Formation characteristics of Fe_3O_4 magnetic particles precipitated from aqueous solutions and their sorption properties

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Effect of temperature and iron concentration in solution on the phase composition, particle size, and magnetization was studied. It is shown that amount of the magnetite phase increases with the temperature increase. The magnetization slightly decreases with increase in the initial iron concentration. It is found that, regardless of the deposition conditions, spherical particles are formed, the average size of which varies within 7 to 15 nm. Comparison between the for removal efficiency and sorption capacity of the particles with the magnetite and hematite phase for cobalt was carried out. The sorption capacity of the particles is essentially independent of the phase composition and is about 18 mg/g for cobalt. For preparation of sorption material based on Fe_3O_4 magnetic particles, it is recommended to carry out the precipitation at the temperature of not lower than 80°C and the concentration of iron in solution of 0.15 to 0.3 M. The resulting particles comprise not less than 90 wt. % of magnetite phase and are characterized by magnetization of 65 to 70 A·m^2/kg.

Keywords: nanoparticles, Fe_3O_4, magnetization, sorption.

Изучено влияние температуры и концентрации железа в растворе на фазовый состав, размер частиц и их намагниченность. Показано, что чем выше температура, тем больше содержание фазы магнетита в образце. С ростом исходной концентрации железа в растворе намагниченность незначительно уменьшается. Установлено, что независимо от условий осаждения формируются сферические частицы, средний размер которых варьируется в пределах 7 до 15 нм. Проведено сравнение эффективности извлечения и сорбционной емкости по кобальту для частиц с фазой магнетита и гематита. Сорбционная емкость частиц практически не зависит от фазового состава и составляет по кобальту порядка 18 мг/г. Для получения сорбционного материала на основе магнитных частиц Fe_3O_4 рекомендовано проведение осаждения при температуре не ниже 80°C и концентрации железа в растворе 0.15–0.3 M. Полученные частицы содержат не менее 90 мас. % фазы магнетита и характеризуются намагниченностью 65–70 А·м^2/кг.

Особливості формування магнітних часток Fe₃O₄ при осадженні з водних розчинів та їх сорбційні властивості. *О.М.Одноволова, Д.С.Софронов, А.М.Пузан, В.М.Баумер, К.Ю.Брильова, П.В.Матейченко, С.М.Десенко, О.М.Вовк, К.О.Мозуль.*

Досліджено вплив температури та концентрації феруму у розчині на фазовий склад, розмір частинок та намагніченість. Показано, що чим вища температура, тим більше вміст фази магнітиту у зразку. Зі збільшенням вихідної концентрації феруму у розчині намагніченість незначною мірою зменшується. Виявлено, що незалежно від умов осадження формуються сферичні частинки середній розмір яких коливається у межах від 7 до 15 нм. Проведено порівняння ефективності вилучення та сорбційної ємності кобальту для частинок з фазою магнітиту та гематиту. Сорбційна емність частинок майже не залежить від фазового складу і становить для кобальту 18 мг/г. Для одержання сорбційного матеріалу на основі магнітних частинок Fe₃O₄ запропоновано проведення осадження за температури не нижче ніж 80°C, та концентрації феруму у розчині 0,15–0,3 М. Одержані частинки містять не менш, ніж 90 мас. % магнетиту, та характеризуються намагніченістю 65–70 А·м²/кг.

1. Introduction

Magnetic particles are considered as promising material for water purification from heavy metal ions and radioactive nuclides. They have an advantage in comparison with of other sorbents because they can be removed by applying of magnetic field to facilitate isolation, separation and reprocessing in the purification technology [1].Their magnetic properties depend on different factors such as chemical composition, particle size and shape, structure and extent of its deformation, etc., allowing to control magnetic properties of the particles by varying preparation conditions [2]. Generally, Fe_3O_4 is used as magnetic material because of simplicity of the synthesis and high magnetic characteristics as compared to other iron oxides. In addition, it has good sorption properties. In particular, Fe_3O_4 particles efficiently (more than 95 %) remove copper, nickel and cadmium from solutions with pH above 7, as well as Cr(VI) at pH 2–4 [3]. The sorption capacity of the particles at pH 2.5 for lead and CrO_4^{2-} is 29 mg/g [4] and 180 mg/g [5], respectively. Modified magnetic particles (Fe_3O_4/NiO and Fe_3O_4/MnO₂) have the sorption capacity for As(V) of 117.6 mg/g [6] and 69 mg/g [7], respectively.

A principal method of Fe_3O_4 preparation is precipitation from aqueous solutions of Fe^{2+} and Fe^{3+} salts by aqueous ammonia solution. The method is simple and productive. However, when precipitated from aqueous solutions, Fe_3O_4 particles demonstrate changes in magnetization from 5 to 100 A·m²/kg. Reasons for the magnetization changes of the particles in such wide ranges have not been revealed despite of numerous publications on its synthesis and investigation of the properties [8]. The mag-

netization changes of the particles were suggested to associate with changes in their morphological characteristics. For example, it was found that during investigation of magnetic particles, prepared by oxidation $FeCl_2$ solution at 134°C and 2 atm for 3 h, their magnetization varies within 53.3 to 97.4 A·m²/kg and depends on the particles size [9]. The particle magnetization decreases with the size decrease. However, magnetic properties of the particles can be greatly influenced by the phase composition, which in turns can be influenced by the synthesis conditions.

It is necessary to consider not only sorption properties but also magnetic properties during development of the sorption material based on the magnetic particles. Thus, determination of the factors influenced on the magnetization changes of Fe_3O_4 particles, when precipitated from water solutions, is a relevant objective for the development of the efficient magnetic sorption materials.

Accordingly, the aim of the present study is to determine factors influenced on the magnetization of Fe_3O_4 particles when precipitated from water solutions, as well as to compare between sorption properties of magnetic Fe_3O_4 and nonmagnetic Fe_2O_3 particles.

2. Experimental

2.1. Preparation of Fe3O4 particles

For synthesis 40 % aqueous solution ammonia, $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$ (Reachim company) were used. Purification grade of all reagents was chemically pure. All solutions were prepared using distilled water.

Precipitation of Fe_3O_4 was carried out as follows: required amounts of $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ (in the ratio $c(Fe^{3+}):c(Fe^{2+})$ = 2:1) were weighted and dissolved in dis-

tilled water. Total content of iron was in the range of 0.15 to 1 M. Resulting mixture was placed in a thermostat and kept until the required temperature (15, 20, 40, 60 and 90°C) was reached. Then the aqueous ammonia solution was added until pH reached 9 and the resulting solution was stirred for 30 min. Then the precipitate was separated by centrifugation, washed with distilled water until the odor of ammonia was absent, dried in the air at room temperature for 24 h.

2.2. Preparation of Fe_2O_3 particles

Fe_2O_3 particles were prepared as follows: aqueous ammonia solution was added to 100 ml of 0.1 M $FeCl_3$ solution until pH reached 11 and the resulting solution was stirred using a magnetic stir bar for 15 min. The resulting precipitate was filtered, washed several times with distilled water, and dried at the room temperature for 24 h, and then it was calcined at 450°C for 1 h to give α-Fe_2O_3 (hematite). BET surface area of the particles was 150 m^2/g.

2.3. Sorption properties

Sorption was carried out using model solutions containing only cobalt salt at pH 6.5 and in concentration range of 10 to 250 mg/l. Standard cobalt solution with concentration 1 mg/cm^3 (State standard sample of Ukraine No. 022.78-98) was used. The model solution (50 mL) was poured in 100 mL beaker and pH was adjusted by adding nitric acid or aqueous ammonia to predetermined value 6.5. Then 0.1 g of the sorbent was added and the solution was held with stirring for 40 min. In the course of sorption the pH was measured every 10 min and in the case of deviation greater than 0.1 units of pH the suitable adjustment to the setpoint was carried out. After sorption the sorbent was filtered and the metals content in the filtrate was found by atomic emission spectrometry with inductively coupled plasma.

2.4. Equipment

X-ray diffraction analysis of the samples was performed on powder diffractometer Siemens D500 in copper radiation with a graphite monochromator in the secondary beam. Full height X-ray patterns were measured at angles of $10 < 2\theta < 110°$ with a step of 0.02° and 10M s integration time at each point. The value of pH was measured by pH-meter millivoltmeter pH-150 equipped with a glass electrode ECL-43-11
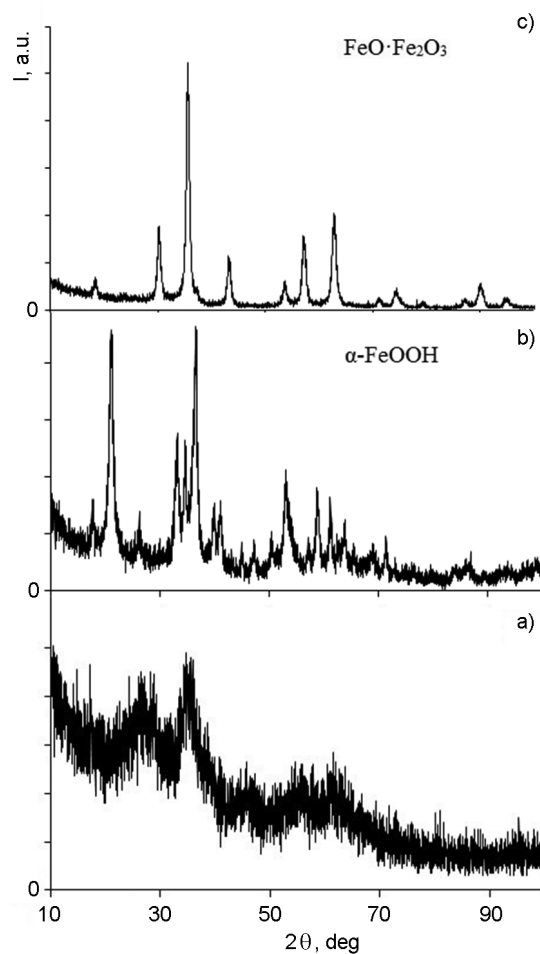

Fig. 1. X-ray patterns of particles, obtained at 15°C (a) and 20°C (b) (total iron concentration in the solution is 1 M) and 90°C (c) (a total iron concentration in the solution is 0.15 M).

and silver chloride reference electrode EVL1MZ. Magnetization was measured using a laboratory-scale pendulum magnetometer at 300 K in the fields significantly higher than effective magnetic anisotropy field [10] (up to 1300 kA/m). The magnetometer was calibrated using electrolytic nickel. Compacted magnetite powder (packing factor $p \sim 0.4$) in amount of 15 to 20 mg was placed in a quartz capsule followed by the particle fixation using glue BF-2. All magnetization curves were recorded using the powder that hadn't been exposed to magnetic field. Investigation of morphology of the resulting powders surface was performed using microscope EM-125 (Selmi, Ukraine). The accelerating voltage of electrons was 125 kV, measurements were done in the light-field mode, images were recorded by CCD matrix. For prepara-
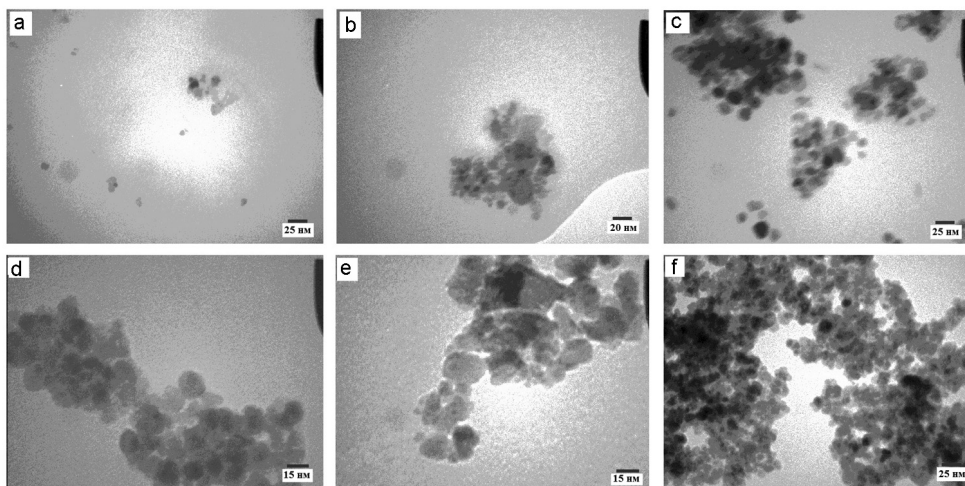
Fig. 2. TEM images of Fe_3O_4 particles obtained from iron chloride and sulphate solutions (in the ratio $c(Fe^{3+}):c(Fe^{2+})$ = 2:1) at pH 8.0 to 9.0: a — T = 15°C and $c(Fe)$ = 0.15 M; b — T = 15°C and $c(Fe)$ = 0.3 M; c — T = 15°C and $c(Fe)$ = 1 M; d — T = 60°C and $c(Fe)$ = 0.15 M; e — T = 60°C and $c(Fe)$ = 0.3 M; f — T = 60°C and $c(Fe)$ = 1 M.

tion of the samples for electron microscopy measurements, suspension of the powders under investigation in water was spread on thin carbon films. Determination of metal concentrations before and after adsorption was performed by the atomic emission spectrometer with inductively coupled plasma TRACE SCAN Advantage (company Thermo Jarrell Ash, USA). The specific surface area was determined by thermal desorption of argon (mixture of 10 % argon in helium) with chromatographic detection, alumina samples with known surface area (4.2 and 52 m^2/g) served as reference.

3. Results and discussion

3.1. Preparation of magnetic particles

Figure 1 shows X-ray patterns of the synthesized powders. The samples prepared at 15°C and iron concentration of 1 M in solution are amorphous (Fig. 1a). Decrease of the iron concentration at precipitation temperature of 15°C does not lead to formation of crystalline precipitate. The crystalline precipitates are formed at 20°C, however, magnetite is not precipitated from the solutions with the iron concentration of 1 M (Fig. 1b). Formation of the pure magnetite is observed at 90°C and the iron concentration of 0.15 M in the solution (Fig. 1c). The X-ray patterns of the samples synthesized at 20 to 90°C reveal reflexes corresponding to magnetite phase (Fe_3O_4), maghemite phase (γ-Fe_2O_3) and goethite phase (α-FeOOH) in different proportions.
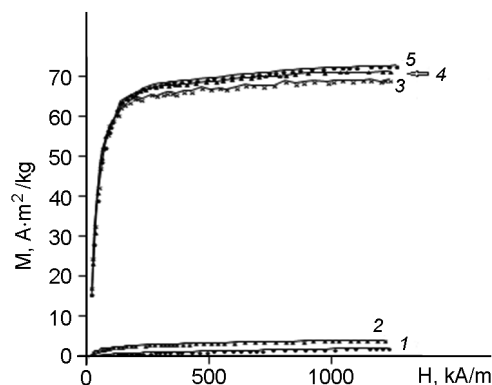

Fig. 3. Magnetization of Fe_3O_4 samples obtained at the precipitation temperature and concentration: *1* — 15°C and 1 M; *2* — 15°C and 0.15 M; *3* — 60°C and 1 M; *4* — 60°C and 0.3 M; *5* — 60°C and 0.15 M.

Table describes quantitative calculation of the phase content according to the Rietveld method. According to the obtained results, content of the magnetite phase significantly depends on precipitation temperature. The content of the magnetite phase grows with the temperature increasing. The initial concentration of iron ions in the solution also influences. The lower iron concentration is in the solution, the higher content of magnetite phase is in the sample. For example, the samples synthesized at 90°C in 0.15 M iron solutions include 100 % of the magnetite phase. The samples synthesized at the temperatures lower than 15°C consist of X-ray amorphous precipitates.

Table. Terms of Fe_3O_4 particle deposition

s/n	Synthesis conditions		Average particle diameter, nm	Compound	Composition[*], wt.% (st. deviation.)	Average particle size[*], nm
	Total iron concentration, M	Deposition temperature, °C				
1	0.15	15	9.5	amorphous	–	–
2	0.3	15	9.5	amorphous	–	–
3	1	15	7.0	amorphous	–	–
4	0.15	20		γ-Fe_2O_3(Maghemite)	7.36 (0.78)	9.9
				Fe_3O_4-Magnetite	85.87 (3.98)	10.8
				α-FeOOH(Goethite)	6.77 (0.44)	9.6
5	1	20		α-FeOOH(Goethite)	100	8.8
6	0.15	40		γ-Fe_2O_3(Maghemite)	8.08 (0.05)	8.4
				Fe_3O_4-Magnetite	91.92 (0.79)	10
7	0.15	60	14.6	γ-Fe_2O_3(Maghemite)	7.29 (0.04)	10.4
				Fe_3O_4-Magnetite	92.71 (0.79)	10.2
8	1	60	10.3	γ-Fe_2O_3	13.3	7.4
				Fe_3O_4-Magnetite	86.7	8.1
9	0.15	90		Fe_3O_4-Magnetite	100	9.5
10	1	90		γ-Fe_2O_3(Maghemite)	4.03 (0.52)	7.2
				Fe_3O_4-Magnetite	82.03 (2.14)	7.6
				α-FeOOH(Goethite)	13.93 (0.49)	9.4

[*] — calculated by the Rietveld method.

Figure 2 shows TEM images of the synthesized particles. Spherical particles with a mean size of about 10 nm are formed at 15°C and the iron concentration of 0.15 M (Fig. 2a). Increase in the total iron concentration up to 0.3 M (Fig. 2b) does not result in significant changes in the particle size. For the powders obtained from 1 M iron solution (Fig. 2c), the mean particle size is slightly reduced to 7 nm. Increase in the precipitation temperature results in the particle enlargement. For example, the particles with the mean size of 15.2 nm are formed in 0.15 to 0.3 M in solutions (Fig. 2d, e), and the particles with the mean size 10.5 nm are formed in 1 M solution. For the particles obtained by simultaneous precipitation from solutions of Fe(III) and Fe(II) (in the ratio $c(Fe^{3+}):c(Fe^{2+}) = 2:1$) and in the precipitation temperature range of 15−90°C, the value of BET surface area is 120−130 m^2/g. Thus, the value of BET surface area (S_{sur}) only slightly depends on the iron ion concentration in the reaction mixture and synthesis temperature.

3.2. Magnetization of Fe_3O_4 particles

Figure 3 shows results of magnetization measurements. It can be seen from Fig. 3 that unsaturability of the specific magnetization is observed. It indicates, along with reduced values of the magnetization in the maximum field compared to macrosample [11], considerable contribution of the surface layer with beveled magnetic structure and correspondingly small particle size ($d < 100$ nm) [12]. The samples obtained at 15°C are characterized by very low values of magnetization of no more than 5 $A{\cdot}m^2/kg$ (Fig. 3a, b). The magnetization of the samples obtained at 60°C is about 70 $A{\cdot}m^2/kg$ (Fig. 3c, d), slightly increasing with the decrease of the initial iron concentration in the solution. It should be noticed that the higher content of the magnetite magnetic phase is in the sample, the larger value of
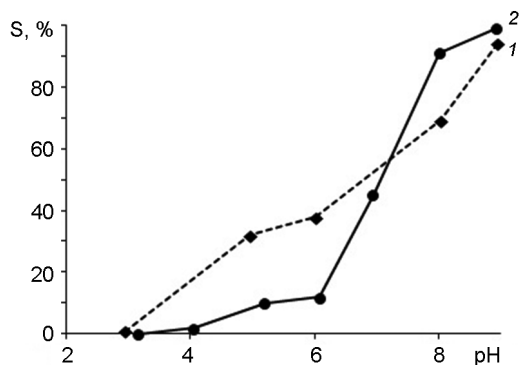
Fig. 4. Influence of pH on cobalt removal efficiency using hematite particles (*1*) and magnetite particles (*2*).

Fig. 5. Sorption isotherms of cobalt on the nanoparticles: α-Fe_2O_3 — (*1*) and Fe_3O_4 — (*2*).

the magnetization it has. In addition, the particles with the larger sizes have the large magnetization values. Thus, the magnetization of the particles depends not only on the particle size but also on their phase composition.

3.3. Sorption properties of the particles

In order to compare properties of the magnetic and nonmagnetic particles, test subjects were chosen as follows: the particles obtained at 90°C from 0.15 M iron solution (100 % magnetite content) and the hematite particles obtained after calcination at 450°C for 4 h. Cobalt was used as sorbate. Cobalt has radioactive isotope Co^{60} (activity of 1 g is 41.8 TBq, half-life is 5.2 years), which is used in the manufacture of gamma radiation sources with energies of about 1.3 MeV. However, when entering to the natural objects, this element constitutes the high danger.

Figure 4 illustrates a plot of cobalt removal efficiency versus pH for the different particles. Degree of cobalt removal increases with pH increase in the both cases. However, use of Fe_2O_3 particles as sorbents in acidic medium allows achieving higher degrees of cobalt removal compared to Fe_3O_4 particles. The maximum removal is observed at pH 9 for both Fe_2O_3 and Fe_3O_4 that is associated with formation of insoluble $Co(OH)_2$.

In order to determine sorption capacity, sorption isotherms were plotted for cobalt ions (Fig. 5) and different parts of the isotherms were fitted by the Langmuir equation. The isotherms are of *S*-type. This type of the isotherms indicates heterogeneity of the sorbent surface. Attainment of the plateau indicates the monolayer formation. For the cobalt concentration in solution of more than 200 mg/l, the excessive adsorption as-
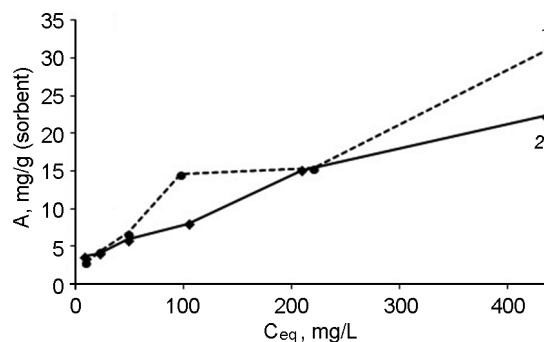
sociates with another more complicated mechanism [13]. The sorption capacity of α-Fe_2O_3 particles for cobalt is 18.7 mg/g ($R^2 = 94.64$ %), and the sorption capacity of Fe_3O_4 is 17.3 mg/g ($R^2 = 92.30$ %). As it follows from the obtained results, the value of the sorption capacity is practically independent of the iron oxide phase.

4. Conclusions

Influence of precipitation conditions (temperature, iron concentration in the solution) on the phase composition, the particle size and their magnetization was studied. Removal efficiency and sorption capacity for cobalt were compared between the magnetite and hematite phases. Formation of the magnetite phase was found to be significantly affected by the precipitation temperature. The magnetite phase content in the sample increases with the temperature increase. Carrying out synthesis at 90°C in 0.15 M iron solutions promote formation of the powder with 100 % (by weight) magnetite phase content (Fe_3O_4) and characterized by the magnetization of 70 $A \cdot m^2/kg$. The magnetization slightly decreases with increase in the initial iron concentration in the solution.

Regardless of the precipitation conditions, spherical particles are formed with the mean size of 7 to 15 nm. The precipitation temperature increase and iron concentration decrease promotes formation of the powder with larger particles characterized by the higher magnetization values.

The sorption capacity is practically independent of the phase content and is about 18 mg/g for cobalt.

It should be recommended for preparation of Fe_3O_4 based sorption material, carrying out the precipitation at temperature of at least 80°C and the iron concentration

in the solution of 0.15 to 0.3 M to obtain particles with the maximum magnetite phase content (more than 90 % by weight).

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