

## SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

# Sorbents Based on Highly Dispersed Boehmite Surface-Modified with Phosphonic Complexones: Preparation and Characterization

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**Abstract**—New complexing sorbents have been manufactured via chemical surface-modification of highly dispersed boehmite ( $\gamma$ -AlO(OH)) by phosphonic complexones (PCs), namely, by nitrilotri(methylenephosphonic) acid (NTP), 1-hydroxyethane-1,1'-diphosphonic acid (HEDP), *N*-hydroxyethylimino-*N,N*-di(methylenephosphonic) acid (HEIDP), and imino-*N,N*-diacetic-*N*-methylenephosphonic acid (IDAMP). The manufactured PC-boehmite materials have been characterized by XRD, BET, SEM, TEM, and IR spectroscopy. Modified boehmites, in which the modifier anchor is one of the phosphonic functions of the complexone, exhibit the properties of a complexing support for double-charged metal ions. The kinetic characteristics and sorption capacities of PC-boehmites have been determined. The complexing selectivity on the modified surface are arranged in the following decreasing order: Pb(II) > Cu(II) > Zn(II)  $\approx$  Ni(II)  $\approx$  Co(II)  $\approx$  Cd(II) > Ca(II). The stability of the sorbed state of metal ions changes along the series of surface-anchored complexones in the following order: IDAMP > NTP > HEDP > HEIDP. The trends elucidated point to a close correlation between complexa formation involving phosphonic complexones in solution and on the boehmite surface.

**Keywords:** nanosized boehmite, chemical surface modification, phosphonic complexones, complexing supports

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## INTRODUCTION

Covalent surface modification by organic compounds is the strategy widely used in design of hybrid functional materials based on oxides of Fe, Al, Si, Ti, Zr, Sn, etc. [1, 2]. The functional groups in the organic component that act as ligands with respect to metal ions make it possible to design materials with complexing properties; such materials are of great interest for sorption preconcentration and separation of metal ions, for the removal of toxic metals from natural and waste waters, as well as for manufacturing supported metal catalysts [3–6]. The use of organic phosphorus(V) acids for the preparation of surface-modified materials with a mineral oxide support is a new approach to the production of diverse hybrid supports [7, 8]. The ease of formation and the hydrolytic stability of M–O–P bond make it possible, under certain conditions, to obtain a monolayer coating of the surface due to the replacement of the hydroxo surface groups of oxides by phosphonic groups. Among the studied phosphonic modifiers of oxide surfaces, long-chain alkylphosphonic acids, phenylphosphonic acid, fluorinated phosphonic acids, diphosphonic acids, and some others are well described, while modifiers having complexing functions are studied insufficiently [9–12]. Therefore, our work that will be described

below was targeted at manufacturing new oxide materials functionalized by complexing derivatives of phosphonic acids and at studying their sorption properties with respect to selected metal ions.

## EXPERIMENTAL

The material used to manufacture organomineral sorbents was synthetic aluminum hydroxide, namely, boehmite ( $\gamma$ -AlO(OH)); its surface modifiers were commercially available phosphonic complexones, which have good complexing properties in solutions [13, 14]. The boehmite  $\gamma$ -AlO(OH) was prepared via low-temperature alkaline hydrolysis of Al(NO<sub>3</sub>)<sub>3</sub> as described elsewhere [15, 16]. The agents used to modify the boehmite surface were phosphonic complexone (Table 1): nitrilotri(methylenephosphonic) acid (NTP), 1-hydroxyethane-1,1'-diphosphonic acid (HEDP), *N*-hydroxyethylimino-*N,N*-di(methylenephosphonic) acid (HEIDP) (all purchased from Zschimmer and Schwarz), and imino-*N,N*-diacetic-*N*-methylenephosphonic acid (IDAMP) (Sigma-Aldrich). The chemical modification of boehmite surface by phosphonic complexones (PCs) involved the exposure of boehmite samples to aqueous solutions of complexones under optimal conditions as determined

**Table 1.** Characteristics of the studied boehmite-based sorbents

Complexone	Sorbent	Surface functional group	Grafted group concentration, mmol/g
—	Boehmite	—OH	0.86
HEDP: 1-Hydroxyethane-1,1'-diphosphonic acid $\begin{array}{c} \text{CH}_3 \\   \\ (\text{HO})_2\text{OP}-\text{C}-\text{PO}(\text{OH})_2 \\   \\ \text{OH} \end{array}$	HEDP-boehmite	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}-\text{PO}(\text{OH})_2 \\   \\ \text{OH} \end{array}$	0.69
HEIDP: <i>N</i> -Hydroxyethylimino- <i>N,N</i> -di(methylenephosphonic) acid $(\text{HO})_2\text{OP}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{PO}(\text{OH})_2 \\   \\ \text{CH}_2-\text{OH}$	HEIDP-boehmite	$-\text{CH}_2-\text{N}-\text{CH}_2-\text{PO}(\text{OH})_2 \\   \\ \text{CH}_2-\text{OH}$	0.58
NTP: Nitrilotri(methylenephosphonic) acid $(\text{HO})_2\text{OP}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{PO}(\text{OH})_2 \\   \\ \text{CH}_2-\text{PO}(\text{OH})_2$	NTP-boehmite	$-\text{CH}_2-\text{N}-\text{CH}_2-\text{PO}(\text{OH})_2 \\   \\ \text{CH}_2-\text{PO}(\text{OH})_2$	0.77
IDAMP: Imino- <i>N,N</i> -diacetic- <i>N</i> -methylenephosphonic acid $(\text{HO})_2\text{OP}-\text{CH}_2-\text{N}-\text{CH}_2\text{COOH} \\   \\ \text{CH}_2\text{COOH}$	IDAMP-boehmite	$-\text{CH}_2-\text{N}-\text{CH}_2\text{COOH} \\   \\ \text{CH}_2\text{COOH}$	0.53

in preliminary experiments (4–6 h at 20°C, pH 2, 1 mmol PC/1 g oxide). The concentration of surface OH groups of the boehmite was determined by substituting them by fluoride ions; the surface PC concentration was determined by analysis for phosphorus [16].

X-ray powder diffraction spectra were obtained on a DRON-3.0 diffractometer (Burevestnik) using monochromated  $\text{FeK}_\alpha$  radiation ( $\lambda = 0.193735$  nm) in the Bragg angle range 12°–105° in the step scan mode with 0.1° steps and an exposure time per point of 15 s.

The particle morphology and mean particle size were determined using electron microscopy. SEM images were obtained on a Camscan-S2 (Cambridge Instruments) electron microscope at an accelerating voltage of 20 kV and a focal length of 10 mm in the secondary electrons mode. A gold–palladium coating was sputtered on a powder sample prior to the experiment. The elemental composition of the surface was determined using an FEI Inspect S50 (FEI) scanning electron microscope equipped with an energy-dispersive X-ray microanalysis system. Transmission electron microscopy (TEM) experiments were carried out using a Jem-1011 (JEOL) instrument at an accelerating voltage of 80 kV. A test sample was applied to a carbon film via ultrasonic dispersion of an aqueous suspension.

The specific surface area and porosity were determined by the BET method using low-temperature sorption–desorption isotherms measured on a TriStar 3020 (Micromeritics) automated gas adsorption surface and porosity analyzer. Prior to measurements, test samples were degassed in vacuo at a residual pressure of  $10^{-2}$  atm at 230°C for 5 h (boehmite) and at 80°C for 48 h (NTP-boehmite). Specific surface areas were calculated by the five-point BET method based on the sorption branch of the isotherm in the partial pressure range  $p/p_0 = 0.1$ –0.4. The pore size distribution was derived by processing the analyzer data from the desorption branch using the BJH method.

The Fourier-transform IR spectra of prepared samples were recorded on an FSM-2201 (Infraspek) IR spectrometer in the frequency range 400–4000  $\text{cm}^{-1}$  (2- $\text{cm}^{-1}$  steps) as KBr disks (2.5 mg per 250 mg KBr) made with a manual hydraulic press. The optical density of solutions was measured on an UNICO 1201 (United Products & Instruments) spectrophotometer. pH measurements in solutions were on an I-160 MI (Izmeritelnaya Tekhnika) pH meter.

In order to study the hydrolytic stability of a grafted layer, a modified boehmite was exposed to an  $\text{HNO}_3/\text{KOH}$  aqueous solution at a constant ionic strength of 0.1 mol/L ( $\text{KNO}_3$ ) for 2 h and then the

residual amount of the complexone on the surface was determined.

The copper(II) sorption kinetics was studied in a batch mode via measuring the potential of a copper-selective electrode (Elit-227) in solution in the course of sorption, as follows: to a solution containing 0.1 mmol/L Cu(II) with the set initial pH of 7 and a constant ionic strength  $I = 0.1$  mol/L (KNO<sub>3</sub>), the Cu(II)-ISE was immersed, and after a sorbent was added (concentration: 1 g/L), the decrease in electrode potential was recorded during 150 min under continuous stirring.

The effect of solution acidity on sorption of metals (Cu(II), Pb(II), Ni(II), Co(II), Zn(II), Cd(II), Ca(II)) was studied in solutions with a constant concentration and a constant ionic strength  $I = 0.1$  mol/L (KNO<sub>3</sub>) at  $20 \pm 1^\circ\text{C}$ . 0.1 mmol/L metal salt solutions were prior prepared, in which the pH was adjusted (using HNO<sub>3</sub>/KOH) in the range 2–9 depending on the system under study. The upper pH bound was set to exclude metal hydroxide precipitation and complexone desorption from the boehmite surface. To a 25-mL portion of the thus-prepared solution, a 25-mg sorbent sample was added; the suspension was shaken for 2 h. The chosen sorption time was longer than necessary for sorption equilibrium to be attained (~60 min). After the sorbent was removed by centrifugation, the residual concentration of metal ions in the solution was determined spectrophotometrically by the reactions of formation of colored pyridylazoresorcinol complexes. The degree of sorption was calculated as  $R(\%) = 100 \times (c_0 - c)/c_0$ , where  $c_0$  and  $c$ , respectively, are the initial and equilibrium concentrations of metal ions in the solution. The relative determination error for  $R$  was 5–10%.

Desorption experiments were carried out as follows: A 10-mg test sample where the amount of the sorbed metal was known was treated with 2 mL of 0.01 mol/L HNO<sub>3</sub> (pH 2.1) for 20 min under stirring. The metal stripping was calculated from the spectrophotometrically measured metal concentration in the solution.

The sorption capacity of a sorbent was determined under batch conditions based on the Cu(II) sorption isotherms with the initial Cu(II) concentration varying in the range 0.1–5.0 mmol/L at equilibrium pH of  $4.5 \pm 0.2$  and a sorption time of 2 h.

## RESULTS AND DISCUSSION

The textural and morphological characteristics of boehmite  $\gamma\text{-AlO}(\text{OH})$ , which determine its functional properties for subsequent use as a support, depend on the preparation process and its parameters: temperature, pressure, solution acidity, precursors, etc. [17–19]. For example, alkaline hydrolysis of inorganic Al(III) salts can yield both amorphous Al(III) hydroxide and crystalline trihydroxides (bayerite  $\alpha\text{-Al}(\text{OH})_3$

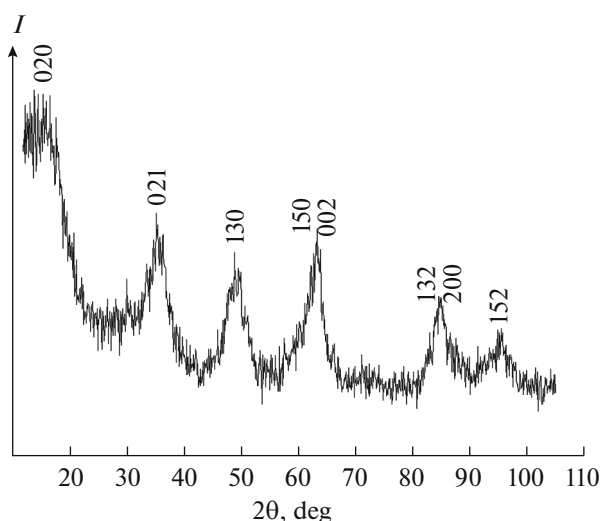


Fig. 1. X-ray diffraction pattern of highly dispersed boehmite.

and gibbsite  $\gamma\text{-Al}(\text{OH})_3$ ), as well as oxyhydroxide boehmite  $\gamma\text{-AlO}(\text{OH})$  [15, 20–22]. Under the synthetic conditions we chose in the present work (slow addition of NaOH solution to a Al(NO<sub>3</sub>)<sub>3</sub> solution to reach the molar ratio  $\text{Al}(\text{III}) : \text{OH}^- = 1 : 3.04$ , followed by the exposure of the precipitate at  $90^\circ\text{C}$  for 4 h, filtration and washing of the precipitate, heating at  $220^\circ\text{C}$  for 4 h in a ShS-80-01 (Smolenskoe SKTB SPU) drier [16]), the product was boehmite as identified by X-ray powder diffraction (JCPDS card 5-190) (Fig. 1). Unlike well-crystallized boehmite [18, 19], the prepared sample featured broadening of diffraction lines in the X-ray spectra and some changes in intensity ratios, as observed for samples prepared by other researchers [17, 20, 23, 24]. These features argue that the synthetic conditions we used in this work yield highly dispersed boehmite (nanoboehmite, pseudoboehmite). The mean crystallite size for the prepared nanoboehmite sample calculated by the Debye–Scherrer relationship (from the half-widths of the 021, 130, and 002 lines), is  $5.6 \pm 0.9$  nm. The phosphonic complexone modifier (NTP) does not change the crystal structure of the thus-prepared nanoboehmite, as probed by X-ray powder diffraction, and does not affect the crystallite size ( $5.0 \pm 0.5$  nm) [16].

The low-temperature nitrogen adsorption–desorption isotherms on intact boehmite and modified boehmite feature a characteristic hysteresis loop in the partial pressure range  $p/p_0 > 0.4$ , indicating a mesoporous structure of the supports (Fig. 2). The prepared boehmite has a high specific surface area, which varies in the range  $S_{\text{sp}} = 230\text{--}250$  m<sup>2</sup>/g, i.e., is far higher than for coarse-grain crystalline boehmite samples (5–100 m<sup>2</sup>/g). The phosphonic complexone modifier (NTP) decreases the specific surface area of the boehmite to  $S_{\text{sp}} = 90\text{--}110$  m<sup>2</sup>/g, while changing

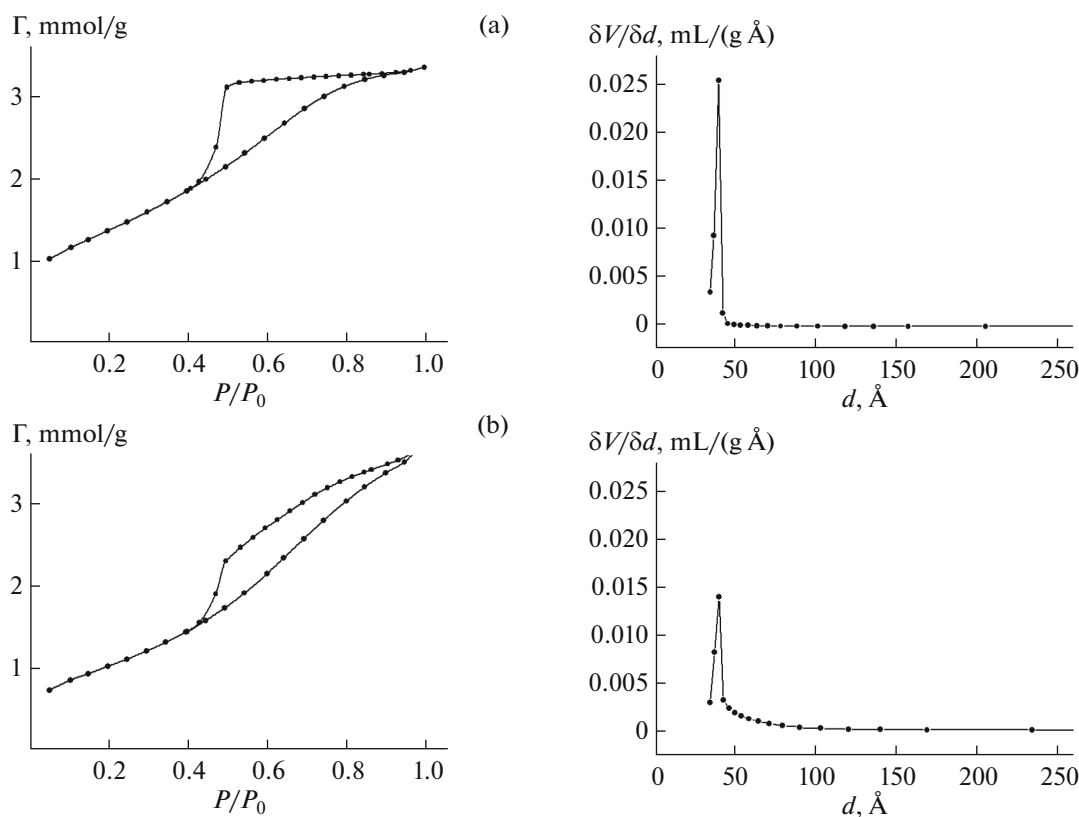


Fig. 2. Nitrogen sorption–desorption isotherms and pore size distribution on (a) intact boehmite and (b) NTP–boehmite.

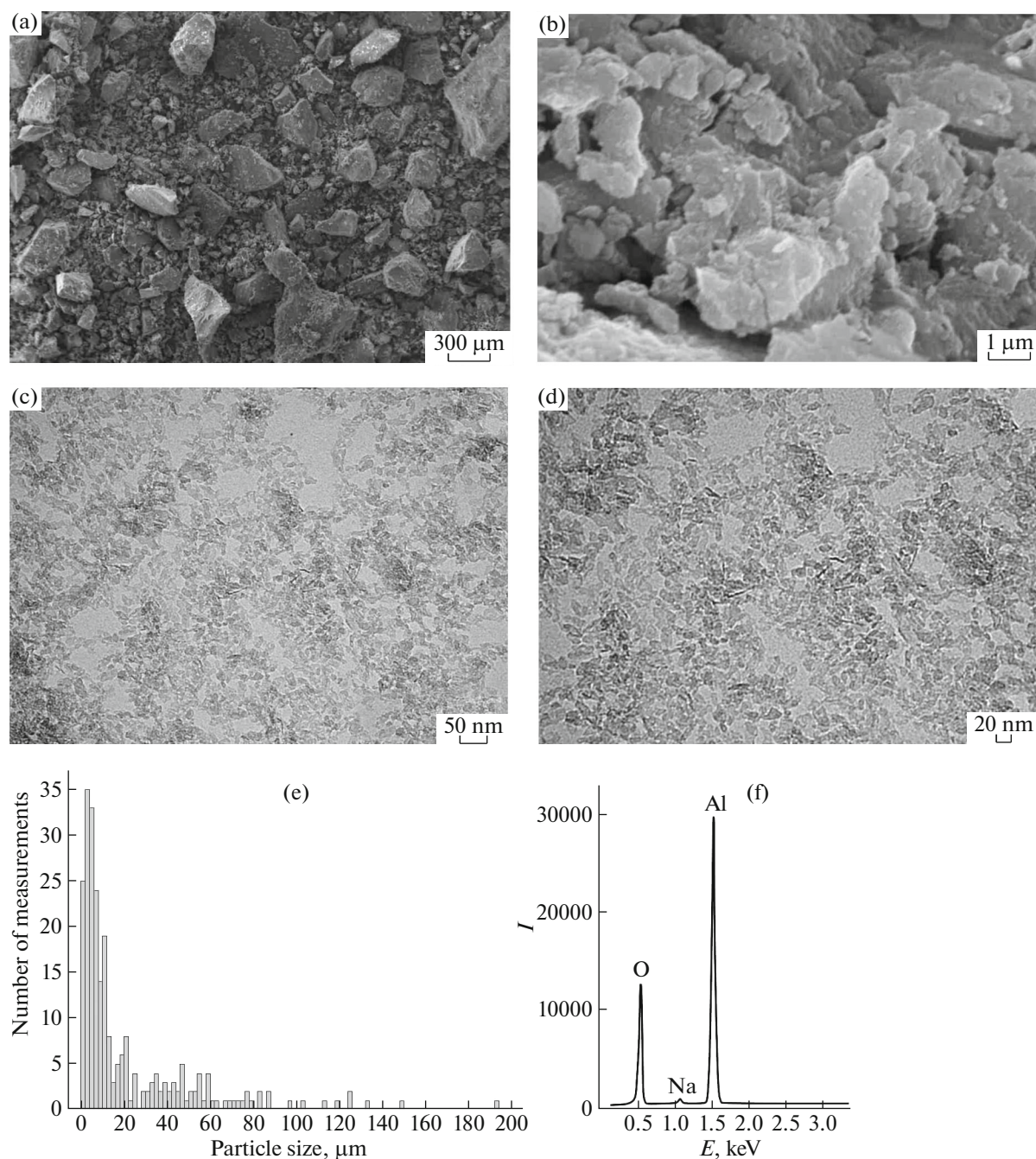
only insignificantly the total pore volume ( $V_p = 0.11–0.12$  mL/g), the pore size distribution, and the mean pore size ( $d_p = 4–6$  nm) (Fig. 2).

As probed by SEM, the prepared highly dispersed boehmite samples are agglomerates sized  $0.5–400$   $\mu\text{m}$  with the greatest amount of  $2–4$   $\mu\text{m}$  agglomerates (Figs. 3a, 3b, 3e). TEM (Figs. 3c, 3d) can elucidate the morphology of the prepared boehmite particles, which are ellipsoidal platelets collected in ribbons, with an average particle size of  $<10$  nm in consistence with XRD results. SEM shows that the NTP modification of boehmite induces the degradation of coarse ( $>50$   $\mu\text{m}$ ) agglomerates, and slightly smaller particles ( $1–2$   $\mu\text{m}$ ) than in unmodified boehmite are in the greatest amount (Figs. 4a, 4b, 4e). TEM (Figs. 4c, 4d) detects a greater dispersion of boehmite particles after NTP treatment; the shapes and sizes of nanosized boehmite particles in agglomerates remain unchanged. Energy dispersive X-ray analysis shows the major elements in the boehmite samples, namely, O (42 at %) and Al (57 at %), and trace Na (1 at %) (Fig. 3f). In the spectrum of NTP-modified boehmite, the oxygen fraction is higher (O, 54 at %; Al, 38 at %) and a phosphorus signal appears (8 at %), arguing for the presence of phosphonic complexones on the surface (Fig. 4f).

The IR spectrum of the prepared boehmite (Fig. 5) features absorption bands at  $476$ ,  $623$ , and  $735$   $\text{cm}^{-1}$

(the stretching vibrations of Al–O) and at  $3430$  and  $1635$   $\text{cm}^{-1}$  (the stretching and bending vibrations of O–H, respectively, in surface OH groups and adsorbate water molecules). The characteristic boehmite bands at  $1072$  and  $1150$   $\text{cm}^{-1}$  are due to the symmetrical and asymmetrical bending vibrations of O–H in interlayer hydroxo groups of boehmite [15, 18, 19, 21]. A narrow strong spike at  $1384$   $\text{cm}^{-1}$  relates to chemisorbed  $\text{NO}_3^-$  ions which arise from the aluminum nitrate used as a precursor in the synthesis. In the IR spectra of boehmites modified with phosphonic complexones, the most pronounced changes are observed in the range  $1000–1400$   $\text{cm}^{-1}$  (Fig. 5, inset), where there is enhanced absorption due to the stretching vibrations of bonds involving the phosphorus atoms of the  $\text{PO}(\text{OH})_2$  groups of the anchored complexone [25].

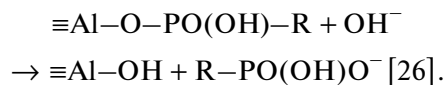
Analysis for phosphorus shows that the concentration of phosphonic complexones on boehmite is  $0.50–0.80$  mmol/g. Referring to the specific surface areas of the modified supports, the surface area per phosphonic complexone molecule is  $0.22–0.29$   $\text{nm}^2$ , which is comparable with the area occupied by a phosphonic group in a dense monolayer coverage ( $0.23$   $\text{nm}^2$ ). Thus, the phosphonic coating on the boehmite surface approaches monolayer coverage. The study of the



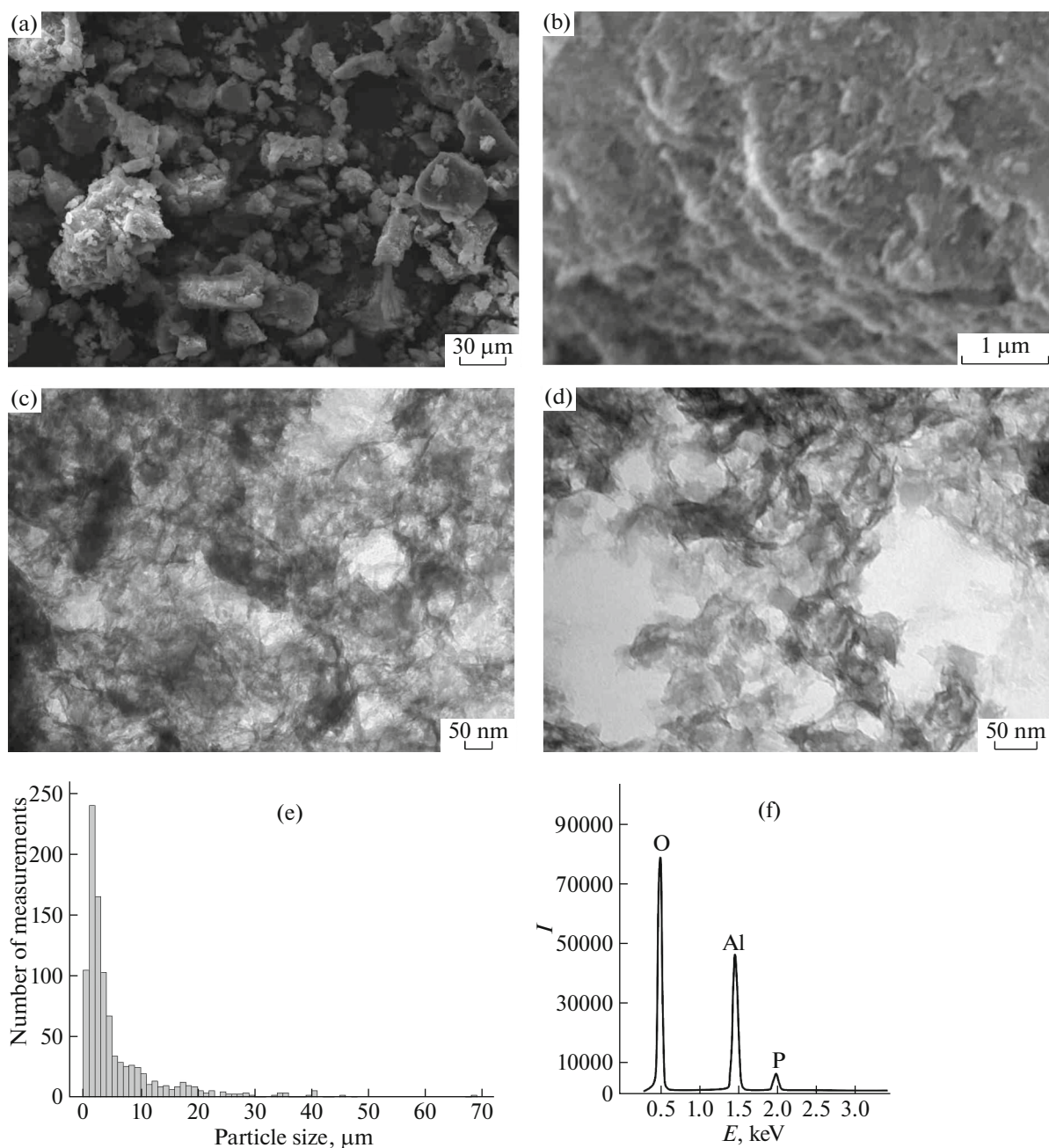
**Fig. 3.** (a, b) SEM images, (c, d) TEM images, (e) agglomerate size distribution, and (f) energy-dispersive X-ray spectrum of boehmite.

hydrolytic stability of phosphonic coating on boehmite shows that the degree of stripping upon 2-h exposure to aqueous solutions with pH 2–9 (at the end of the treatment, pH was 3–7) is no more than 2%, with the exception of the HEDP coating, for which the degree of stripping is higher (10–15%). At higher alkalities (pH 10–12 in the initial solution, and pH 8–10 in the equilibrium solution), desorption increases to 10–30%. Thus, the phosphonic coating formed on

boehmite is hydrolytically stable at pH 2–7. The instability of the sorbate state of phosphonic complexones on iron oxides under alkaline conditions was also elucidated earlier due to the reaction



The ideas about the interaction of the studied phosphonic complexones with the surface of iron



**Fig. 4.** (a, b) SEM images, (c, d) TEM images, (e) agglomerate size distribution, and (f) energy-dispersive X-ray spectrum of NTP-modified boehmite.

(hydr)oxides [26] and aluminum (hydr)oxides [27] imply that only one phosphonic group of the complexone serves as an anchor in binding all phosphonic complexones to the boehmite surface (Table 1). An argument for this scheme is the fact that the amount of all phosphonic complexones on boehmite approaches the amount of surface OH groups therein, and this can be only if the modification reaction has the following scheme:  $\equiv\text{Al}-\text{OH} + -\text{R}-\text{PO}(\text{OH})_2 \rightarrow \equiv\text{Al}-\text{O}-\text{PO}(\text{OH})\text{R} + \text{H}_2\text{O}$ . This suggests that only one phosphonic group interacts with the surface according to a

mononuclear, monodentate binding scheme [6, 8]. Thus, the presence of functions unbound to the surface in the modified support is a prerequisite for the manifestation of complexing properties in modified boehmite.

The adsorption of metal ions on complexing supports is most frequently described as involving the formation of surface metal ion complexes with grafted functions of the support. The theory of surface complexation is well developed for the quantitative interpretation of the sorption of metal ions by iron, alumi-

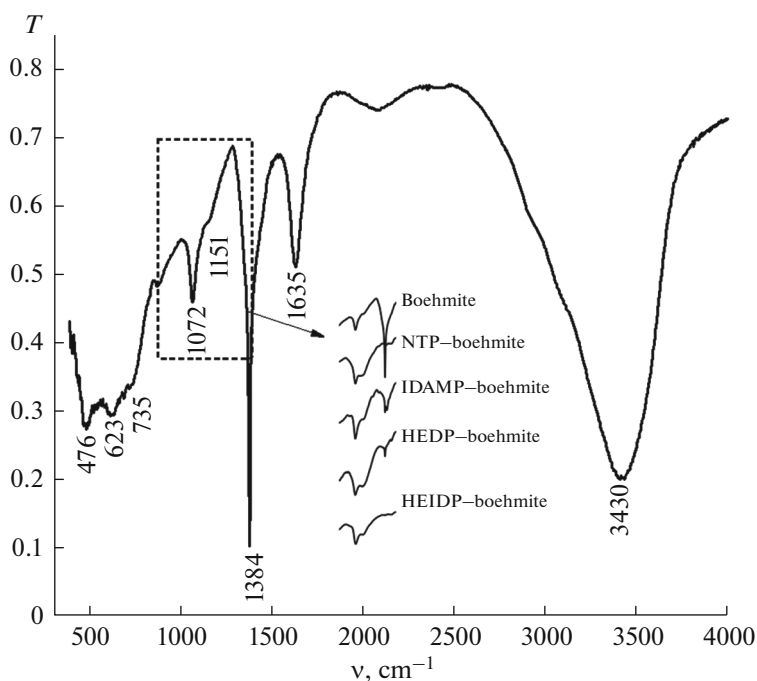


Fig. 5. IR spectra of intact boehmite and boehmites modified by phosphonic complexones (the inset).

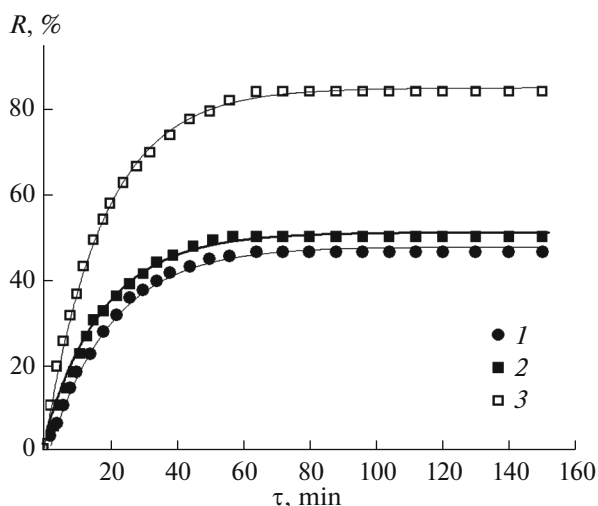
num, and manganese hydroxides, in which the surface hydroxide groups act as the simplest ligands with respect to metal ions [28]. A quantitative description of complexation of metal ions on a surface with more complex functional groups the result of which would be the determination of the composition and stability of surface complexes, is encountered in the literature far more rarely. We chose to study the complexing properties of supports of most common heavy metal ions, namely, Cu(II), Pb(II), Ni(II), Co(II), Zn(II), and Cd(II), as well as Ca(II), which is a macrocomponent of many natural and man-made water systems.

The acquisition rate of sorption equilibrium involving complexing sorbents is important for use in the sorption concentration and separation of metal ions, especially under dynamic conditions (columns, inserts, and cartridges). In the general case, the acquisition time of sorption equilibrium depends on the initial concentration of the metal in the solution, the sorbent content, its porosity and particle size, solution pH, temperature, stirring speed, etc. The kinetics of sorption of metal ions by modified boehmite was studied using the example of Cu(II) ions; the change in Cu(II) concentration in the solution during sorption was directly monitored using a copper-selective electrode, the potential of which decreased when the sorbent was inserted into the Cu(II) solution. Under the chosen experimental conditions, sorption equilibrium was acquired in ca. 60 min both for the intact and for modified boehmite regardless of the nature of the grafted phosphonic complexone (Fig. 6). The rather slow acquisition of equilibrium can be because of the

diffusion control of the sorption process when a highly dispersed narrow-pore sorbent is used. All sorption curves are well fitted ( $R^2 = 0.99$ ) by a pseudo-first-order kinetic equation with the rate constants  $k_1 = 0.052 \pm 0.001 \text{ min}^{-1}$  (boehmite),  $k_1 = 0.056 \pm 0.001 \text{ min}^{-1}$  (NTP-boehmite), and  $k_1 = 0.057 \pm 0.001 \text{ min}^{-1}$  (IDAMP-boehmite). The data gained may be compared to the sorption kinetics of heavy-metal ions on silica gels with grafted groups of aminopolycarboxylic complexones (IDA, NTA, EDTA, and DTPA), for which the following values were obtained:  $k_1 = 0.0009\text{--}0.0014 \text{ min}^{-1}$  (Co(II), Ni(II) ions on EDTA-SiO<sub>2</sub>, DTPA-SiO<sub>2</sub> [29]);  $k_1 = 0.339 \text{ min}^{-1}$  (Cu(II) ions on NTA-SiO<sub>2</sub>); and  $k_1 = 0.105 \text{ min}^{-1}$  (Cd(II) ions on NTA-SiO<sub>2</sub>) [30]. The equilibration time varied from 20 min to 24 h [29–32].

Changes in the state of sorption centers caused by the surface modification of boehmite are most clearly manifested in the effect of solution acidity on metal ion sorption. The recovery of all metal ions on modified sorbents increases in response to increasing solution pH to reach 90–100% at pH 7 (Fig. 7). The quantitative stripping of metal ions is reached via treatment of the sorbent with HNO<sub>3</sub> having pH ~ 2 for 20 min, upon which the sorbent itself is regenerated and can subsequently be reused.

The solution acidity that corresponds to 50% sorption of the sorbent (pH<sub>50</sub>) can serve as the simplest quantitative characteristic referring to the ability of a metal ion to form surface complexes. The sorption



**Fig. 6.** Kinetic curves for copper(II) ion sorption on (1) boehmite, (2) NTP-boehmite, and (3) IDAMP-boehmite. The lines drawn on the basis of calculated constants of a pseudo-first-order kinetic equation.  $\text{pH}_{\text{in/eq}}$ : (1) 7.3/6.0, (2) 7.2/5.7, and (3) 7.2/5.0.  $c_{\text{Cu(II)}} = 0.1$  mmol/L;  $c_{\text{sorbent}} = 1$  g/L; the solution volume (mL)/sorbent weight (g) ratio  $V/m = 10^3$ .

curves and  $\text{pH}_{50}$  values for modified supports shift toward the lower solution acidities relative to the respective items of the parent boehmite (Fig. 7a), arguing for the higher stability of surface complexes that involve the functions of phosphonic modifiers compared to the stability of complexes with surface OH groups of unmodified boehmite. It is known [13, 14] that all of the studied phosphonic complexones ( $\text{H}_n\text{L}$ ) in aqueous solutions form 1 : 1 (mol/mol) complexes with doubly charged metal ions ( $\text{M}^{2+}$ ) with various degrees of protonation,  $\text{MH}_i\text{L}^{i+2-n}$  ( $i = 0, 1, 2, \dots, n - 1$ ):

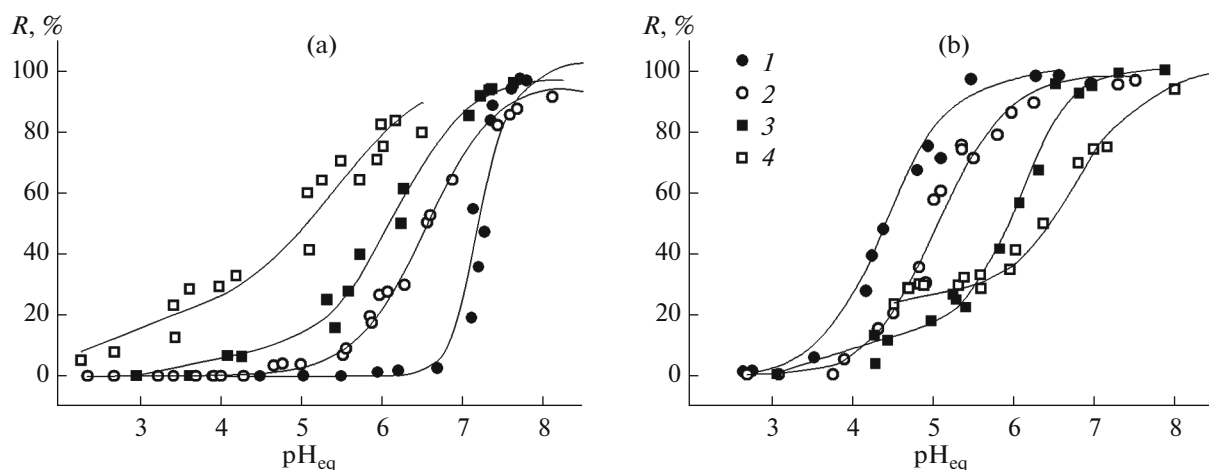


We may presume that, in the case of surface-grafted complexones, metal ion binding occurs in similar surface reactions:



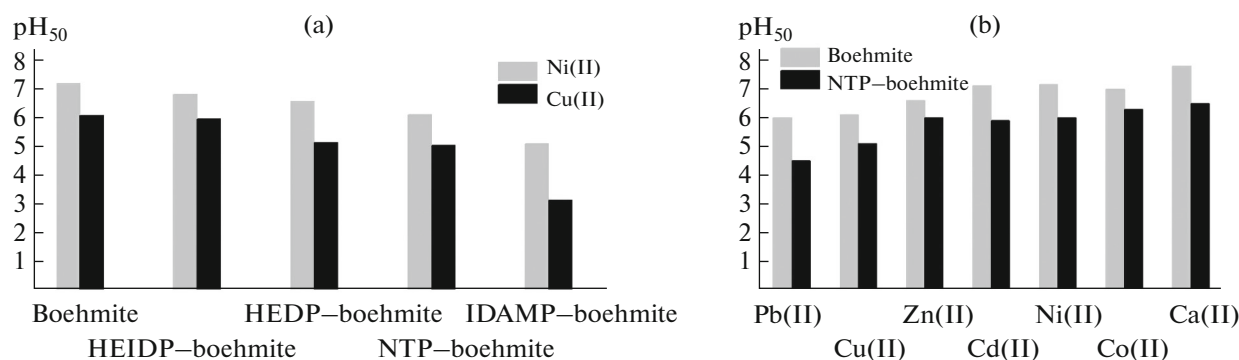
A comparison of Ni(II)/Cu(II) sorption on various modified supports shows that the nature of the surface function of the grafted phosphonic complexone determines the stability of surface complexes to a considerable extent (Fig. 7a). The value of  $\text{pH}_{50}$  (Fig. 8a) implies that an anchored iminodiacetate group (IDAMP-boehmite) provides the best binding of metal ions. This sorbent is, in fact, an analogue of widespread sorbents based on silica gel with grafted iminodiacetic acid groups (IDA-SiO<sub>2</sub>) [31, 33–35]. NTP-boehmite, which is the phosphonic analogue of IDAMP-boehmite containing an iminodi(methylenephosphonic) group instead of iminodiacetate group, binds to metal ions more weakly, and the replacement of one methylenephosphonic group by hydroxyethyl (HEIDP-boehmite) further reduces the complexing ability of the grafted complexone. In general, the resulting sequence of  $\text{pH}_{50}$  values (Fig. 8a) correlates with the decreasing order of Ni(II)/Cu(II) complexing abilities of the studied complexones in aqueous solutions: IDAMP > NTP > HEDP > HEIDP [14]. All modified sorbents bind Cu(II) more strongly than Ni(II), in the same way as in solutions.

The influence of the nature of the metal on the stability of sorption complexes was studied on NTP-boehmite (Fig. 7b). The metals studied are arranged, based on their  $\text{pH}_{50}$  values on NTP-boehmite, in the following decreasing order of selectivities: Pb(II) > Cu(II) > Zn(II)  $\approx$  Ni(II)  $\approx$  Co(II)  $\approx$  Cd(II) > Ca(II) (Fig. 8b). The highest sorption affinity of NTP-boeh-



**Fig. 7.** (a) Nickel(II) sorption on (1) intact boehmite, (2) HEDP-boehmite, (3) NTP-boehmite, and (4) IDAMP-boehmite versus solution acidity. (b) Sorption of (1) Pb(II), (2) Cu(II), (3) Cd(II), and (4) Ca(II) on NTP-boehmite versus solution acidity.  $c_{\text{M(II)}} = 0.1$  mmol/L;  $c_{\text{sorbent}} = 1$  g/L; the solution volume (mL)/sorbent weight (g) ratio  $V/m = 10^3$ ; sorption time: 2 h.





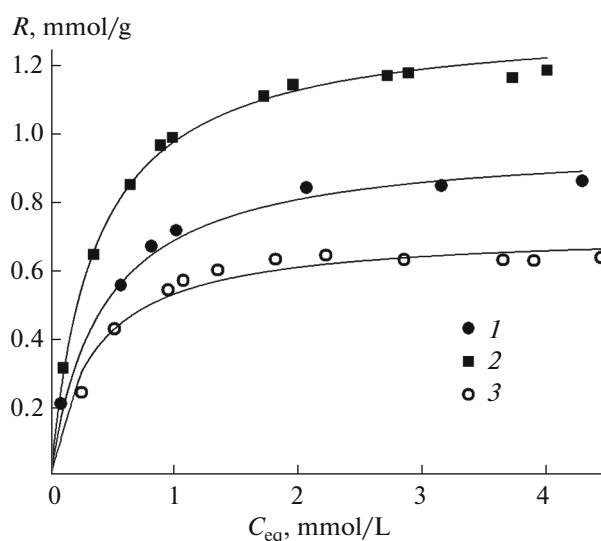
**Fig. 8.** (a) pH of 50% Ni(II) and Cu(II) sorption on intact boehmite and modified boehmites and (b) pH of 50% sorption on intact boehmite and NTP-modified boehmite for various metals.  $c_{M(II)} = 0.1$  mmol/L;  $c_{\text{sorbent}} = 1$  g/L; the solution volume (mL)/sorbent weight (g) ratio  $V/m = 10^3$ ; sorption time: 2 h.

mite toward Cu(II) and Pb(II) ions in comparison to the other studied ions correlates with the higher stability of their homogeneous complexes with NTP. The Ca(II) ion, which ends the series, forms the least stable complexes with NTP in solutions. Thus, the stabilities of surface complexes of metal ions on modified boehmite correlate with the stabilities of their homogeneous analogues in solutions.

Sorption capacity is an important characteristic of complexing sorbents, which determines the effectiveness of their use for sorption recovery/preconcentration of metal ions. For the parent boehmite, the Cu(II) sorption capacity (0.85 mmol/g) almost coincides with the concentration of its surface OH groups (Fig. 9). For OEDP-modified boehmite, the sorption capacity is 0.62 mmol/g, approaching the surface concentration on this complexone, while for NTP-boehmite, the sorption capacity (1.15 mmol/g) is higher than the grafted group concentration. The results point to the formation of  $M:L = 1:1$  (mol/mol) surface complexes on HEDP-boehmite and the formation of  $M:L = 1:1$  complexes as well as  $M:L = 2:1$  complexes (in an excess of metal ions) on NTP-boehmite. The sorption capacities of modified boehmites are comparable with those of silica gels containing grafted iminodiacetate and aminodiphosphonic groups: 0.3–0.4 mmol/g (Cu(II), Pb(II), and Ni(II) on IDA-SiO<sub>2</sub>) [34], 1.23 mmol/g (Cu(II) on IDA-SiO<sub>2</sub>) [29], 0.09–0.14 mmol-equiv/g (Zn(II) on IDA-SiO<sub>2</sub>) [35], and 0.3 mmol/g (Cu(II) on ADPA-SiO<sub>2</sub>) [36].

A scheme of metal ions binding to modified boehmite may be suggested proceeding from the coordination possibilities of the functions of grafted phosphonic complexones (Table 1). A complexone that contains a free phosphonic group(s) (HEDP-boehmite, HEIDP-boehmite, or NTP-boehmite) in an acid solution forms surface complexes involving two oxygen atoms of the phosphonic group to close the four-member ring. A similar scheme was described for complexation of metal ions with phosphonic com-

plexones in solutions [13] and for binding of metal ions to phosphonic/aminophosphonic ion exchangers [37] and silica gels having grafted phosphonic/aminophosphonic groups [9]. The complexing iminodiacetate group of IDAMP-boehmite in acid solution binds metal ions via dissociated carboxy group(s). At higher alkalinity, the surface-anchored aminophosphonic complexones (in HEIDP-boehmite and NTP-boehmite) and an iminodicarboxylic complexone (IDAMP-boehmite) can more strongly bind a metal ion due to the formation of a five-membered chelate ring(s) involving the oxygen atom of the phosphonic/carboxylic group(s) and the deprotonated nitrogen atom, as in solutions and on the surface [9, 37].



**Fig. 9.** Copper(II) sorption isotherms on (1) intact boehmite, (2) NTP-boehmite, and (3) HEDP-boehmite.  $\text{pH}_{\text{eq}}$ : (1) 4.8, (2) 4.5, and (3) 4.5.  $c_{\text{sorbent}} = 1$  g/L; the ratio solution volume (mL)/sorbent weight (g)  $V/m = 10^3$ ; sorption time: 2 h. The lines drawn on the basis of calculated constants of the Langmuir equation.

The complexing supports that we have manufactured can be used for the sorption group preconcentration of the studied heavy metals. Modified supports adsorb these metal ions from solutions of higher acidity than parent boehmite does (the shift is one to two pH units), and this reduces the adverse effects of hydrolysis and precipitation on sorption. The interference of Ca(II) ions, which are abundant macrocomponents of many aqueous systems, is expected in the group concentration of poorly adsorbed heavy metal ions (Ni(II), Co(II), Zn(II), and Cd(II)), while the concentration selectivity for Pb(II) and Cu(II) ions in the presence of Ca(II) is fairly high. The manufactured  $\gamma$ -AlO(OH)-based complexing sorbents can supplement the range of sorbents with similar functions that have already found practical application, where the inorganic support is SiO<sub>2</sub> and the grafted groups are aminopolycarboxylic acids (IDA, NTA, EDTA, etc.). The surface modification of aluminum and iron (hydr)oxides by phosphonic acid derivatives occur under mild conditions in a one-step reaction, which is far more facile than the synthesis of similar complexing silica gel sorbents. In view of a plurality of commercially available phosphonic complexones, the developed method for modifying oxide surfaces opens up the possibility of providing a variety of functional materials, including complexing species.

### CONCLUSIONS

The above-presented results show that a phosphonic complexone (NTP, HEDP, HEIDP, or IDAMP) can be immobilized on the surface of synthetic nanoboehmite to form a dense monolayer coverage. Modified boehmite can perform as a complexing support for metal ions (Pb(II), Cu(II), Ni(II), Co(II), Zn(II), Cd(II), Ca(II)) due to the phosphonic complexone functions that are free from interacting with the surface. The trends intrinsic to complexation in solutions involving phosphonic complexones hold when the complexones are anchored to the surface, too. Therefore, the body of data on complex formation in homogeneous systems can serve as the basis for making a reasoned choice of the modifying phosphonic complexone for solving particular problems in the provision of a surface-anchored state of some metal.

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### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest that would be disclosed in this paper.

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