DEVISING A COMPREHENSIVE TECHNOLOGY FOR TREATING INDUSTRIAL IRON SULFATE-CONTAINING EFFLUENTS OF GALVANIC PRODUCTION

The object of the research is complex electrochemical and ferritic decontamination of iron sulfate-containing waters. Processing of liquid waste is carried out by electrochemical treatment using two- and three-chamber electrolyzers. This paper investigates the processes of electrodialysis purification of simulated solutions with an $FeSO_4$ compound concentration of 5 g/dm^3 and an H_2SO_4 compound concentration of 300–2100 mg-equiv/dm^3. A plate made of stainless steel was used as the cathode, and a plate made of titanium covered with ruthenium oxide and lead was used as the anode. It is shown that the highest current yield of electrodialysis products of 84.5 % was obtained when using a three-chamber electrolyzer with MA-41 anion exchange membranes. It was found that when using the specified electrolyzer, the concentration gradient, the value of which is directly proportional to the difference in the concentrations of the initial solutions filled with the electrode chambers, has a significant effect on the process of separation of impurities. It is shown that for a two-chamber electrolyzer, the current output reaches 72 %, which is explained by the harmful effect of a significant concentration gradient and is manifested in the rapid mechanical blocking of the membrane and the slowing down of the ion migration process, as well as the increase in energy consumption. In a two-chamber electrolyzer, H_2SO_4 with a concentration of 18.3 % was obtained, which is suitable for repeated use in etching baths. It was found that as a result of electrodialysis separation and additional oxidation, it is advisable to use concentrated iron sulfate solutions for obtaining ferrite material of a crystalline structure with particle sizes of 2–20 μm. Within the framework of the circular economy, an ecologically safe technology for decontamination of industrial iron-containing sulfate solutions of galvanic production using a complex of electrodialysis and ferrite methods is proposed

Keywords: electrodialysis, galvanic effluents, iron sulfate-containing solutions, three-chamber electrolyzer, ferrite method

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1. Introduction

One of the biggest polluters of the water environment are enterprises related to metalworking industries, in particular galvanic industries. When using relatively small volumes of water, effluents that are formed as a result of technological processes contain a significant amount of heavy metal ions, the anthropogenic entry of which into surface waters has recently led to the pollution of both surface and underground waters [1]. In addition, as a result of accumulation and various chemical transformations, heavy metal ions can transform into more dangerous water pollutants [2, 3].

Etching solutions, the volumes of which reach 0.1 m³/ton of steel, make up a significant amount of waste from electroplating production [4]. According to statistical data [5], the annual discharge of iron ions in the composition of untreated and insufficiently treated wastewater into surface water bodies of Ukraine is 414 tons on average. When iron-containing effluents enter river basins, in particular, after etching processes, the coloration of natural waters increases, which is especially characteristic of reservoirs of the Dnieper Cascade in Ukraine [6]. In addition, as a result of the monitoring of the state of transboundary rivers within the framework of bilateral agreements [7], an unacceptable excess of the content of iron ions was recorded. All these facts require the urgent application of environmental pollution prevention methods.

It should also be noted that in order to ensure a closed cycle of production within the framework of the circular economy, devising environmentally safe technology for the disposal of liquid industrial waste containing iron ions remains relevant.

2. Literature review and problem statement

Paper [8] shows that even with complex use, recently developed methods of removing ions from water, including ion

exchange, evaporation, membrane, or thermal distillation, do not solve the problem of its purification without the formation and accumulation of concentrates. The formation of liquid water treatment waste requires the implementation of additional measures to solve the problem. Iron sulfate solutions, which are formed in significant quantities after etching operations of various steels and subsequent washing stages, are particularly difficult to clean, and require the latest environmentally safe disposal methods. An innovative method of wastewater purification from iron ions is filtration using capillary materials [9]. However, its use is possible only for the extraction of impurities from low-concentration solutions at the level of pollution of natural waters, which is not inherent in wastewater from galvanic production. In addition, the environmentally friendly technology for removing Fe^{2+} ions from more concentrated iron-containing solutions should be distinguished by the prospect of recycling or secondary use of waste. Currently, it is known that iron-containing oxides, obtained from aqueous solutions of iron salts, are a highly demanded commercial product for use in environmental purposes. In particular, work [10] noted the possibility of targeted use of iron oxides in the field of catalytic purification of gas emissions from carbon monoxide. Iron oxides are also proposed to be used for sorption of heavy metals from polluted industrial effluents [11]. Another way of using iron-containing oxides is their use in the production of building materials [12].

It was shown in [13] that the use of the reagent method allows achieving high levels of purification of industrial effluents but leads to the formation of contaminated oxide material that is difficult to separate from sparingly soluble salts. At the same time, the formed compounds are not only impossible to use in nature protection directions but also need to be buried at special storage facilities, the construction and operation of which is expensive and undesirable. In addition, when using the reagent method, unacceptable secondary water pollution occurs [14].

An option to overcome the relevant difficulties may be the electrochemical treatment of polluted industrial effluents by electrolysis, which is characterized by perspective and ecological expediency. The advantage of this method is the absence of the use of additional chemical reagents [15]. But, despite a number of significant advantages, the main disadvantage of electrochemical cleaning is high electricity consumption. An effective way to optimize the use of electrolysis processes is to conduct it to obtain products ready for further use – reactive mixtures, acid solutions, etc. [8, 16].

Therefore, the electrodialysis method with the use of ion exchange membranes is precisely the actual technique of electrochemical decontamination of galvanic effluents, which makes it possible to obtain ready-made valuable products for secondary use by separating and oxidizing dangerous wastewater impurities.

It is advisable to use the electrodialysis method of wastewater treatment for wastewater with a salt concentration of up to 10 g/dm^3. It is possible to intensify the process by increasing the current density to a certain limit since in this case the limiting factor will be the concentration polarization that occurs near the surface of the ion exchange membrane. This disrupts the operating mode of the electrolyzer, reducing the permeability of the membrane itself, thereby increasing the technological time of cleaning and increasing the voltage on the electrolyzer, and as a result, causing an increase in electricity consumption. It is possible to reduce such a negative factor by using the method of concentrating iron-containing solutions to a certain value during electrodialysis purification. Subsequently, the resulting

concentrates can be used for ferritic wastewater treatment [17] and the resulting ferritic sediments can be used in environmental protection technologies [10–12].

The process of energy-saving ferrite treatment of galvanic effluents consists in the formation of inert sediments of various phase composition in the presence of iron ions and their separation by magnetic separation [18]. The advantages of this method are high efficiency, the possibility of its application for the removal of heavy metal ions from widespread galvanic processes of galvanizing [19] and nickel plating [20], cheapness due to the repeated use of commercial products. Such processes using iron salts [18] are of industrial importance.

Obtaining magnetic particles of high dispersion from a mixture of ferric and ferric sulfates by precipitating them with alkali makes it possible to significantly reduce the duration of the process, simplify it, and increase the productivity of the equipment [17]. At the same time, there is also no need to control the course of the reaction of the formation of magnetic particles since their characteristics are determined by the composition of the initial solutions and the conditions of their deposition. The essence of the method is rapid precipitation with alkali with or without heating with constant stirring of a mixture of iron salts. This method is most widely used in technologies for the preparation of magnetic fluids, where particles of magnetite or ferrites are the main component. To obtain particles with maximum magnetic properties, the consumption of iron (II) is 0.5 mg per 1 mg of Fe^{3+} ions.

Thus, each of the considered methods has strengths and weaknesses. Among the weak positions, the following can be highlighted:

– the impossibility of disposal of reagent waste treatment;

– concentration limitation of the application of filtration using capillary materials;

– the problem of disposal of spent regeneration solutions and washing waters of the ion exchange method;

– high consumption of electricity when using electrochemical methods.

Based on the review and systematization of literary sources, it can be stated that it is expedient to conduct a study that considers the electrochemical purification of iron sulfate-containing effluents with the subsequent use of solutions of iron (II) and iron (III) sulfates to obtain ferritic materials as a commercial product. This study could make it possible to ensure complex and effective cleaning of galvanic drains and reduce costs for implementation.

3. The aim and objectives of the study

The purpose of research is to devise an integrated technology for the neutralization of industrial iron-containing sulfate solutions of galvanic production using a combination of electrodialysis and ferrite methods.

To achieve the goal, the following tasks were solved:

– to investigate the influence of concentrations of iron sulfate (II) solution in the cathode chamber and sulfuric acid in the anode chamber in a two-chamber electrolyzer on the process of separating impurities, taking into account the replacement of the anode material from titanium to lead;

– to evaluate the possibility of using a three-chamber electro dialyzer with anion-exchange membranes to separate impurities with sodium hydroxide solution in the cathode chamber, sulfuric acid solution in the anode chamber and ferrous sulfate-containing waters in the intermediate chamber;

– to investigate the possibility of oxidation of iron (II) ions in the anode chamber of a two-chamber electrolyzer in the presence of sulfuric acid in the cathode chamber;

– to investigate the physical and chemical state of the ferrite material obtained from the commercial product of electrodialysis – a concentrated solution of iron sulfate (III);

– to propose a technological scheme for integrated de-contamination of industrial iron-containing sulfate solutions with obtaining products suitable for repeated use.

4. The study materials and methods

4. 1. The object and hypothesis of the study

The object of our research is comprehensive electrochemical and ferritic decontamination of iron sulfate-containing waters.

The subject of the study is an ecologically safe technology for processing washing waters of galvanic industries.

The research hypothesis assumes the possibility of concentration of iron (II) sulfate in the near-cathode area and sulfuric acid in the near-anode area of the electrodialysis unit of a two- and three-chamber electrolyzer, taking into account the concentration polarization of the anion exchange membrane.

Accepted assumptions provide for the use of a chemically resistant anion exchange material that allows a high concentration of sulfuric acid.

Adopted simplifications imply the use of simulating solutions that model the composition of washing iron sulfate-containing waters of galvanic production.

4. 2. Materials and equipment used in the experiment

Electrochemical and ferrite methods were used. A first – electrochemical – method was used for the disposal of liquid iron-containing waste, and a second – ferritic – method was applied to obtain ferrite particles of a given size for reuse in the technological processes of other industries.

Solutions of iron sulfate (II) and sulfuric acid were used as simulation solutions, which realistically reflected the composition of wastewater from the etching department of electroplating production. Reagents for solutions were provided by TOV Khimlaborreaktiv LLC (Ukraine, Brovary).

The schematic diagram of the installation of electrodialysis treatment of spent ferrous sulfate-containing galvanic effluents in a two-chamber electrolyzer is given in [21] and in a three-chamber electrolyzer is shown in Fig. 1.

Electrodialysis treatment of wastewater was carried out in two- and three-chamber electrolyzers, the working and intermediate chambers in which had a volume of 100 cm^3 each and were separated by MA-41 anion exchange membranes. The surface of MA-41 membranes, obtained on the basis of synthetic ion-exchange resin AB-17 by pressing a mixture of ionite powder and polyethylene, is reinforced with Capron mesh to ensure mechanical strength. These membranes are characterized by chemical stability, which makes it possible to use them for a long time in concentrated solutions of acids and alkalis [22].

A 12X18N10T stainless steel plate was used as a cathode, and a titanium plate covered with ruthenium oxide and lead was used as an anode. The area of the electrodes was $S_K=S_A=0.12 \text{ dm}^2$. Electrolysis was performed at current densities in the range of $1.7–8.3 \text{ A/dm}^2$.

When using a two-chamber electrolyzer for the separation of impurities, the cathode chamber was filled with a working solution of wastewater – a solution containing $FeSO_4$ and H_2SO_4 with concentrations of 5 g/dm^3

and $550–2100 \text{ mg-equiv/dm}^3$, respectively. The anode chamber of the two-chamber electrolyzer was filled with sulfuric acid solutions with a concentration of $50–2100 \text{ mg-equiv/dm}^3$. In the case of using a two-chamber electrolyzer for the oxidation of impurities, the anode chamber was filled with a solution of iron (II) sulfate with a concentration of $5–20 \text{ g/dm}^3$, and the cathode chamber with sulfuric acid with a concentration of $200–400 \text{ mg-equiv/dm}^3$.

When using a three-chamber electrolyzer (Fig. 1), the working solution containing iron sulfate (II) and sulfuric acid with concentrations of 5 g/dm^3 and $300 \text{ mg-equiv/dm}^3$, respectively, was placed in the middle intermediate chamber. The cathode chamber was filled with an alkali solution with a concentration of $275 \text{ mg-equiv/dm}^3$, and the anode chamber with a solution of sulfuric acid with a concentration of 50 mg-equiv/dm^3.
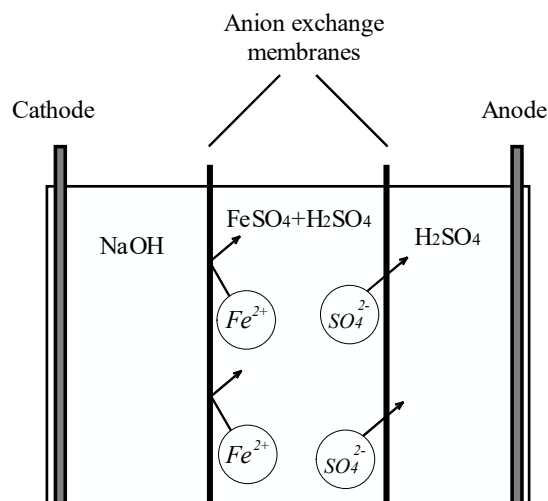

Fig. 1. Diagram of the installation for electrodialysis treatment of spent ferrous sulfate-containing galvanic effluents in a three-chamber electrolyzer

4. 3. Methodology of electrodialysis of ferrous sulfate-containing solutions

Acidity and alkalinity in the anodic and cathodic chambers were monitored during electrolysis, with a periodicity of 2 times per hour. The acidity and alkalinity of the solutions were determined using the classical titrimetric method using 0.1 M HCl and 0.1 M NaOH and indicators, respectively, phenolphthalein and methyl orange [23].

The output of electrolysis products by current was calculated as the ratio of the theoretical and practical amount of electricity, which is spent on transferring the equivalent of the substance:

$$B = \frac{q_{pract}}{q_{theor}} \times 100\,\% = \frac{m_{pract}}{m_{theor}} \times 100\,\%, \qquad (1)$$

where q_{pract} is the amount of electricity actually spent on transferring the equivalent of the substance; q_{theor} is the theoretical amount of electricity spent on substance transfer; m_{pract} is the mass of the substance obtained (transferred to another chamber) during the actual electrolysis process, g; m_{theor} is the mass of the substance received (transferred to another chamber), calculated theoretically, g.

The actual amount of the transferred substance is determined by the change in its concentration in the full volume of the solution:

$$m_{pract} = V \times (C_0 - C), \quad (2)$$

where V is the volume of the treated solution, dm^3; C_0 – initial concentration of the component, g-equiv/dm^3, C – final concentration of the component after treatment, g-equiv/dm^3.

The theoretical amount of transferred substance was determined according to Faraday's law:

$$m_{theor} = Ke \times I \times t, \quad (3)$$

where Ke is the electrochemical equivalent $Ke=$ $=0.03731$ g-equiv/(A·h); I is the current, A; t is time, hours.

4. 4. Methodology for the process of obtaining ferrite material from concentrated solutions of iron (II) and iron (III) sulfate

The process of formation of ferrite material – magnetite was carried out by mixing the solutions of iron (II) and iron (III) sulfate formed as a result of electrodialysis with a ratio of $[Fe^{2+}]/[Fe^{3+}]=0.5$. A 10 % solution of sodium hydroxide was gradually added to the mixture of solutions with constant stirring until pH=9.5 according to [17]. The deposition process is described by the equation:

$$FeSO_4 + Fe_2(SO_4)_3 + 8NaOH \rightarrow$$
$$\rightarrow 4Na_2SO_4 + Fe_3O_4 \downarrow + 4H_2O. \quad (4)$$
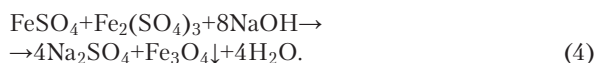
The physicochemical state of the ferrite material obtained according to equation (4) was determined after its thorough purification from sodium sulfate by 3-fold washing, settling, and decantation. In order to obtain an image of the surface of the object with high spatial resolution and establish the qualitative and quantitative elemental (chemical) composition, the ferrite material was studied using a scanning electron microscope with an energy dispersive microanalyzer REM 106I.

5. Results of investigating the electrodialysis disposal of spent ferrous sulfate-containing galvanic effluents to obtain a marketable product

5. 1. Influence of concentrations of ferrous sulfate-containing galvanic effluents on the process of separation of impurities in a two-chamber electrolyzer

During electrodialysis treatment of wastewater in a two-chamber electrolyzer, concentration of iron sulfate solution was observed in the cathode chamber, and sulfuric acid was observed in the anode chamber (Fig. 2). The speed of the process depended on the difference in concentration of the initial solutions and significantly increased with its increase (Fig. 2, a–c). This effect is explained by the growth of the concentration gradient, which in this case is the driving force of the ion migration process through the membrane. An additional confirmation of this was the increase in the current yield of the main product – sulfuric acid from 35.7 to 72 % (Fig. 3). In addition, replacing the anode material from titanium to lead to level the polarizing effect of the current on the membrane did not affect the yield of products by current and the kinetics of electrolysis (Fig. 2, d–f).
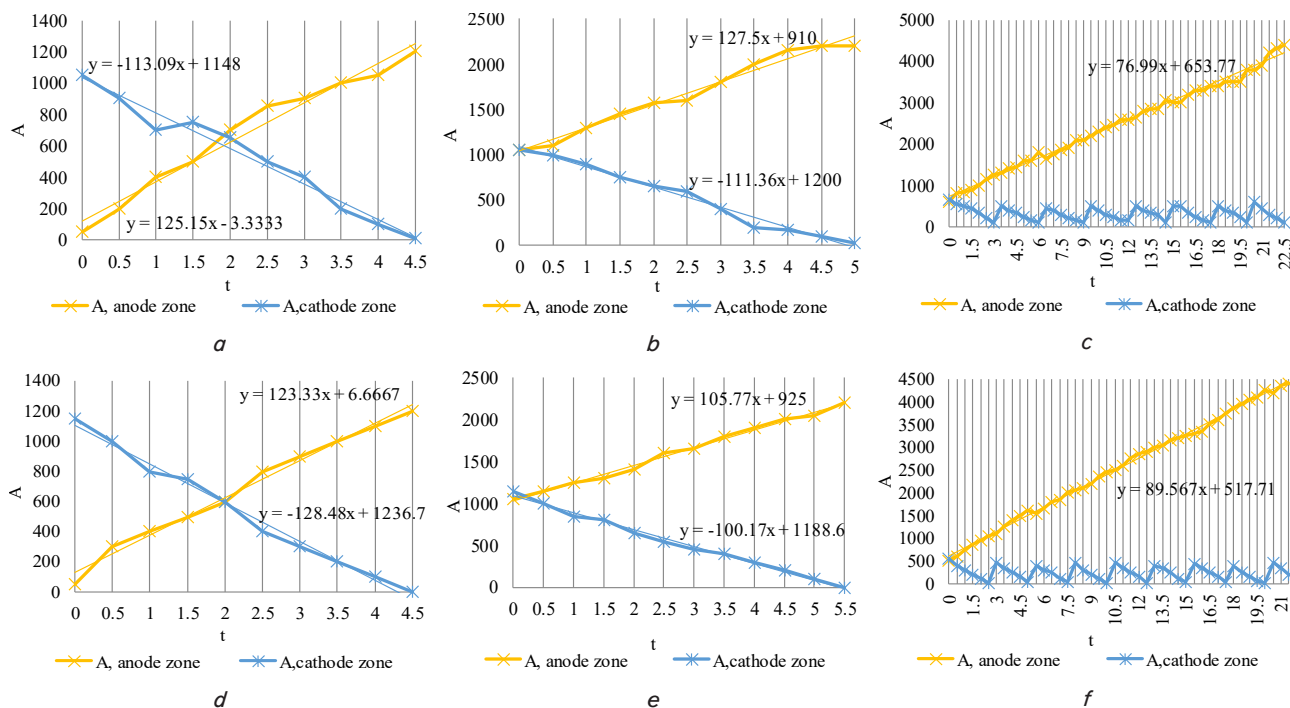

Fig. 2. Change in acidity (K) in the anode and cathode zones during electrodialysis of wastewater in a two-chamber electrolyzer (cathode – steel, current strength – 1 A, [FeSO$_4$]$_{cathode}$=5 g/dm^3):
a – anode: Ti, [H$_2$SO$_4$]$_{anode}$=50 mg-equiv/dm^3, [H$_2$SO$_4$]$_{cathode}$=1050 mg-equiv/dm^3, β_{medium}=68.5 %;
b – anode: Ti, [H$_2$SO$_4$]$_{anode}$=550 mg-equiv/dm^3, [H$_2$SO$_4$]$_{cathode}$=550 mg-equiv/dm^3, β_{medium}=61.6 %;
c – anode: Ti, [H$_2$SO$_4$]$_{anode}$=1050 mg-equiv/dm^3, [H$_2$SO$_4$]$_{cathode}$=1050 mg-equiv/dm^3, β_{medium}=45.3 %;
d – anode: Pb, [H$_2$SO$_4$]$_{anode}$=50 mg-equiv/dm^3, [H$_2$SO$_4$]$_{cathode}$=1050 mg-equiv/dm^3, β_{medium}=68.5 %;
e – anode: Pb, [H$_2$SO$_4$]$_{anode}$=550 mg-equiv/dm^3, [H$_2$SO$_4$]$_{cathode}$=550 mg-equiv/dm^3, β_{medium}=63.4 %;
f – anode: Pb, [H$_2$SO$_4$]$_{anode}$=1050 mg-equiv/dm^3, [H$_2$SO$_4$]$_{cathode}$=1050 mg-equiv/dm^3, β_{medium}=48.6 %

As can be seen from Fig. 2, the concentration of sulfuric acid can be achieved in the range of 1200–2200–4400 mg-equiv/dm^3 or 5–9.16–18.3 % at a current density of 8.3 A/dm^2. The maximum acid concentration was obtained in the case of using a lead anode of 4400 mg-equiv/dm^3 or 18.3 % of sulfuric acid (Fig. 2, f) in 21.5 hours. In addition, this electrode is characterized by greater durability and cheapness.

It is known that in the technological processes of metal processing, for steel etching operations before the application of galvanic coatings, solutions of 15–20 % sulfuric acid, or a mixture of 15 % hydrochloric and 10 % sulfuric acids in a ratio of 1:1 [24, 25] are used. Therefore, it is quite fair to assert the possibility of obtaining an industrial concentrated product for use in etching baths as a result of electrolysis.
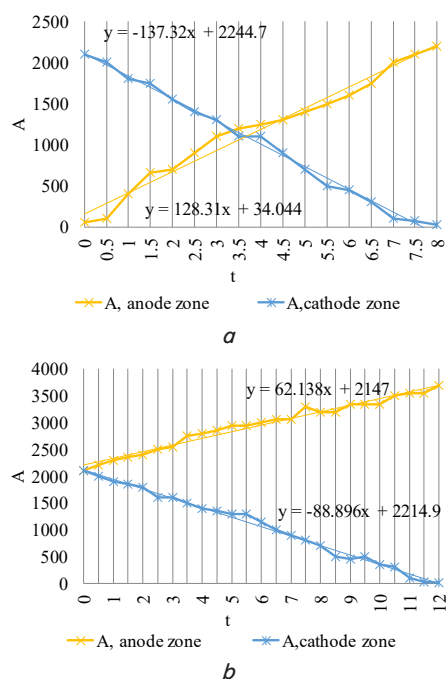

Fig. 3. Change in acidity (K) in the anode and cathode zones during electrodialysis of wastewater in a two-chamber electrolyzer (cathode — steel, anode — Ti, current strength — 1 A, [H$_2$SO$_4$]$_{cathode}$=2100 mg-equiv/dm^3, [FeSO$_4$]$_{cathode}$=5 g/dm^3):
a — [H$_2$SO$_4$]$_{anode}$=50 mg-equiv/dm^3, β$_{medium}$=72 %;
b — [H$_2$SO$_4$]$_{anode}$=2100 mg-equiv/dm^3, β$_{medium}$=35.7 %

In the case of an increase in the concentration of sulfuric acid in the cathode zone and anode zone (Fig. 3), it was possible to achieve acid concentration up to 2200 and 3700 mg-equiv/dm^3, or 9.2 and 15.4 %, respectively, with a much shorter duration of the electrolysis process – 7 and 12 hours.

5. 2. The use of two anion exchange membranes for the separation of impurities in a three-chamber electrolyzer

During electrolysis in a three-chamber electrolyzer (Fig. 1, 4), it was the use of two anion exchange membranes that made it possible to speed up the wastewater treatment process. At the same time, lower values of the current density were used in comparison with electrolyzers, where both anion and cation exchange membranes were used to separate the chambers [16].

In a three-chamber electrolyzer, the cathode chamber is filled with a sodium hydroxide solution, the intermediate working chamber is filled with ferrous sulfate-containing effluents from galvanic production, and a sulfuric acid solution is concentrated in the anode with a current yield of up to 84.5 %. In this case, sulfuric acid with a concentration of 310 mg-equiv/dm^3 or 1.3 % was obtained for 5 hours of concentration with a current density of 1.7 A/dm^2, which confirmed the possibility of using a three-chamber electrolyzer with anion exchange membranes for the separation of impurities. Further research is planned to meaningfully study the separation of iron sulfate (II) and sulfuric acid in a three-chamber electrolyzer using different concentrations of reagents, anode material, and current strength.
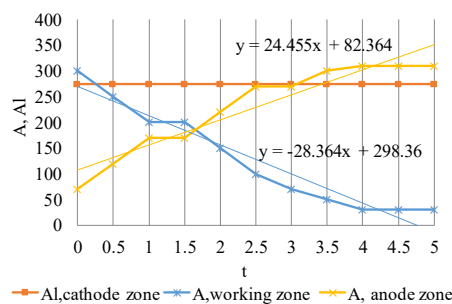

Fig. 4. Change in acidity (K) in the anode and intermediate zones, alkalinity (A) in the cathode zone during electrodialysis of wastewater in a three-chamber electrolyzer: cathode — steel, anode — Ti, current strength — 0.2 A, [H$_2$SO$_4$]$_{anode}$=50 mg-equiv/dm^3, [H$_2$SO$_4$]$_{intermediate}$=300 mg-equiv/dm^3, [FeSO$_4$]$_{intermediate}$ =5 g/dm^3, [NaOH]$_{cathode}$=275 mg-equiv/dm^3, β$_{medium}$=84.5 %

5. 3. Oxidation of iron (II) ions in the anode chamber of a two-chamber electrolyzer in the presence of sulfuric acid in the cathode chamber

Concentration of ferrous sulfate (II) and its subsequent oxidation in the anode region of the electrolyzer was carried out to obtain a concentrated solution of ferrous sulfate (III). Further targeted application of iron (III) sulfate was determined in the direction of ferrite production or use as a coagulant for industrial wastewater treatment [26]. Of course, the use of a smaller volume of reagent with a higher concentration reduces the material costs of obtaining ferrite.

During the operations of further oxidation of the iron-containing sulfate solution, two-chamber electro dialyzers with an anion exchange membrane were used with a current of 0.5 A. It should be noted that in this case, the increase in the difference in the concentration of the solutions in the cathode and anode chambers did not lead to an acceleration of the concentration process. A larger concentration gradient, on the contrary, contributed to the mechanical clogging of the membrane pores by iron ions (Fig. 5) and the increase in voltage on the electrolyzer.

However, iron (II) sulfate concentrates obtained in this way with subsequent oxidation to ferric iron are an excellent cheap raw material obtained as a by-product of the disposal of iron-containing galvanic effluents for use in ferritic purification methods.
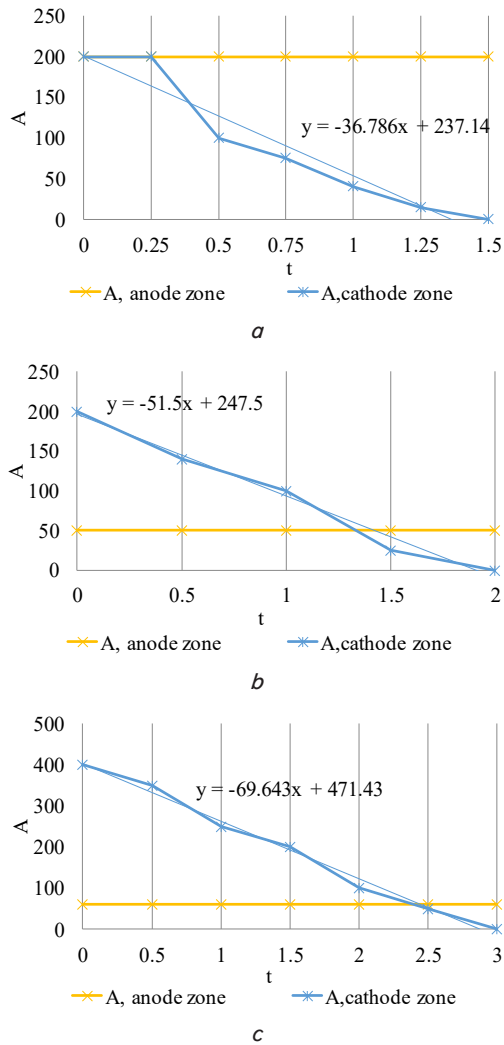
$$y = -36.786x + 237.14$$

a

$$y = -51.5x + 247.5$$

b

$$y = -69.643x + 471.43$$

c

Fig. 5. Change in acidity (A) in the cathodic and anodic zone of wastewater solutions during purification in a two-chamber electrolyzer (cathode — steel, anode — Ti, current strength — 0.5 A): a — $[FeSO_4]_{anode}$=5 g/dm^3, $[H_2SO_4]_{cathode}$=200 mg-equiv/dm^3; b — $[FeSO_4]_{anode}$=10 g/dm^3, $[H_2SO_4]_{cathode}$=200 mg-equiv/dm^3; c — $[FeSO_4]_{anode}$=20 g/dm^3, $[H_2SO_4]_{cathode}$=400 mg-equiv/dm^3

5. 4. The physical-chemical state of ferrite nano-material obtained from a concentrated solution of iron (III) sulfate

As can be seen from Fig. 6, the obtained ferrite material – magnetite has a crystalline structure with particle sizes of 2–20 μm, which fully confirms the results of research into the production of magnetic particles by the ferrite method [17]. Particles of magnetite of the specified size were also obtained by water condensation from solutions of iron-containing salts with a ratio of iron (II) ions to iron (III) ions equal to 0.5.

Fig. 7, 8 show the results of establishing the qualitative and quantitative elemental (chemical) composition of the ferrite material in 2 locations of the maximally expanded portion of magnetite.

The obtained X-ray spectra prove the presence of pure iron oxide material with a predominance of the content of the iron component without sodium sulfate impurities with

certain differences in the weight and atomic ratio. The obtained results can be explained by the inhomogeneity of applying magnetite particles to the adhesive tape when fixing the experimental material for research (Fig. 7, 8).
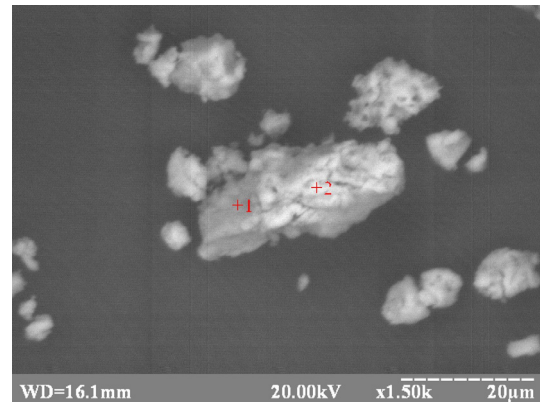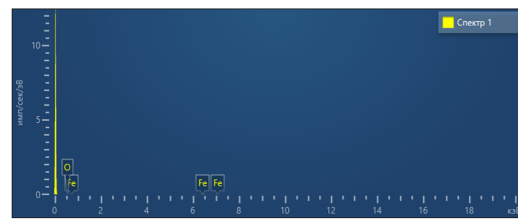

Fig. 6. Image of the surface of a ferrite material cleaned of salts — magnetite, obtained using a scanning electron microscope with an energy dispersive microanalyzer PEM 106I

Spectrum 1				
Element	Line type	Weight %	Sigma weight %	Atom %
O	K-range	5.66	4.59	17.33
Fe	K-range	94.34	4.59	82.67
Totally		100.00		100.00

Fig. 7. X-ray spectrum of 1 ferrite material purified from salts — magnetite, obtained using a scanning electron microscope with an energy dispersive microanalyzer REM 106I
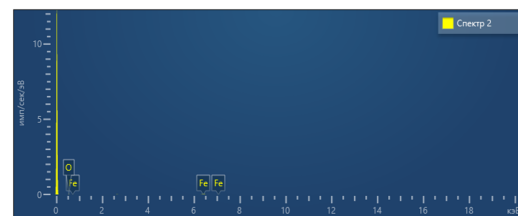
Spectrum 2				
Element	Line type	Weight %	Sigma weight %	Atom %
O	K-range	20.13	4.63	46.80
Fe	K-range	79.87	4.63	53.20
Totally		100.00		100.00

Fig. 8. X-ray spectrum of 2 ferrite material purified from salts — magnetite, obtained using a scanning electron microscope with an energy dispersive microanalyzer REM 106I

It is known that the conditions for using the ferrite method are strict adherence to the concentrations of iron (II) and (III) ions in the solution and the achievement of the appropriate pH. For this reason, it should be taken into account that during the precipitation of a mixture of iron salts

with a NaOH solution at a temperature of 20 °C, magnetite is formed already at pH=4, although the pH of complete precipitation of magnetite reaches 9.5±1.5 [17]. Its formation takes place due to the presence of high local concentrations of OH⁻ ions. When the suspension is stirred, freshly formed magnetite turns into a-FeOOH. In the interval pH=4–8, the formation of magnetite takes place according to the following equations:

$$Fe(OH)_2+FeOOH\rightarrow Fe(OH)OFe(OH)_2, \qquad (5)$$

$$Fe(OH)OFe(OH)_2+FeOOH\rightarrow Fe_3O_4, \qquad (6)$$

$$Fe(OH)_2+2Fe(OH)_3\rightarrow Fe_3O_4. \qquad (7)$$

The process of magnetic phase formation in the described technologies is not instantaneous [17]. In this case, the incubation period lasts 8–10 seconds. After this period, magnetite crystals with the minimum possible size of 38–40 A° are formed in the solution, which eventually grow to sizes of 70 A°. The processes of particle formation and their growth take place in the solution independently of each other. In 10 min after deposition, the processes of formation and growth of particle size practically stop, while the degree of transition of amorphous iron compounds into magnetite crystals approaches 100 %, while the average particle size is estimated at 9 μm.

Thus, in compliance with the requirements for water condensation of magnetite particles, as a result of the research,

ferrite material Fe_3O_4 with a crystalline structure with a predominant particle size of 2–20 μm was obtained.

5. 5. Devising a technological scheme of the process of comprehensive decontamination of industrial solutions

The basic ecologically safe technological scheme of comprehensive disposal of industrial iron-containing sulfate solutions of galvanic production with obtaining products suitable for repeated use is shown in Fig. 9.

As can be seen from Fig. 9, from the receiving chamber 1, ferrous sulfate galvanic wastewater is fed into the intermediate chamber of the three-chamber electrolyzer 2, in the anode chamber of which H_2SO_4 is concentrated, which is later used in the etching processes of galvanic production. In the two-chamber electrolyzer 7, concentration takes place in the cathode chamber, and in the anode chamber of the two-chamber electrolyzer 6, iron (II) sulfate is oxidized with the transition to iron (III) sulfate. The formed iron-containing concentrates from tanks 4 and 9 are mixed in a ferritizer reactor 10 with a stirrer 11 with a sodium hydroxide solution from a waste tank 5 with the formation of a ferritic precipitate, which is removed in a magnetic separator 12. Further, after transportation, the ferritic sludge is sent for drying in a dryer 16. After during the moisture removal process, the ferrite material is crushed to the required size in a ball mill 17 in order to use it as a catalyst for carbon monoxide neutralization or safe burial [11]. After the ferrite sludge separation processes are completed, the purified water is poured into the sewer or reused in the technological process for applying galvanic coatings.
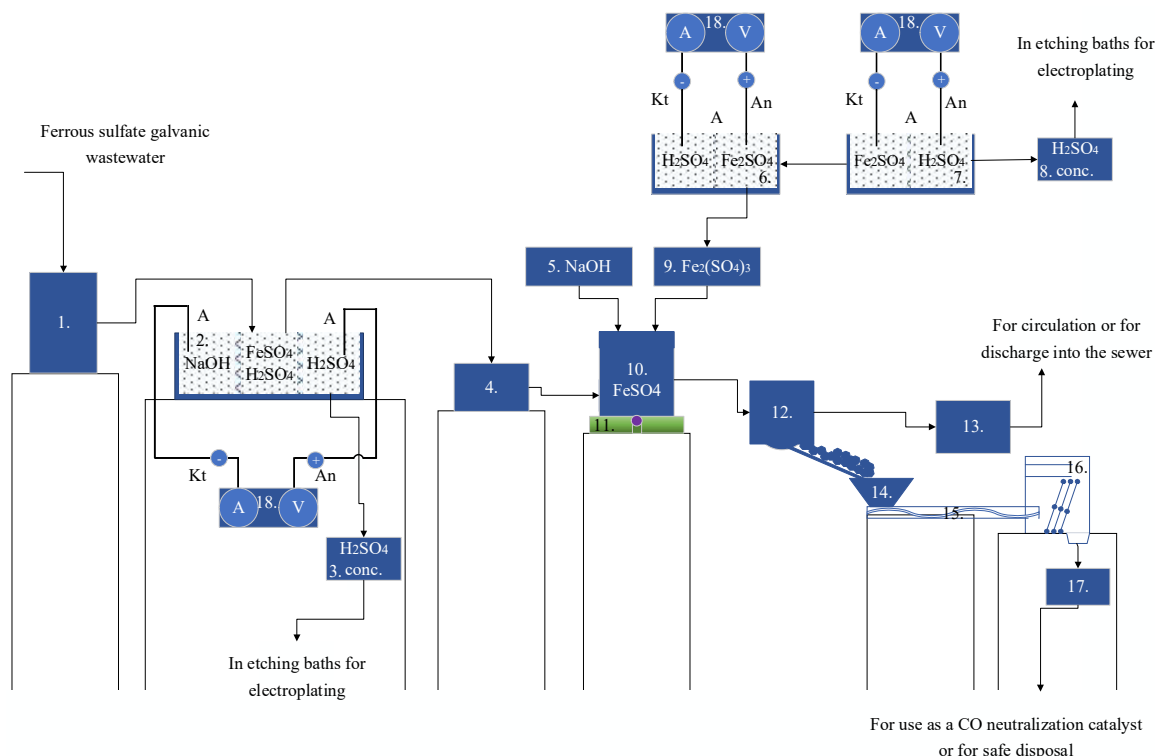

Fig. 9. Ecologically safe basic technological scheme of electroplating waste processing: 1 — receiving chamber of iron sulfate electroplating effluents; 2 — three-chamber electrolyzer with anion exchange membranes; 3 — H_2SO_4 concentration tank in the process of electrolysis in a three-chamber electro dialyzer; 4 — storage tank of iron sulfate solution (II); 5 — consumption tank of NaOH solution; 6 — two-chamber iron (II) oxidation electrolyzer with an anion exchange membrane; 7 — two-chamber electrolyzer with an anion exchange membrane; 8 — H_2SO_4 concentration tank in the process of electrolysis in a two-chamber electrolyzer; 9 — consumption tank of $Fe_2(SO_4)_3$ solution; 10 — ferritizer reactor; 11 — electric stirrer; 12 — magnetic separator; 13 — purified water tank; 14 — receiving capacity of ferritic sediment; 15 — screw; 16 — dryer of ferrite sediment; 17 — ball mill for grinding ferritic sediment; 18 — source of direct current

6. Discussion of results of investigating the processes of electrodialysis treatment of ferrous sulfate-containing effluents with the production of a marketable product

According to the results of studies of processes of electrodialysis neutralization of iron sulfate-containing effluents, when using a three-chamber electrolyzer with anion-exchange membranes, it was possible to achieve a current yield of sulfuric acid up to 84.5 % (Fig. 4). This indicator for a two-chamber electrolyzer reaches 72 % (Fig. 3, *a*), which is significantly higher than the previously obtained results [16], in which the output of sulfuric acid by current reached 50.2 %. At the same time, in a two-chamber electrolyzer, it was possible to obtain sulfuric acid with a concentration of 18.3 % (Fig. 2, *f*), which is quite suitable for use as a commercial product for reverse use in etching baths of galvanic production.

Concentrated sulfate solutions of iron (III) obtained as a result of electrodialysis separation and additional oxidation (Fig. 5) are proposed to be used for decontamination of galvanic effluents by the method of ferritization with subsequent formation of multifunctional ferritic materials from the resulting sediments. However, the conditions for using the ferrite method are strict adherence to the concentrations of iron ions (II) and (III) in the solution and the achievement of the appropriate pH. Therefore, if the requirements for water condensation of magnetite particles are met, the obtained ferrite material – Fe_3O_4 has a crystalline structure with particle sizes of 2–20 microns (Fig. 6), (6), (7), which can be used for environmental purposes. As can be seen from Fig. 7, 8, in magnetite the weight ratio is Fe:O=72.4 %:27.6 %, the atomic ratio is Fe:O=42.9 %:57.1 %. In addition, this fact proves the impossibility of formation of intermediate hydroxide forms (5).

Another way of using iron sulfate (III) is its use as a commercial product – a coagulant. Currently, water treatment processes in Ukraine use the Ferix-3 coagulant produced by Kemira, which is 36 % $Fe_2(SO_4)_3$ (about 10 % $Fe^{3+)}$ and is supplied as a solution both in tanks and in polyethylene containers. At the same time, the sulfate-iron-containing coagulant is supplied in the form of solutions that are easily dissolved in water, have good coagulation properties in the entire range of applied temperatures, which is being purified, and in a wide pH range [27]. In the case of using a less concentrated ready-made solution of iron sulfate (III) with a concentration of 20 g/dm^3 (Fig. 5, *c*) in water treatment, it has ecological feasibility as an indisputable advantage of the effective disposal of electroplating waste.

In addition, for devising an environmentally safe technology for cleaning industrial iron-containing effluents of galvanic production by the electrodialysis method, a necessary process is the production of non-toxic and limitedly biodegradable substances. At the same time, the obtained materials should be close to natural minerals in terms of chemical composition [28]. Accordingly, the safety of burying ferritic sludge sediments is based on the correspondence of its chemical composition to the analogue of magnetite distributed in the Earth's crust [17]. In addition, the application of the ferrite method also ensures residual concentrations of iron ions in purified water corresponding to discharge standards. Thus, the obtained research results in the direction of creating a "green" technology for the processing of galvanic

production waste using a comprehensive of electrodialysis and ferrite methods are undoubtedly appropriate in the direction of improving the environmental safety of the mechanical engineering industry.

Therefore, the application of the electrodialysis method of wastewater treatment of galvanic production makes it possible to effectively solve the problem of comprehensive decontamination of industrial iron-containing sulfate solutions with the production of ready-made products suitable for repeated use. The production of concentrated sulfuric acid and a concentrated solution of iron (III) sulfate as a result of the disposal of industrial effluents only increases the economic feasibility of using this method to obtain ready-to-reuse electrolysis products.

Limitations of the use of electrodialysis cleaning are an increase in the current density above 8 A/dm^2, which can lead not only to the blocking of membranes and an increase in system resistance but also to the exothermic effect of sulfuric acid concentration.

In the future, research is planned to evaluate the possibilities of using the obtained ferrite materials as the active phase of fibrous catalysts for the catalytic neutralization of carbon monoxide emissions.

7. Conclusions

1. It was determined that in a two-chamber electrolyzer with an anion exchange membrane for cleaning iron sulfate-containing washing waters of galvanic industries, effective concentration of solutions is provided only with an optimal concentration difference. Otherwise, the harmful effect of a significant concentration gradient manifests itself in the rapid mechanical blocking of the membrane and, as a result, the slowing down of the ion migration process and the increase in energy consumption. When using a lead anode at a current density of 8.3 A/dm^2, the maximum concentration of sulfuric acid was achieved up to 4400 mg-equiv/dm^3 or 18.3 %, which is quite suitable for use as a commercial product for reverse use in etching baths of galvanic production.

2. When using a three-chamber electrolyzer, the concentration gradient, the value of which is directly proportional to the difference in the concentrations of the starting solutions filled with the electrode chambers, has a significant effect on the process of separation of impurities. At the same time, it is possible to achieve a current output of commercial products suitable for use up to 84.5 %, compared to the same indicator for a two-chamber electrolyzer – 72 %.

3. It was found that in the process of oxidation of an iron-containing sulfate solution in a two-chamber electrolyzer with an anion exchange membrane, an increase in the difference in the concentration of solutions in the cathode and anode chambers did not lead to an acceleration of the concentration process. A larger concentration gradient, on the contrary, contributed to the mechanical clogging of the membrane pores by iron ions and the increase in voltage on the electrolyzer.

4. It is shown that as a result of electrodialysis separation and additional oxidation, it is advisable to use concentrated ferrous sulfate solutions for the production of ferritic material. The resulting magnetite has a crystalline structure with particle sizes of 2–20 μm, which allows it to

be used in environmentally friendly disposal technologies or safe disposal.

5. An environmentally safe technological scheme for decontamination of industrial iron-containing sulfate solutions of galvanic production using a combination of electrodialysis and ferrite methods is proposed. Its features include, in addition to the disposal of liquid waste, obtaining marketable products suitable for reuse in galvanic production and use for environmental purposes in other industries. Given this, global trends in the circular economy can be implemented.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

Data availability

All data are available in the main text of the manuscript.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the presented work.

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