Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.786654

52 (2014) 324–330
January

Taylor & Francis
Taylor & Francis Group

Removal of Cr(VI) from aqueous solutions by magnetite nanoparticles with different sizes and crystal structure

Oleg Linnikov[a,*], Irina Rodina[a], Vladimir Shevchenko[a], Irina Medvedeva[b], Michael Uimin[b], Nina Schegoleva[b], Anatoly Yermakov[b], Vladimir Platonov[c], Vladimir Osipov[c]

[a]*Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, 91 Pervomayskaya St, 620990 Ekaterinburg, Russia*
Tel. +7 343 3623519; Fax: +7 343 3744495; email: linnikov@mail.ru
[b]*Institute of Metal Physics, Ural Branch of the Russian Academy of Sciences, 18 S. Kovalevskaya St, 620099 Ekaterinburg, Russia*
[c]*Institute of Electrophysics, Ural Branch of the Russian Academy of Sciences, 106 Amudsena St, 620016 Ekaterinburg, Russia*

Received 15 October 2012; Accepted 9 March 2013

ABSTRACT

In this work a few nanopowders of magnetite (Fe_3O_4) produced by different methods were used as a sorbents. Three techniques were applied to make the nanopowders: (1) gas-phase synthesis, (2) chemical precipitation from water solution, and (3) laser atomization. Using these methods, the particles with different sizes and crystal structure have been produced. The effects of the particles size and structure of nanopowders on the removal of toxic Cr(VI) from an aqueous solution imitating ground waters and wastewaters with pH = 7.4–7.8 were studied at different solution temperatures. It is shown that magnetite is effective sorbent for the removal of Cr(VI) from polluted natural waters and sewage. It is found that sorption of Cr(VI) by magnetite is irreversible and has chemisorption character, and even small rise in temperature of the solution during the sorption process sharply increases efficiency of the sorption.

Keywords: Adsorption; Aqueous solutions; Sorption; Nanoparticles; Magnetite; Sorbents; Cr(VI)

---

1. Introduction

Purification of natural waters and wastewaters from Cr(VI) represents extremely important problem on account of high toxicity of chrome(VI). There is a variety of methods for the removal of Cr(VI) from water solutions. However, almost all of them are connected with use of various chemical reagents. In result, after their use, the total mineralization of the refined sewage grows and often they become unsuitable for dump into environment or wastewater systems. Especially, it concerns sewage in which concentration of Cr(VI) exceeds 5–10 mg/l.

One of the perspective ways of removal Cr(VI) from solutions is a sorption method. Its main advantage is that it practically does not bring into refined solutions new ions and substances. It allows to use the given method for regeneration of some

---

*Corresponding author.

1944-3994/1944-3986 © 2013 Balaban Desalination Publications. All rights reserved.

technological solutions (for example, in galvanic technology), and also for purification of polluted natural waters for the purposes of their subsequent use in municipal services.

The sorption capacity of sorbents is substantially defined by their specific surface area, which increases with reduction in sizes of particles of the sorbents. However, the small size of sorbent particles complicates processes of separation of them from solutions by traditional methods of precipitation and filtration. Therefore, the important problem is production of sorbents that (1) have good sorption properties and (2) may be easily separated from solutions. This problem can be solved, if powders of small ferromagnetic particles are used like sorbents. And after sorption of pollutants, the powders may be separated from solution under action of magnetic field. One of the examples of such ferromagnetic sorbent for the removal of Cr(VI) from solutions is magnetite Fe_3O_4 [1–6].

The purpose of the present work was to research a possibility to apply powders of magnetite as sorbents for the removal of Cr(VI) from natural waters and wastewaters. As these powders had different structure and size of particles and were produced by various methods, a question on influence of these parameters on sorption properties of magnetite also represented a great interest.

2. Experimental

The study of sorption of Cr(VI) by magnetite was carried out in a water solution imitating natural waters and sewage. It should be noted that often industrial wastewaters (for example, in galvanic technology) have only two components: Na_2SO_4 and K_2CrO_4. Therefore, for their imitation, a solution with such composition may be used. The solution was prepared by dissolving sodium sulfate (Na_2SO_4) and potassium chromate (K_2CrO_4) in distilled water. Volume of the imitating solution in each experiment was 50 ml. Concentration of sodium sulfate in the imitating solution (before sorption) was equal 400 mg/l, and Cr(VI)–50 mg/l. After preparation, the solution had pH = 7.4–7.8. The researches were performed in static conditions with use of a series of 70-ml glass flasks, at different temperatures and at periodic mechanical agitation of the solutions in the glass flasks. After introduction of a powder of magnetite into the imitating solution the total time of exposition of the solution was varied from about 24 h (sorption at temperatures of 30–80°C) to seven and more days (sorption at a room temperature 25 ± 2°C). At sorption at temperatures of 30–80°C, the series of 70-ml glass flasks was placed into special air thermostat with the required temperature where they were periodically agitated. Concentration of Cr(VI) in solutions was determined by colorimetric analysis with diphenylcarbazide at 540 nm [7]. For this the Russian spectrophotometer KFK-2 was used. As a sorbent a few samples of nanopowders of magnetite obtained by different methods were used. Three techniques were used to make nanopowders: (1) method of gas-cycle synthesis [8], (2) method of chemical precipitation from water solutions of $FeSO_4$ [9] and (3) method of laser atomization [10].

At the gas-cycle method, a strongly overheated drop of molten iron was evaporated in a buffer Ar gas media containing some percent of oxygen [8]. Some variation of the partial argon pressure and of the speed of its leakage near the evaporation zone allowed to change the average particle size. The method of chemical precipitation consisted in precipitation of $Fe(OH)_2$ at pH = 10–12 from solution of $FeSO_4$ with following aeration of the obtained suspension by air and heating it to 60–90°C [9]. At laser atomization magnetite was prepared by evaporation of target from a powder of Fe_2O_3 using impulse-periodic laser.

The structure and size of the obtained particles of magnetite were analyzed by X-ray and TEM. The specific surface area was evaluated by BET method (from desorption of Ar). Magnetization was measured with the help a Vibrating Sample Magnetometer in fields to 27 kOe at a room temperature. TEM research was carried out with microscope Philips CM30.

3. Results and discussion

Some physical properties of the tested magnetite samples are summarized in Table 1. Fig. 1 displays visual and TEM images of one of them.

The synthesized powders of magnetite had a dark brown colour, and they consisted of separate particles in the range of 16–54 nm in diameter. The average size of the particles determined by means of the X-ray analysis was close to results of its calculation using data about their specific surface area (the magnetite density used at these calculations was taken as 5,180 kg/m^3 [11]). Besides, direct microscopic measurements of the sizes of the obtained particles of magnetite also have confirmed it (Fig. 2). This proves that all obtained powders of magnetite really consisted from separated nanoparticles of above sizes and did not represent porous agglomerates.

At placing of the synthesized powders into the imitating solution a formation of large aggregates of nanoparticles of magnetite was found. The aggregates had sizes above several microns. The particle-size

Table 1
Properties of Fe_3O_4 nanopowders produced by different methods (dav–the average diameter of particles; Ssp–the specific surface area of particles)

Sample	Preparation method	Structure	Magnetization, A m^2/kg	Ssp (BET), m^2/g	dav (BET/X-ray), nm
1	1	Orthorombic	81	44.3	26/22
2	1	Orthorombic	70	71.2	16/21
3	2	Tetragonal	82	21.9	53/32
4	1	Tetragonal	84	21.4	54/54
5	3	Cubic	76	68.8	17/-
6	3	Cubic	74	49.9	23/-

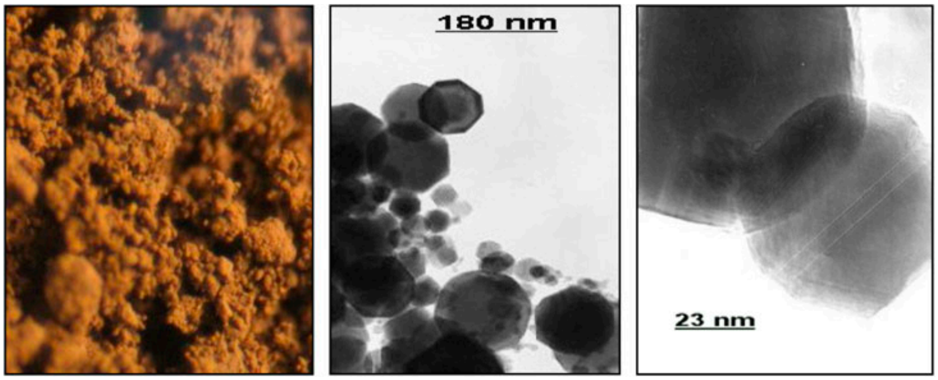

Fig. 1. Typical visual and TEM images of prepared magnetite powder (sample 4).

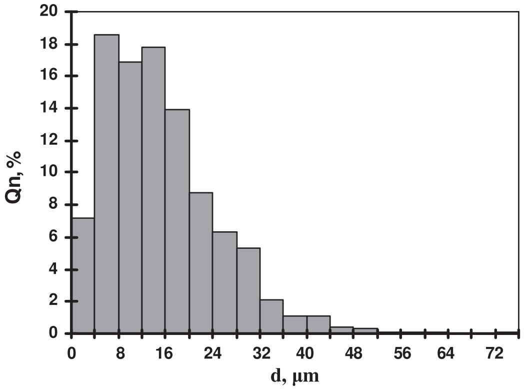

Fig. 2. Size distribution of magnetite particles in sample 5. Q_n is the fraction of particles of size (diameter) *d*.

distribution of these aggregates has been defined by photo-sedimentation method using a speed of their sedimentation in the imitating solution [12]. The calculated specific surface area of these aggregates (the calculation was done using the average size of these aggregates) was about 1,000 times less the specific surface area of the initial nanoparticles of magnetite. These formed aggregates were very steady and were not completely destroyed during mechanical agitation of solutions. However, ultrasound treatment of the suspension resulted in some partial destruction of the aggregates (Fig. 3). In particular, their average size decreased and their calculated specific surface area increased almost in 10 times.

The chemical analysis of the solutions after their exposition during seven days at a room temperature has shown that with increase in mass of magnetite in them, the concentration of Cr(VI) in the solutions decreased, that is a process of sorption of Cr(VI) was observed. However, the influence of the ultrasound resulting in increase of the calculated specific surface area of the formed aggregates of nanoparticles of magnetite (see Fig. 3) did not lead to the subsequent decrease in concentration of Cr(VI) in the solutions (Fig. 4). It points out that the ultrasound did not change the real surface area of the particles of magnetite in the solutions. Hence, in spite of aggregation of nanoparticles of magnetite in the solutions, all their surface remained accessible for sorption. It, in turn, has allowed to compare among themselves sorption efficiency of the powders of magnetite synthesized by different methods (Fig. 5).

From Fig. 5, it is seen that magnetite is enough effective sorbent for the removal of Cr(VI) from

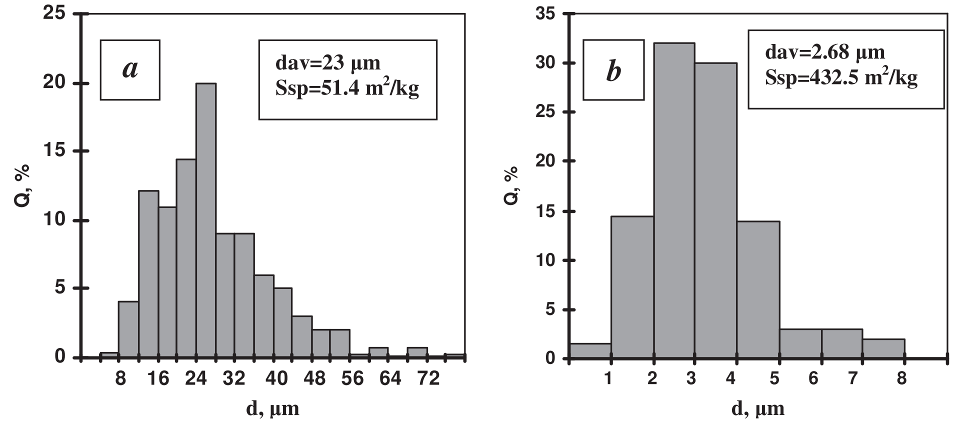

Fig. 3. Influence of ultrasound on particle-size distribution of aggregates of particles of magnetite (sample 1) in the imitating solution: *a*-particle-size distribution of aggregates of magnetite particles in the imitating solution before ultrasound; *b*-the same after ultrasound. *Q* is the mass fraction of aggregates (particles) of diameter (size) *d*.

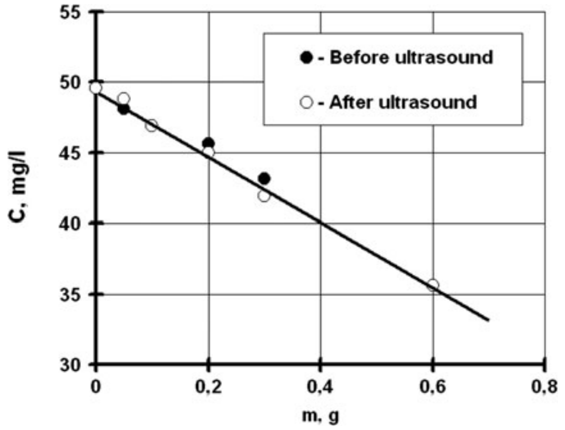

Fig. 4. Ultrasound influence on sorption of Cr(VI) by magnetite (sample 3) at temperature 25 ± 2°C. C is the concentration of Cr(VI) in the imitating solution after sorption; m is the mass of magnetite in the solution.

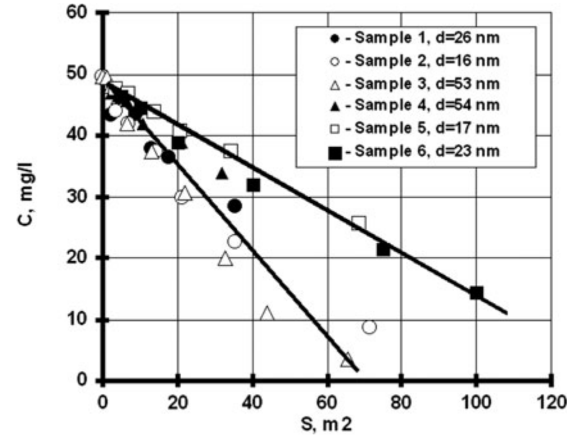

Fig. 5. Change of concentration of Cr(VI) in the imitating solution after sorption at temperature 25 ± 2°C. S is the total surface area of particles of magnetite placed in the solution.

solutions. At its placing in the imitating solution, considerable reduction in concentration of Cr(VI) was reached. This coordinates well with results of [1–6] where adsorption of Cr(VI) by magnetite was also observed.

From Fig. 5, one can see that two straight lines can approximate all received experimental data. The experimental points for the powders of magnetite, which have been obtained by methods of gas-cycle synthesis (samples 1, 2, 4) and by chemical precipitation from water solutions (sample 3) lay down onto the bottom straight line in Fig. 5. And experimental points of the nanoparticles of magnetite produced by the method of laser atomization (samples 5, 6) fall onto the upper straight line in Fig. 5. It is seen that the last powders possess lower sorption ability. However, for all synthesized powders of magnetite, irrespective of the method of their production, in the studied range of their sizes the absence of influence of structure and size of the particles on their sorption ability is observed.

To find out the reason for the lowered sorption ability of samples 5 and 6 an additional more thorough research of them has been conducted. So, X-ray analysis of the nanopowders has shown that they consist of monophase and have maghemite structure with a cubic crystal lattice of type P4332. However, the values of parameters of the lattices of these powders ($a = 8.357 \pm 0.0015\,\text{Å}$ and $a = 8.3627 \pm 0.0008\,\text{Å}$) were considerably more than for Fe_2O_3 ($a = 8{,}34\,\text{Å}$)

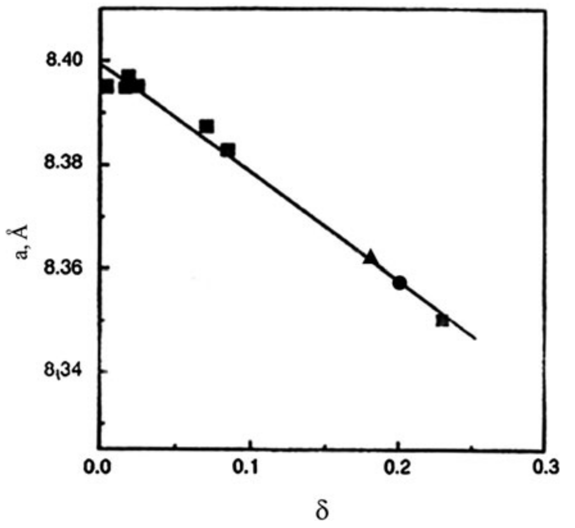

Fig. 6. Influence of size of non-stehiometry δ in $Fe_{3-\delta}O_4$ on the parameter a of a crystal lattice: ■-the data of work [13]; ●-sample 5; ▲-sample 6.

and less than for Fe_3O_4 ($a = 8.396$ Å). This fact may be explained if it is assumed that these nanopowders in comparison with Fe_2O_3 have some deficiency of oxygen, and the part of ions of iron is in a bivalent condition. To check this assumption, we used linear approximation of a dependence of the parameter of the crystal lattice of Fe_3O_4 on a degree of nonstoichiometry δ (Fig. 6) presented in [13]. From this, it follows that sample 5 corresponded to structure of $Fe_{2,8}O_4$ while nanopowder 6 corresponded to structure $Fe_{2,82}O_4$.

The made experiments have shown that efficiency of removal of Cr(VI) from a solution at use of magnetite can be greatly increased if to carry out the sorption process at high temperatures (Fig. 7(a)). As a result, it is possible to reach complete removal (within sensitivity of the method of chemical analysis) of Cr (VI) from the imitating solution. Besides, in this case it is not observed any considerable differences in sorption abilities of the nanopowders of magnetite obtained by different methods. All experimental points, irrespective of the size of the particles of the nanopowders of magnetite and the method of their production, lay down practically onto one and the same straight line (Fig. 7(b)).

Additional experiments have shown that sorption of Cr(VI) by magnetite is an irreversible process. So placement of the samples of magnetite after sorption process at high temperatures into pure (without chrome) imitating solution does not lead to appearance of ions of chrome in the solution. It points out that sorption of Cr(VI) by magnetite is a chemisorption process. A long time required for reaching equilibrium of the sorption process also confirms this (Fig. 8).

Apparently from Fig. 8, the sorption of ions of Cr(VI) by magnetite at a room temperature proceeds very slowly, and even after 80 days from the beginning of the sorption process it does not reach an equilibrium state. Such slow interaction is a characteristic of chemical

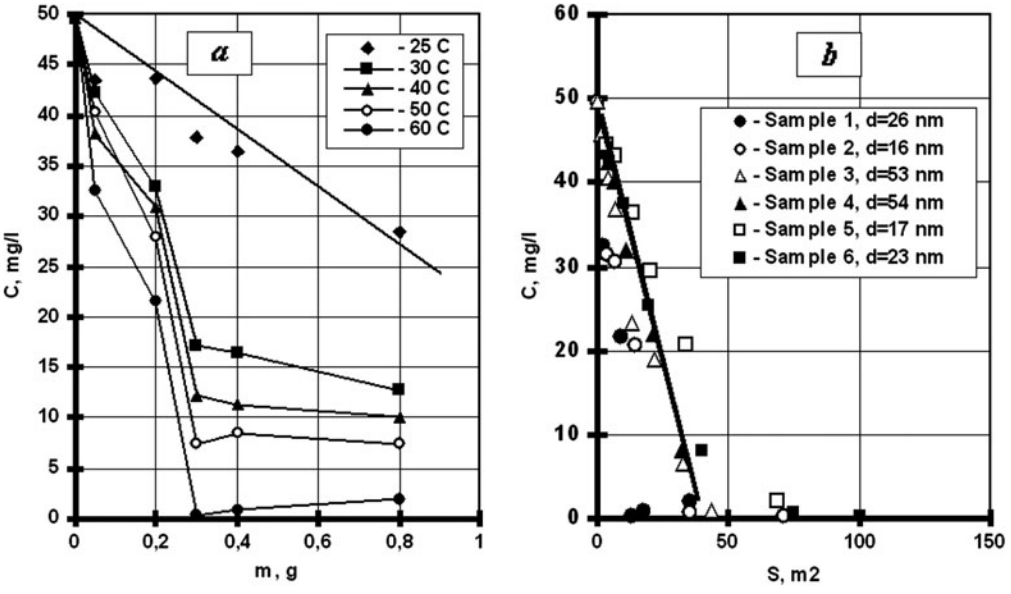

Fig. 7. Influence of temperature on process of sorption of Cr(VI) by nanoparticles of magnetite: (a) sample 1, sorption at different temperatures of the imitating solution; (b) sorption at temperatures 60–80˚C.

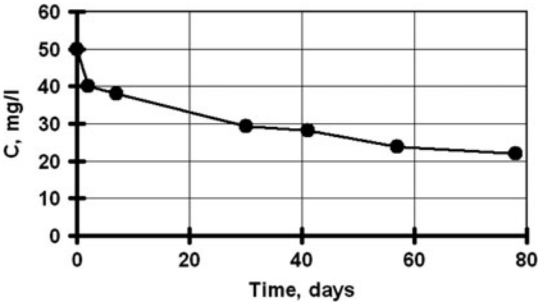

Fig. 8. Kinetics of sorption of Cr(VI) by magnetite at temperature 25 ± 2˚C, sample 2.

reactions with high activation energy and it is not typical for adsorption processes, which are usually coming to an end for 0.5–2 h. From this, it follows that experimental data in Fig. 5 are not in equilibrium, that is, represent not isotherms of adsorption and reflect some intermediate status of the system, and, therefore, the use of adsorption isotherms such as the Langmuir isotherm and Freundlich isotherm in this case is incorrect. Further, it is quite natural that the rise in temperature of realization of the chemical reaction of interaction of Cr(VI) with magnetite leads to significant acceleration (Fig. 7) of the sorption process. On the contrary, the simple physical adsorption supposes the presence of dynamic balance between adsorbent and adsorbate and should decrease with the rise in temperature of the process [14,15]. However, as it was mentioned previously, the made experiments testify that sorption of Cr(VI) by magnetite, on the contrary, increases when temperature rises (see Fig. 7). One can assume that at the interaction of Cr(VI) with magnetite some oxidation–reduction reaction takes place in which Cr(VI) is deoxidized to Cr(III), and Fe(II) in magnetite is oxidized to Fe(III). If this assumption is true, then it becomes clear that the low sorption efficiency of samples 5 and 6 is caused by reduced (in comparison with pure magnetite) content of Fe(II) in them. The given assumption, however, requires an additional experimental check.

It is necessary to notice that a possibility of chemisorption at removing of Cr(VI) from aqueous solutions by magnetite was also mentioned in works [1–5]. So in [1] some traces of additional phases, which could not be identified were observed in a deposit of magnetite after sorption process. In work [2], it was established that process of desorption of Cr(VI) proceeded not completely.

According to very careful research [5] at adsorption of Cr(VI) by magnetite Cr(VI) is deoxidized to Cr(III) and probably even replaces Fe (III) in the lattice of magnetite. Results of the present experiments by indirection confirm this assumption. So in the conditions of our experiments (pH > 7) solubility of Fe(III) and Cr(III) is very, very small. Chemical analysis of the solutions after sorption process showed the absence of ions Fe (II), Fe(III) and Cr(III) in them. TEM analysis also did not establish new solid particles in the sediment. Therefore, formation of Cr(III) is possible only in thin surface layer of particles of magnetite.

4. Conclusions

Results of this study allow to draw following conclusions:

(1) Magnetite is a highly effective sorbent for the removal of Cr(VI) from polluted natural waters and sewage.
(2) Even a small rise in temperature sharply increases efficiency of the sorption process.
(3) Process of sorption of Cr(VI) by magnetite is irreversible and has a chemisorption character.
(4) For all synthesized powders of magnetite, irrespective of a method of their production, in the studied range of their sizes the absence of influence of structure and the sizes of the particles on their sorption ability is observed.
(5) Nanoparticles of magnetite form large aggregates of micron sizes in water solutions. However, it does not influence on process of sorption and all surfaces of the nanoparticles of magnetite in the aggregates are accessible for sorption.
(6) After completion of sorption process, magnetite, thanks to formation of large aggregates from its nanoparticles, can be easily separated from the solution by usual methods used in industry (desilting, filtration).

The mechanism of interaction of Cr (VI) with magnetite is not clear yet and investigation in this direction will be continued.

Acknowledgements

This work was financially supported by the Ural Division of the Russian Academy of Sciences.

References

[1] J.V. Topkin, I.G. Roda, N.V. Anfinogenov, N.N. Prishchep, Removal of ions of heavy metals from a solution by ferrite method, Chem. Technol. Water 12 (1990) 895–897, (in Russian).
[2] A.I. Lesnikovich, S.A. Vorobyova, N.V. Karpenko, Adsorption of Cr (VI) from water solutions by ferrites of cobalt, manganese and iron, Zh. Prikl. Khim. 67 (1994) 500–502, (in Russian).
[3] S.S. Banerjee, M.V. Joshi, R.V. Jayaram, Removal of Cr(VI) and Hg(II) from aqueous solutions using fly ash and impregnate fly ash, Sep. Sci. Technol. 39 (2004) 1611–1629.

[4] J. Zhao, X. Guan, H. Unuma, Preparation of Fe_3O_4 nanoparticles and their application to composite biosorbent, J. Ceram. Soc. Jpn. 115 (2007) 475–478.

[5] R.R. Sheha, A.A. Ei-Zahhar, Synthesis of some ferromagnetic composite resins and their metal removal characteristics in aqueous solutions, J. Hazard. Mater. 150 (2008) 795–803.

[6] P. Yuan, M. Fan, D. Yang, H. He, D. Liu, A. Yuan, J. Zhu, Montmorillonite-supported magnetite nanoparticles for removal of hexavalent chromium [Cr(VI)] from aqueous solutions, J. Hazard. Mater. 166 (2009) 821–829.

[7] The Unified Methods of the Analysis of Sewage, second ed., under the edit. of J.J. Lure, Chemistry, Moscow, 1973 (in Russian).

[8] V.S. Kortov, A.Ye. Yermakov, A.F. Zatsepin, M.A. Ujmin, S.V. Nikiforov, A.A. Mysik, V.S. Gaviko, Features of luminescent properties of nanostructural alumina, Phys. Solid State. 50 (2008) 916–920, (in Russian).

[9] I.A. Weinstein, Clearing and use of sewage of etching branches, Metallurgy, Moscow, 1986, pp. 82–83 (in Russian).

[10] Jur.A. Kotov, V.V. Osipov, M.G. Ivanov, O.M. Samatov, E.I. Azarkevich, A.M. Murzakaev, A.I. Medvedev, V.V. Platonov, Research of characteristics of oxide nanopowders received at target evaporation by impulsno-periodic CO_2-laser J. Techn. Phys. 72 (2002) 76–82 (in Russian).

[11] The short directory of the chemist, 4th ed., under the edit. of O.D. Kurilenko, Naukova Dumka, Kiev, 1974 (in Russian).

[12] P.A. Kouzov, The basic of particle-size distribution analysis of industrial dusts and grinded materials, Chemistry, Leningrad, 1971 (in Russian).

[13] J.B. Yang, X.D. Zhou, W.B. Yelon, W.J. James, Q. Cai, K.V. Gopalakrishnan, S.K. Malik, X.C. Sun, D.E. Nikles, Magnetic and structural studies of the Verwey transition in $Fe_{3-\delta}O_4$ nanoparticles, J. Appl. Phys. 95 (2004) 7540–7542.

[14] J.H. de Boer, The Dynamical Character of Adsorption, Clarendon Press, Oxford, 1953.

[15] Jur. G. Frolov, Course of Colloid Chemistry. The Superficial Phenomena and Disperse Systems, second ed., Chemistry, Moscow, 1988 (in Russian).