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COLLOID REMOVAL FROM AQUA MEDIA VIA MAGNETITE-BASED REAGENT

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Abstract. A new method has been developed to prepare an inexpensive magnetite-based reagent with balanced magnetic and sorption properties for colloidal removal from water solutions. The reagent has been obtained from the salts of ferrous iron at the room temperature. The kaolinite solution with the concentration range of 10 to 30 mg/l was chosen to carry out laboratory tests. The relationship between pH of the solution under treatment and the zeta potential of the reagent was investigated. It was found that the most effective heterocoagulation takes place at $pH = 6.0–6.5$. At $pH > 7.5$, the efficiency of water treatment decreases steeply because of the same sign of the charge and the minimal difference of potentials between the particles of the reagent and kaolinite.

Keywords: magnetite-based reagent, kaolinite, suspended solids, water treatment, zeta potential.

1. Introduction

Widespread in nature, iron oxides find application in different areas of human activities [1, 2], including the nanotechnologies that have progressed rapidly in the last few years [3-7]. Although the researchers go on with investigations of maghemite (g-Fe_2O_3) and hematite (a-Fe_2O_3) [1, 8-11], it is magnetite (Fe_3O_4) that has been most deeply studied recently [12-18]. There are two big areas in the application of magnetite on which particular emphasis should be laid. On the one hand, this is medicine with magnetic resonance imaging, development of immunoassays, magnetic hyperthermia and targeted drug delivery vehicles [3, 19-23]; on the other hand, this is removal of different contaminations from aqueous media [14, 17, 18, 24-29]. Magnetite may be used either in its pure form [16, 30] or as a composite [14, 15, 17, 22, 24-26]. There are different methods to produce magnetite including thermal decomposition [12, 13], coprecipitation of Fe^{3+} and Fe^{2+} with an aqueous NaOH or NH_4OH solution [3, 18, 31], oxidation with hydrogen peroxide H_2O_2 of ferrous hydroxide $Fe(OH)_2$ in the form of suspension [16, 34, 35], microemulsion technique [37] and ultrasound irradiation [22].

Preparation of magnetic nanoparticles with adjustable morphology and properties can be of great importance (*e.g.* for magnetic hyperthermia) [16] or does not matter a lot (*e.g.* for removal of heavy metal ions from wastewater) [4, 8, 27, 32, 33]. In keeping with the application purpose, the preparation technique should be chosen, that also affects the price of the synthesized nanoparticles.

The aim of this study was the synthesis of inexpensive magnetite-based reagent for removal of colloidal particles from aqueous media as well as the investigation of its properties under different conditions (pH of the reagent obtaining, pH of the medium, the solution temperature, the stirring gradient *etc*.). The application of pure magnetite as a reagent does not pay off, because it has a low adsorption capacity, possessing, however, good magnetic properties, which allow sludge separation by devices creating external magnetic fields [38, 39]. Elimination of the colloidal particles occurs *via* the heterocoagulation of the positively charged reagent with the negatively charged particles of suspended solids like kaolinite, bentonite, vermiculite, *i.e.* the mineral particles with the average size of 0.1–4 µm, and the specific surface of 100–750 m^2/g. The heterocoagulation takes place at pH values bellow the point of zero charge (PZC) of the reagent [40, 41]. The magnetite-based reagent in this study was obtained by the air blowing of ferrous solution containing iron in the divalent state with preliminary introduction of alkali to obtain pH > 7, instead of conventional technique of magnetite preparation *via* coprecipitation of ferric and ferrous salts, such as $FeCl_2·4H_2O$ and $FeCl_3·6H_2O$ [3, 18, 22, 31, 42] or $FeSO_4·7H_2O$ and $FeCl_3·6H_2O$ [30].

2. Experimental

2.1. Preparation of the Magnetite-Based Reagent

The general technique of the reagent obtaining consists of the following steps: the preparation of the Fe(II) solution; alkalization of the solution; the partial oxidation of the iron ions to produce the magnetite-based reagent. $FeSO_4$ and distilled water were used to obtain the Fe(II) solution. The iron ions concentration was 5 g/l. The solutions with pH ranged from 10 to 11.5 were prepared *via* alkalization using sodium hydroxide. The ionic strength was adjusted by an inert electrolyte (sodium chloride). After that, the air with the flow rate of 0.7–0.9 cm^3/s was blown to produce the nanoparticles of magnetite. The magnetite-based reagent was obtained after 40 min of blowing at room temperature.

2.2. Preparation of the Kaolinite Solution

Kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) was chosen to simulate mineral colloidal contaminations of water. The suspension of kaolinite was prepared using distilled water at pH = 7 and room temperature.

2.3. Zeta Potential Determination

The zeta potential was estimated using a microphoretic cell made of optical glass and then calculated as the arithmetic average of twenty measurements carried out at the constant ionic strength. It was achieved by the use of indifferent electrolyte (sodium chloride). The zeta potential was estimated 24 h after the reagent had been prepared.

3. Results and Discussion

The removal of mineral colloidal contaminations from water with the use of the magnetite-based reagent occurs by means of heterocoagulation followed by the withdrawal of the agglomerated particles with the help of a magnetic filter. The surface charge of the particles is of paramount importance in the process. The zeta potential allows estimating the surface charge.

There are factors that may have an influence on the zeta potential, such as temperature and salt content. However, they can be neglected, as applied to superficial water [43].

The correlation between the zeta potential, pH of the reagent preparation and pH of the treated aqueous medium is presented in Fig. 1. As evident from the figure, the PZCs of the magnetite-based reagent shift to the left, into the zone of neutral pHs, as pH of the reagent preparation increases. The reason is that the oxidation of Fe(II) is more intensive at higher pHs, and the content of the hydrated magnetite

($FeO \cdot Fe_2O_3 \cdot nH_2O$) in the prepared reagent rises. Later, the PZC of the reagent shifts to the zone of the low pHs, as the investigation of the one-year old reagent shows (Fig. 1). This is because the solid phase is dehydrated and the oxyhydrated forms turn to the oxide ones.
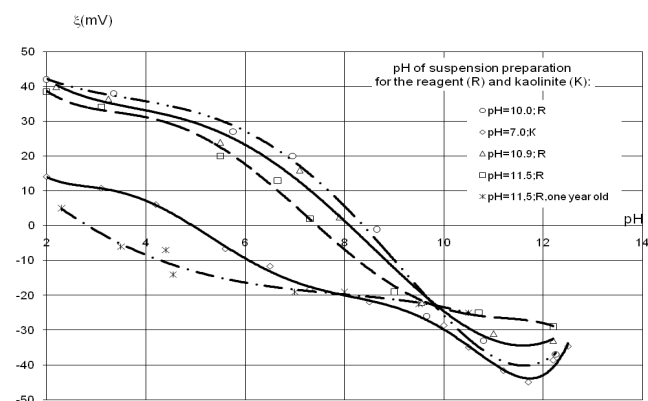

Fig. 1. Relationship between the zeta potential and pH of treated aqueous medium

The correlation between the zeta potential of kaolinite and pH of the solution is presented in Fig. 1 as well. The ionic strength of the solution was constant at different pHs. The PZC of kaolinite corresponds to pH = 5. The zeta potential is equal to 15 mV at the neutral pH, as shown in Fig. 1.

When the zeta potential of kaolinite is compared with that of the magnetite-based reagent, it is apparent that the signs of potentials are different and their difference makes up about 30 mV at pH = 5.5–7.0. The heterocoagulation must be the most effective in this range.
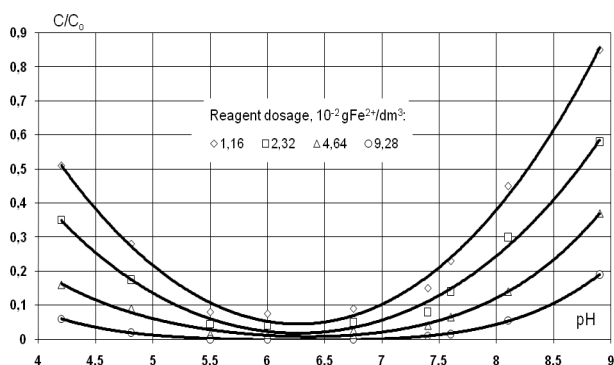

Fig. 2. Efficiency of kaolinite removal as a function of pH. Initial concentration of kaolinite is 20 mg/l, pH of the reagent preparation is 10.0

It was confirmed in the course of the further laboratory investigations. The reagent was dropped into the water with kaolinite. After that the solution was run through

a magnetic filter. Fig. 2 presents the removal of kaolinite as a function of pH. Here C_0 is the initial concentration of kaolinite; C is the concentration of kaolinite after the filter. Because of big linear dimensions of the units in filtering medium and its big porosity (see Table 1), the removal of nonferromagnetic substances is less than 5 % (by mass) at filtration rate of 40 m/h.

Table 1

Filter bed porosity of crushed barium ferrite

Diameter of fraction, mm	Porosity[a], %	
	Packed filter bed	Bulked filter bed
7–10	48.4–56.0	51.7–70.0
5–7	48.5–55.6	54.7–68.7
3.5–5	50.0–54.6	56.7–67.5

[a]The first value is for the unmagnetized material and the second one is for magnetized material

The efficiency of the kaolinite removal decreases steeply at pH > 7.5 as shown in Fig. 2. This is consistent with the abatement of difference between the zeta potentials of kaolinite and the magnetite-based reagent under alkaline conditions (Fig. 3). At pH > 8.5 the zeta potential of both kaolinite and reagent has the same sign. Moreover, the amount of anionic groups, which hinder heterocoagulation being adsorbed on the kaolinite surface, increases with pH.
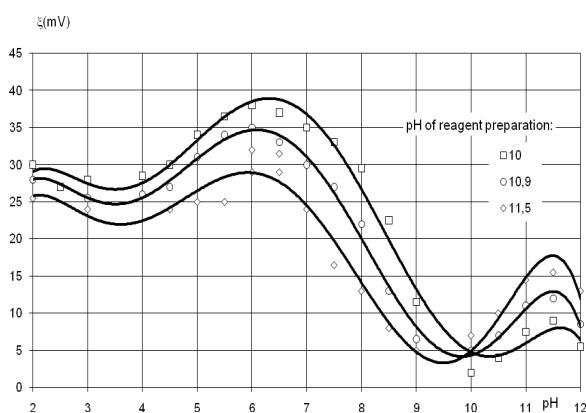
Fig. 3. Difference between the zeta potentials of kaolinite and the magnetite-based reagent

At lower pHs, when the zeta potential of kaolinite gets over its zero value and obtains the same sign as the reagent, the efficiency of kaolinite-reagent interaction doesn't decrease, because there is no anionic groups adsorbed on the surface.

In the pH range of the reagent preparation from 10.0 to 11.5, the smaller value of pH corresponds to the bigger value of zeta potential, that causes more effective heterocoagulation of kaolinite and the magnetite-based reagent. The application of the reagent prepared at pH = 10.0 makes it possible to reduce the kaolinite concentration in the solution more then in case of the reagents prepared at pH 10.9 or 11.5, as shown in Fig. 4.
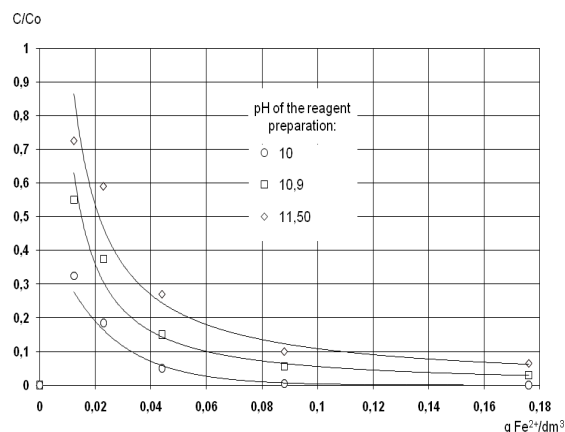
Fig. 4. Relationship between the kaolinite removal and the reagent dosage. Initial concentration of kaolinite is 20 mg/l, pH of the solution is 7.8
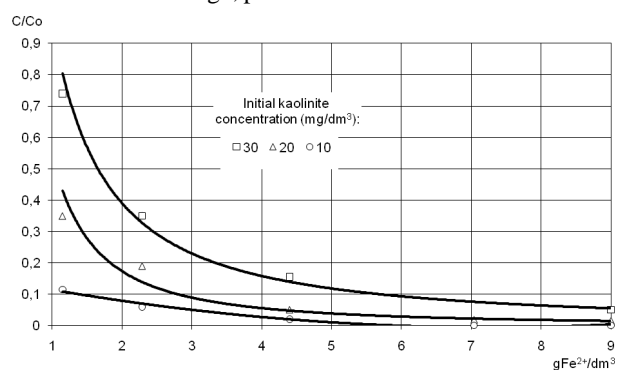
Fig. 5. Efficiency of water treatment at different initial concentrations of kaolinite as a function of the reagent dosage. pH of the reagent preparation is 10.0

To reach the value $C/C_0 = 0.1$, it is necessary to take $3.5 \cdot 10^{-2}$, $6.5 \cdot 10^{-2}$ and $9.0 \cdot 10^{-2}$ g Fe^{2+}/dm^3 reagent, prepared at pH = 10.0, 10.9 and 11.5, respectively. However, only the reagent dosage of $4.7 \cdot 10^{-2}$, $11.3 \cdot 10^{-2}$ and $24.4 \cdot 10^{-2}$ g Fe^{2+}/dm^3 respectively, allows decreasing of C/C_0 to the value of 0.05. Thereby, pH of the reagent preparing is very important to achieve the high quality of water treatment.

The spread of the specific reagent dosages (per 1 mg of suspended solids) reduces as the degree of purification increases (Fig. 5). It is necessary $1.5 \cdot 10^{-2}$; $3.6 \cdot 10^{-2}$; $5.86 \cdot 10^{-2}$ g Fe^{2+}/dm^3 to reach $C/C_0 = 0.1$ at the initial kaolinite concentrations of 10, 20 and 30 mg/dm³, respectively. The specific reagent dosage is equal to $1.5 \cdot 10^{-2}/10 = 0.15 \cdot 10^{-2}$ g Fe^{2+}/mg; $3.6/20 = 0.18 \cdot 10^{-2}$ g Fe^{2+}/mg; $5.86/30 =$

=0.20·10⁻² g Fe²⁺/mg for C/C_0 = 0.1 and 2.7·10⁻²/10 = =0.27·10⁻² g Fe²⁺/mg; 5.5·10⁻²/20 = 0.275·10⁻² g Fe²⁺/mg; 9.0·10⁻²/30 = 0.3·10⁻² g Fe²⁺/mg for C/C_0 = 0.05. The reason is that the higher degree of purification requires the bigger amount of the reagent. In consequence of this, the number of particles in solution and the frequency of collisions increase, culminating in agglomeration of particles with big magnetic moment that can be easily removed by a magnetic filter.

The frequency of particle collisions increases with the stirring rate and the stirring time. The residual concentration of kaolinite in the solution falls exponentially with the stirring time, as presented in Fig. 6. 90 % of the initial suspended solids are removed within the first five minutes.

The effect of the time and rate of stirring was estimated based on the Camp term [44], conventionally used to appreciate, how the stirring parameters impact on agglomeration/disagglomeration of particles [45-49]. The Camp term GT is the product of velocity gradient G and the stirring time T. The velocity gradient was estimated as follows:

$$G = \sqrt{\frac{P}{Vm}} \qquad (1)$$

where V is the mixer volume (m³), m is the dynamic viscosity of the fluid (kg/m/s), P is the average power consumption (W), obtained *via*:
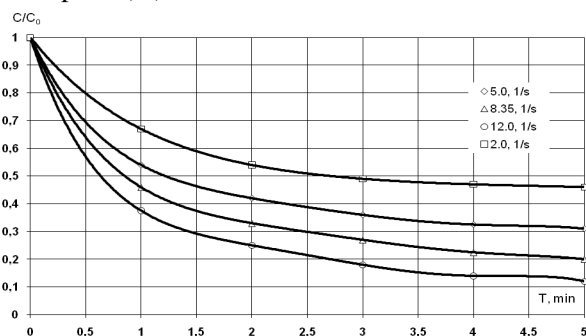

Fig. 6. Relationship between the stirring time and efficiency of kaolinite removal. Initial concentration of kaolinite is 20 mg/l; the temperature of the solution is 289 K; pH of the solution is 7.2; pH of the reagent preparation is 10.0; the reagent dosage is 2.32·10⁻² g Fe²⁺/dm³

$$P = 1.1 r N^3 D^5 \qquad (2)$$

where r is the fluid density (kg/m³), N is the rotational speed of the impeller (s⁻¹), D is the diameter of the impeller (m).

Based on the Camp term, the relationship between C/C_0 and lg(GT) was developed for the stirring parameters, laying in the range from 2 to 12 s⁻¹ (stirring rate) and from 0.5 to 70 min (stirring time). The residual concentrations of kaolinite reach their minimum at $GT = 10^8$–10^9, as shown in Fig. 7. After that, the slight increasing of residual concentrations occurs pertaining to the reagent altering.
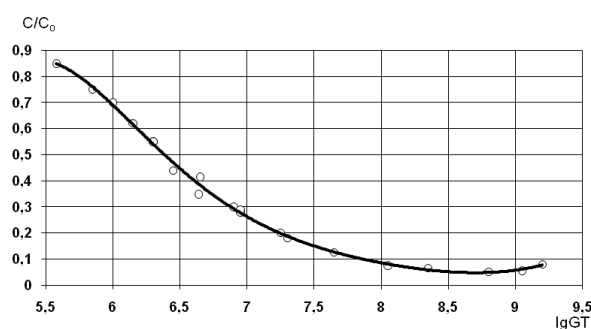

Fig.7. Residual kaolinite concentration as a function of Camp term

The magnetite-based reagent compared to the conventional coagulant ($Al_2(SO_4)_3$) and flocculant (polyacrylamide) [43] has the advantage of wide range of operating temperatures. The temperature has a greater impact on the treatment efficiency, when a coagulant is used (see Table 2). The residual concentration of kaolinite in solution rises twice as the temperature decreases from 293 to 278 K (in case of coagulant) [43]. As for a flocculant, the temperature decreasing improves the treatment efficiency [43]. The magnetite-based reagent is unsusceptible to the temperature owing to the preformed structure of its particles and the absence of chemical conversions after adding the reagent to the solution.

Table 2

The influence of the solution temperature on the residual concentration of kaolinite[a],%

Type of the reagent	Temperature, K											
	274				283				293			
	Time of treatment, min											
	5	10	20	50	5	10	20	50	5	10	20	50
Coagulant ($Al_2(SO_4)_3$)	83	70	54	39	80	57	39	29	69	58	28	17
Flocculant (polyacrylamide)	72	50	19	16	72	50	20	17	79	59	28	20
Magnetite-based reagent	—	—	—	—	20	18	18	18	19	18	18	18

[a] The dosage of coagulant is 20 mg/dm³; flocculant is 0.25 mg/dm³; magnetite-based reagent is 20 mg/dm³; at n = 5 s⁻¹; the residual concentration is given as a percentage of the initial concentration.

The settling velocity of aggregated particles after the treatment with the magnetite-based reagent is slightly over the settling velocity of the particles after the coagulant treatment. The process time shortens as the stirring rate increases and/or percolation of the solution through a magnetic filter is carried out. Moreover, the magnetite-based reagent allows considerable decreasing of the process time compared with coagulant or flocculant on retention of the treatment efficiency, as it is presented in Fig. 8.
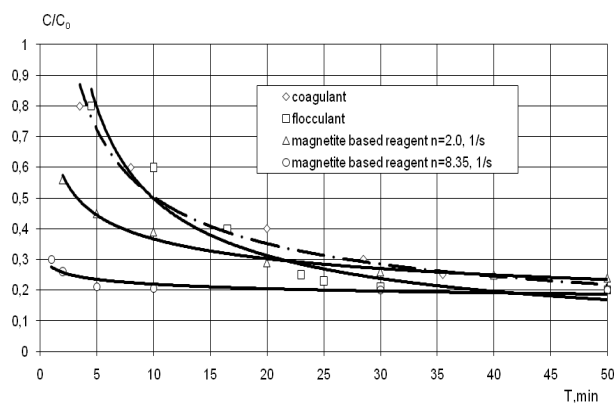

Fig. 8. Efficiency of the kaolinite removal with coagulant, flocculant and magnetite-based reagent (pH of reagent preparation is 10.0, pH of the solution is 7.2, the dosage of magnetite-based reagent is 2.32 mg/dm^3, the coagulant dosage is 20 mg/dm^3, the flocculant dosage is 0.25 mg/dm^3)

The equal residual concentrations of kaolinite in the solution are obtained after 50 min with coagulant, 20 min with flocculant and 5 min with the magnetite-based reagent (the Camp term $GT = 3.9 \cdot 10^5$, filtering velocity is 40 m/h).

The heterocoagulation of kaolinite and the magnetite-based reagent go faster with increasing of the stirring rate. Even at the stirring rate $n = 12s^{-1}$ and $GT = 7.1 \cdot 10^8$, there is no destruction of aggregated particles and the residual concentration of kaolinite is less than 2 % on retention of other initial conditions (the temperature of the solution, the concentrations of kaolinite and the magnetite-based reagent).

4. Conclusions

A new method has been developed to prepare an inexpensive magnetite-based reagent with balanced magnetic and sorption properties for removal of colloidal particles from aqua media. The reagent has been obtained from the salts of ferrous iron at the room temperature. In this case, the formation of the reagent goes through the stage of the mix of the ferrous and ferric iron hydrates, then the stage of oxyhydrates and finally to the compounds of hydrated oxides and oxyhydrates. The sorptive capacity decreases and the magnetic susceptibility grows along this chain. Being optimized relative to the concentration, the speed of the oxidizer inlet and pH of the solution, the reagent with balanced magnetic and sorption properties were obtained.

The weak solution of kaolinite that has the commensurable size of particles with the magnetite-based reagent was used to investigate the removal of inorganic colloidal contaminations from water. The kaolinite concentration was 10–30 mg/dm^3. The reagent was prepared at pHs of 10.0; 10.9 and 11.5. The water treatment consisted of dropping of the magnetite-based reagent into the kaolinite solution, mixing and filtering through the magnetic filter. The use of the reagent obtained at pH of 10.0 allows the better removal of kaolinite compared to the higher pH values (10.9 and 11.5). The reason is that the sorption component decreases and the magnetic component of the reagent increases with the growth of pH.

pH of the aqua medium has an effect on the zeta potentials of the reagent and kaolinite and finally on the treatment efficiency. In the pH range from 6.0 to 6.5 the heterocoagulation is maximal, and the residual kaolinite concentration in the treated solution is less than 5 % of the initial concentration. The interaction between the particles of the reagent and kaolinite abates as pH increases because the difference of their zeta potentials gets smaller. Moreover, the amount of hydroxyl groups, which are adsorbed on the surface of particles and inhibit their aggregation, rises.

The particles interact more intensive as the speed and the time of mixing increase, that leads to the exponential decreasing of the residual kaolinite concentration. The minimal residual concentration of suspended solids were observed at the Camp term $GT = 10^8–10^9$. There is a small rise in the residual concentration as the Camp term increases further. This is because of the partial desorption of suspended solids owing to the reagent syneresis.

Acknowledgments

References

[1] Teja A. and Koh P.: Progr. Crystal Growth & Character. Mater., 2009, **55**, 22.
[2] Cornell R. and Schwertmann U.: The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses. 2nd edn. Wiley-VCH, Weinheim 2003.
[3] Zhao D.-L., Zeng X.-W., Xia Q.-S. and Tang J.-T.: J. Alloys Compd., 2009, **469**, 215.
[4] Majewski P. and Thierry B.: Critical Rev. in Solid State and Mater. Sci., 2007, **32**, 203.
[5] Sun C., Lee J. and Zhang M.: Adv. Drug Delivery Rev., 2008, **60,** 1252.

[6] Zhang J. and Misra R.: Acta Biomater., 2007, **3**, 838.
[7] Yang H. *et al.*: Anal. Chem., 2004, **76**, 1316.
[8] Yusuf S. *et al.*: Physica B, 2009, doi:10.1016/j.physb.2009.11.040
[9] de Almeida M. *et al.*: J. Alloys Compd., 2009, doi:10.1016/j.jallcom.2009.10.245
[10] Zhang Z. and Chen X.: J. Alloys Compd., 2009, **488**, 339.
[11] Gurmen S. and Ebin B.: J. Alloys Compd., 2009, doi:10.1016/j.jallcom.2009.11.186
[12] Pei W. *et al.*: J. Magn. Magn. Mater., 2007, **310**, 2375.
[13] Maity D. *et al.*: J. Magn. Magn. Mater., 2009, **321**, 3093.
[14] Hu H. *et al.*: J. Alloys Compd., 2009, doi:10.1016/j.jallcom.2009.11.204
[15] Hong R. *et al.*: J. Alloys Compd., 2009, **476**, 612.
[16] Chen J. *et al.*: J. Alloys Compd., 2009, **475**, 898.
[17] Zhao X. *et al.*: J. Haz. Mat., 2010, **173**, 102.
[18] Illes E. and Tombacz E.: J. Colloid Interface Sci., 2006, **295**, 115.
[19] Qiang Y. *et al.*: J. Nanoparticle Res., 2006, **8**, 489.
[20] Xu Z. *et al.*: Chemical Engineering Sci., 2006, **61**, 1027.
[21] Gonzales M. and Krishnan K.: J. Magn. Magn. Mater., 2005, **293**, 265.
[22] Zhao D.-L. *et al.*: J. Alloys Compd., 2009, **477**, 739.
[23] Feng B. *et al.*: J. Alloys Compd., 2009, **473**, 356.
[24] Ozay O. *et al.*: Water Res., 2009, **43**, 4403.
[25] Yuan P. *et al.*: J. Haz. Mater., 2010, **173**, 614.
[26] Chang Y.-C. and Chen D.-H.: J. Colloid Interface Sci., 2005, **283**, 446.
[27] Hu J., Lo I. and Chen G.: Separ. Purif. Technol., 2007, **56**, 249.
[28] Kushka O., Kochetov G. and Stepova N.: Ekotechnologii i Resursosberegenie, 2003, **2**, 52.
[29] Kushka O., Stepova N. and Kochetov G.: Ekotechnologii i Resursosberegenie, 2001, **4**, 44.
[30] Valenzuela R. *et al.*: J. Alloys Compd., 2009, **488**, 227.
[31] Frimpong R., Dou J., Pechan M. and Hilt J.: J. Magn. Magn. Mater., 2010, **322**, 326.
[32] Hu J., Chen G. and Lo I.: Water Res., 2005, **39**, 4528.
[33] Oliveira L., Petkowicz D., Smaniotto A. and Pergher S.: Water Res., 2004, **38**, 3699.
[34] Rossi L., Quach A. and Rosenzweig Z.: Anal. Bioanal. Chem., 2004, **380**, 606.
[35] Tada M. *et. al.*: J. Appl. Phys., 2003, **93**, 7566.
[36] Kushka O. and Stepova N.: Abstracts of the 65th conference in Kyiv National University of Construction and Architecture, 2004, Part 2, 41.

[37] Lee K., Sorensen C., Klabunde K. and Hadjipanayis G.: IEEE Trans. Magn., 1992, **28**, 3180.
[38] Booker N. *et al.*: Water Sci. Technol., 1991, **23**, 1703.
[39] Orbell J. *et al.*: J.Chem.Educ., 1997, **74**, 1446.
[40] Tombacz E. *et al.*: Organic Geochem., 2004, **35**, 257.
[41] Tombacz E., Csanaky Cs. and Illes E.: Colloid & Polym. Sci., 2001, **279**, 484.
[42] Sun Z., Su F., Forsling W. and Samskog P.: J. Colloid Interface Sci., 1998, **197**, 151.
[43] Montadi M. and Rao R.: Water Res., 1973, **5**, 747.
[44] Camp T.: Transact. Am. Soc. Civil Eng., 1954, **120**, 1.
[45] Ormeci B. and Ahmad A.: Water Res., 2009, **43**, 3249.
[46] Cuthbertson A. *et al.*: Coast. Eng., 2009, doi:10.1016/j.coastaleng.2009.11.011
[47] Pejrup M. and Mikkelsen O.: Estuar. Coast. Shelf Sci., 2009, doi:10.1016/j.ecss.2009.09.028
[48] Stricot M. *et al.*: Water Res., 2010, doi:10.1016/j.watres.2009.12.021
[49] Bridgeman J., Jefferson B. and Parsons S.: Adv. Eng. Software, 2010, **41**, 99.

ВИЛУЧЕННЯ КОЛОЇДІВ З ВОДНИХ СЕРЕДОВИЩ ЗА ДОПОМОГОЮ ФЕРОРЕАГЕНТУ

Анотація. Розроблено новий метод для приготування недорогогоферореагенту зі збалансованими магнітними та сорбційними властивостями для вилучення колоїдів з водних розчинів. Реагент отриманий із солей двовалентного заліза при кімнатній температурі. Для проведення лабораторних досліджень використовувався розчин каолініту у діапазоні концентрацій від 10 до 30 мг/л. Досліджений зв'язок між рН оброблюваного розчину та дзета-потенціалом ферореагенту. Встановлено, що найбільш ефективно гетерокоагуляція відбувається при рН = 6.0–6.5. При рН > 7.5 ефективність очищення води різко зменшується внаслідок однакового знаку поверхневого заряду та мінімальної різниці потенціалів між частками реагенту та каолініту.

Ключові слова: реагент на основі магнетиту, каолініт, завислі речовини, очищення води, дзета-потенціал.