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Removal of Zn^{2+} ions from wastewater using iron-containing sorbents

Usuwanie jonów Zn^{2+} ze ścieków stosowanie sorbentów zawierających żelazo

Anastasia Sosedko, Dmitry Samchenko*)

Keywords: *magnetic sorbents, washing wastewater, zinc ions, ultrasound treatment.*

Abstract

The possibility of increasing the level of environmental safety for industrial enterprises as a result of implementation of the latest sorption technologies for the purification of washing wastewater are considered. Analysis of effectiveness of the existing methods of sorption treatment of zinc-containing wastewater was carried out. Magnetic sorbents was obtained by the method of hydrophase ferritization and their structural analysis was studied. The sorption capacity of different phase composition for zinc ions removal from wastewater was fulfilled. The influence of pH value on the purification process of washing wastewater was determined. In this work ultrasound was used to increase the efficiency of wastewater treatment by magnetic sorbents. The most effective results for water purification were achieved using a sorbent containing 61.3% of δ-FeOOH, 38.7% of Fe_3O_4, as well as 100% Fe_3O_4. Application of ultrasound and increasing the pH value to 10 a high level of zinc ions removal is achieved – more than 98.9%. The obtained purified solution meets the current standards for water use in the operations of washing parts in galvanic facilities. Implementation of research results at enterprises will prevent environmental pollution with toxic substances and change outdated wastewater treatment technologies. Spent sorbents are chemically stable and have ferromagnetic properties; thay can be recycled into commercial products.

Słowa kluczowe: *sorbenty magnetyczne, ścieki z przemywania, jony cynku, oczyszczanie ultradźwiękowe.*

Streszczenie

Rozważa się możliwość podniesienia poziomu bezpieczeństwa ekologicznego przedsiębiorstw przemysłowych w wyniku wdrożenia najnowszych technologii sorpcyjnych do oczyszczania ścieków popłucznych. Przeprowadzono analizę skuteczności istniejących metod sorpcyjnego oczyszczania ścieków zawierających cynk. Sorbenty magnetyczne otrzymano metodą ferrytyzacji hydrofazowej i przeprowadzono badania ich analizy strukturalnej. Zdolność sorpcyjna o różnym składzie fazowym do usuwania jonów cynku ze ścieków została spełniona. Określono wpływ wartości pH na proces oczyszczania ścieków po przemywaniu. W pracy wykorzystano ultradźwięki do zwiększenia efektywności oczyszczania ścieków za pomocą sorbentów magnetycznych. Najbardziej efektywne wyniki oczyszczania wody uzyskano stosując sorbent zawierający 61,3% δ-FeOOH, 38,7% Fe_3O_4 i 100% Fe_3O_4. Zastosowanie ultradźwięków i podniesienie wartości pH do 10 pozwala uzyskać wysoki poziom usuwania jonów cynku – ponad 98,9%. Otrzymany oczyszczony roztwór spełnia aktualne normy dotyczące wykorzystania wody w operacjach mycia części w obiektach galwanicznych. Wdrożenie wyników badań w przedsiębiorstwach zapobiegnie zanieczyszczeniu środowiska substancjami toksycznymi i zmieni przestarzałe technologie oczyszczania ścieków. Zużyte sorbenty są stabilne chemicznie i mają właściwości ferromagnetyczne; Można je poddać recyklingowi w produkty komercyjne.

Introduction

Water is one of the most important and strategic resources for human life, industry and the environment. It is estimated that only 10% of available water in the world is for domestic use. According to the World Health Organization and UNICEF, about 768 million people do not have access to clean water [21]. Therefore, environmental protection and rational use of water resources is of great importance. Wastewater from galvanic production is one of the most dangerous liquid wastes of industrial enterprises. In connection with the diversity of the chemical composition, properties and consumption of wastewater, it is necessary to provide for the use of special methods at such enterprises, as well as facilities with preliminary and complete purification of these water from various pollutants. The surface treatment and coating operations end with the washing of parts, as a result galvanic production is inextricably connected with wastewater discharge. Depending on the production capacity, 0.2 ÷ 5 m^3 of water is used to wash 1 m^2 of the coating surface [13]. In general, according to the types of electroplating, the largest volume of production falls on the galvanizing line, namely 40 ÷ 50% [10]. In this regard, treatment of washing water in order to remove metal ions, return of purified water to production and prevention of pollution of the environment is an urgent problem.

Currently, a significant number of methods based on various physical and chemical processes are used to purify aqueous solutions from heavy metal compounds. The most common are reagent based methods of wastewater treatment at galvanic productions, their share is more than 80% [22]. However, sorption methods are very popular in recent years. They are characterized by ease of operation, low cost and high level of purification. The development of environmentally friendly and cost-effective sorbents from waste is a modern research trend. However, disposal of exhausted sorbents is a big problem to avoid environmental risks.

* **Anastasia Sosedko** (snitko2311@gmail.com, ORCID ID 0000-0003-4644-7302), **Dmitry Samchenko** (sama314@ukr.net, orcid.org/0000-0003-3305-8180)
KYIV NATIONAL UNIVERSITY OF CONSTRUCTION AND ARCHITECTURE

There are known numerous studies on the use of magnetic sorbents for the removal of pollutants from industrial wastewater. The most widely used magnetic materials are magnetite Fe_3O_4 and maghemite γ-Fe_2O_3 and hematite α-Fe_2O_3. To improve sorption capacity of magnetic sorbents, it is advisable to use in the process of their obtaining processing methods such as stirring, vibration, grinding and ultrasonic treatment at ambient temperature or elevated temperature. Regarding the global production of porous composites with iron oxides, it is shown that by 2024 the scale of their global market will reach 7.5 billion US dollars [5]. Hematite, magnetite, and maghemite are significantly superior to other iron oxides due to their unique magnetic, catalytic, and other properties [2]. Hematite is the most stable modification of iron oxides and its structure has a different morphology, which makes hematite well adapted to the needs of further application [19]. Iron oxide in the form of magnetite is easily oxidized to Fe_2O_3 or dissolves in an acidic medium, so anaerobic conditions should be ensured during synthesis to avoid oxidation [24]. Therefore, it is obvious that many factors influence the synthesis of magnetic particles of hematite, magnetite and maghemite, which, in turn, increases the complexity of the method. The efficiency of sorption of heavy metals is influenced by the following factors: pH, contact time, temperature, adsorbent dose and initial concentration of ions [20] (in Table 1).

Table 1 Efficiency of zinc ions removal from wastewater by magnetic sorbents

Tabela 1 Skuteczność usuwania jonów cynku ze ścieków za pomocą sorbentów magnetycznych

№	Magnetic sorbents	Sorbtion capacity, mg/g	Time, min	pH	Temperature °C	Reference
1	γ-Fe_2O_3	111.1	-	6	25	[10]
2	Fe_3O_4 nanotubes	107.27	60	6	25	[11]
3	γ-Fe_2O_3 nanotubes	86.95	-	-	-	[12]
4	Fe_3O_4-SiO_2	81.6	60	5	-	[13]
5	Fe_3O_4-SiO_2-TiO_2	137.0	30	-	-	[14]
6	Fe_3O_4-MnO_2	100.24	-	-	25	[15]
7	$MnFe_2O_4$	454.4	120	6	25	[16]
8	$CoFe_2O_4$	384.6	120	6	25	[16]

By synthesizing magnetic iron oxides in laboratory conditions, it is possible to control the particle size and achieve better water purification, using various methods, such as hydrothermal, solvothermal, ferritization, thermal decomposition, microemulsion, electrochemical, and microwave [7]. Among mention methods, the use of ferritization is promising due to its simplicity of synthesis [12]. Production of iron-containing sorbents by the energy-saving ferritization method of spent etching soltions at low temperatures. Adjusting the technological parameters of the ferritization process, it is possible to obtain magnetic sorbents of preset phase composition.

The physical conditions of the sorption process also determine the efficiency of removal of heavy metal ions from wastewater. The traditional method of sorption is carried out by dynamic mixing at different speeds [14]. To intensify the sorption process, ultrasound is used, in particular for the purification of wastewater from organic and bacterial pollution [4]. Thus, the effective use of iron-containing sorbents obtained from the liquid waste of galvanic industries during ultrasound treatment makes it expedient to provide complex technological wastewater treatment at industrial enterprises, according current standards; returning up to 95% of purified water to the closed water supply system of enterprises; low cost of purification; use of compact installations; recycling of valuable components.

The purpose of the work is obtaining of iron-containing sorbents and study of sorption removal of zinc ions from washing wastewater of galvanic facilities.

To achieve the goal, the following tasks were set:

- to determine the influence of the pH value of the solution and ultrasound treatment of sorbent on the efficiency of removal of zinc ions by various iron-containing sorbents;
- to investigate the structure of spent sorbents.

Experimental research methods

Iron-containing sorbents were obtained by the ferritization method of spent ething solutions on the installation described in [17]. Samples of various sorbents were obtained using the technological parameters of the process: initial concentration of iron ions 14.5 g/dm^3; pH = 10.5; the duration of the process is 30 minutes; with different methods of activation of the reaction mixture [12].

The phase analysis of the sorbents was carried out by X-ray diffractometry in a step-by-step mode with Cu-Kα radiation on the Ultima IV device. The shooting was carried out in the range of angles 2θ 6 ÷ 65° with a scan step of 0.05° and exposure time at a point of 2 s.

The sorption capacity of the obtained materials was studied for purification of a model solution for washing wastewater of zinc galvanic line with an initial concentration of Zn^{2+} ions – 30 mg/dm^3 and pH value 5.6. The sorption process was carried out with dynamic mixing at a speed of 800 rpm (Fig. 1a), as well as ultrasonic treatment with a frequency of 40 kHz on the TUN-13 laboratory device (Fig. 1b). Initial and residual concentrations of zinc ions were determined on a Hach DR3900 spectrophotometer.

Fig. 1. Laboratory equipment for sorption purification of wastewater using: a – dynamic mixing, b – ultrasound.

Rys. 1. Urządzenia laboratoryjne do sorpcyjnego oczyszczania ścieków z wykorzystaniem: a – mieszania dynamicznego, b – ultradźwięków

The sorbent powder was added to the model solution at the ratio of 300 mg per 30 mg/dm^3 of zinc ions. The sorption process was carried out during 60 min in the pH range from 5.6 to 10.0. After the process was completed, the sorbent was separated on a filter with a mesh size of 10 µm.

Images of the surface structures were obtained using a scanning electron microscope (SEM) "JEOL" JSM-6510LV.

The dispersion and error limits of the experiments to determine the residual concentrations of zinc ions after the sorption process were evaluated according to the method [8] with a confidence probability of 0.95.

Results and discussion

Results of study of the phase composition for obtained sorbent samples are presented in Table 2.

Research of zinc ions removal by these iron-containing sorbents are shown in the diagrams of Figure 2. Ultrasonic treatment of a sorbent (Fig. 2 b) increases the degree of removal of zinc ions by

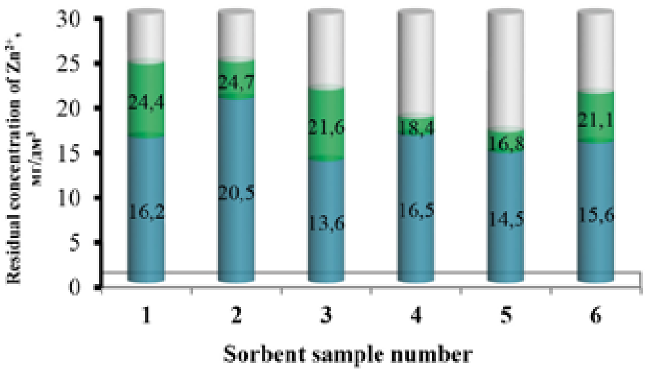
Table 2 Phase composition of sorbents

Tabela 2 Skład fazowy sorbentów

Sample №	Phase content, %			
	γ-FeOOH	δ-FeOOH	Fe_3O_4	γ-Fe_2O_3
1	25.9	74.1	-	-
2	30.2	40.1	29.6	-
3	-	61.3	38.7	-
4	-	31.7	68.3	-
5	-	-	100	-
6	-	-	-	100

an average of 10%. This can be explained by the fact that ultrasound causes the effect of acoustic cavitation. The formation, growth and chaotic collapse of bubbles in an aqueous solution creates short-term local "hot spots" and a pressure of hundreds of atmospheres, which contributes to a more efficient passage of the sorption process.

Increase the pH value of wastewater contributes to the improvement of purification level. It is known [10] that the pH value directly affects the ability of ions to compete for active sites on the surface of the sorbent. According to the authors [18], the maximum sorption capacity is observed at pH from 6 to 9, and in most known studies, the optimal sorption capacity is reached at pH 5 ÷ 7.



a

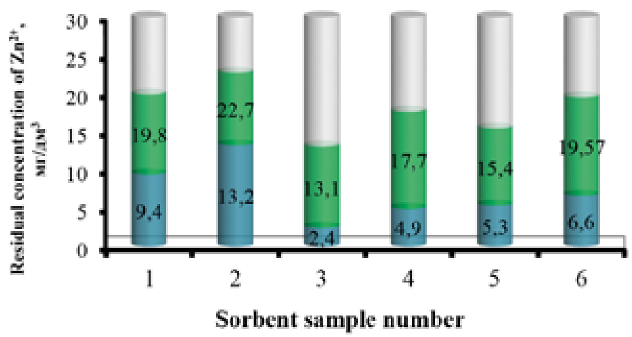


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Fig. 2. The results of sorption wastewater treatment by iron-containing sorbents: a – dynamic mixing; b – ultrasound processing; pH: ■ – pH 5.6; ■ – pH 8

Rys. 2. Wyniki sorpcyjnego oczyszczania ścieków sorbentami zawierającymi żelazo: a – mieszanie dynamiczne; b – obróbka ultradźwiękowa; pH: ■ ▯ pH 5,6; ■ – pH 8

As can be seen from the comparative analysis of the data presented in fig. 2a and b, with growth of pH value from 5.6 to 8.0 the degree of purification for zinc ions increases. The study iron--containing sorbents at different phase composition indicated, that the most effective sorbent contains 61.3% of the phase δ-FeOOH and 38.7% Fe_3O_4.

Using sample No. 3 (Table 2) gives the lowest concentration of zinc ions in the purified solution is 2.4 mg/dm^3, the degree of purification is 92.0%. This is explained by the fact that the sorbent sample has a large mass fraction of the ferroxygite phase δ-FeOOH in its structure, which is unstable in alkaline medium. During ultrasound treatment the δ-FeOOH phase is destroyed and in the presence of zinc ions it is able to form other more stable structures of zinc ferrite and magnetite. It should be noted that despite the high degree of removal of zinc ions from wastewater. However, the quality of the obtained purified solution at the best sorption conditions does not meet the requirements of current standards for zinc ions for reuse water in galvanic productions. In addition, obtaining the desired phase content of metal oxohydroxides in real conditions is very difficult, since the spent steel ething solutions at galvanic plants have different residual concentrations of iron ions. Therefore, to obtain sorbents by the ferritization method, it is always necessary accurately to select and control the technological parameters of this process. As shown by previous studies [11], such synthesis conditions are achieved when sediments contain exclusively magnetite phase. In addition, magnetite is environmentally safe substance. Thus, further research had been focused on the use of this sorbent. shows the results of removal of zinc ions by magnetite are shown in Table 3. The analysis of the obtained data shows that the highest sorption capacity of magnetite is observed at pH value of 10 and simultaneous treatment by ultrasound. At the same time, the residual concentration of zinc ions is 0.3 mg/dm^3 with a degree of wastewater purification of 98.9 %. Such water meets the requirements both for reuse at the galvanic productions in washing operations, and discharge into the central sewage network for further purification at city treatment facilities.

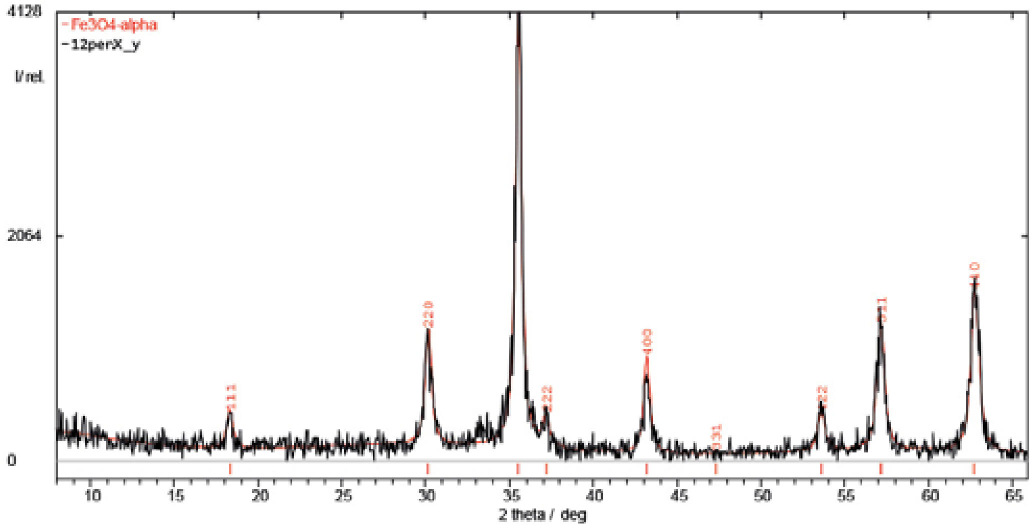
Table 3 Results of the efficiency of wastewater treatment from zinc ions with magnetite sorbent

Tabela 3 Wyniki efektywności oczyszczania ścieków z jonów cynku sorbentem magnetytowym

Conditions of sorption purification	Initial concentration of Zn ions, mg/dm^3	Residual concentrationions Zn from the pH value of wastewater, mg/dm^3			Degree of purification of zinc ionsfrom the pH value of wastewater, %		
		5.6	8.0	10.0	5.6	8.0	10.0
Dynamic mixing	30	16.84	14.52	3.78	43.8	51.6	87.4
Ultrasound treatment		15.43	5.31	0.31	48.5	82.3	98.9

To detect the immobilization of zinc ions, the structure of spent sorbents used at pH 10 was studied. According to the results of X-ray phase analysis (Fig. 3a, b) only the magnetite phase was identified in samples of spent sorbents. The zinc ferrite phase was not detected on the diffractogram, In our opinion, it is due to the fact that the crystal lattices of the spinel structure of the magnetite and zinc ferrite phases are identical.

The results of SEM studies (Fig. 4) serve as evidence of our assumption: both samples are characterized by the presence of structures with different morphology of particles and aggregates. Among them spherical magnetite and zinc ferrite particles are segregated.



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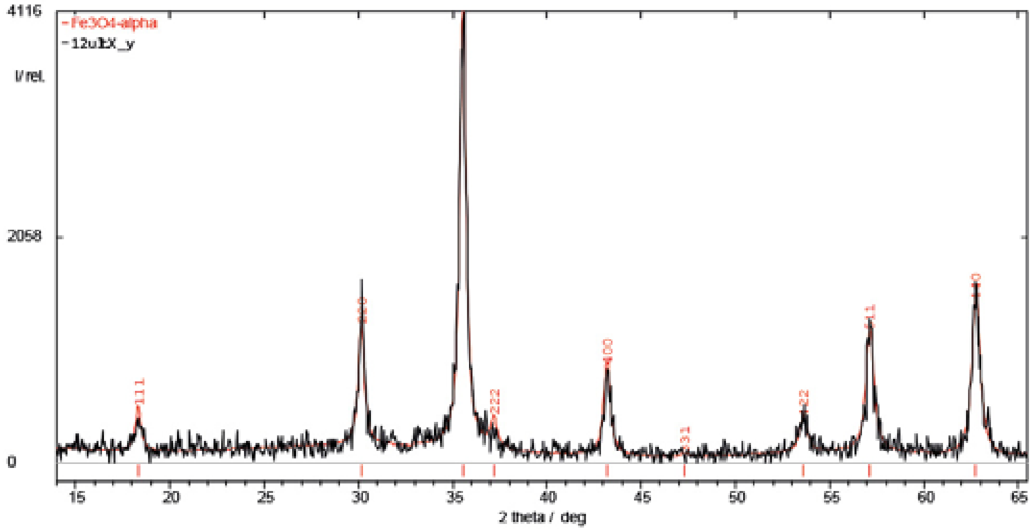

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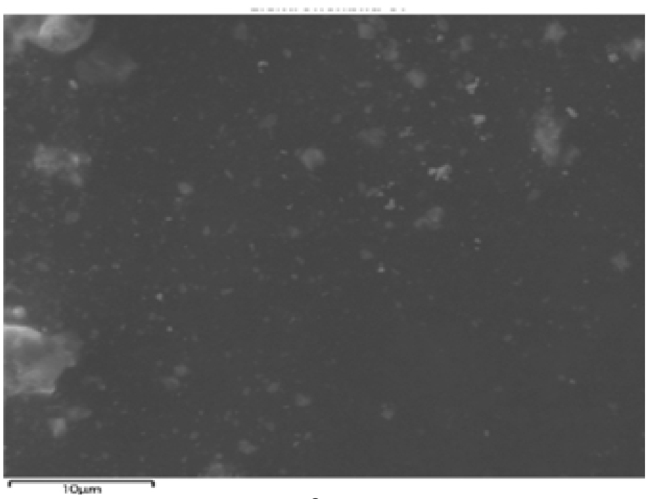
Fig. 3. X-ray diffractograms of spent sorbents treated by: a –dynamic mixing; b – ultrasound treatment

Rys. 3. Dyfraktogramy rentgenowskie zużytych sorbentów poddanych obróbce: a – mieszaniu dynamicznemu; b – leczenie ultradźwiękowe



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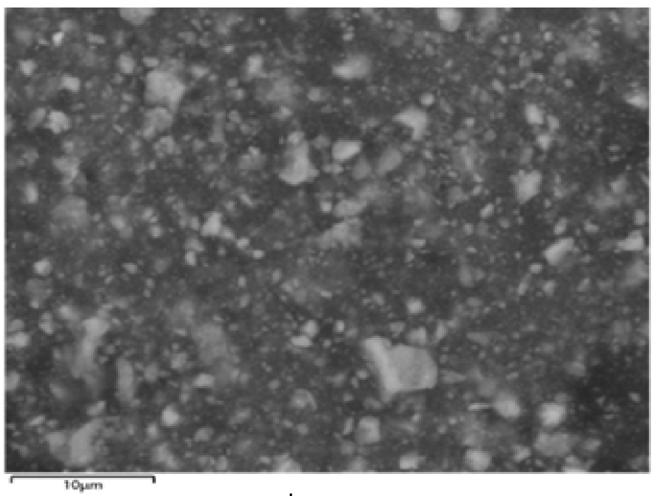

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Fig. 4. SEM images of magnetite aggregates at a with the inclusion of zinc ions in its structure; the sorbent treated by: a – dynamic mixing, b – ultrasound treatment. Magnification of 5000 times.

Rys. 4. Obrazy SEM agregatów magnetytu w punkcie a z włączeniem w ich strukturę jonów cynku; sorbent poddany obróbce poprzez: a – mieszanie dynamiczne, b – obróbkę ultradźwiękową. Powiększenie 5000 razy

In the sample of spent sorbent with using ultrasound treatment (Fig. 4b), there are more spherical irregular shapes compared to the traditional sorption process (Fig. 4a), which obviously indicates higher content of the spinel phases.

The residual concentration of zinc ions in purified water as a result of their sorption by a sample of magnetite with ultrasound treatment (Table 3), as well as the results of structural studies of this sample (Fig. 4) proved the high efficiency and perspective of implementation of the obtained sorbent at industrial productions. It is important to investigate the kinetics of the sorbtion process in our subsequent studies.

Conclusions

Samples of iron-containing sorbents with different phase composition were obtained by the ferritization process of spent steel etching solutions. Sorption capacity of the samples for zinc ions was studied. Ultrasound was used to intensify the sorption process. The most effective results for removal of zinc ions were achieved using sorbents with containing phases: 61.3% δ-FeOOH, 38.7% Fe_3O_4 and 100% Fe_3O_4. Using ultrasound and pH value 10 allows to achieve high degree of zinc ions removal – more than 98.9%. As a result of implementation of the proposed sorption process, the necessary quality of water purification is ensured its reuse at industrial productions in washing operations. The analysis and generalization of the obtained data confirm the perspective of using effective and environmentally friendly magnetic sorbents for the purification of washing wastewater of galvanic industries from Zn^{2+} ions.

Electron microscopy data showed the presence of structures with different morphology of particles and aggregates with predomination of spherical spinel-type particles. Under the conditions of formation of magnetite or zinc ferrite stable phases, the spent sorbent is appropriate for further utilization in building materials.

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REFERENCES

[1] Ahmadi A., Heidarzadeh S.,……Harouni HA Optimization of Heavy Metal Removal from Aqueous Solutions by Maghemite (γ-Fe2O3) Nanoparticles Using Response Surface Methodology. J. Geochem. Explor. 2014. No. 147. P.151-158.

[2] Aredes S., Klein B., Pawlik M. The Removal of Arsenic from Water Using Natural Iron Oxide Minerals. J. Clean. Prod. 2012. No. 29. P. 208-213.

[3] Asadi R., Abdollahi H., Gharabaghi M., Boroumand Z. Effective Removal of Zn (II) Ions from Aqueous Solution by the Magnetic MnFe2O4 and CoFe2O4 Spinel Ferrite Nanoparticles with Focuses on Synthesis, Characterization, Adsorption, and Desorption. Adv. Powder Technol. 2020. No. 31. P. 1480-1489.

[4] Bernatska N. Establishing optimal conditions for water purification using ultrasound. East European Journal of Advanced Technologies ISSN 1729-3774. 4/10 (76) 2015. P. 8-12.

[5] Dontsova T.A. Metal oxide nanomaterials and nanocomposites for environmental purposes: monograph / T.A. Dontsova. - Kyiv: "Polytechnic". 2021. – 323 p.

[6] Habila MA, Alothman ZA, ……Soylak M. Synthesis and Application of Fe3O4@SiO2@TiO2 for Photocatalytic Decomposition of Organic Matrix Simultaneously with Magnetic Solid Phase Extraction of Heavy Metals Prior to ICP-MS Analysis. Talent. 2016. No. 154.S. 539-547.

[7] Hrubyak A.B., Kotsyubynskyi V.O., Moklyak V.V. Methods of synthesis of nanodispersed iron oxides. Solid state physics and chemistry. 2015. No. 16 (1). P. 193 – 201.

[8] Justin, JM On Generalized Variance Functions for Sample Means and Medians. JSM 2018 – Survey Research Methods Section. 2018. P. 584 – 594.

[9] Karami H. Heavy Metal Removal from Water by Magnetite Nanorods. Chem. Eng. J. 2013. No. 219. P. 209-216.

[10] Klymenko M.O., Bedunkova O.O. Cycle of heavy metals in aquatic ecosystems: monograph. Rivne: NUVHP. 2008. 216 p.

[11] Kochetov G., Samchenko D., Lastivka O. Determining the rational parameters for processing spent etching solutions by ferritization using alternating magnetic fields. Eastern-European Journal of Enterprise Technologies. 2022. No. 3 (10). P. 21 – 28.

[12] Kochetov H.M., Samchenko D.M. Improvement of the ferritization technology of wastewater treatment: electromagnetic impulse activation of the process. Water supply and drainage. 2015. Issue 3. P. 20-26.

[13] Plyatsuk L.D., Melnyk O.S. Analysis of galvanic wastewater treatment technologies in Ukraine. Bulletin of Sumy State University. 2008. No. 2. P. 51-56.

[14] Puzanov A., Samchenko D., Kochetov G., Sosedko A., Yemchura B. Research on purification of washing wastewater from zinc ions by magnetic sorbents. Problems of water supply, drainage and hydraulics. 2023, Issue 43. P. 64-73.

[15] Ren Y., Abbood HA, He F., Peng H., Huang K. Magnetic EDTA-Modified Chitosan/SiO2/Fe3O4 Adsorbent: Preparation, Characterization, and Application in Heavy Metal Adsorption. Chem. Eng. J. 2013. No. 226. P. 300-311.

[16] Roy A., Bhattacharya J., Removal of Cu (II), Zn (II) and Pb (II) from Water Using Microwave-Assisted Synthesized Maghemite Nanotubes. Chem. Eng. J. 2012. No. 211–212. P. 493 – 500.10

[17] Samchenko D.M., Kochetov G.M., Derecha DO, Skirta YB Sustainable approach for galvanic waste processing by energy-saving ferritization with AC-magnetic field activation. Cogent Engineering. 2022. No. 9 (1), 2143072.

[18] Shaker MA Adsorption of Co (II), Ni (II) and Cu (II) Ions onto Chitosan-Modified Poly (Methacrylate) Nanoparticles: Dynamics, Equilibrium and Thermodynamics Studies. J. Taiwan Inst. Chem. Eng. 2015. No. 57. P. 111 – 122.

[19]]Tadic M., Trpkov D., …… Panjan M. Hydrothermal Synthesis of Hematite (α-Fe2O3) Nanoparticle Forms: Synthesis Conditions, Structure, Particle Shape Analysis, Cytotoxicity and Magnetic Properties. J. Alloy. Compd. 2019. No. 792. P. 599 – 609.

[20] Wadhawan S., Jain A., Nayyar J., Mehta SK Role of Nanomaterials as Adsorbents in Heavy Metal Ion Removal from WasteWater: A Review. J. Water Process Eng. 2020. No. 33. 101038.

[21]]WHO/UNICEF Progress on Sanitation and Drinking-Water — Update 2013. Available online: https://apps.who.int/iris/handle/10665/81245 (accessed on 28 August 2022).

[22] Yang X. et al. Surface functional groups of carbon-based adsorbents and their roles in the removal of heavy metals from aqueous solutions: a critical review. Chem. Eng. J. 2019. No. 366. P. 608 - 621..

[23] Kochetov G., Samchenko D., Lastivka O. Determining the rational parameters for processing spent etching solutions by ferritization using alternating magnetic fields. Eastern-European Journal of Enterprise Technologies. 2022. No. 3 (10). P. 21 – 28.

[24] Zhao J., Liu J.,…..Cui F. Highly Efficient Removal of Bivalent Heavy Metals from Aqueous Systems by Magnetic Porous Fe3O4-MnO2: Adsorption Behavior and Process Study. Chem. Eng. J. 2016. No. 304. P. 737 – 746.

[25] Zia M., Phull AR, Ali JS Challenges of Iron Oxide Nanoparticles. Powder Technol. 2016. No. 7. P. 49 – 67.