



ELECTROCHEMICAL METHOD FOR PRODUCING MAGNETITE FOR WASTEWATER TREATMENT

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As a result of the expanding directions of application of magnetic liquids, it becomes necessary to obtain a large amount of magnetite. The most common method of obtaining magnetite is its chemical condensation, both from pure components and from iron-containing waste of machine-building industries. Magnetite obtained from waste is as high as magnetite obtained from pure components. In addition, the cost of such magnetite is much lower. The article describes an electrochemical method for obtaining magnetite for wastewater treatment of electroplating production from the waste of cutting sheets of steel. A solution of sodium chloride was chosen as the electrolyte. The article presents the main stages of obtaining electrochemical magnetite, the results of measuring the saturation magnetization of samples of dispersed magnetite. The measurements were carried out at room temperature using a vibrating magnetometer in magnetic fields up to 1 Tl. We obtained the Mossbauer spectrum of an electrochemical magnetite sample. Magnetite, obtained by the electrochemical method, was used for the treatment of electroplating production washing wastewater as an adsorbent of copper ions. The paper presents the process of magnetite adsorption of copper ions and the scheme of the purification method. Studies of adsorption treatment of electroplating wastewater from copper ions show the high efficiency process level up 92.0-98.4%.

Introduction

The most common method of producing magnetite is chemical condensation. It uses a mixture of trivalent and divalent iron salts as raw material and ammonium hydroxide as an alkalisng reagent [1-13]. The disadvantages of this method are the high cost of the starting reagents by the classification rules "chemically pure" (CP) and "pure for analysis" (PA).

The development and optimisation of methods for obtaining magnetite using industrial waste as a feedstock solves both the problem of improving the environmental safety of enterprises and decreasing the costs of the produced material - magnetite, suitable for use in a number of engineering and technological fields.

In our work we obtained magnetite by electrochemical dissolution of waste material from cutting sheets of the most widely used steel St3 under direct current in a heated, electrically



conductive medium. For the production of magnetite nanoparticles by electrochemical method, an aqueous sodium chloride solution was chosen as the electrolyte. The reasons were its high electrical conductivity, low impurity content, insolubility of magnetite in the electrolyte solution, as well as relatively low cost and availability. In addition, chlorine ions activate the state of the electrode surface, increasing the period of operation before passivation [14-16]. The method includes an electrolysis in a sodium chloride (NaCl) solution preheated to a temperature providing the ferritisation process, while oxidising the resulting intermediate compounds (hydroxides) with supplied air oxygen.

Methodology

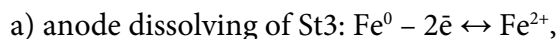
The synthesis of magnetite main stages:

1. The obtaining of magnetite by electrochemical method using waste St3 (shavings and trimming) and sodium chloride solution (NaCl) as an electrolyte was carried out with the following parameters: NaCl solution concentration - 0.5%, electrode voltage - 26 V, specific air flow rate - 52 l/h·l, temperature 60-90 °C.

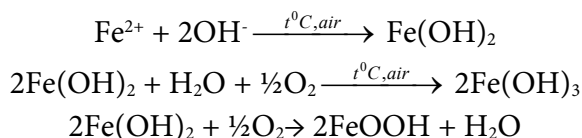
The following reactions occur:



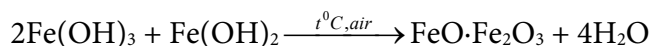
1.2. On the anode



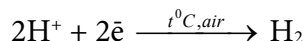
1.3. Gradual formation of 2- and 3-valent iron hydroxides and iron oxyhydroxide during bubble aeration:



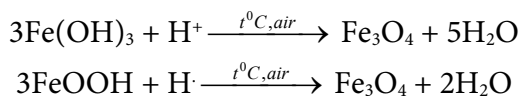
1.4. Ferritization by the acidic character of trivalent iron hydroxide and the basic character of divalent iron hydroxide:



1.5. Hydrogen is generated on the cathode, which prevents the oxidation of 2-valent iron to 3-valent iron:



1.6. On the cathode, the reduction reactions of 3-valent iron hydroxide and iron oxyhydroxide with hydrogen also take place:



2. Sedimentation of the magnetite suspension using permanent magnets and removal of the sedimented water;

3. Drying at 100 °C for three hours.



According to X-ray diffractometry, this way synthesised powder is magnetite with an average particle size of ~13 nm.

Results and discussion

We measure the saturation of magnetisation the samples of dispersed magnetite obtained by the method described above. Measurements were taken at room temperature using a vibrating magnetometer in magnetic fields up to 1 Tesla. The measurement uncertainty was 4%. The highest saturation magnetisation $I_s = 282$ kA/m was recorded for the sample obtained at 80 °C. The magnetite obtained electrochemically from waste cut sheets (shavings) of steel has a slightly higher magnetisation and is cheaper than dispersed magnetite obtained from industrial waste by chemical condensation method. The Mössbauer spectrum of the sample obtained at 80 °C shown in the Fig. 1. The study was conducted at room temperature.

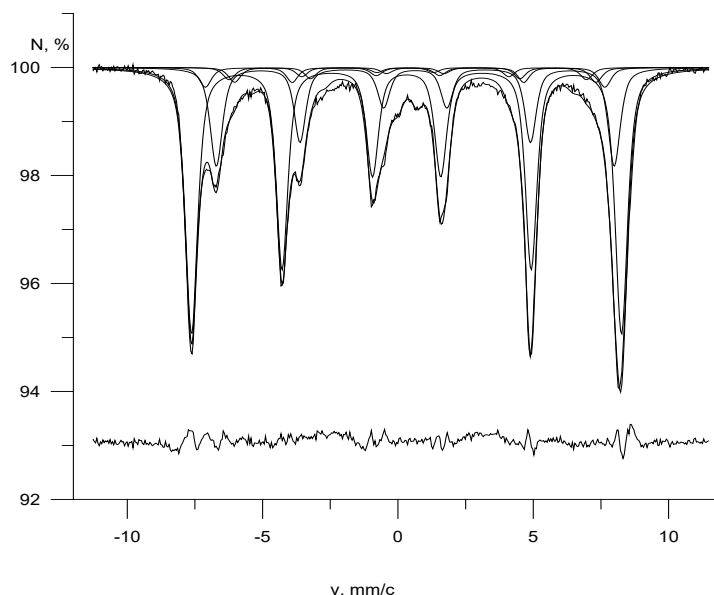


Fig. 1. Mössbauer spectrum of an electrochemical magnetite sample

The spectra were processed using the Spectrum software, based on their configuration, assuming six sextets. The parameters of the magnetite sample are shown in Table 1.

N_{eff} – is the fields at the iron nuclei; δ – is the isomeric shift of the Mössbauer line; ε – is the quadrupole shift of the spectrum components; S – is the area of the partial spectrum.

Table 1. Mössbauer spectrum of an electrochemical magnetite sample parametres

Non-equivalent positions of iron ions	N_{eff} , kE	δ , mm/sec	ε , mm/sec	S , mm/sec
A ₁	493,30±0,06	0,3184±0,0006	-0,0029±0,0005	0,643 ±0,004
B ₁	456,50± 0,18	0,6407±0,0023	-0,0002±0,0016	0,2382±0,0019
A ₂	458,5±1,1	0,3184±0,0006	-0,054±0,007	0,0477±0,0028
B ₂	414,7±1.1	0,6407±0,0023	0,001±0,010	0,0357±0,0019
A ₃	410,0±1,2	0,3184±0,0006	0,046±0,013	0,0293±0,0014
B ₃	369,8±1,2	0,6407±0,0023	-0,113±0,014	0,0239±0,0013



The treatment results are strongly agree with theoretical and experimentally obtained spectrum of the electrochemical magnetite sample. By the values of the effective fields at the iron nuclei and the intensity of the corresponding partial spectra, the effective magnetic fields at the ^{57}Fe nuclei of A_1 and B_1 partial spectra correspond to the iron ions belonging to the inner region of the particle and located in the A- and B- places of the magnetite lattice. The pairs of effective magnetic fields A_2, B_2 and A_3, B_3 appear to be related to iron ions in the surface layer of the magnetite particle. The areas corresponding to these sextets are significantly lower for A_1, B_1 .

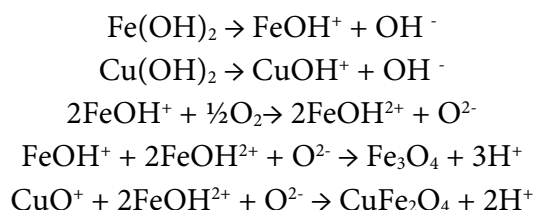
The effective magnetic fields A_3 and B_3 corresponding to the lowest intensity sextets probably refer to iron ions on the particle surface itself. They differ from the nearest surface iron ions in the symmetry of the ligand environments by the corresponding values. Apparently only the long recording time of the described spectra, which provided large statistics, allowed these two types of surface iron ions to be distinguished.

An assessment of the particle sizes based on the ratio of "surface" to "inner" sextet intensities according to the method [17] showed that these sizes are within the margin of error in agreement with X-ray diffractometry data and are (13 ± 2) nm.

Magnetite produced by the electrochemical method was used as an adsorbent for copper ions in the galvanic industry treatment of wastewater.

Particles of $\text{Fe}_2\text{O}_3\cdot\text{FeO}$ magnetite in aqueous solution due to ionic-electrostatic, magnetic and molecular forces are in a shell consisting of hydroxyl ions and iron hydroxides, forming a supermicellular aggregate [18].

The process of adsorption treatment of galvanic wastewater from copper ions is represented by the equations:



The scheme of the sorption purification method is shown in Fig. 2.

To determine adsorption purification parameters, five experiments were carried out in three replications using electrochemically produced magnetite at a ratio of copper ions to magnetite of 1:1; 1:3; 1:6; 1:12; 1:16 respectively. The wastewater and sorbent were stirred on a laboratory shaker for 5 minutes. The results of the experiments are summarized in Table 2.

Based on the Table 2 a histogram was constructed that reflects the dependence of the degree of purification on the mass of the sorbent loading, shown in Fig. 3.

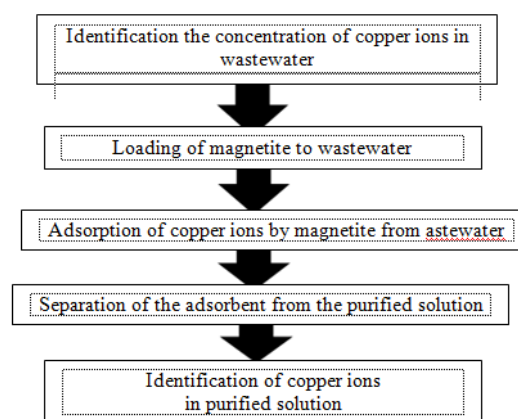
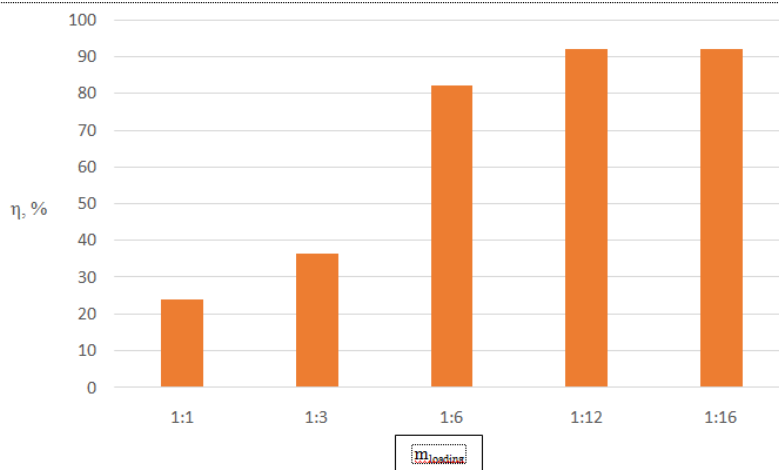


Fig. 2. Diagram of a magnetite-based adsorption treatment of galvanic wastewater from copper ions

**Table 2.** Determining the best sorbent loading weight

Initial concentration of copper ion in waste water, mg/dm ³	1250				
Ratio of copper ions to magnetite	1:1	1:3	1:6	1:12	1:16
Copper ion concentration after treatment, mg/dm ³	800	950	220	100	100
Degree of purification, %	24	36.4	82	92	92

**Fig. 3.** Histogram "Degree of wastewater treatment as a function of sorbent load weight"

By Fig. 3, maximum degree of purification is achieved at a copper ion load of 1:12. A further increase in the charge weight is not reasonable as there is no visible increase of purification degree.

As the sorbent load mass has been determined, it is necessary to find sufficient time for the adsorption process. To achieve this, experiments were carried out with wastewater interacting with magnetite for 5, 10, 15 and 25 minutes. The results of the experiments are summarized in Table 3.

Table 3. Determination of sufficient time for adsorption purification

Time of interaction sorbent and wastewater, min	5	10	15	25
Copper ion concentration after treatment, mg/dm ³	100	20	85	93
Degree of purification, %	92	98.4	93.2	92.6

By Table 3, sufficient and optimum time for adsorption treatment of galvanic wastewater from copper ions on magnetite is 10 minutes.

Thus, magnetite synthesised by electrochemical method from steel sheet cutting waste can be used as an adsorbent for treatment of electroplating wastewater from copper ions with an efficiency of 92–98,4%.

References

1. Berkovsky B.M., Medvedev V.F., Kraskov M.S. Magnetic liquids. Moscow: Khimiya, 1989. 240 p. (in Russian).
2. Uheida A., Iglesias M., Fntas C., Hidalgo M., Salvado V., Zhang Y., Muhammed M. Sorption of palladium (II), rhodium (III), and platinum (IV) on Fe₃O₄ nanoparticles. *J. Colloid and Interface Sci.* 2006. V. 301. N 2. P. 402-408.



3. **Egunova O.R., German S.V., Vrabie Y.A., Shtykov S.N.** Synthesis of monodisperse magnetite. *Izvestiya Saratovskogo universiteta. Novyye serii. Seriya Khimiya. Biologiya. Ekologiya.* 2015. V. 15. N 4. P. 10-14. DOI: 10.18500/1816-9775-2015-15-4- 10-14 (in Russian).
4. **Marnautov N.A., Komissarova L.H., Tatikolov A.S., Larkina E.A., Elfimov A.B., Vasilkov O.O.** Working out the optimal method to obtain chemical-and-size homogenous in magnetite nanoparticles for biomedical purposes. *Uspechi sovremennogo yestestvoznaniya.* 2017. N 6. P. 23-27 (in Russian).
5. **Kalaeva S.Z., Markelova N.L., Makarov V.M.** Obtaining magnetite by reduction of iron-containing wastes. *From chemistry towards technology: step by step.* 2021. V. 2. N 1. P. 79-85. DOI: 10.52957/27821900_2021_01_79. (in Russian).
6. Patent RF N 2750429. Method of magnetite production / Bibaneva S.A., Pasechnik L.A., Skachkov V.M. Publ. 28.06.2021. Bul. N 19 (in Russian).
7. Patent RF N. 2433956. Method of magnetite production / Krause E., Rehm W. Publ. 20.11.2011. Bul. N 32 (in Russian).
8. Patent RF N 2461519. Method of obtaining magnetite with a developed surface / Ikaev A.M., Agaeva F.A., Avguzarova V.A., Esieva L.K., Dzaraeva L.B. Publ. 20.09.2012. Bul. N 26 (in Russian).
9. Patent RF N. 2610506. Method of obtaining magnetite nanoparticles (variants) / Grishechkina E.V., Dosovitsky A.E., Mikhlin A.L. Publ. 13.02.2017. Bul. N 5 (in Russian).
10. **Gordeev B.A., Maslov G.V., Okhulkov S.N., Osmekhin A.N.** On Developing a Magneto-rheological Transformer That Operates in Orthogonal Magnetic Fields. *Journal of Machinery Manufacture and Reliability.* 2014. V. 43. N 2. P. 99-103. DOI: 10.3103/S105261881402006X.
11. **Belyaev E.S., Ermolaev A.T., Titov E.Y., Tumakov S.F.** Magnetorheological fluids: technologies of creation and application: monograph. M.: Nizhegorodskiy gosudarstvennyy tekhnicheskii universitet imeni R.E. Alekseyeva, 2017. 94 p. (in Russian).
12. **Hoang C.T., Yurmazova T.A., Vaitulevich E.A.** Magnetite with modified surface for water treatment. *Izvestiya Tomskogo Politeknicheskogo Universiteta. Inzhiniring Georesursov.* 2019. V. 330. N 8. P. 163-172. DOI: 10.18799/24131830/2019/8/2222 (in Russian).
13. **Lebedev A.V., Lysenko S.N., Gileev V.G.** Poly (dymethylsiloxane) stabilized magnetic fluid remains flowable in the absence of a carrier medium. *Kolloidnyy zhurnal.* 2020. V. 82. N 3. P. 339-345. DOI: 10.31857/S0023291220030064 (in Russian).
14. **Rotinyan A.L., Tikhinov K.I., Shoshina I.A.** Theoretical electrochemistry. L.: Khimiya, 1981. 424 p. (in Russian).
15. **Uhlig G.G., Revie R.W.** Corrosion and Corrosion Control. Introduction to Corrosion Science and Technology. L.: Khimiya, 1989. 456 p. (in Russian).
16. **Kesche G.** Corrosion of metals. Moscow: Metallurgizdat, 1984. 400 p. (in Russian).
17. **Zakharova I.N., Nikolaev V.I., Shipilin A.M.** On estimation of nanoparticles sizes by Mössbauer effect. *Zhurnal fiziki tverdogo tela.* 2001. V. 43. N 8. P. 1455-1457 (in Russian).
18. **Hoang C.T., Yurmazova T.A., Vaitulevich E.A.** Magnetite with modified surface for water treatment. *Izvestiya Tomskogo Politeknicheskogo Universiteta. Inzhiniring Georesursov.* 2019. V. 330. N 8. P. 163-172. DOI: 10.18799/24131830/2019/8/2222 (in Russian).

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