\ \\ \text{HOOC}-\text{C}-\text{CH}_2-\text{COOH} \\ \\ \text{COOH} \end{array}$

dry powders and suspensions) are strongly attracted by a permanent magnet, which makes it easy to separate them from the aqueous phase.

The commercial preparations of phosphonic complexones (Table 1) from Zschimmer and Schwarz of the Cublen® series were used: NTMP (AR 1), HEDP (K 60), EDTMP (E 34135P), HEIDPH (R 60), and PBTC (P 50). Complexone solutions (0.05 mol/dm³) were prepared by dissolving a sample of preparations in distilled water, followed by standardization by potentiometric titration. Modification of the surface of MIOs was carried out by treating the sorbents with PC solution (1 mmol PC/g sorbent) at the selected values of the acidity of the medium (pH 2–11), temperature (20 and 55°C), and processing time (2 and 24 h). After modification, the sorbent was filtered off, washed with distilled water, and dried in air. The content of PC on the surface was determined from its residual concentration in the solution by the spectrophotometric method (the reaction of formation of phosphorus-molybdenum blue), after preliminary oxidation of complexone with ammonium persulfate. Experiments on desorption of PC from the surface of MIOs were carried out by treatment with aqueous solution with different pH values (pH 2, 6, 11) for 24 h.

The acid–base properties of MIOs were studied by pH-metric titration (I-160 MI ionomer) of a suspension (concentration is 1 g/dm³) with a standard KOH solution at a constant ionic strength of the solution ($I = 0.1$ mol/dm³, KNO₃).

Sorption of metal ions (Cu(II), Cd(II)) on MIOs was studied in the static mode at 20°C with continuous shaking for 30 min in the presence of a background electrolyte (0.1 mol/dm³ KNO₃). The required acidity of the medium was created with HNO₃ and KOH solutions. The sorbent was filtered through a paper filter (“blue ribbon”), the pH of the equilibrium solution was measured, and the residual concentration of metal ions was determined in it. The residual concentration of Cu(II) and Cd(II) cations was determined by anodic stripping voltammetry using a PU-1 universal polarograph. In this case, a system of three electrodes was used: glassy carbon (working), platinum (auxiliary), and saturated silver-chloride (reference electrode). Voltammograms were taken against a background of 0.05 mol/dm³ HCl with the addition of 10⁻⁴ mol/dm³ Hg(NO₃)₂ with the following parameters: accumulation potential is –0.8 V; accumulation time is 60 s; scanning amplitude from –0.8 to 0.2 V;

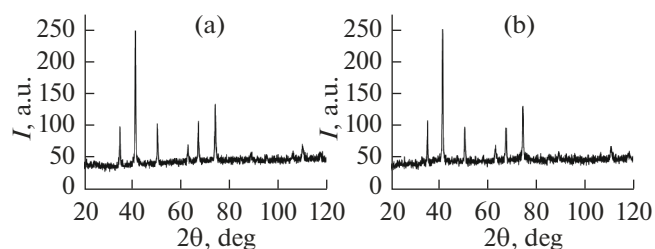


Fig. 1. Powder diffraction pattern of (a) magnetite and (b) maghemite.

scanning speed is 50 mV/s, regeneration potential is 0.4 V; regeneration time is 60 s.

The X-ray powder diffraction patterns of MIOs were obtained on a DRON-6 diffractometer ($\text{FeK}\alpha$ radiation, interval of scattering angles is 20° – 120° with a step of 0.05°). The specific surface area of MIOs was determined on the basis of the isotherms of low-temperature nitrogen sorption using the four-point BET method on a Sorbi-M® instrument. Thermal characteristics of sorbents were obtained on a Diamond TG/DTA derivatograph (Perkin-Elmer) (air atmosphere, temperature range is 50 – 1050°C , heating

rate is $10^\circ\text{C}/\text{min}$). FTIR spectra of the samples (in the form of tablets with KBr) were recorded on an FSM 2201 IR spectrometer in the frequency range of 400 – 4000 cm^{-1} .

RESULTS AND DISCUSSION

The obtained diffraction patterns of synthesized MIOs (Fig. 1) are in good agreement with the literature data [14] and indicate the isostructural nature of magnetite and maghemite (spinel structure). The average size of spherical crystallites of MIOs was calculated using the Debye–Scherrer formula: $D = K\lambda/\beta\cos\theta$, where $K = 0.89$ (Scherrer constant), $\lambda = 0.19360\text{ nm}$ (X-ray wavelength), β is the width of the reflex at half maximum (in radians, in units of 2θ), and θ is the diffraction angle. The obtained value of D is the same for both MIOs and amounts to $30.2 \pm 0.1\text{ nm}$. The specific surface area of MIOs determined by the BET method was $S_{\text{sp}} = 36.8 \pm 4.1\text{ m}^2/\text{g}$ (magnetite) and $S_{\text{sp}} = 35.7 \pm 3.3\text{ m}^2/\text{g}$ (maghemite).

To characterize the changes associated with chemisorption of phosphonic complexes on the surface of MIOs, the method of IR spectroscopy was used. The IR spectra of MIOs (Fig. 2) contain charac-

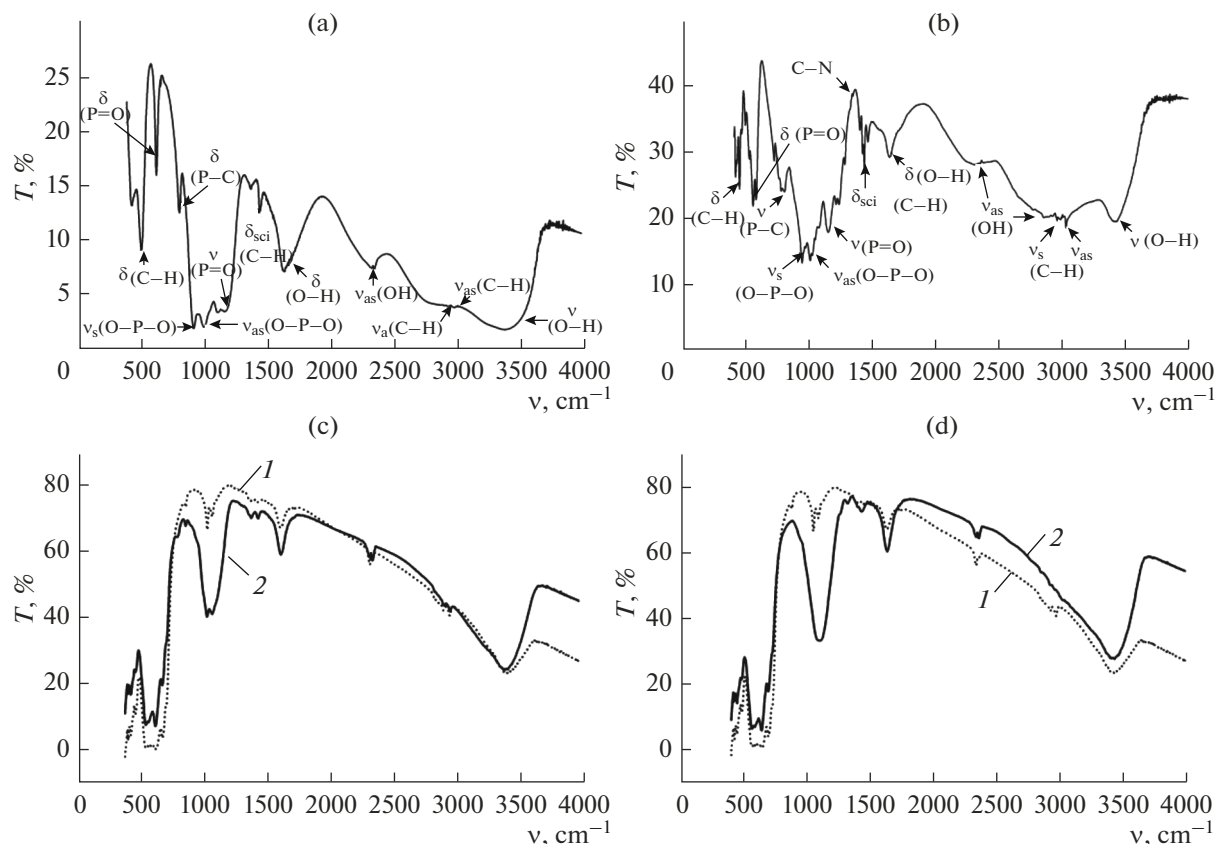


Fig. 2. IR spectra of (a) HEDP, (b) NTMP, (c) (1) maghemite and (2) HEDP–maghemite, and (d) (1) maghemite and (2) NTMP–maghemite.

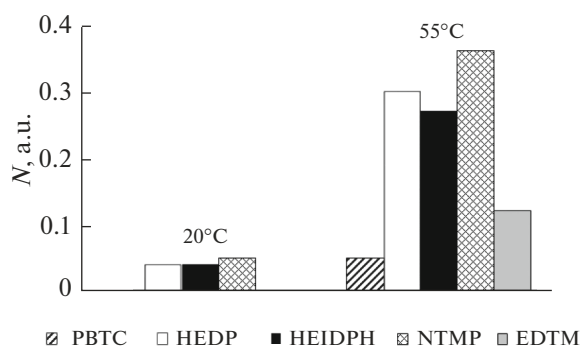


Fig. 3. Relative content of various phosphonic complexes on the surface of maghemite at modification temperature of 20 and 55°C. Modification time is 2 h, pH 1.5–2.5.

teristic bands at 559 and 632 cm^{-1} (maghemite) and at 580 cm^{-1} (magnetite) caused by stretching vibrations of the Fe–O bond [13], as well as bands at 3450 and 1633 cm^{-1} (stretching and deformation vibrations of O–H, respectively, of OH-surface groups and sorbed water molecules). Small “extraneous” peaks at 1140 and 1020 cm^{-1} are associated with chemisorbed SO_4^{2-} ions, since FeSO_4 is a precursor of the synthesis of MIOs. The IR spectra of pure PC preparations in the region of phosphonic group vibrations (900–1400 cm^{-1}) contain characteristic bands related to stretching vibrations of the phosphoryl group P=O (1112 cm^{-1} (HEDP), 1147 cm^{-1} (NTMP)) and stretching vibrations of the P–O bond (asymmetric and symmetric) PO_3^{2-} and HPO_3^- groups (1024 and 931 cm^{-1} (HEDP); 1002 and 939 cm^{-1} (NTMP)) [15]. In the spectra of modified MIOs, in comparison with the initial samples, there is a significant increase in the absorption intensity in the region of vibrations of phosphonic groups, which unambiguously indicates that the modifier is fixed on the surface. The shape of the absorption band of the surface-fixed phosphonic group differs significantly from that observed for the complexes themselves, as was also observed in [16]. When PC is fixed on the surface, the fine structure of the band becomes much less pronounced (compared to free complexes), which indicates the presence of more equivalent P–O bonds in the sorbed state.

To study the conditions under which modification of the MIOs surface is most effective, the dependence of the surface content of PC on time and temperature of treatment, acidity of the medium, and the nature of the complexone modifier was studied. To quantify the relative content of PC on the surface of MIOs, the IR absorption band of phosphonic groups were numerically integrated in the region from 900 to 1400 cm^{-1} . The obtained value was further attributed to the absorption of the sorbent itself, determined by integration in the region of 400–1000 cm^{-1} .

It was found that, at a modification temperature of 20°C, the content of PC on the surface is very insignificant, and an increase in the modification time from 30 min to 24 h does not lead to its further growth (Fig. 3). With an increase in temperature to 55°C, a five- to sevenfold increase in the amount of all PCs on the surface of MIOs is observed. Comparing the results of the content of various phosphonic complexes fixed on the surface, we should keep in mind the unequal amount of phosphonic groups in their composition (Table 1). Accordingly, a number of modifying abilities of complexes is as follows: $\text{NTMP} \approx \text{HEDP} \approx \text{HEIDPH} > \text{EDTMP} > \text{PBTC}$. Complexes containing one (PBTC) and four (EDTMP) phosphonic groups are significantly worse bound to the surface of MIOs than complexes containing two (HEDP, HEIDPH) or three (NTMP) phosphonic groups. Thus, only one phosphonic group is not sufficient for strong binding to the surface of MIOs, and low modifying activity of EDTMP is probably associated with a steric factor—blocking of part of the surface by this bulk molecule. Indeed, as was shown by the authors of [17], the maximum degree of sorption of PC on goethite decreases in the series $\text{HEDP} > \text{NTMP} > \text{EDTMP} > \text{DTPMP}$.

The interaction of PC (H_nL) with the surface of oxides is a reaction of nucleophilic substitution of surface OH groups with phosphonic ones according to the scheme: $\equiv\text{FeOH} + \text{L}^{n-} \leftrightarrow \equiv\text{Fe}-\text{L}^{1-n} + \text{OH}^-$. This reaction is facilitated by an increase in the acidity of the medium, which has been shown for other iron (hydr)oxides (goethite $\alpha\text{-FeOOH}$) [17]. We also found that, with an increase in the alkalinity of the NTMP solution used to modify the solution from pH 2 to pH 6–11, *ceteris paribus*, the complexone content on the surface of maghemite decreases by about three times. Studying the stability of the coating during treatment of the modified MIOs (NTMP–maghemite/magnetite) with alkaline aqueous solutions (pH 10–11) for 30 min shows that the amount of PC on the surface decreases by 5–10% compared to the initial one, i.e., to modify the surface of MIOs and stability of the resulting coating, a medium with pH < 7 is required.

Thus, the following optimal conditions are necessary for effective modification of MIOs with phosphonic complexes: the temperature is 50–60°C, the modification time is 2–6 h, the acidity of the complexone used to modify the solution is in the pH range of 2–3, the ratio of complexone/sorbent = 1 mmol PC/g, and the phosphonic complexone should contain two or three phosphonic groups.

The results of thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) show significant differences for initial and modified carriers (Fig. 4). A decrease in mass (by ~1–2%) for unmodified MIOs at temperatures below 200°C is associated with the removal of loosely bound water, and at tem-

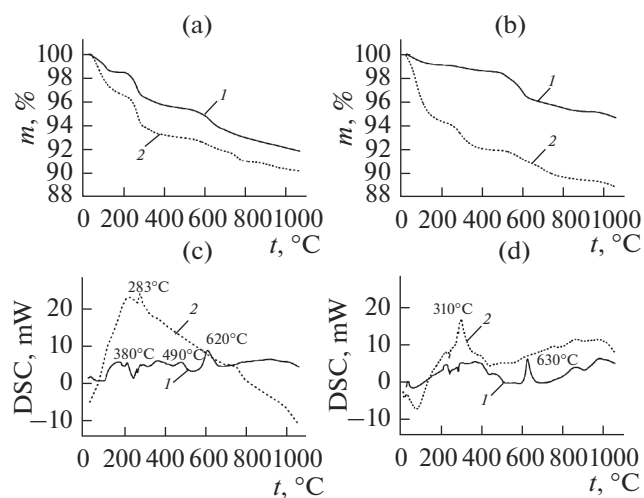


Fig. 4. Curves of (a, b) thermogravimetric analysis and (c, d) differential scanning calorimetry for (a, c) (1) magnetite and (2) HEDP-magnetite and (b, d) (1) maghemite and (2) NTMP-maghemite.

peratures of 200–300°C with the removal of structural water (endo peaks at 250–290°C). For magnetite, a series of low-intensity exothermic peaks is located in the temperature range of 300–500°C, accompanied by only insignificant mass loss, which may indicate magnetite oxidation to maghemite $4\text{Fe}_3\text{O}_4 + \text{O}_2 \rightarrow 6\gamma\text{-Fe}_2\text{O}_3$ (peak 380°C) and phase transition of maghemite $\gamma\text{-Fe}_2\text{O}_3 \rightarrow \text{hematite } \alpha\text{-Fe}_2\text{O}_3$ (peak 490°C). An intense exoeffect with a maximum at 620°C is associated with completion of the maghemite \rightarrow hematite phase transition, as well as the formation of hematite from the residual magnetite that has not previously converted to maghemite. In the case of maghemite, the maghemite \rightarrow hematite phase transition occurs in the temperature range of 300–700°C (an intense exopeak at 630°C). The total mass loss when heated to 1000°C is ~8% (magnetite) and ~5% (maghemite). For modified MIOs, the weight loss in the temperature range of 200–600°C is 3–6% more than for unmodified ones. The observed intense exoeffects at these temperatures (maximums at 283 and 310°C) indicate thermal decomposition of phosphonic complexones with the formation of various products (amino-, iminophosphonic acids, phosphoric and phosphorous acids) [11]. The estimation of the PC content on the surface according to the TG data corresponds to 0.1–0.2 mmol/g, which is in good agreement with the data obtained on the basis of the spectrophotometric determination of the residual PC content in the solutions after modification.

Fixation of HEDP and NTMP on the MIOs leads to a change in the acid–base properties of the surface, which is reflected in the titration curves of the suspension of sorbents with alkali solution (Fig. 5). The titration curve of unmodified magnetite/maghemite indi-

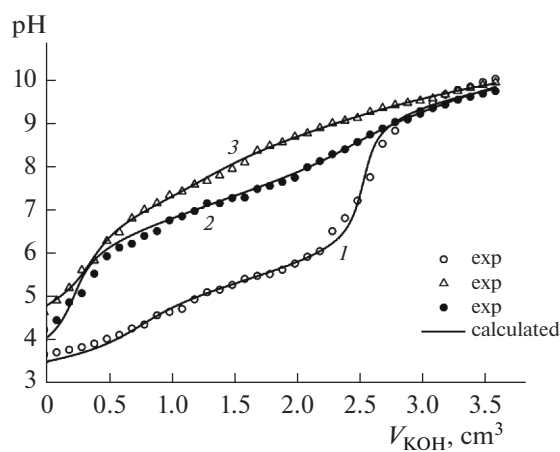


Fig. 5. Acid–base titration curves of (1) magnetite, (2) HEDP-magnetite, and (3) NTMP-magnetite. $C_{\text{MIO}} = 1 \text{ g/dm}^3$, $C_{\text{KOH}} = 0.01 \text{ mol/dm}^3$.

cates the presence of sufficiently strong acid centers on their surface, which are protonated hydroxogroups $\equiv\text{FeOH}_2^+$ formed during hydration of the surface of this oxide. The step-by-step dissociation constants of these groups for magnetite calculated in the framework of the nonelectrostatic model of the theory of surface complexation ($\equiv\text{FeOH}_2^+ \leftrightarrow \equiv\text{FeOH} + \text{H}^+$, $\text{pK}_{a1} = 5.5 \pm 0.1$; $\equiv\text{FeOH} \leftrightarrow \equiv\text{FeO}^- + \text{H}^+$, $\text{pK}_{a2} = 9.8 \pm 0.1$), as well as the points of zero surface charge ($\text{pH}_{\text{PZC}} = 7.7 \pm 0.2$), are in the range of values given for magnetite in the literature [13]. The titration curves of modified MIOs significantly differ from the titration curves of the initial sorbents (Fig. 5), which unambiguously indicates the appearance of new acid–base centers on the surface. Compared to solutions in which HEDP is a tetrabasic (H_4L), and NTMP is a hexabasic (H_6L) acid [11], the basicity of surface-fixed complexones decreases, which is associated with the participation of their phosphonic groups in interaction with the surface. The obtained titration curves can be satisfactorily described by a model that includes the presence of acidic centers of $\equiv\text{Fe-LH}_3$ on the surface (HEDP-magnetite: $\text{pK}_{a1} = 6.6 \pm 0.2$, $\text{pK}_{a2} = 7.7 \pm 0.1$, $\text{pK}_{a3} = 9.3 \pm 0.1$) and $\equiv\text{Fe-LH}_5$ (NTMP-magnetite: $\text{pK}_{a1} = 4.5 \pm 0.3$, $\text{pK}_{a2} = 7.1 \pm 0.2$, $\text{pK}_{a3} = 8.5 \pm 0.2$, $\text{pK}_{a4} = 9.5 \pm 0.1$, $\text{pK}_{a5} = 10.4 \pm 0.1$).

Thus, based on the totality of the obtained data, one can make an suggestion about the mechanism of fixation of phosphonic complexones on the surface of MIOs. According to numerous studies [7], binding of phosphonic groups to the surface of various metal (hydr)oxides can occur as a result of mono-, bi-, or tridentate coordination of the phosphonic group. In this case, interaction can be carried out with one, two, or even three metal atoms (mono-, bi-, and trinuclear complexes, respectively). In case of polyphosphonic

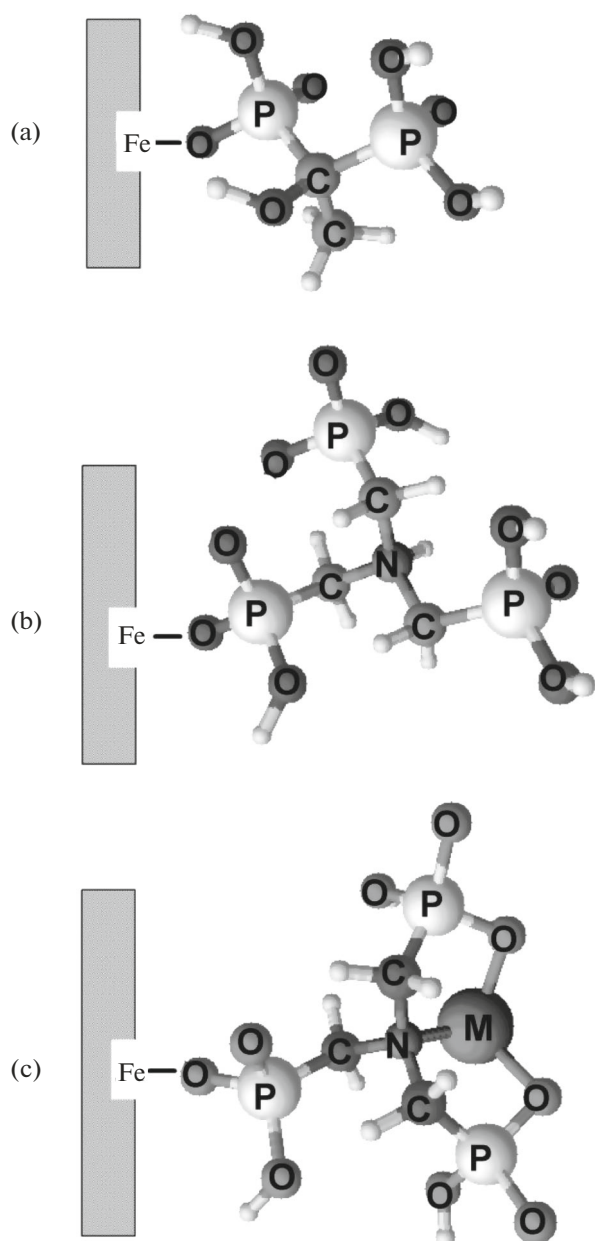


Fig. 6. Schemes of binding of (a) HEDP and (b) NTMP to the surface of magnetic iron oxides. (c) Metal cation by NTMP-modified magnetic iron oxides.

derivatives, which include phosphonic complexones (HEDP, NTMP, EDTMP, DTPMP), the proposed binding mechanism of iron and aluminum (hydr)oxides to the surface consists in coordinating only one of the phosphonic groups with the formation of mononuclear monodentate complexes [16–18]. Taking into account the basicity of surface-fixed complexones that we have established, it can be also assumed that only one phosphonic group of HEDP and NTMP binds to the MIO surface (Figs. 6a, 6b) and PC groups not involved in binding to the surface are new functionally

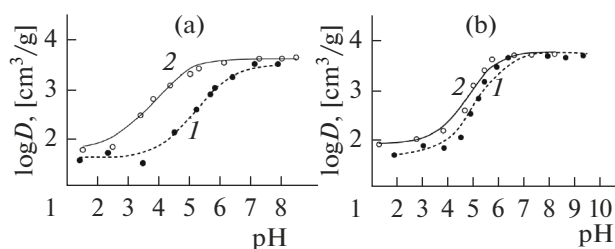


Fig. 7. Effect of medium acidity on the distribution coefficient of (a) Cd(II) ions for (1) maghemite and (2) NTMP-maghemite and (b) Cu(II) ions for (1) magnetite and (2) NTMP-magnetite.

active centers, which can participate in the coordination of ions of various metals.

A study of the sorption of metal ions (Cu(II), Cd(II)) by the initial and NTMP-modified MIOs depending on the acidity of the medium (Fig. 7) showed that, with increasing pH, the degree of extraction, presented as distribution coefficient of ions D , increases significantly, reaching values of the order of $5 \times 10^3 \text{ cm}^3/\text{g}$. Moreover, for modified sorbents in acidic medium, the D values are five to ten times higher than for the initial sorbents. The acidity of the medium at which an increase in the sorption of cations on NTMP-modified sorbents is observed corresponds to the regions of pH complexation of Cu(II) and Cd(II) with NTMP in aqueous solutions ($\text{MH}_n\text{L}^{n-4}$ complexes ($n = 1-4$) at pH 3–8, ML^{4-} complex at pH 8–12 [11, 19]). This suggests that the binding of metal cations to NTMP-modified iron oxides occurs similarly to the process in solutions—as a result of coordination of the metal cation by phosphonic groups not participating in binding to the surface and a nitrogen atom with the formation of two stable five-membered rings (Fig. 6c). Thus, phosphonic complexones grafted to the surface act as heterogenized complexing agents that efficiently extract metal cations from aqueous solutions.

CONCLUSIONS

The results obtained indicate that phosphonic complexones have a high affinity to the surface of magnetic iron oxides due to the good anchor properties of phosphonic groups toward many oxide surfaces. Under the optimal modification conditions established in the course of this work, the maximum grafting density of phosphonic complexones is 0.1–0.2 mmol/g or 1.6–3.2 groups/nm², which can be compared with the number of OH groups on the MIO surface (on average, 5 groups/nm² [13]). The greatest amount of bound complexone is achieved when two or three phosphonic groups are present in its composition. As a result of modification by phosphonic complexones, new functional groups appear on the surface of MIOs, which are part of the complexone and are free from

binding to the surface ($-\text{PO}(\text{OH})_2$, $-\text{COOH}$, $-\text{OH}$, tertiary N atom), which change acid–base and adsorption properties of surface. The resulting modified carriers, like complexones in solution, primarily show the properties of complexing materials towards ions of various metals. In this regard, they complement such well-known complexing carriers as chemically modified silicas and complexing ion exchangers. In addition to the binding of metal ions, the resulting sorbents can be promising for fixing organic molecules, including biologically important ones. The disadvantages of MIOs modified with phosphonic complexones are a relatively low grafting density, which is inherent in all oxide carriers, and instability of the modifying layer, which is inherent in all oxide carriers, and instability of the modifying layer under alkaline conditions. An important advantage of the obtained modified carriers is their strong magnetic properties, which is a decisive factor for all various areas of practical use of MIOs, including sorption extraction, separation, and concentration of metal ions.

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