SORPTION
AND ION EXCHANGE PROCESSES

Use of Micrometer Hematite Particles and Nanodispersed Goethite as Sorbent for Heavy Metals

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Abstract—Sorption properties of micrometer hematite particles and goethite nanoparticles were studied. Goethite nanoparticles were produced by chemical precipitation from iron nitrate and stabilized with potassium hydro-tartrate. Data on how the sorption properties of goethite nanoparticles depend on temperature and acidity of the medium were used to determine the optimal values of these parameters, at which the maximum sorption of metals are obtained. The higher sorption properties of goethite nanoparticles with respect for all the heavy metal ions under study were found as compared with the micrometer hematite and published data. The results obtained can be used in purification of wastewater containing heavy metal ions.

In the XXI century, the contamination of water with heavy metal ions is among the principal ecological problems. The steadily increasing requirements to the quality of water treatment processes force technologists to search for new, more ecologically safe and economical ways to remove heavy metal ions.

The efficiency of practical use of any kind of sorbent is determined by two parameters: sorption efficiency α (mg g^{-1}) (the ratio between the amount of substance removed from a liquid medium and that of the sorbent used for this purpose) and by the degree of recovery, R, calculated as the ratio between the concentrations of a substance under study in an aqueous solution after the sorption to that before.

For substance to be used as a sorbent, it is necessary that it should be, together with having pronounced sorption properties (large parameters α and R), ecologically safe and economically accessible. Rather promising in this regard are various methods for removing heavy metal ions from water with metal oxides [1, 2]. Oxides of trivalent iron (hematite, goethite, magnetite) are strongest adsorbents of heavy metals and, therefore, attract close attention as candidates for being used in purification of wastewater and soil. Hematite $\alpha\text{-}Fe_2O_3$ and goethite $\alpha\text{-}FeOOH$, which occur in nature in the form of minerals, are rather attractive as sorbents. These substances attract researchers' and technologists' attention because of being possibly applied in the form of dispersed particles to purify wastewater due to their high efficiency, ecological safety, and economical accessibility.

The practice of using sorbents has shown that the recovery of toxic metals from aqueous media depends on numerous factors: temperature, pH of the medium, presence of surfactants, nature and concentration of a sorbent and metal ions, and specific surface area of the sorbent. In recent years, large expectations for solving the problems of metal ions sorption have been associated, due to the development of nanotechnologies, with application and development of various sorbents in the form of nanoparticles, including those of hematite.

The sorption capacity of particles and nanoparticles of hematite $\alpha\text{-}Fe_2O_3$ and goethite $\alpha\text{-}FeOOH$ for a number of heavy metal ions was studied in relation to experimental conditions: sorbent and sorbate concentrations, pH, temperature, microwave treatment, etc., in [3–15]. As indicated by published data goethite and hematite

are rather promising as sorbents for heavy metals and their sorption capacity and degree of recovery widely vary, depending on numerous factors: particle size and surface morphology of a sorbent, pH of the medium, concentrations of the sorbent and a substance being adsorbed, etc. A review of published data demonstrated that there is evidence about the sorption capacity of hematite and goethite microparticles and hematite nanoparticles, with a wide scatter in values of α and R existing at the same time. There are data [12, 14] on high sorption characteristics of goethite nanoparticles, but the methods employed in these studies to precipitate heavy metal ions hinder their practical application. In [12], UV light was used to reach a sorption capacity α of goethite in the range from 34.84 to 84.46 mg g^{-1}. When using the method suggested in [14], it is necessary to perform sorption with nanogoethite in an acid medium (pH 2.4) at 80°C in the course of 4 h, which complicates their practical application.

The goal of our study was to examine sorbents based on hematite and goethite that would be promising for practical use (sufficiently low cost) and could operate under conditions close to a neutral medium at nearly room temperatures. To achieve this goal, we used powdered hematite, which is manufactured as an iron oxide pigment, contains 96% micrometer hematite particles (α-Fe$_2$O$_3$), and is an inexpensive large-tonnage chemical product. Goethite nanoparticles were synthesized, together with α-Fe$_2$O$_3$, by a comparatively simple method. The optimal sorptin conditions were determined for micrometer hematite particles and goethite nanoparticles produced in the present study and the sorption capacities and degrees of recovery of a number of heavy metal ions (Cu^{2+}, Ni^{2+}, Cr^{6+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}) were compared. To evaluate the efficiency of the sorbents considered in the study, we compared their sorption characteristics with the related published data.

EXPERIMENTAL

Aqueous solutions of metals were prepared with reagents of chemically pure grade: copper sulfide pentahydrate (CuSO$_4$·5H$_2$O), nickel(II) nitrate hexahydrate [Ni(NO$_3$)$_2$·6H$_2$O], potassium chromate (K$_2$Cr$_2$O$_7$), cadmium nitrate tetrahydrate [Cd(NO$_3$)$_2$·4H$_2$O], anhydrous cobalt dichloride (CoCl$_2$), lead(II) nitrate [Pb(NO$_3$)$_2$], zinc sulfide heptahydrate (ZnSO$_4$·7H$_2$O).

The starting solutions of heavy metal salts with a concentration of 10^{-2} M were prepared by dissolution of weighed portions of the substances under study in distilled water. Solutions of required concentrations in the range 10^{-2}–10^{-5} M were prepared from the starting solutions by successive dilutions.

We studied the sorption properties of micrometer hematite particles by using the iron oxide pigment containing 96% hematite (α-Fe$_2$O$_3$). To study the sorption properties of goethite nanoparticles, they ere synthesized from the following reagents of chemically pure grade: iron nitride nonahydrate [Fe(NO$_3$)$_3$·9H$_2$O], acid potassium tartrate [HOOC(CHOH)$_2$COOK], 25% aqueous ammonia, and ammonium oxalate monohydrate [(NH$_4$)$_2$C$_2$O$_4$·H$_2$O]; acid-base indicator lacmoid with a coloration variation range pH 4.4–6.4; and absolute ethanol.

The particle size distribution of hematite was determined with an SALD 7071 laser analyzer (Shimadzu, Japan), which enables measurements on a real-time basis. IR spectra were recorded with a Bruker Optik GmbH FTIR spectrometer. X-ray phase and thermal analyses were made with a DRON-3.0 diffractometer and Q-1000 derivatograph, respectively.

Analytical studies were performed using the methods of iodometric titration, complexonometric titration, flame atomic-absorption spectrometry with an AAC-7000 atomic-absorption spectrometer (Shimadzu, Japan), photometric method with a KFK-2MP photoelectric concentration calorimeter. The pH values of the solutions were monitored with an OP-264/1 potentiometer (Redelkis, Hungary). The analyses were made using the procedures described in [16, 17]. We also employed the following four procedures.

(1) Quantitative chemical analysis of water. Procedure for measuring the mass concentration of chromium ions in natural and wastewater by the photometric method with diphenyl carbazide. PND (Nature-protective Regulatory Document) F 14.1:2.52–96 (approved by the Ministry of Natural Resources of the Russian Federation on 20.03.1996).

(2) Quantitative chemical analysis of water. Procedure for measuring the mass concentration of nickel in wastewater by the photometric method with dimethyl glyoxime. PND F 14.1.46–96.

(3) Quantitative chemical analysis of water. Procedure for measuring the mass concentration of cadmium in surface and underground fresh water and wastewater by
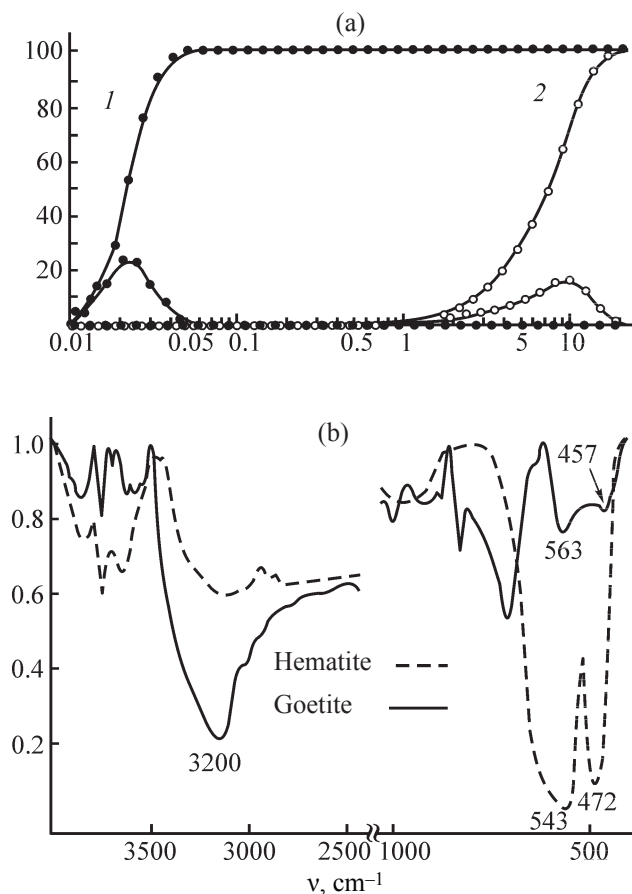
Fig. 1. (a) Integral and differential particle size distributions for (*1*) goethite nanoparticles and (*2*) hematite microparticles. (b) IR spectra of hematite and goethite nanoparticles. (v) Wave number.

the photometric method with bromo benzothioazo. PND F 14.1P2:3.180–2002 (FR.1.31.2007.03801, approved by the Federal State-Financed Institution, Federal Central Administrative District, on 21.03.2012).

(4) Quantitative chemical analysis of water. Procedure for measuring the mass concentrations of cobalt, nickel, zinc, chromium, manganese, iron, silver, cadmium, and lead in samples of potable, natural, and wastewater by atomic-absorption spectrometry. PND F 14.1:2:4.139–98.

The published methods for obtaining goethite nanoparticles are comparatively few in number [18–23], there is a review of these techniques [24]. In [24], needle-like crystals of goethite were obtained at large pH values; in [20], an ionic fluid was used as a medium; in [21], air was passed through an aqueous solution containing iron sulfide and sodium hydroxide. The closest to the method we used in the present study is that reported in [18, 23], in

which goethite nanoparticles were produced by mixing of iron nitrate and hydrazine sulfate solutions. In the present study, we replaced the toxic and expensive hydrazine sulfate with ammonia and used potassium tartrate as a particle size stabilizer.

Samples of goethite nanoparticles for sorption tests were synthesized as follows: a preliminarily prepared solution of iron(III) nitrate (60 g of the salt per 240 mL of distilled water) was poured into a 250-mL round-bottom flask and the solution was brought to boiling. Then, 54 mL of concentrated ammonia was gradually added to the boiling solution in two portions: 36 mL immediately after the onset of boiling and 18 mL more in 15 min. Further, 0.35 g of potassium tartrate was added in small portions to the boiling mixture. After that the mixture was boiled for 2.5 h. After the synthesis was complete, the mixture was cooled and filtered through a pleated filter, with the filtrate separated from the precipitate. The resulting red-brown powder was washed several times with a 25% solution of ammonium oxalate to a nearly neutral reaction of the medium (pH $\approx$ 6.5–7). Further, the powder was washed with distilled water and dried in a drying box at 100°C. The suggested method is simple in use and requires inexpensive and nontoxic reagents. As demonstrated further studies, the application of potassium tartrate made it possible to obtain goethite nanoparticles stable in the course of time.

Measurements of the particle size of the hematite powder demonstrated that the powder particle sizes fall within the range 1–20 μm (Fig. 1, curve *2*), with 50% of the particles being smaller than 7 μm in size. Particle size measurements of the synthesized powder demonstrated that the powder particle sizes fall within the range 10–50 nm, wit a maximum at 20 nm (Fig. 1, curve *1*). Repeated measurements of the particle sizes with a laser analyzer on the real-time basis demonstrated that the dispersion of goethite nanoparticles with an average size of 20 nm in an aqueous medium is stable during a long time, a curve 1 identical to that in Fig. 1a was observed on the display screen. Measurements of IR absorption spectra demonstrated (Fig. 1b) the presence of absorption lines at 543 and 472 cm^{-1}, characteristic of deformation vibrations in hematite [25]. Measurements of IR spectra of the synthesized powder demonstrated (Fig. 2b) the presence of absorption lines at 3200–3125 cm^{-1}, which are characteristic of goethite [26] and correspond to stretching vibrations of OH groups of iron hydroxide (goethite), and also lines at 563 and 457 cm^{-1}, associated

with asymmetric stretching vibrations of Fe–Oh groups. A thermal analysis indicated that the sample remains unchanged up to 900°C and there is a small exothermic effect peake at 340°C, which shows that there are internal stresses appearing in a sample in the course of its fabrication (Fig. 2a, dashed lines). As the temperature is raised, these defects are annealed out and manifested in the DTA curve as an exothermic effect. The presence of the exothermic peak in the DTA curve indicates that the solid has an excess enthalpy [27] associated with the presence in the crystal lattice of hematite of structural defects that appeared when the hematite powder was synthesized. A thermal analysis of the synthesized powder revealed an endothermic effect with a minimum at 245°C and a significant decrease in the sample mass in the temperature range 200–300°C, which is due [28] to the decomposition of hydroxy groups of goethite and its transformation to hematite (Fig. 2, solid curves). An X-ray diffraction analysis demonstrated the presence of the phases known from the literature: the hematite phase was found in the iron oxide pigment, and the goethite phase, in the powder synthesized in the study. Thus, our analysis of the samples shows that the powder has micrometer particles with an average size of 7 μm, whereas the synthesized powder is goethite with an average particle size of 20 nm. Further, these powders were used to evaluate their sorption properties for a number of heavy metal ions.

The sorption of a number of heavy metal cations (Cu^{2+}, Ni^{2+}, Cr^{6+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}) on the surface of micrometer hematite particles and stabilized goethite nanoparticles was studied in the static mode. A 250-mL conical flask was charged with a 10-mL portion of a salt solution. Then hydrochloric acid or potassium hydroxide was added to create the required acidity and the solution volume was brought to 25 mL. After that, 1 g of a sorbent was introduced and the mixture was shaken on an oscillating agitator for 30 min. Changing the sorbent mass demonstrated that a mass of 1 g per 25 mL of a solution is the optimal value: making the sorbent mass larger did not lead to any noticeable increase in the sorption capacity, whereas making it smaller resulted in a decrease in the sorption of ions. Further, the filtrate was separated from the sorbent by filtration through dry pleated filters.

To choose the optimal conditions for sorption of heavy metal ions from aqueous solutions, we experimentally determined the conditions of the sorption concentration of a number of heavy metal cations (pH value of the
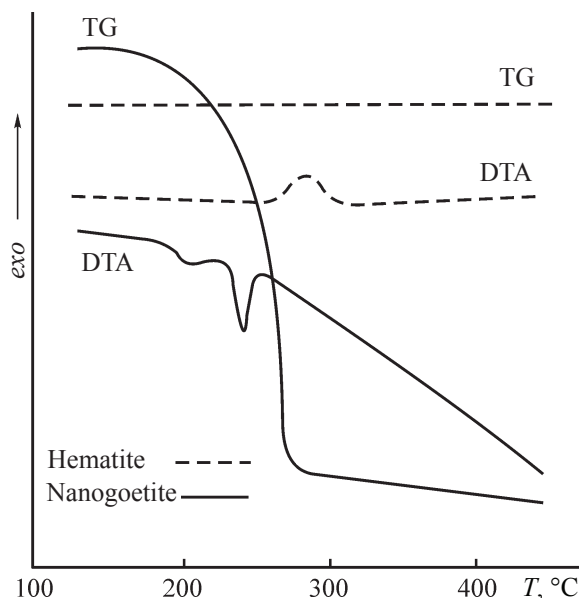

Fig. 2. Results of a thermal analysis: DTA and loss-of-mass (TG) curves for goethite nanoparticles and hematite microparticles. (*T*) Temperature.

medium, temperature, time of attainment of the sorption equilibrium) for hematite and goethite particles. Because close optimal values of the parameters were obtained, only data for goethite nanoparticles are presented below.

We commenced our study of the sorption of metal ions by experimentally determining the optimal sorption temperature. For this purpose, we measured temperature dependences of the sorption capacity of hematite and goethite particles in the range 20–90°C.

Figure 3 shows how the degrees of recovery of lead (a) and copper (b) ions by goethite particles depend on temperature. It can be seen that the maximum value of R is observed at 30°C. Similar results were obtained for other metal ions.

Further, it was necessary to find the optimal acidity of the medium, corresponding to the maximum sorption of the metal cations under study because the concentration of hydrogen ions H^+ is an important factor governing the equilibrium in sorption processes. For this purpose, we plotted dependences of the degree of recovery (R, %) by goethite nanoparticles on the acidity of the medium at various pH values of the medium for each of the cations under study, with the value of R for each point taken as an average from three independent runs. A study of the influence exerted by the solution acidity in the range pH 4.5–9 on the sorption of cations by goethite
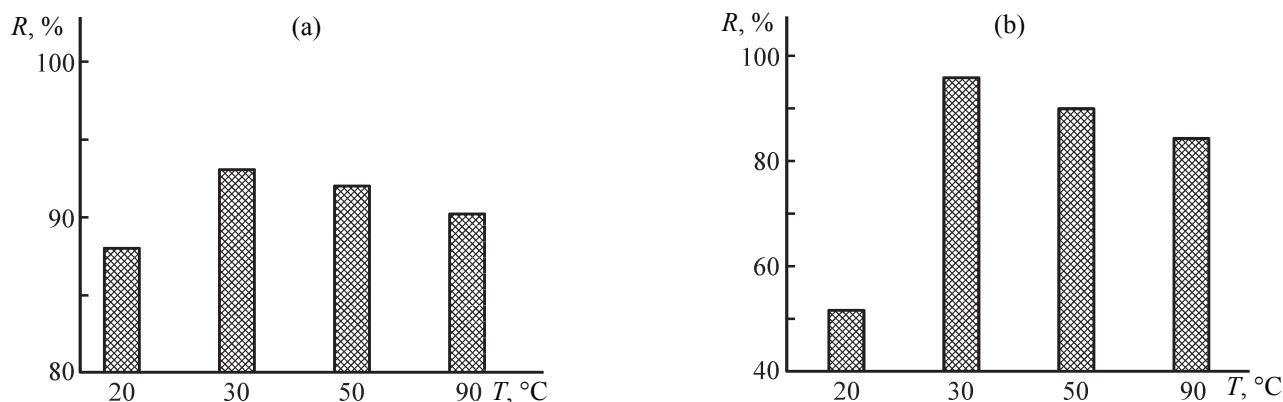
Fig. 3. Dependence of the degree of recovery (R) of (a) Pb^{2+} and (b) Cu^{2+} ions with goethite nanoparticles on temperature T.

nanoparticles demonstrated that the maximum recovery is observed at pH values in the range from 6.1 to 6.5. The results obtained for cobalt and cadmium ions on goethite nanoparticles are presented in Fig. 4. It can be seen that the sorption process strongly depends on the pH of the medium.

Together with determining the dependence of the sorption capacity on temperature and pH, we also found the time required for performing the sorption process. We measured R in aqueous solutions with certain pH values and concentrations in the range 20–60 min. It was found that the optimal time of contact between the sorbent and sorbates, at which the degree of recovery of metal ions is at a maximum, is 30 min.

Thus, we determined the optimal cation sorption conditions in the static mode: temperature 30°C, sorption
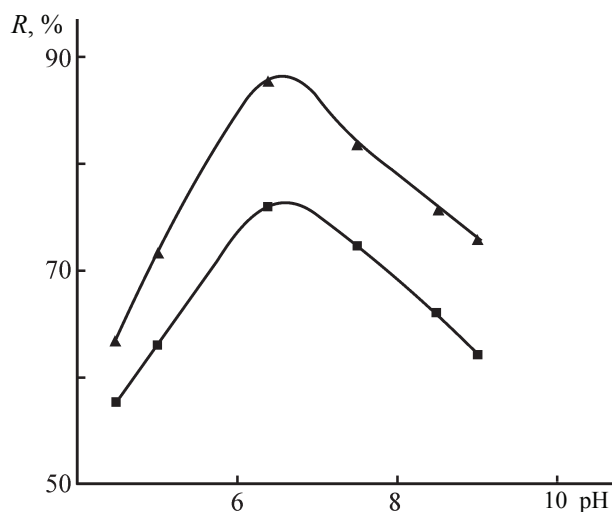

Fig. 4. Dependence of the degree of recovery (R) of (*1*) cadmium and (*2*) cobalt ions on pH at 30°C.

equilibrium time 30 min, process pH 6.1–6.5. At the optimal values of the pH of the medium, temperature at sorption equilibrium time, we measured the sorption capacity and degree of recovery on hematite and goethite particles and plotted sorption isotherms for goethite nanoparticles. For all the metal ions under consideration, we plotted isotherms of sorption on goethite nanoparticles (Fig. 5). It can be seen in Fig. 5 that a sorbent concentration of about 0.06 M is sufficient for an effective sorption of all the metal ions.

Figure 6 shows the sorption capacities of hematite microparticles and goethite nanoparticles. It can be seen that goethite nanoparticles stabilized with potassium hydrotartrate have a substantially higher sorption capacity for the cations under study. To compare the efficiencies of hematite and goethite particles of varied dispersity, the results obtained in the present study and published data are listed in Tables 1 and 2.

RESULTS AND DISCUSSION

To evaluate the efficiency of a sorbent, it is necessary to take into account numerous factors: ecological safety and simplicity of fabrication, high sorption properties, accessible cost, possible further processing of slurry formed upon sorption. Tables 1 and 2 present the results obtained in measurements of the sorption properties of hematite and goethite with varied dispersity, in comparison with published data. We used the iron oxide pigment as a powder of hematite microparticles. The pigment contains 96% hematite (α-Fe_2O_3) and is an inexpensive large-tonnage chemical product, which can be used in large amounts to purify industrial wastewater. It can be seen in Table 1 that the sorption capacity of hematite
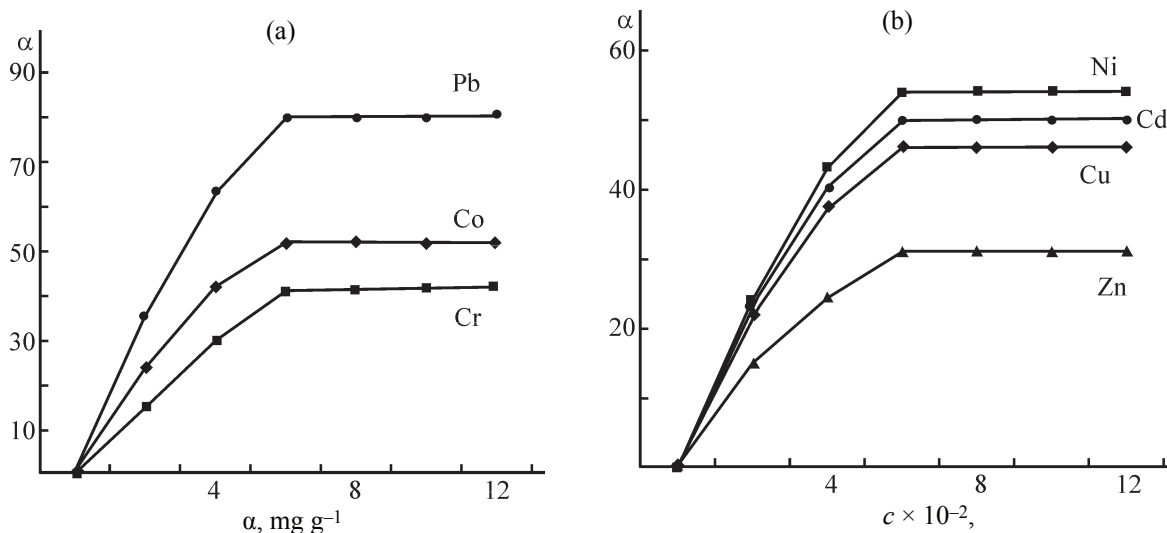
Fig. 5. Isotherm of metal sorption by goethite nanoparticles. (α) Sorption capacity and (c) sorbent concentration. (a) Pb, Co, CR; (b) Ni, Cd, Cu, Zn.

Table 1. Sorption capacity of various forms of iron oxides for metal ions

Metal ion	pH$_{opt}$	Sorption capacity α, mg g^{-1}				
		microhematite		nanohematite, published data	nanogoethite	
		this study	published data		this study	published data
Cr^{6+}	6.1	5	4.47 [7]	30 [8], 6.33–200 [10]	42	35.0 [5], 19.76 [14]
Ni^{2+}	6.5	17			54	42.5 [5]
Cd^{2+}	6.3	19	7 [4]		50	
Co^{2+}	6.5	23			52	30.0 [5]
Pb^{2+}	6.5	46	12.5 [4]		80	79.0 [14]
Zn^{2+}	6.2	10			31	30.0 [5]
Cu^{2+}	6.2	46		34.84–84.46 [12]	47	50.0 [5], 36.85 [14], 90.09 [15]

Table 2. Degree of recovery of a number of metal ions from aqueous solutions with various forms of iron oxides

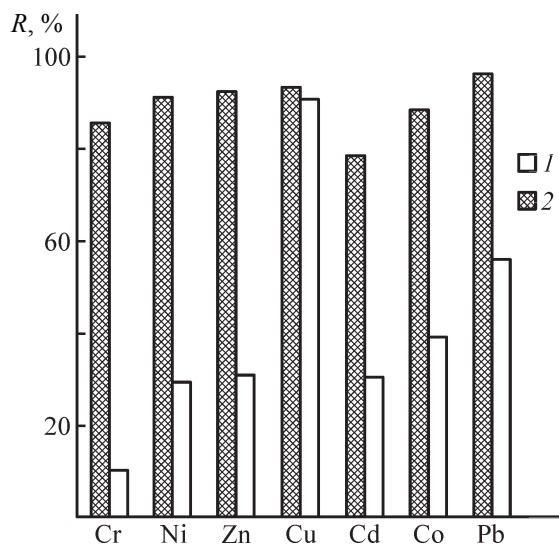| Metal ion	R, %				
	microhematite		microhematite	nanogoethite	
	this study	published data		this study	published data
Cr^{6+}	10		95 [5], 53 [10]	86	70 [5]
Ni^{2+}	29		85 [5], 50 [9]	91	85 [5]
Cd^{2+}	30	78 [13]	94 [3], 45.5 [6], 65 [9]	78	78 [7]
Co^{2+}	39		70 [5], 97 [9]	88	60 [5]
Pb^{2+}	56	100 [13]	100 [3], 98 [6]	96	100 [7]
Zn^{2+}	31	56 [13]	80 [5], 100 [3], 79.6 [6]	92	60 [5], 56 [7]
Cu^{2+}	91	88 [13]	20 [5], 89 [3], 30.4 [6], 100 [9]	93	100 [5], 88 [7]

Fig. 6. Degree of recovery (*R*) of metal ions by (*1*) micrometer hematite particles and (*2*) goethite nanoparticles at 30°C.

micriparticles exceeds the related published values and the suggested hematite microparticles can be used because of the low cost of hematite. The sorption capacity of hematite nanoparticles having a larger specific surface area noticeably exceeds that for hematite microparticles, but, at the same time, is inferior to the values of α for goethite nanoparticles, obtained in the present study. Only in a single case [12], with the sorption process performed under UV irradiation, the sorption capacity for copper ions was obtained in the range $\alpha = 34$–84 mg g^{-1} for hematite nanoparticles, with these values exceeding those for goethite ($\alpha = 47$ mg g^{-1}). The values obtained for lead ions ($\alpha = 80$ mg g^{-1}) are comparable with the results of [14] ($\alpha = 79$ mg g^{-1}). However, it should be taken into account here that the data of [14] have been obtained under more severe (pH 2.5) and labor- and time-consuming conditions ($T = 80$°C, minimum processing duration 4 h). Moreover, the results obtained in the present study also surpass the corresponding published values for goethite nanoparticles (Ni^{2+}, Cr^{6+}, Co^{2+}, and Zn^{2+} ions). Only for Cu(II) a value $\alpha = 34$–84 mg g^{-1} exceeding that in the present study ($\alpha = 47$ mg g^{-1}) was obtained with the sorption process performed under UV irradiation [12]. The values of α for Ni^{2+}, Cr^{6+}, Cd^{2+}, Co^{2+}, and Zn^{2+} ions also exceed the corresponding values for goethite microparticles. The results of [5] are the closest to our data in the sorption characteristics for zinc and copper ions. The values of α, obtained in [5] for chromium, nickel, and cobalt ions, are larger by 20, 28, and 73%, respectively.

We can attribute to shortcomings of [5], compared with our study, the sorption in an acid medium (pH 3–6) and the two times longer process duration.

An important parameter characterizing the sorption properties is the degree of recovery from aqueous solutions. Table 2 lists data of hematite and goethite with varied dispersity. The degrees of recovery (*R*) for hematite microparticles, obtained in the present study, are sufficiently large for most of ions (with the exception of lead), although being inferior to the values of *R* for the sorbent based on hematite nanoparticles. The values of R for stabilized nanogoethite, obtained in the present study, in most cases (Ni^{2+}, Cd^{2+}, Co^{2+}, Pn^{2+}, Zn^{2+} cations) exceed the published values for goethite nanoparticles. It is noteworthy, when comparing the degrees of recovery of the ions by hematite microparticles and goethite nanoparticles, that the most pronounced changes are observed for Cr^{6+}: the value of *R* changes by a factor of 8–9 on passing from hematite to goethite, whereas for Cu^{2+}, *R* changes only slightly. A similar behavior, a weak dependence of the sorption characteristics for copper ions on the size of hematite particles, was observed in [11].

As positive factors, in comparison with all the published data presented in this communication, can serve good sorption characteristics reached in a short time (30 min) and the simplicity of obtaining goethite nanoparticles. One more argument in favor of the suggested method for sorption of heavy metal ions with hematite and goethite of varied dispersity is the optimal sorption temperature of 30°C, found in the study. This temperature, close to that of the ambient, makes it possible to do without gross expenditure for maintaining a constant temperature during sorption of heavy metal ions with hematite and goethite. The range of optimal pH values (6.1–6.5), found for various metal ions, is close to pH 7 for the neutral medium, which also favor practical industrial implementation of sorption processes. And finally, the sorption yields purified water and a slurry in the form of a powder containing oxides of iron and adsorbed metals. This slurry can be rather easily processed by using the well-known metallurgical techniques.

CONCLUSIONS

(1) It was found that goethite nanoparticles having high sorption capacity for heavy metal ions can be synthesized by a comparatively simple method with accessible reagents. Measurements demonstrated that

IR spectra and X-ray and thermal characteristics of goethite nanoparticle samples are the same as those for bulk goethite samples. It was determined that the size of goethite nanoparticles can be stabilized via introduction of potassium tartrate into solution.

(2) A comparison with published data revealed in most cases the advantage of the sorption characteristics of the suggested sorbents based on hematite and on goethite nanoparticles. If, however, the sorption characteristics of hematite and goethite nanoparticles were close to the related published data, an advantage was observed in the cost, simplicity of synthesizing the sorbent, and sorption process conditions (nearly room temperature, short sorption duration of 30 min, nearly neutral pH value, and no need for any additional treatment, such as, e.g., UV irradiation.

(3) It was demonstrated that, owing to their low cost, versatility, and comparatively high efficiency, sorbents based on hematite microparticles can be recommended for practical application as a reagent for wastewater purification to remove a number of heavy metal ions (Cu^{2+}, Ni^{2+}, Co^{2+}, Cr^{6+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}). The same refers to goethite nanoparticles thanks to their versatility, simple synthesis and high sorption efficiency at nearly room temperatures (30°C) and nearly neutral pH values (weakly acidic medium, pH ≈ 6.1–6.5).

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