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INFLUENCE OF VARIOUS FACTORS ON THE FERRIC α-OXYHYDROXIDE SYNTHESIS

Liliya A. Frolova, Tatyana V. Hrydnieva

Ukrainian State University of Chemical Technology, Dnipro, Ukraine

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Abstract

At present, synthetic oxides and oxyhydroxides in the form of pigments, adsorbents, and magnetic carriers are widely used in industry. This is due to their non-toxicity, chemical stability, durability, a wide variety of colours and low cost. The properties of the obtained pigments are determined primarily by the dispersion of the obtained product and its phase composition, specific surface of the powders. The problem of improving the quality of the final product is mainly a technological problem and it can be solved by improving the technological stages, especially precipitation and oxidation.

In this work, the dependence of the phase composition of the products on the synthesis conditions is investigated. Oxyhydroxides and ferric oxides are synthesized by oxidation ferrous hydroxides obtained by precipitation. Air was used as an oxidizer of Fe^{2+} ions. The study of the influence of synthesis parameters on the precipitation of α-oxyhydroxide nanoparticles was studied by the experimental design method. Particles with a different form factor and specific surface were formed depending on temperature, initial concentrations of salt and precipitant, air flow rate.

It has been established that the concentration of iron(II) sulphate has a decisive influence on the particle size of α-FeOOH and its specific surface, to a lesser extent on the concentration of sodium hydroxide and rate oxidation.

Key words: iron oxides; precipitation; oxidation; pigments; α-oxyhydroxide.

ВПЛИВ РІЗНИХ ФАКТОРІВ НА СИНТЕЗ α-ОКСИГІДРОКСИДУ ФЕРУМУ

Лілія А. Фролова, Тетяна В. Гриднєва

ДВНЗ «Український хіміко-технологічний університет»

Анотація

В даний час синтетичні ферум(III) оксиди і оксигідроксиди у вигляді пігментів, адсорбентів і магнітних носіїв широко використовуються в промисловості. Це пов'язано з їх нетоксичністю, хімічною стабільністю, довговічністю, широким розмаїттям кольорів і низькою вартістю.

Властивості отриманих пігментів визначаються, перш за все, дисперсністю отриманого продукту і його фазовим складом, питомою поверхнею порошків. Проблема підвищення якості кінцевого продукту є перш за все технологічною проблемою і може бути вирішена шляхом покращення технологічних стадій, особливо осадження і окислення.

У даній роботі досліджена залежність фазового складу продуктів від умов синтезу. Оксигідроксиди і оксиди заліза синтезували окисленням ферум(II) гідроксиду, отриманого осадженням. В якості окислювача іонів Fe^{2+} використовувався повітря. Методом планування експерименту вивчено вплив параметрів синтезу на процес утворення наночастинок α-оксигідроксида. Частинки з різним форм-фактором і питомою поверхнею формувалися в залежності від температури, вихідних концентрацій солі і осаджувача, швидкості подачі повітря.

Встановлено, що вихідна концентрація ферум(II) сульфату має суттєвий вплив на розмір частинок α-FeOOH і його питому поверхню. У меншій мірі впливає концентрація гідроксиду натрію і швидкість подачі повітря.

Ключові слова: ферум(III) оксиди; осадження; окислення; пігменти; α-оксигідроксид.

**Corresponding author: Tel. +380973846557 ; e-mail address: 19kozak83@gmail.com*

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ВЛИЯНИЕ РАЗЛИЧНЫХ ФАКТОРОВ НА СИНТЕЗ α-ОКСИДГИДРОКСИДА ЖЕЛЕЗА

Лилия А. Фролова, Татьяна В. Гриднева
ГВУЗ «Украинский государственный химико-технологический университет»

Аннотация
В настоящее время синтетические оксиды и оксигидроксиды железа в виде пигментов, адсорбентов и магнитных носителей широко используются в промышленности. Это связано с их нетоксичностью, химической стабильностью, долговечностью, широким разнообразием цветов и низкой стоимостью.
Свойства полученных пигментов определяются, прежде всего, дисперсностью полученного продукта и его фазовым составом, удельной поверхностью порошков. Проблема повышения качества конечного продукта является в основном технологической проблемой и может быть решена путем улучшения технологических стадий, особенно осаждения и окисления.
В данной работе исследована зависимость фазового состава продуктов от условий синтеза. Оксигидроксиды и оксиды железа синтезировались путем окисления гидроксидов железа, полученных осаждением. В качестве окислителя ионов Fe^{2+} использовался воздух. Методом планирования эксперимента изучено влияние параметров синтеза на процесс образования наночастиц α-оксигидроксида. Частицы с различным форм-фактором и удельной поверхностью формировались в зависимости от температуры, исходных концентраций соли и осадителя, скорости подачи воздуха.
Установлено, что исходная концентрация сульфата железа(II) оказывает существенное влияние на размер частиц α-FeOOH и его удельную поверхность. В меньшей степени концентрация гидроксида натрия и скорость подачи воздуха.

Ключевые слова: оксиды железа(III); осаждение; окисление; пигменты; α-оксигидроксид.

Introduction

Currently, iron oxides are commercially represented by a large group of pigments. This is due to their non-toxicity, chemical stability, durability, a wide variety of colours and cheapness [1–4].

There are many studies devoted to various methods of obtaining of goethite, magnetite, maghemite, hematite [3–10], described in literature. Such pigments are used in the paint and varnish industry for the production of various enamels, primers. They not only determine the coating colours, but also affect their technological characteristics.

The iron oxides, commonly used as pigments, are coloured in black, red, brown or yellow. A special place is occupied by a group of iron oxide pigments in the yellow-orange colour scheme (goethite, acaganèite, ferrohydride). The properties of the resulting pigments are determined primarily by the dispersity and phase composition of the product obtained [11–14].

The problem of improving the quality of the final product is mainly a technological problem and can be solved by improving all the processing steps (sedimentation, dehydration). So, achieving the necessary developed surface, necessary particles shape and powder phase composition is determined by the technological mode selection [15–21].

The establishment of the basic technological regularities in the synthesis of the dispersed systems with crystallographic particles anisotropy, as well as shape anisotropy, will make it possible to obtain goethite particles with the maximum form factor.

Experimental Section

The pigments were obtained in the laboratory facility by precipitation from the standard solutions of iron sulphates with caustic soda. The precipitation was conducted in a three-necked flask.

The flask was set on a hotplate equipped with a mercury thermometer and a water refrigerator. During the experiment the required amount of metal sulphate necessary for the experiment with a concentration of 0.5 mol/l was placed in the three-necked flask; different amounts of sodium hydroxide were added and the mixture was stirred with a magnetic mixer.

During all the experiment nitrogen was added into the flask and the temperature about 30–45°C was supported. The value of pH was measured with a pH-meter.

At the moment when the temperature and pH of the medium reached their nominal values, the mixing was stopped. Then compressors were connected to oxidize the mixture with oxygen. The oxidation time was 1.5–2 hours. The mixture was filtered, the resulting paste was dried and ground. The filtrate was analyzed for the presence of cations and OH^-groups according to the known methods. 3 parallel experiments were conducted.

The influence of different principal variables: concentration of $FeSO_4$, concentration of NaOH, air feed rate and temperature were investigated using factorial matrix (($2^{k-1,}$ k being the number of factors; k = 4). In this case, a half-replica type was used to plan the fractional factorial experiment.

The plan was given by the generating relation $x_4 = x_1 \cdot x_2$.The coefficients of the model were calculated using the half difference between the arithmetic average of the response values when the associated coded variable is at level (+1) and the arithmetic average of the response values when the associated coded variable is at level (−1). The experimental range investigated and the code values are shown in Table 1.

Table 1

Experimental range and levels of chosen variables

Factor	Name	Units	Levels			
			High (+1)	Low (−1)	Middle (0)	Interval
X_1	C($FeSO_4$)	mol/l	1.0	0.3	0.65	0.35
X_2	C (NaOH)	mol/l	1.5	0.5	1.0	0.5
X_3	Air feed rate	·min^{-1}	50	5	27.5	22.5
X_4	Temperature	°C	45	30	37.5	7.5

Results and discussion

According to preliminary experiments, the main technological factors that influence the shape, size and morphology of goethite particles are the concentration of ferrous sulphate, the concentration of sodium hydroxide, temperature and air feed rate. To determine the limits of these factors changes, which affect the product output with the maximum particles anisotropy, an optimization of the experimental statistical mathematical model was carried out. This model was constructed using the results of a series of experiments implemented according to the plan for a full four-factor experiment.

As a limiting conditions were chosen the following values of factors (Table 2).

Table 2

Experimental matrix and responses for the factorial design

X_1	X_2	X_3	X_4	Y_1	Y_2
+	+	+	+	3	63
–	+	+	–	9.6	39
+	–	+	-	4.5	52
–	–	+	+	11.1	42
+	+	–	+	4.7	62
–	+	–	–	11.8	38
+	–	–	–	6.9	52
–	–	–	+	14.1	40

As the response functions the form factor value (Y_1) characterized by the shape anisotropy and the specific surface value (Y_2) were chosen. The calculation of the equation coefficients, determination of their significance, verification of the model adequacy were performed by means of the program STATSGRAPHICS 10.0.

The dependence of the form factor value on the above factors is adequately described by the equation:

$$Y_1=12.54 - 9.01x_1 - 0.79x_2+3.86x_1^2+1.5x_1x_2$$

In Fig. 1. the dependence of the form factor from the independent variables is presented: iron (II) sulphate concentration and sodium hydroxide concentration.

The greatest influence on the particles habitus is exerted by the ferrous sulphate concentration. With its increase the length of the particles is decreasing.

The concentration of sodium hydroxide acts in the same way.

In the investigated range, the largest value of the form factor is attained at the points $x_1 = 0.3$ and $x_2 = 0.5$.

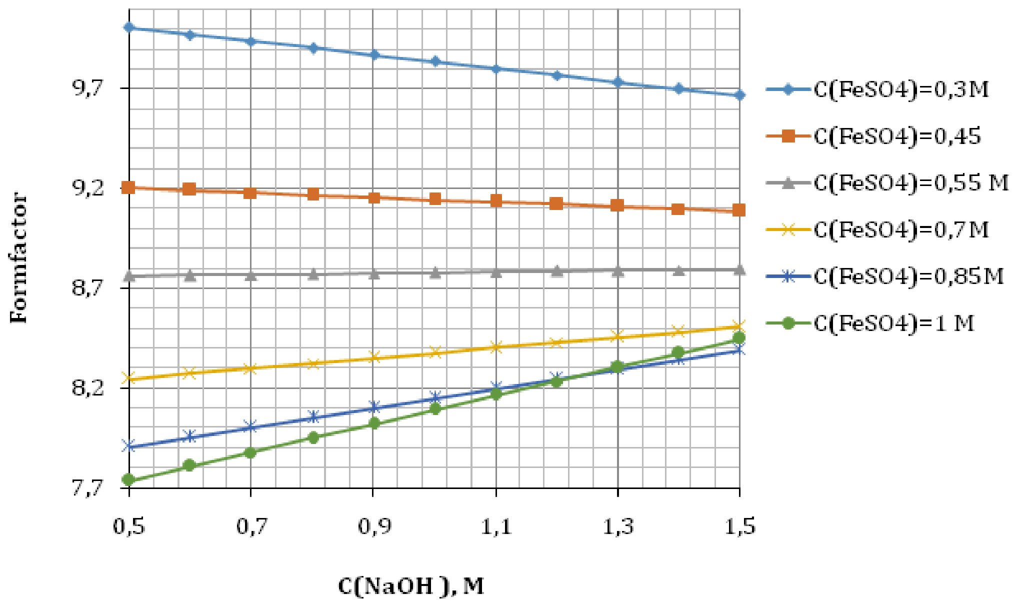

Fig. 1. Dependence of the form factor value on the concentration of sodium hydroxide

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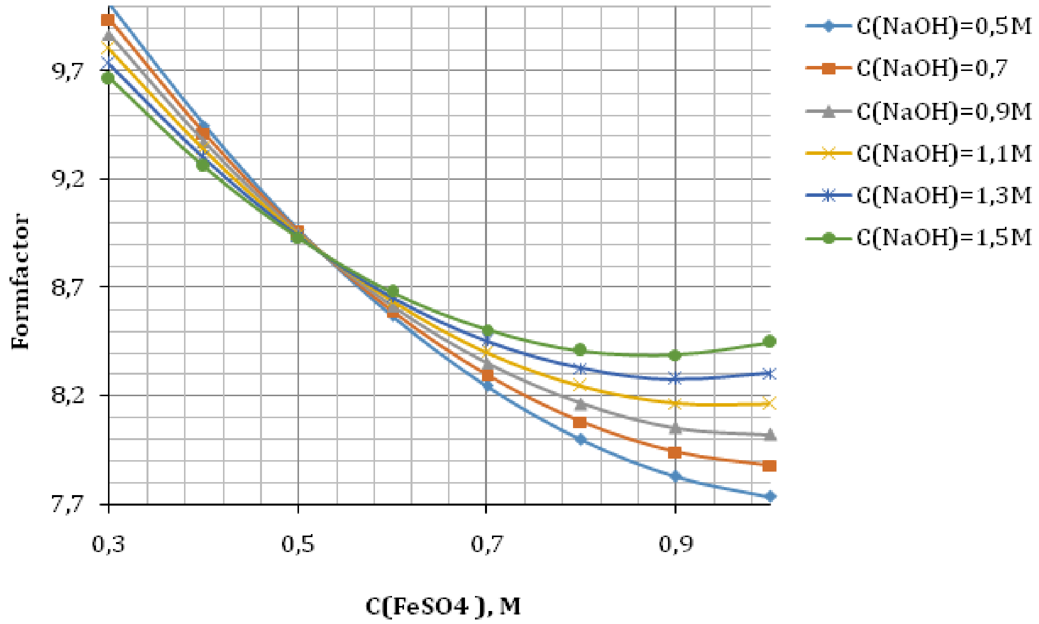

Fig. 2. Dependence of the form factor on the ferrous sulphate concentration

To verify the results of the calculation of the experimental statistical model, an additional experiment was carried out. At these levels of factors, the value of the original variable, which is in good agreement with the theoretical model, was obtained.

The dependence of the specific surface value on the above factors can be adequately described by the equation:

Y_2=6.74 – 3.26x_1 + 8.93x_2 + 0.128x_3 + 0643x_4 + + 26.87x_1^2 – 0.0021x_3^2 – 7.475x_1x_2

In Fig. 3, 4 the dependence of the specific surface on the independent variables is shown: the concentration of ferrous sulphate and the concentration of sodium hydroxide.

The greatest influence on the specific surface is exerted by the concentration of ferrous sulphate. With the increase of the ferrous sulphate concentration the specific surface area increases too. With the increase of sodium hydroxide concentration, the specific surface area decreases. In the investigated range the maximum value of the specific surface of goethite was reached at the point x_1= 0.9 and x_2 = 0.5. The use of caustic soda of higher concentration leads to the formation of a mixture of goethite and magnetite.

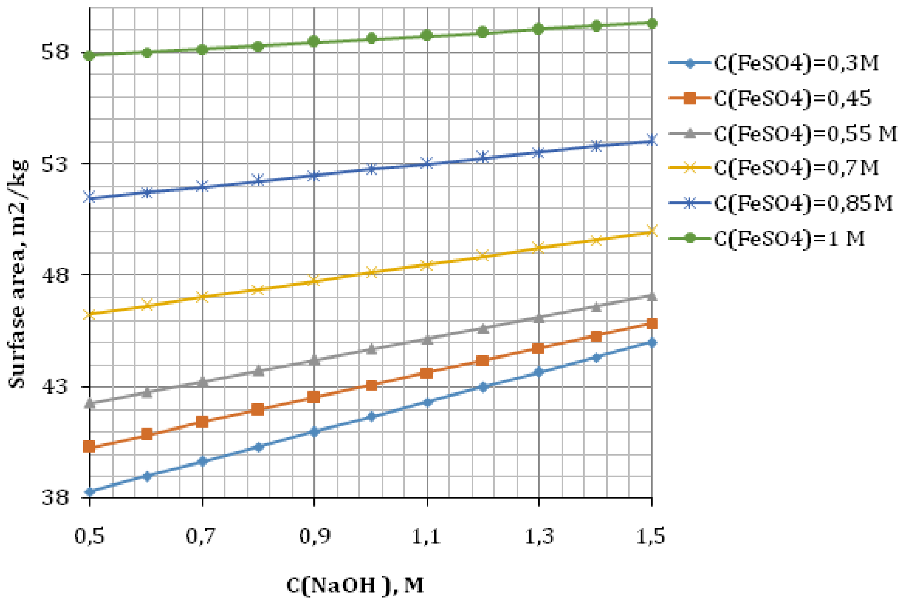

Fig. 3 Dependence of the specific surface area on the concentration of the sodium hydroxide (temperature 30°C effective air supply rate of 45°C)

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The initial concentration of ferrous(II) sulphate has the determining effect on the particle size and its specific surface. The concentration of sodium hydroxide has a lesser effect, as well as the pH of the start of oxidation and the rate of oxidation. It should be noted that the use of the caustic soda of a high concentration leads to the formation of magnetite. The temperature also has a great influence on the phase composition of the final product.

It is obvious that the temperature of the oxidation in the range 35-45°C has a significant effect on the course of the oxidation and the formation of a new phase. In addition, the X-ray analysis confirms the presence of the impurities of magnetite in the goethite obtained at a high temperature.

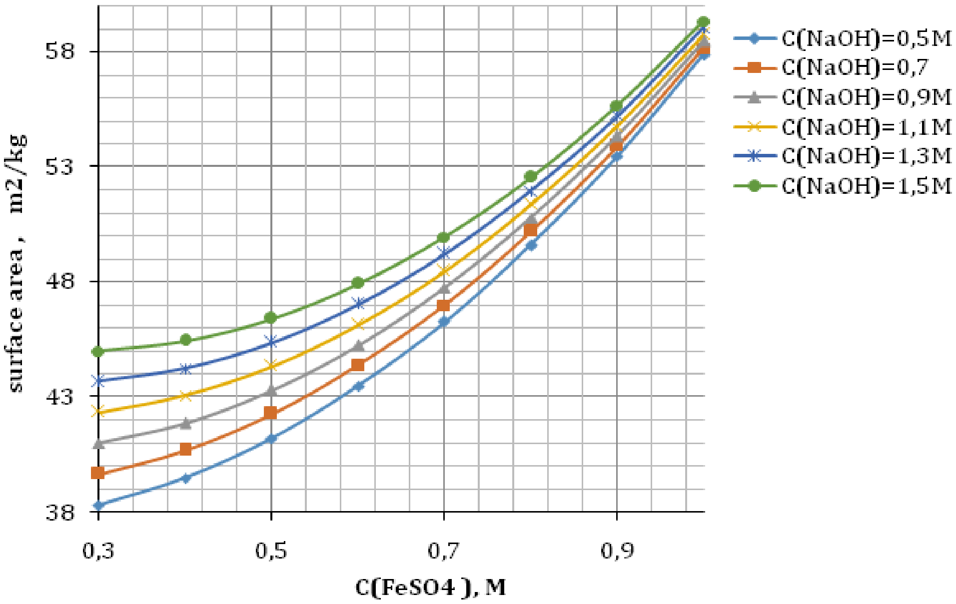

Fig. 4. Dependence of the specific surface area on the concentration of ferrous sulphate (temperature 40°C, effective air supply rate of 10 min^{-1})

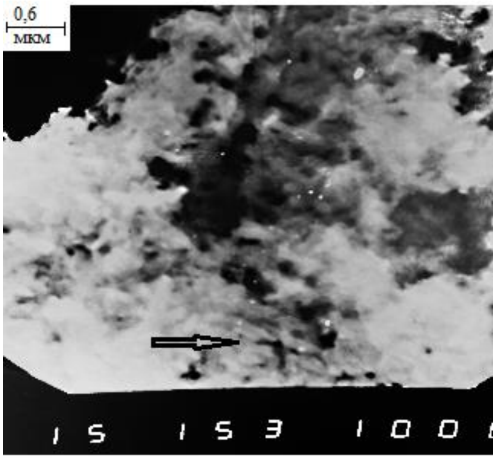

Fig.5. SEM micrograph of goethite powder

In Fig. 5 the photomicrograph of a powder of goethite obtained under the following conditions: C($FeSO_4$)= 0.3 mol/l, C(NaOH) = 0.5 mol/l, t = 30°C, W = 45 min^{-1} is shown.

The SEM micrograph of the goethite product (Fig. 5) showed that the formfactor was 10. The particles of bright yellow goethite were needle-like in shape and fairly monodispersing.

The XRD analysis of the powder showed the goethite to be the main phase. The slight broadening of the XRD lines (Fig. 6) may be due to the poor crystallinity and small particle sizes.

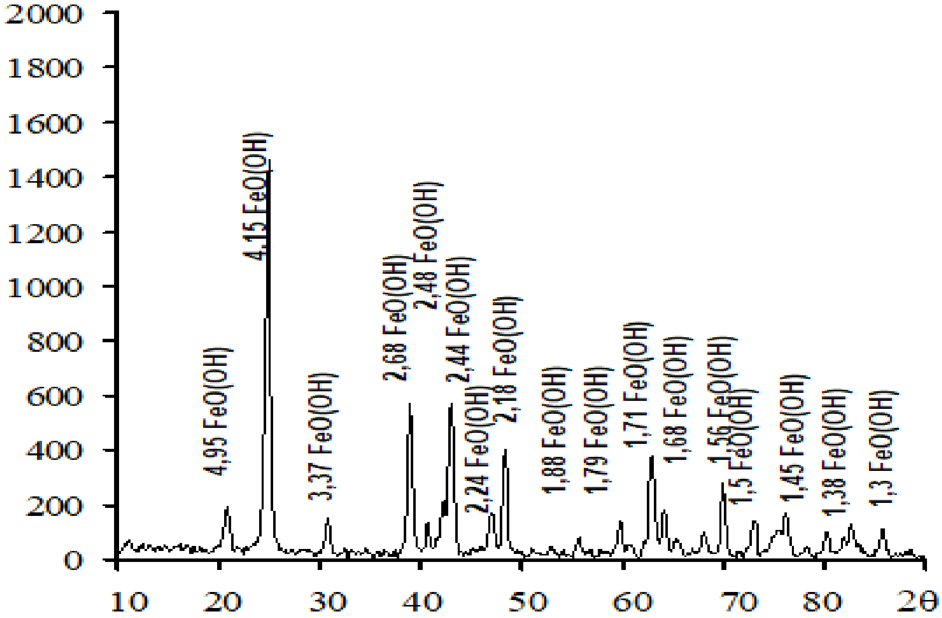

Fig.6. X-ray diffractogram of goethite powder

Conclusion

The determining effect on the size and specific surface of the α-FeOOH particles is exerted by the concentration of iron(II) sulphate. To a lesser extent it is affected by the concentration of sodium hydroxide, as well as by the pH of the onset of oxidation and its rate. It should be noted, that the use of caustic soda with a high concentration leads to the formation of magnetite.

The experimental data shows that with the increase of the temperature and air feed rate the oxidation time decreases. However, according to the X-ray data at the temperature above 40 °C a mixture of goethite and magnetite is formed.

The phase and dispersed composition of the iron oxide compounds obtained by air oxidation of iron(II) compounds depend on the pH of the iron(II) salt solution, the temperature of the reaction medium and the air feed rate.

Bibliography

[1] Litynska M. Ferric oxyhydroxide as fouling prevention reagent for low-pressure membranes / M.Litynska, R. Antoniuk, N. Tolstopalova, I.M. Astrelin // Journal of Ecological Engineering. – 2019. – Vol. 20, N 3. – P. 77–84.

[2] Frolova L. A. Production conditions of iron oxide black from pickle liquors / L. A. Frolova // Metallurgical & Mining Industry. – 2014. – Vol. 4. – P. 65–69.

[3] Synthesis of ferric oxyhydroxide nanoparticles and ferric oxide nanorods by reflux assisted coprecipitation method and comparative study of their thermal properties / S. R. Khan, S. Jamil, M. R. S. A. Janjua, R. A. Khera // Materials Research Express. – 2017. – Vol. 4, N 11. – P. 115019.

[4] Synthesis of highly-specific stable nanocrystalline goethite-like hydrous ferric oxide nanoparticles for biomedical applications by simple precipitation method /. E. L. Kolychev, E. N. Mochalova, V. R. Cherkasov, M. P. Nikitin// Journal of colloid and interface science. – 2019. – Vol. 541. – P. 143–149.

[5] Microwave-assisted synthesis of goethite nanoparticles used for removal of Cr(VI) from aqueous solution / V. D. Nguyen, J. Kynicky, P. Ambrozova, V. Adam // Materials. – 2017. – Vol. 10, N 7. – P. 783.

[6] Enhancement of anti-corrosion and mechanical properties of alkyd-based protective paints for steel petroleum structures incorporating natural limonite pigment / M.I. Abdou, Hany El-Sayed Ahmed, M. A. Wahab Gaber, A. M. Fadl // Cogent Engineering. – 2018. – Vol. 5, N 1. – P. 1427844.

[7] Zhang M. Comparison of arsenic adsorption on goethite and amorphous ferric oxyhydroxide in water / M. Zhang, M. Dai, S. Song // Water, Air, & Soil Pollution. – 2017. – Vol. 228, N 11. – P. 427.

[8] Goethite as an efficient heterogeneous Fenton catalyst for the degradation of methyl orange / Y. Wang, Y. Gao, L. Chen, H. Zhang // Catalysis Today. – 2015. – Vol. 252. – P. 107–112.

[9] Synthesis and characterization of iron oxide pigments through the method of the forced hydrolysis of inorganic salts / M. Müller, J. C. Villalba, F. Q. Mariani [et al.] // Dyes and Pigments. – 2015. – Vol. 120. – P. 271–278.

[10] Kong D. Synthesis and characterization of cellulose-goethite composites and their adsorption properties with roxarsone / D. Kong, L. D. Wilson // Carbohydrate polymers. – 2017. – Vol. 169. – P. 282–294.

[11] Cornell R. M. The iron oxides: structure, properties, reactions, occurrences and uses / R. M. Cornell, U. Schwertmann // Weinheim, Cambridge:John Wiley & Sons, 2003. – 137 p.

[12] Goethite, α-FeO(OH), from single-crystal data / H. Yang, R. Lu, R. T. Downs, G. Costin // Acta Crystallographica Section E: Structure Reports Online. – 2006. – Vol. 62, N 12. – P. 250–252.

[13] XAS studies of pressure-induced structural and electronic transformations in α-FeOOH / N. Trcera, S. Layek, M. Shulman, A. Polian [et al.] // Journal of

Physics: Condensed Matter. – 2019. – Vol. 31, N 32. – P. 325401.
[14] Frolova L. Obtaining of brown pigments from concentrated waste water containing nickel / L. Frolova, A. Pivovarov // Chemistry & Chemical Technology. – 2016. – Vol. 10, N 2. – P. 209–212.
[15] Suppiah D. D. One step facile synthesis of ferromagnetic magnetite nanoparticles / D. D. Suppiah, S. B. A. Hamid // Journal of Magnetism and Magnetic Materials. – 2016. – Vol. 414. – P. 204–208.
[16] Dutrizac J. E. Behaviour of the rare earths during goethite (α-FeOOH) precipitation from sulphate-based solutions / J. E. Dutrizac, C. Soriano // Hydrometallurgy. – 2018. – Vol. 176. – P. 87-96.
[17] Burleson D. J. Two-step growth of goethite from ferrihydrite. One step facile synthesis of ferromagnetic magnetite nanoparticles / D. J. Burleson, D. D. Suppiah, S. B. A. Hamid// Journal of Magnetism and Magnetic Materials. – 2016. – Vol. 414. – P. 204-208.
[18] Walter D. The mechanism of the thermal transformation from goethite to hematite / D. Walter, G. Buxbaum, W. Laqua // Journal of Thermal Analysis and Calorimetry. – 2001. – Vol. 63, N 3. – P. 733–748.
[19] Khoiroh L. M. Synthesis of Goethite (α-FeOOH) Pigment by Precipitation Method from Iron Lathe Waste/ L. M. Khoiroh, E. D. Nuraini, N. Aini // ALCHEMY. – 2018. – Vol. 6, N3. – P. 65–69.
[20] Synthesis of acicular goethite with surfactants / R. Frost, H. Y. Zhu, P. Wu, T. Bostrom // Materials Letters. – 2005. – Vol. 59, N 17. – P. 2238–2241.
[21] Frolova L. Non-equilibrium plasma-assisted hydrophase ferritization in Fe^{2+}–Ni^{2+}–SO_4^{2-}–OH^- System / L. Frolova, A. Pivovarov, E. Tsepich // Nanophysics, Nanophotonics, Surface Studies, and Applications. Springer Proceedings in Physics. – 2016. – Vol. 183, – P. 213–220.

References

[1] Litynska, M., Antoniuk, R., Tolstopalova, N., Astrelin, I.M. (2019). Ferric Oxyhydroxide as Fouling Prevention Reagent for Low-Pressure Membranes. *IEE Journal of Ecological Engineering*, *20*(3), 77–84.
[2] Frolova, L.A. (2014). Production conditions of iron oxide black from pickle liquors. *Metallurgical & Mining Industry*, 4, 65–69.
[3] Khan, S. R., Jamil, S., Janjua, MRSA., Khera, RA. (2017). Synthesis of ferric oxyhydroxide nanoparticles and ferric oxide nanorods by reflux assisted coprecipitation method and comparative study of their thermal properties. *Materials Research Express*, *4*(11), 115019.
[4] Lunin, A. V., Kolychev, E. L., Mochalova, E. N., Cherkasov, V. R., Nikitin, M. P. (2019). Synthesis of highly-specific stable nanocrystalline goethite-like hydrous ferric oxide nanoparticles for biomedical applications by simple precipitation method. *Journal of colloid and interface science*, 541, 143–149.
[5] Nguyen, V. D., Kynicky, J., Ambrozova, P., Adam, V. (2017). Microwave-assisted synthesis of goethite nanoparticles used for removal of Cr(VI) from aqueous solution. *Materials*, *10*(7), 783.
[6] Abdou, M.I., Ahmed, Hany El-Sayed, Wahab Gaber, M. A., Fadl, A. M. (2018). Enhancement of anti-corrosion and mechanical properties of alkyd-based protective paints for steel petroleum structures incorporating natural limonite pigment. *Cogent Engineering*, *5*(1), 1427844. https://doi.org/10.1080/23311916.2018.1427844
[7] Zhang, M., Dai, M., Xia, L., Song, S. (2017). Comparison of arsenic adsorption on goethite and amorphous ferric oxyhydroxide in water. *Water, Air, & Soil Pollution*, 228 (11), 427.
[8] Wang, Y., Gao, Y., Chen, L., & Zhang, H. (2015). Goethite as an efficient heterogeneous Fenton catalyst for the degradation of methyl orange. *Catalysis Today*, 252, 107–112.
[9] Müller, M. Villalba, J. C., Mariani, F. Q., Dalpasquale, M., Lemos, M. Z., Gonzalez Huila, M. F., Anaissi, F. J. (2015). Synthesis and characterization of iron oxide pigments through the method of the forced hydrolysis of inorganic salts. *Dyes and Pigments*, 120, 271–278.
[10] Kong, D., Wilson, L.D. (2017). Synthesis and characterization of cellulose-goethite composites and their adsorption properties with roxarsone. Carbohydrate polymers, 169, 282–294. http://doi.org/10.1016/j.carbpol.2017.04.019 0144-8617
[11] Cornell, R. M., Schwertmann, U. (2003). The iron oxides: structure, properties, reactions, occurrences and uses. Weinheim, Cambridge: John Wiley & Sons.
[12] Yang, H., Lu, R., Downs, R. T., Costin, G. (2006). Goethite, α-FeO(OH), from single-crystal data. *Acta Crystallographica Section E: Structure Reports Online*, *62* (12), 250–252. http://doi.org/10.1107/S1600536806047258
[13] Trcera, N., Layek, S., Shulman, M., Polian, A., Irifune, T., Itié, J. P., Rozenberg, G. K. (2019). XAS studies of pressure-induced structural and electronic transformations in α-FeOOH. *Journal of Physics: Condensed Matter*, *31*(32), 325401.
[14] Frolova, L, Pivovarov A. (2016). Obtaining of brown pigments from concentrated waste water containing nickel. Chemistry & Chemical Technology, *10*(2), 209–212.
[15] Suppiah, D. D., Hamid, S. B. A. (2016). One step facile synthesis of ferromagnetic magnetite nanoparticles. *Journal of Magnetism and Magnetic Materials*, 414, 204-208.
[16] Dutrizac, J. E., Soriano, C. (2018). Behaviour of the rare earths during goethite (α-FeOOH) precipitation from sulphate-based solutions. *Hydrometallurgy*, 176, 87–96.
[17] Burleson, D. J., Suppiah, D. D., Hamid, S. B. A. (2016). Two-step growth of goethite from ferrihydrite. One step facile synthesis of ferromagnetic magnetite nanoparticles. *Journal of Magnetism and Magnetic Materials*, 414, 204–208.
[18] Walter, D., Buxbaum, G., Laqua, W. (2001). The mechanism of the thermal transformation from goethite to hematite. *Journal of Thermal Analysis and Calorimetry*, *63*(3), 733–748.
[19] Khoiroh, L. M., Nuraini, E. D., Aini, N. (2018). Synthesis of Goethite (α-FeOOH) Pigment by Precipitation Method from Iron Lathe Waste. *ALCHEMY*, *6*(2), 65–69.
[20] Frost, R., Zhu,H. Y., Wu, P., Bostrom, T. (2005). Synthesis of acicular goethite with surfactants. *Materials Letters*, *59*(17), 2238–2241.
[21] Frolova, L., Pivovarov, A., Tsepich, E. (2016). Non-equilibrium plasma-assisted hydrophase ferritization in Fe^{2+}–Ni^{2+}–SO_4^{2-}–OH^- System. *Nanophysics, Nanophotonics, Surface Studies, and Applications. Springer Proceedings in Physics*, 183, 213–220.