

Optimum Conditions for Applying the Magnetic Absorption Method for Decontamination of Ferrous Sulphate and Chromate-Containing Wastewater

Vyacheslav Radovenchyk¹, Olena Ivanenko¹, Olena Otrokh¹, Tetiana Overchenko¹, Serhii Ivaniuta^{2*}, Daniel Benatov¹, Svitlana Frolenkova³, Liudmyla Hurieva¹

¹ Faculty of Chemical Engineering, Igor Sikorsky Kyiv Polytechnic Institute, Beresteyskyi Avenu, 37/4, 03056 Kyiv, Ukraine

² Institute of Physics and Technology, Igor Sikorsky Kyiv Polytechnic Institute, Beresteyskyi Avenu, 37/4, 03056 Kyiv, Ukraine

³ Faculty of Chemical Technology, Igor Sikorsky Kyiv Polytechnic Institute, Beresteyskyi Avenu, 37/4, 03056 Kyiv, Ukraine

* Corresponding author's e-mail: ivanyuta.sergiy@gmail.com

ABSTRACT

The article deals with the acute issue of intensive contamination of surface and underground waters with iron and chromium ions, which reduces the amount of water suitable for consumption. It was noted that because of monitoring the state of transboundary rivers of Ukraine within the framework of bilateral agreements, an unacceptable excess of the content of heavy metal ions was recorded. The main polluters of the water environment are machine-building enterprises that discharge untreated or insufficiently treated metal-containing wastewater from the processes of steel etching, chrome plating, etc. Recently, the processing of these solutions to obtain a suspension of highly dispersed particles with magnetic properties – magnetite has been increasingly practiced. One of the directions of its use is the sorption of various pollutants in water environments, i.e., the application of the magnetic absorption method. Our study shows the advantages of using magnetite obtained from sulphate solutions in comparison with the traditional sulphate-chloride solution, the influence of the ratio of iron (II) and (III) ions, temperature, pH, nature of the precipitant, salinity on the dispersion of the obtained magnetic particles. When applying the magnetic absorption method, it was determined that hydrolyzed forms of iron (III) ions are best sorbed on magnetite, the removal process of which from aqueous solutions occurs quite intensively during the first two minutes. During the study of various samples of magnetite, it was established that in acidic solutions, with an increase in the ratio of iron (II) and (III) ions, the efficiency of iron ion removal decreases; in neutral and alkaline solutions, such a dependence is not observed. In the proposed technological scheme, purifying wastewater containing 10–100 mg/dm³ of iron ions is advisable by adding 100–1000 mg/dm³ of magnetite suspension and alkali solution to a pH of 8–9. The study showed that during the treatment of chromate-containing waters with magnetite, in addition to the processes of reduction of chromate ions, oxidation of surface Fe²⁺ ions to Fe³⁺, sorption of Cr³⁺ ions or Cr(OH)₃ hydroxides, the reduction of chromate anions on its surface is observed, the basis of which may be the formation chemical compounds, as well as the sorption mechanism. The optimal conditions for removing chromium (VI) compounds from model solutions are to conduct the process at an elevated temperature and use magnetite with a 20 mg per 1 mg Cr⁶⁺ consumption.

Keywords: purification, magnetite, iron sulphate-containing solutions, chromates, hydrolysis, sorption, magnetic absorption method, wastewater.

INTRODUCTION

As a result of anthropogenic human activity, intensive pollution of surface and underground waters is observed every year, which reduces the amount

of water suitable for consumption. For example, today, most water bodies in Ukraine are characterized as polluted and dirty (III and IV quality classes) (Karpenko et al., 2023). In some regions of Ukraine, including the basins of the Dnipro, Siversky Dinets,

and Azov Rivers, the water is classified as “very dirty” (V quality class). A significant amount of waste from galvanic production consists of pickling solutions, which reach 0.1 m³/t of steel (Frolova 2018). Injection of sulphate In-house pickling lines can produce a low salt concentration of 100–300 g/dm³ (Ivanenko et al., 2022). According to statistical data (Statistical publication 2020), the average amount of ions released into the surface water bodies of Ukraine from the storage of untreated and insufficiently treated wastewater is 414 tons. When iron-containing wastewater enters river basins, after digestion processes, the colour of natural waters increases, which is especially typical for reservoirs of the Dnieper cascade in Ukraine (according to the MPC for fishery reservoirs 0.1 mg/dm³) (Natsionalna dopovid 2021). In addition, because of monitoring the state of transboundary rivers within the framework of bilateral agreements, an unacceptable excess of the content of iron ions was recorded. In addition, when chromium is used in passivation processes at machine-building enterprises, a large amount of wastewater contaminated with chromates is generated.

The problem of neutralizing chromates is complicated by the extreme toxicity of these compounds since they are among the most environmentally hazardous, with general toxic, cumulative, allergenic, carcinogenic, and oxidative effects (Donchenko et al., 2018). The detrimental effect of chromium(VI) ions on flora and fauna leads to inhibition of the self-purification processes of water sources; its influence also worsens the formation of sediments in settling tanks and increases the formation of films on biofilters at a water treatment plant. Chromium(VI) accumulates in plant tissues and negatively affects their development, so water containing even traces of chromium should not be used for irrigation. According to statistical data (Statistical publication 2020), the annual discharge of hexavalent chromium ions into the surface water bodies of Ukraine in the composition of untreated and insufficiently treated wastewater is, on average, 1.3 tons. Of course, this amount of Cr(VI) ions is significantly less compared to the annual discharge of iron ions in the amount of 414 t in the composition of iron-containing effluents; however, in the process of monitoring the state of water bodies in Ukraine, an excess of the average annual concentration of Cr(VI) ions (according to the MPC for fishery reservoirs 0.001 mg/dm³) is observed in the pools, Visly, in the city of Pripyat (Natsionalna dopovid

2021). All these facts require the urgent application of methods to prevent environmental pollution by cleaning iron- and chromate-containing wastewater. Existing reagent methods allow for complete wastewater purification but lead to the formation of contaminated oxide material, which is difficult to separate from poorly soluble salts (Trus et al., 2018). The vast majority of washing wastewater from galvanic production has a concentration of iron compounds above the limit standards for discharge into sewers, amounting to 2.5 mg/dm³. Solutions with iron (III) compounds are neutralized, resulting in Fe(OH)₃ precipitation. Iron (II) compounds are oxidized to iron (III), and then the water is neutralized with alkaline reagents. Chromium (VI) compounds are not hydrolyzed when the pH is adjusted and cannot be extracted by traditional reagent methods. To neutralize chromatic wastewater, it is necessary to provide for chromate recovery separately.

In most cases, this is done using chemical reagents and is accompanied by the salinization of water and the formation of a significant amount of highly dispersed sediments that are difficult to separate from the water. Together with sodium bisulphite, hydrogen, carbon, and other substances, iron (II) compounds are often used for these purposes, which form, in addition to the Cr(OH)₃ precipitate, also the Fe(OH)₃ precipitate (Radovenchyk et al., 2020). Therefore, solid waste generated during cleaning does not find practical use. At the same time, the formed compounds not only cannot be used in environmental protection industries but also must be buried in special landfills, the construction and operation of which is expensive and undesirable. In addition, when using the reagent method, unacceptable secondary water pollution occurs (Gomelya et al., 2016). In addition, applying these methods requires the construction of high-volume structures and a significant technological cycle time. Therefore, physical and chemical wastewater treatment methods are more promising, which will solve these technical difficulties and reduce the salinity of treated water and the cost of reagents for their treatment. One of these methods is the magnetic absorption method, which treats a liquid purified by ferromagnetic material (magnetite) segments to deposit substances to be extracted on their surface (Radovenchyk et al., 2020).

The possibility of further separation of ferromagnetic particles in magnetic filters and separators can significantly reduce the technological cycle period and the volume of the resulting sludge. This method's effectiveness has been proven in extracting

copper impurities (Khokhotva et al., 2018) and purifying wastewater from engineering enterprises from associated oil contaminants (Vozniuk et al., 2023). The efficiency of water purification processes depends on the properties of dispersed particles.

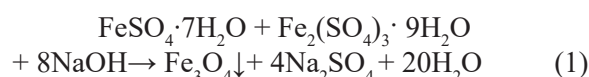
These are particles' dispersity, sorption capacity, and magnetic properties for magnetic sorbents. Existing methods of synthesis of magnetic sorbents (Khokhotva et al., 2018; Samchenko et al., 2022) allow obtaining ferrite particles of high dispersion. However, in each specific case, the particles' shape and size can vary significantly, as they depend on the deposition conditions (the composition of the original solutions and the conditions of their neutralization). It is known that the type of anions in the initial solutions affects the magnetic susceptibility of the obtained magnetite particles (Dudchenko et al., 2011). When magnetite is obtained from sulphate-chloride and chloride-chloride solutions, a higher magnetization is characterized by nano magnetite in sulphate anions. When magnetite is deposited from chloride solutions, the magnetic susceptibility is 1.6 times lower at 40 °C than when using sulfate-chloride solutions. The main reason for this fact is seen in the favourable hydration of the sulphate ion, as opposed to the negative hydration of the chloride anion, which facilitates the hydration of cations and provides magnetite with a more perfect, ordered structure (Bukliv et al., 2008).

The optimization of obtaining magnetite particles using only sulphate-containing solutions to introduce magnetic absorption processing of metal-containing effluents of machine-building enterprises remains quite relevant. Moreover, the issue of sorption of iron ions and chromate anions using magnetite formed from iron sulphates (II) and (III) has not been sufficiently studied. Therefore, the purpose of this work is to study the dispersibility of magnetite particles obtained from a sulphate-containing solution under different conditions, such as storage time, temperature, pH, $(\text{Fe}^{2+}):(\text{Fe}^{3+})$ ratio, salt content, nature of the precipitant, in establishing optimal conditions for water condensation of ferrite material to obtain magnetic particles of the required dispersion for better magneto sorption processes of removing iron compounds and chromium (VI) compounds from model solutions.

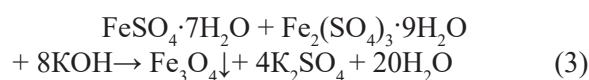
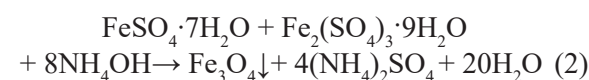
MATERIALS AND METHODS

In this work, magnetite particles were obtained by precipitation from a mixture of solutions of iron (II) and iron (III) salts, and the

particle size distribution was determined by the photoelectric method (Radovenchyk et al., 2020). The process of the experiment involved the preparation of an aqueous solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ i $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ with a concentration of iron ions of 5.59 and 11.17 g/dm³ (16.76 g/dm³ of iron ions), respectively, which corresponds to their stoichiometric ratio $K = (\text{Fe}^{2+}):(\text{Fe}^{3+}) = 0.5$ in the composition of natural magnetite. The equation describes the deposition process using NaOH:



To determine the effect of the precipitant on the change in particle dispersion, NH_4OH and KOH were used, respectively, in the reactions:



Later, the ratio of iron ions (K) was changed to 0.8 (7.45 and 9. g/dm³, respectively); 1 (8.38 and 8. g/dm³, respectively); 1.4 (9.78 and 6.98 g/dm³, respectively); 1.8 (10.78 and 5. g/dm³), 2.0 (11.17 and 5.59 g/dm³, respectively); 2.2 (11.52 and 5.24 g/dm³, respectively); 2.6 (12.10 and 4.66 g/dm³, respectively). A mixture of salts with a concentration ratio of $(\text{Fe}^{2+}):(\text{Fe}^{3+}) = 0.5$ was precipitated with an alkali solution at 20–70 °C to pH = 8–11. The obtained suspension was settled for 30 min and then washed to neutral pH by decantation. After washing, the magnetite suspension was stored in a closed container under distilled water, from which oxygen was previously removed. The precipitation was carried out as follows to determine the influence of applying a magnetic field on the dispersion of magnetite particles. A specially designed glass container containing an aqueous solution of a mixture of iron salts was placed in the working space of the magnetization system (Ivanenko et al., 2020). A magnetic field with a 0 to 76.5 kA/m voltage was created by supplying current to the solenoid in the working volume. Magnetite precipitation was carried out during mixing according to reaction (1) at pH = 9.5. After deposition, the suspension was kept for about 10 minutes, after which the current supply was stopped, and magnetite was washed in a magnetic field.

The method of the magnetostriction extraction of iron and chromate ions experiment consisted

of the preparation of simulated aqueous solutions of FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$ with a concentration of iron(II), (III) ions of 20 mg/dm^3 and $\text{K}_2\text{Cr}_2\text{O}_7$ with a concentration of chromium(VI) ions of $20\text{--}200 \text{ mg/dm}^3$. A dose of magnetite suspension obtained by reaction (1) was added to 100 ml of a model solution with a hydrogen index and temperature determined using NaOH or H_2SO_4 . After stirring for a specified time, the mixture was filtered through an electromagnetic filter as a solenoid, the working volume filled with ferrite particles $1.5\text{--}2.0 \text{ mm}$ in size. Using a direct current source, a magnetic field with a strength of 130 kA/m was created in the working volume of the filter and stirred for 10 min. When filtering a magnetite suspension through such a filter, ferromagnetic particles of magnetite with iron and chromium ions sorbed on its surface were reliably fixed in its pores. The selected filtrate samples were analyzed for iron and chromate ions by a photometric method using sulfosalicylic acid and diphenyl carbazide, respectively (Nabivanets et al., 2007). Periodically, the filter was washed with distilled water through the nozzles with the power source turned off. In the experiments, chemical reagents of the HC qualification were used. 4–6 experiments were conducted in parallel, based on the processing of the results of which curves were constructed, and the main aspects of the investigated process were analyzed. The methods of mathematical statistics

established satisfactory reproducibility of the results. The scheme of the experimental setup is shown in Figure 1.

RESULTS AND DISCUSSION

It is known (Radovenchyk et al., 2020) that even when preserved, the structure of magnetite changes over time. In the deep layers of the magnetite particles, the crystal structure is ordered, while in the upper layers, loosening is observed. Recrystallization processes can also be observed in such suspensions. Accordingly, the dispersion of the solid phase can also change. Our tests showed (Fig. 2) that in the freshly deposited magnetite suspension, there are many particles with a size of less than 10 microns. The processes in the suspension lead to the fact that over time, the number of small particles decreases, and the number of hefty particles increases. Since the maximum number of particles (40–45%) have a size of about 10 microns, particles with a smaller size will be considered negligible, and larger particles will be considered significant.

One of the factors that affects the dispersion of magnetic particles is temperature. As shown by our research (Fig. 3), at a temperature of $20 \text{ }^\circ\text{C}$, a suspension with a maximum content of particles with a diameter of more than 10 microns is formed. Thus, at a temperature of $40\text{--}70 \text{ }^\circ\text{C}$,

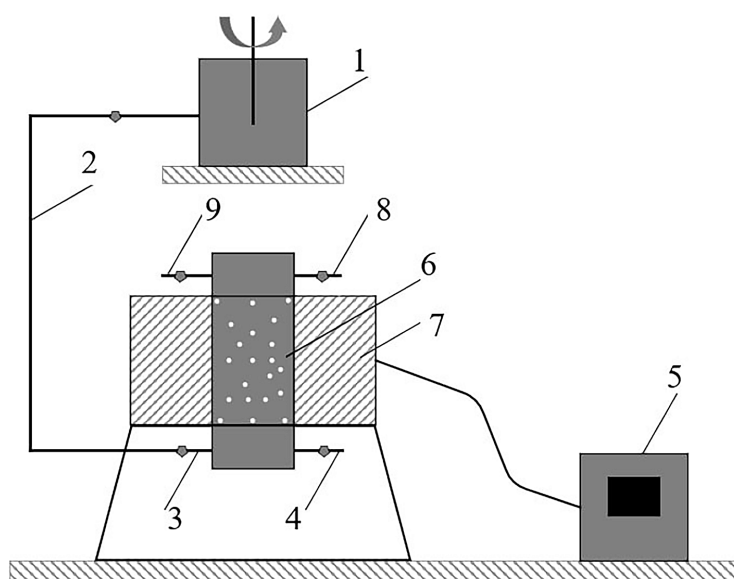


Figure 1. Scheme of the experimental setup: 1 – a glass with a stirrer; 2 – pipeline for the supply of wastewater; 3 – inlet pipe; 4, 8 – flushing nozzles; 5 – power supply unit; 6 – ferromagnetic nozzle; 7 – magnetizing system; 9 – nozzle for draining the filtrate

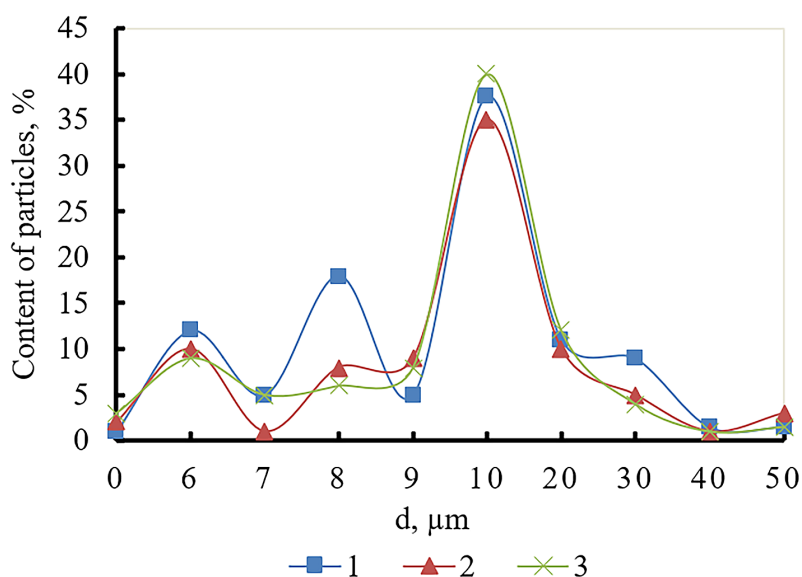


Figure 2. Effect of magnetite aging time at $K = 0.5$ on particle dispersion: 1 – freshly prepared suspension, 2 – 1 day of aging, 3 – 2 days of aging

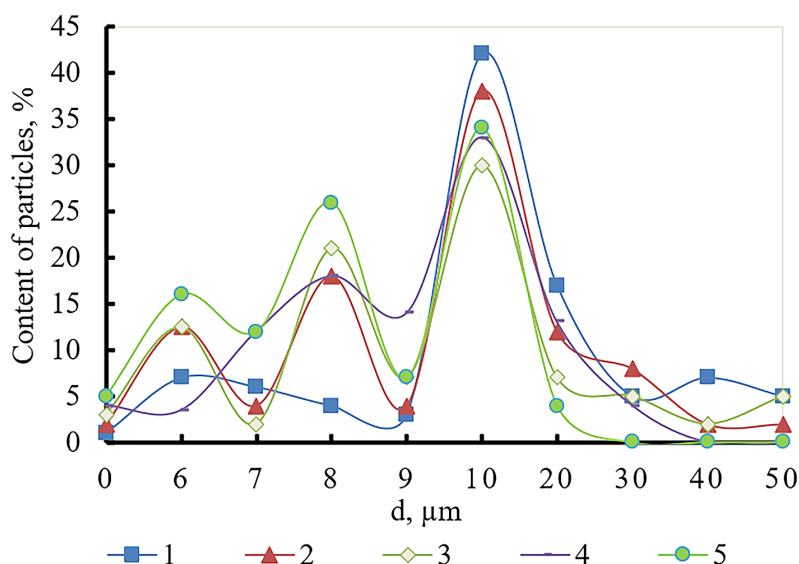


Figure 3. Effect of magnetite preparation temperature on particle dispersion: 1–20 °C; 2–30 °C; 3–40°C; 4–50 °C; 5–70 °C

particles with a size of 8–10 microns prevail in the suspension. It should also be noted that if at temperatures of 20–40 °C, a certain number of particles reaching 65 microns are observed in the solution. At a temperature of 70 °C, the maximum particle size does not exceed 30 microns. The pH at which it precipitates significantly affects the dispersion of magnetite particles. In the conducted experiments, the concentration of iron salts in the solution corresponded to the stoichiometric coefficient $K = 0.5$, and the deposition temperature was maintained at 30 °C. The process was carried out at a pH in the range of

8–11, as seen in Figure 4; with an increase in the pH of the solution, the number of small particles in the suspension increases with a corresponding decrease in the share of large particles. To study the dependence of the dispersion of particles on the ratio of concentrations of iron ions (II) and (III) during the synthesis of magnetite, solutions of iron salts were prepared in the obtained suspensions, considering that the total concentration of iron ions in the solution was constant and equal to 16.76 g/dm³. As our further studies (Fig. 5) established, at $K = 0.8$ and $K = 2.0$, the most significant number of particles with a size of 10

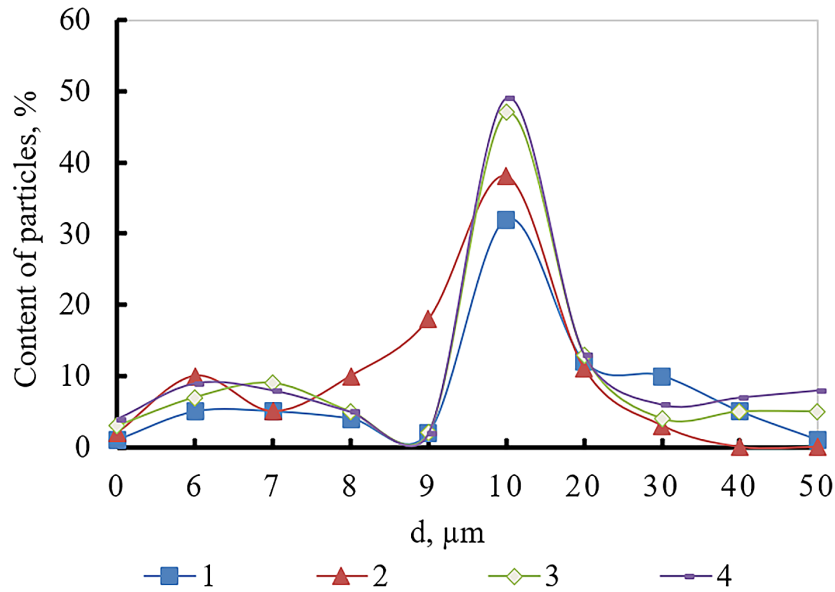


Figure 4. Effect of magnetite deposition pH on particle dispersion: 1 – pH = 8; 2 – pH = 9; 3 – pH = 10; 4 – pH = 11

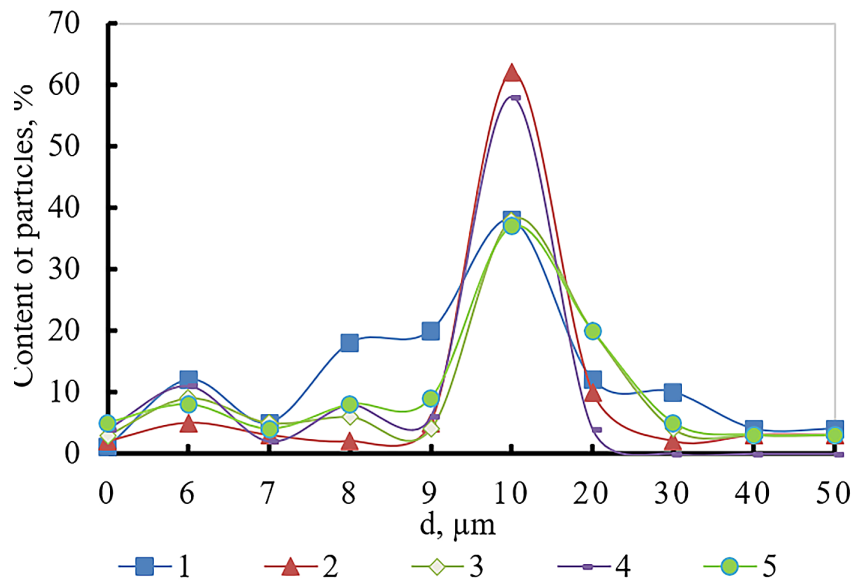


Figure 5. Effect of K on the dispersion of particles: 1 – K = 0.5; 2 – K = 0.8; 3 – K = 1.4; 4 – K = 2.0; 5 – K = 2.6

microns (about 60%) is formed in the solution, while at other ratios, this value does not exceed 40%. However, at $K = 0.5$ and $K = 1.4$, this is compensated by the presence of particles with a size of 30 and even 50 microns, while at $K = 2.0$, there are no particles larger than 35 microns at all. It was also established that an increase in the concentration of the initial solutions is accompanied by an increase in the fraction of small particles and a decrease in the fraction of large particles. An artificial change in salinity by adding Na_2SO_4 showed (Fig. 6) that with an increase in its concentration, the particle size increases with a

decrease in the share of small particles by almost two times. The studies described above were carried out under the influence of such factors as temperature, concentration, and ratio of components in the initial solutions. Considering the presence of magnetite particles with magnetic properties, it can be predicted that applying a magnetic field will significantly affect the dispersion of the suspension. As shown in Figure 7, a suspension with a maximum content of particles with a diameter of 10 microns is formed without the influence of a magnetic field. When the field voltage increases, the particle size first increases, and after a voltage

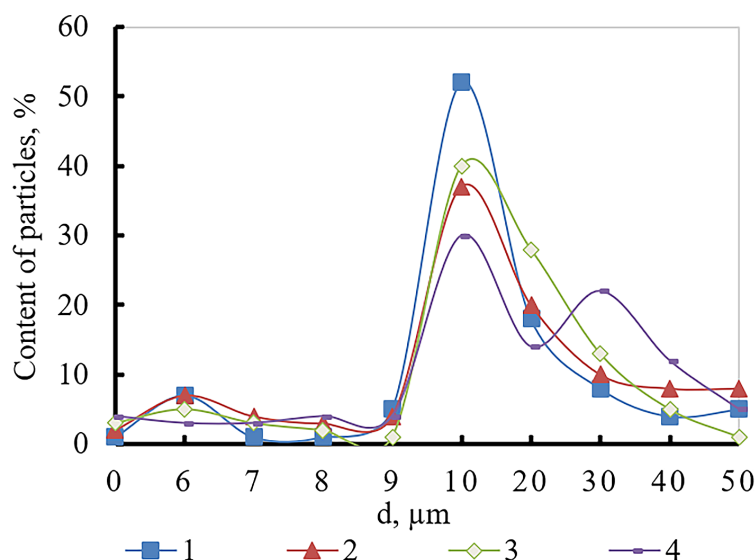


Figure 6. The effect of salinity on the dispersion of particles: 1 – without Na_2SO_4 , 2 – 1 г/л Na_2SO_4 , 3 – 5 г/л Na_2SO_4 , 4 – 50 г/л Na_2SO_4

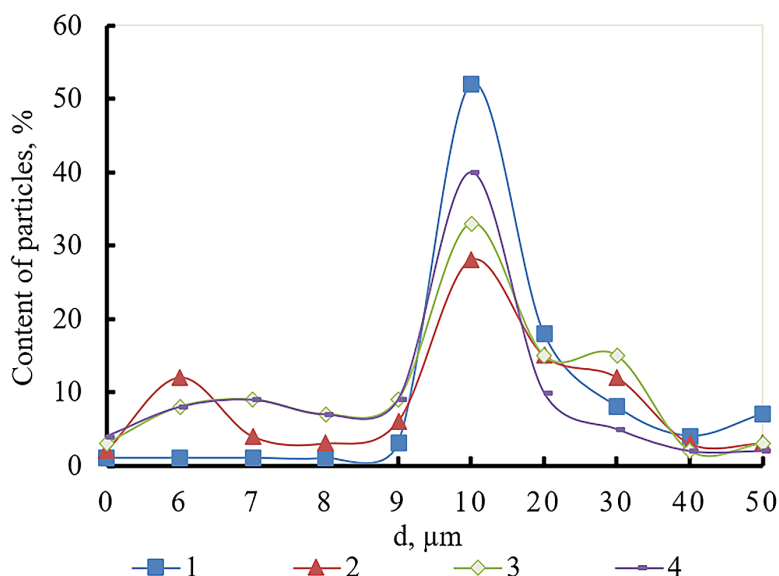


Figure 7. Effect of magnetic field voltage on particle dispersion: 1 – 0 kA/m; 2 – 8.5 kA/m; 3 – 25.5 kA/m; 4 – 76.5 kA/m

of 75.5 kA/m, it begins to decrease again. Intensive solution mixing during deposition also allows you to obtain smaller particles. Testing the influence of the precipitant on the dispersity of the precipitating particles is shown in Figure 8. If an ammonia solution is used as a precipitant, the number of small particles increases relative to NaOH, and the number of hefty particles slightly decreases. When using caustic potash, the number of particles larger than 20 microns is significantly reduced in terms of NaOH and ammonia. To establish optimal conditions for removing iron compounds from model solutions using highly dispersed magnetite

particles obtained from a solution containing iron sulphate, the influence of the hydrogen index on the efficiency of removal of iron ions by magnetite particles was studied (Fig. 9). Since we were primarily interested in the optimal technological parameters of the actual cleaning process, the model solutions were not isolated from air. This affected the results of the experiments in the case of Fe^{2+} , which will be discussed below. Hydrolyzed forms of iron (III) ions are best absorbed. Fe^{3+} ions start and finish hydrolyzing in dilute solutions at pH 1.5 and 4.5, respectively (Radovenchyk et al., 2020). For Fe^{2+} ions, these processes occur at pH 6.5 and

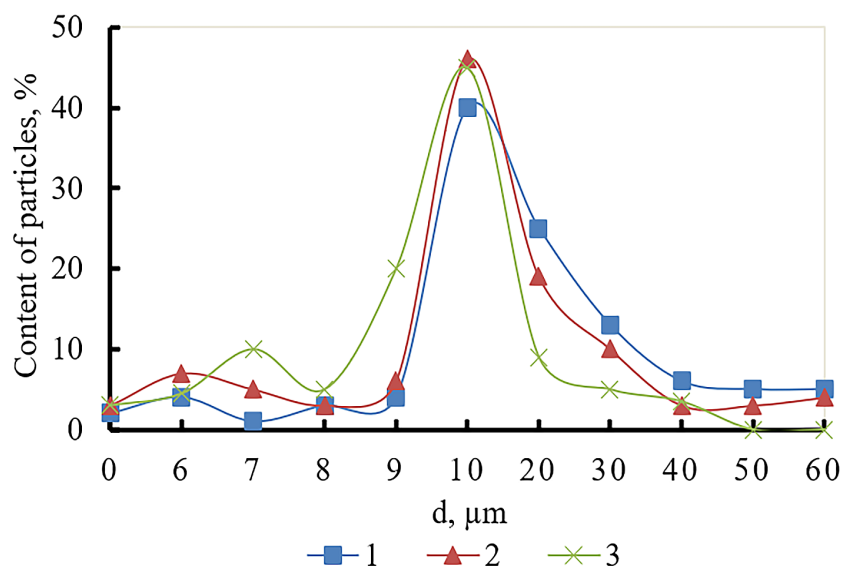


Figure 8. Influence of the nature of the precipitant on the dispersion of particles: 1 – NaOH; 2 – NH₄OH; 3 – KOH

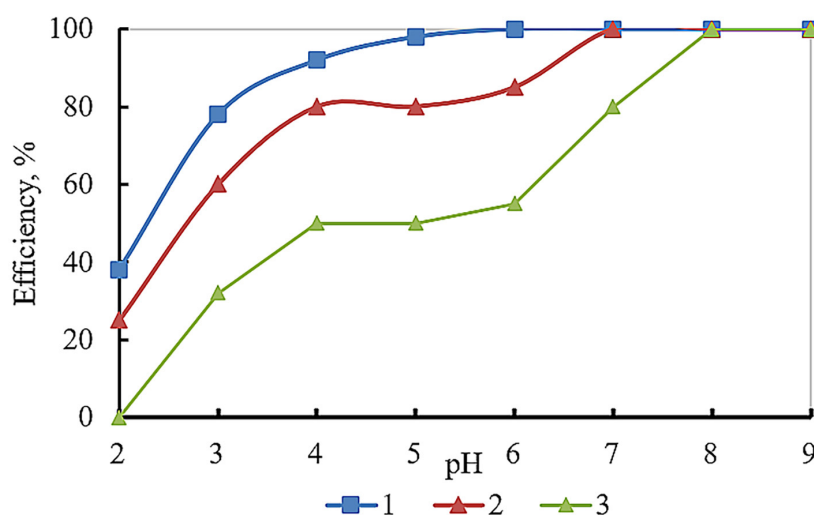


Figure 9. Dependence of the removal efficiency of iron ions on pH ($C_{\text{magn}} = 150 \text{ mg/dm}^3$, $t = 25 \text{ }^\circ\text{C}$, $\tau = 5 \text{ min}$): 1 – (Fe³⁺) = 20 mg/dm³; 2 – (Fe²⁺) = 10 mg/dm³ + (Fe³⁺) = 10 mg/dm³; 3 – (Fe²⁺) = 20 mg/dm³

9.5, respectively. Thus, the extraction efficiency of Fe³⁺ ions increases with increasing pH (Fig. 9, curve 1), and the maximum efficiency of the process corresponds to the pH of complete hydrolysis of Fe³⁺ ions. When Fe²⁺ ions are added to the model solution, the course of the curve changes (Fig. 9, curve 2). In the pH range of 4.0–5.5, a plateau appears on the graph, after which the increase in the efficiency of removal of iron compounds continues. In our opinion, in the pH range of 2–4, the growth of the process efficiency is due to the hydrolysis of Fe³⁺, and the growth after the plateau is due to the hydrolysis of Fe²⁺. In the preparation of solutions, part of Fe²⁺ is oxidized by air oxygen dissolved in

water. Therefore, in this case, the curve will have two characteristic bulges (Fig. 9, curve 3), which coincide with the pH of complete hydrolysis of Fe³⁺ and Fe²⁺, respectively. As the pH increases, the oxidation rate of Fe²⁺ also increases, which cannot help but affect the overall efficiency of the process. Synthetic magnetite particles' sorption process of hydrolyzed iron (III) forms is quite intensive (Fig. 10). It is completed within the first two minutes. The further increase in the duration of contact of magnetite particles with the model solution is not accompanied by a corresponding increase in the extraction efficiency of iron compounds. The authors studied several samples of

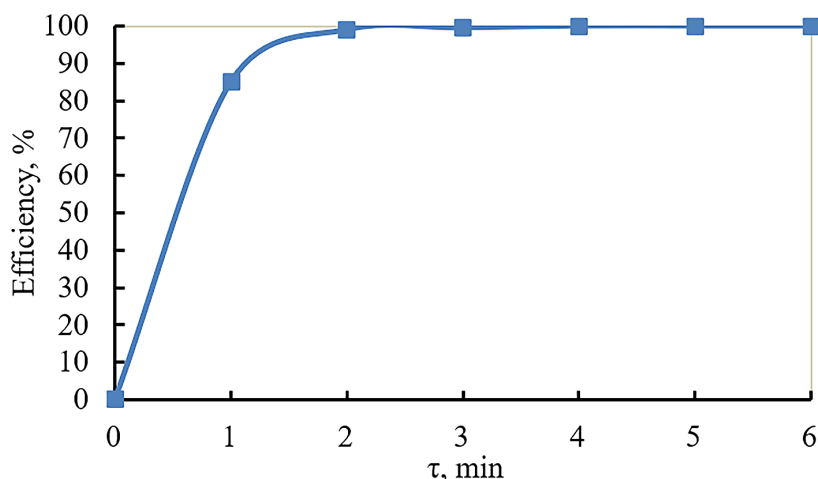


Figure 10. Dependence of the removal efficiency of iron ions on the duration of contact of magnetite particles with the solution (pH = 8, $t = 25\text{ }^{\circ}\text{C}$, $C_{\text{Fe}^{3+}} = 20\text{ mg/dm}^3$, $C_{\text{magn}} = 150\text{ mg/dm}^3$)

magnetite suspension with different ratios of Fe^{2+} and Fe^{3+} concentrations in magnetite particles ($K = (\text{Fe}^{2+})/(\text{Fe}^{3+})$). In the range of $K = 0.2\text{--}2.2$, magnetite particles obtained from sulphate effluents, as well as from sulphate-chloride effluents (Ivanenko et al., 2020), retain magnetic properties sufficient to remove them from the aqueous medium by a magnetic field. In this range, the change in K does not significantly affect the required contact time of the particles with the treated water. Obviously, for the conditions of this experiment, 5 minutes of mixing the mixture of magnetite suspension with the model solution is sufficient. This value must be set experimentally in actual production conditions since it depends on many factors (mixer volume, water velocity, magnetite suspension concentration).

During the study of various magnetite samples, it was established that iron ions' removal efficiency decreases in acidic solutions with increasing K (Fig. 11). No such dependence is observed in neutral and alkaline solutions. In our opinion, this may be due to the processes of desorption of excess ions and elimination of defects in the crystal lattice of magnetite particles. As K increases, the structure's defectivity increases, and magnetite dissolves at $\text{pH} \leq 3$. Therefore, considering the maximum magnetic properties in removing iron ions from aqueous solutions, it is most appropriate to use magnetic particles with $K = 0.5$ since there is no significant increase in the efficiency of the process at other K . In the temperature range of $10\text{--}70\text{ }^{\circ}\text{C}$, no significant changes in the efficiency of the process are observed. This statement is valid for samples of magnetite with $K = 0.2\text{--}2.2$.

Based on the research carried out for removing iron compounds from aqueous solutions at concentrations of $10\text{--}100\text{ mg/dm}^3$, it is possible to recommend the technological scheme shown in Figure 12. Before starting the water purification process, preparing a magnetite suspension is necessary. For this, spent sulfate-containing electrolytes from steel pickling or other sulfate-containing solutions containing a significant amount of iron (II) and (III) ions are used. Obtaining magnetite involves bringing $K = (\text{Fe}^{2+})/(\text{Fe}^{3+})$ to 0.5 in the initial solution, setting $\text{pH} = 9.0\text{--}9.5$ with alkali solutions, and washing the suspension from sulphates (if necessary). Wastewater containing $10\text{--}100\text{ mg/dm}^3$ of iron ions is fed into the mixer, where $100\text{--}1000\text{ mg/dm}^3$ of magnetite suspension and alkali solution are added to bring the pH to 8–9. After stirring for 10–20 min, the mixture is fed to coarse and fine purification magnetic filters, where magnetite particles with sorbed iron compounds are separated from purified water. Purified water is discharged into the sewage system or reused in the technological process. The separated sludge is sent to storage or for further processing (punching and using it as a pigment (Frolova 2018)). Without spent steel pickling solutions, the magnetite suspension can be used repeatedly. A solution containing Fe^{2+} (half of the total sorbed ions) is added to the reactor, and NaOH solution is added to $\text{pH} = 9.5\text{--}10$. With such processing, the main properties of magnetite particles (magnetic and sorption) are restored, and the suspension is fed to the magnetite preparation unit. When treating water according to the given scheme, the residual concentrations of iron

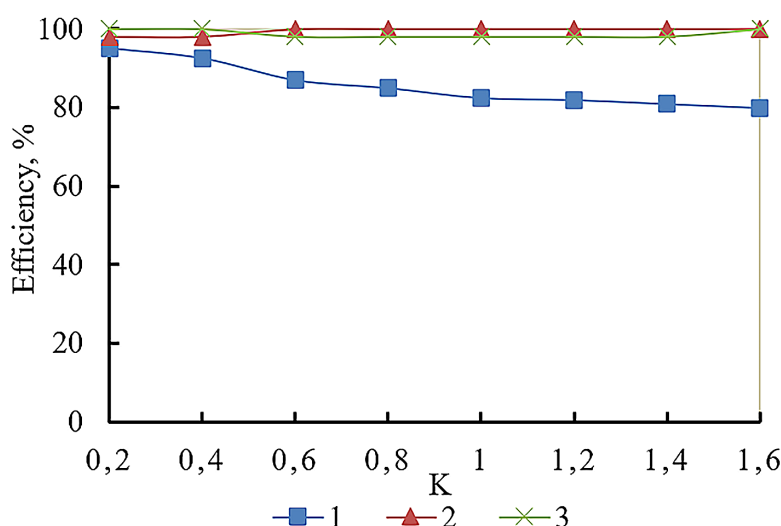


Figure 11. Dependence of the removal efficiency of iron ions on K at different pH ($t = 25\text{ }^{\circ}\text{C}$, $C_{\text{Fe}^{3+}} = 20\text{ mg/dm}^3$, $C_{\text{magn}} = 150\text{ mg/dm}^3$): 1 – pH = 3, 2 – pH = 7, 3 – pH = 10

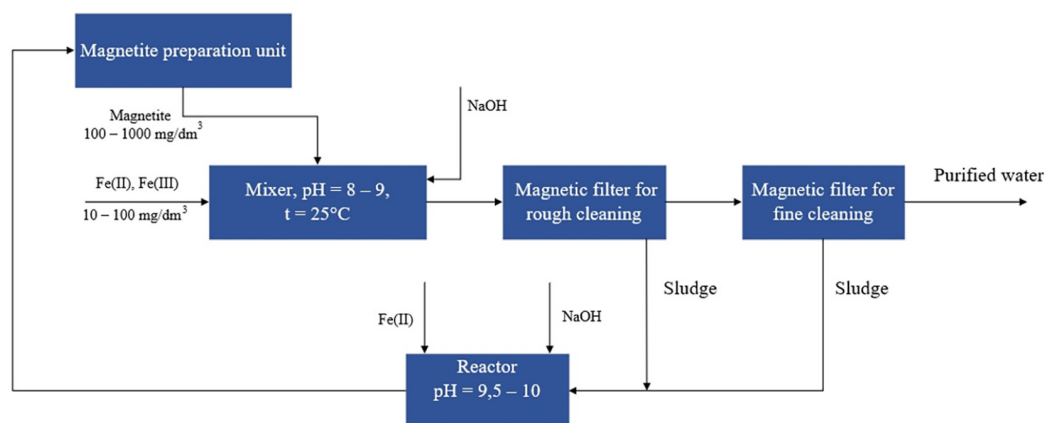


Figure 12. Technological scheme for removing iron ions from aqueous solutions

ions do not exceed the maximum rate for discharge into the sewage system. Further research determined the optimal conditions for removing chromium (VI) compounds from model solutions using highly dispersed magnetite particles from a sulphate-containing solution. As mentioned earlier, the stoichiometric composition of magnetite is described by the formula $\text{FeO} \cdot \text{Fe}_2\text{O}_3$, and in the absence of oxidation of surface Fe^{2+} ions by oxygen dissolved in water, the concentration ratio $(\text{Fe}^{2+})/(\text{Fe}^{3+}) = 0.5$. In natural conditions, this ratio will be even lower, and the amount of Fe^{2+} on the surface of magnetite particles will be smaller. The amount of Cr^{6+} that surface Fe^{2+} ions can reduce will also be negligible. The problem can be solved by increasing the concentration of Fe^{2+} in the surface layer. Earlier (Honcharuk et al., 2003) proposed using magnetite particles with magnetic properties in the range of $K = 0\text{--}3.0$ to remove

Cr^{6+} ions from water, and the maximum of magnetic characteristics corresponds to the stoichiometric composition ($K = 0.5$). When deviating from stoichiometry in any direction, the magnetic properties decrease. A corresponding increase in the number of surface Fe^{2+} ions in magnetite particles accompanies an increase in K from stoichiometry. The removal efficiency of Cr^{6+} ions increases the most when $K > 1.8$. At the same time, it is necessary to consider the corresponding decrease in magnetic properties, especially in the application for separating spent particles from magnetic or electromagnetic filters. Detailed studies carried out in the $\text{pH} = 3\text{--}11$ range for various magnetite samples confirmed almost the same rate of neutralization of chromates in acidic and alkaline environments. A slight increase is observed at $\text{pH} \leq 3$, but since magnetite begins to dissolve at such values, this fact is not essential

from a practical point of view. Still, it is explained by the simple dissolution of particles, accompanied by the transition into a solution of iron ions.

Different concentrations of magnetite are required to treat wastewater with the same concentration of chromates, depending on the conditions. It was established (Fig. 13) that at $K = 2.0$, it is sufficient to remove 100% of chromates using 20 mg of magnetite per 1 mg of Cr^{6+} , at $K = 1.0$ when using 50 mg of magnetite per 1 mg of Cr^{6+} , 70% of the cleaning efficiency is achieved, and at $K = 0.5$, even at a concentration of 50 mg of magnetite per 1 mg of Cr^{6+} , the cleaning efficiency does not exceed 30%. Thus, the effective ratio (magnetite)/

(Cr^{6+}) when using magnetite with $K = 2$ is 20. The concentration of chromates in the initial solutions also significantly affects their removal efficiency. As can be seen from Figure 14, with an increase in the concentration of chromates in the solution for magnetite samples with constant K , their extraction efficiency also increases. It also increases with increasing K . Previously; it was assumed that the process of extracting chromates by magnetite particles is based on the reduction of Cr(VI) by surface Fe^{2+} ions and the sorption of reduced Cr^{3+} ions or their hydrolyzed forms by the surface of magnetite. However, as can be seen from the sorption isotherms (Fig. 14), the efficiency of chromate extraction increases

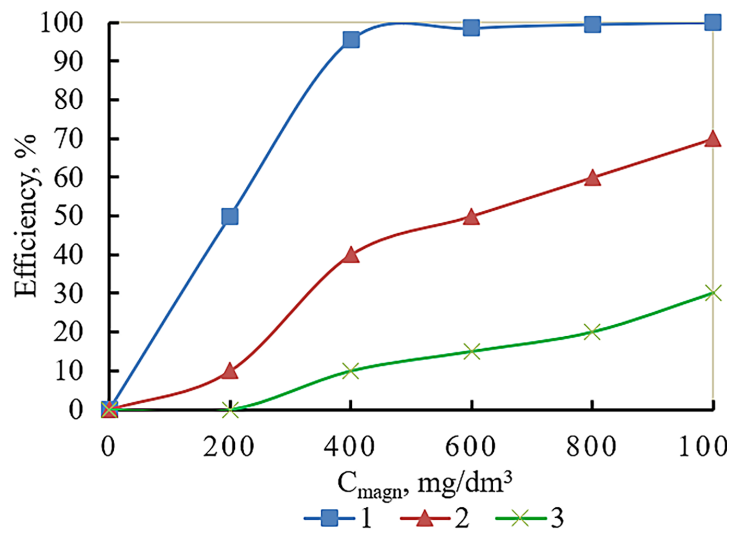


Figure 13. Dependence of chromate removal efficiency on magnetite concentration at $C_{\text{Cr}^{6+}} = 20 \text{ mg/dm}^3$, $\text{pH} = 8$, $t = 25 \text{ }^\circ\text{C}$ and different K : 1 – 2; 2 – 1; 3 – 0.5

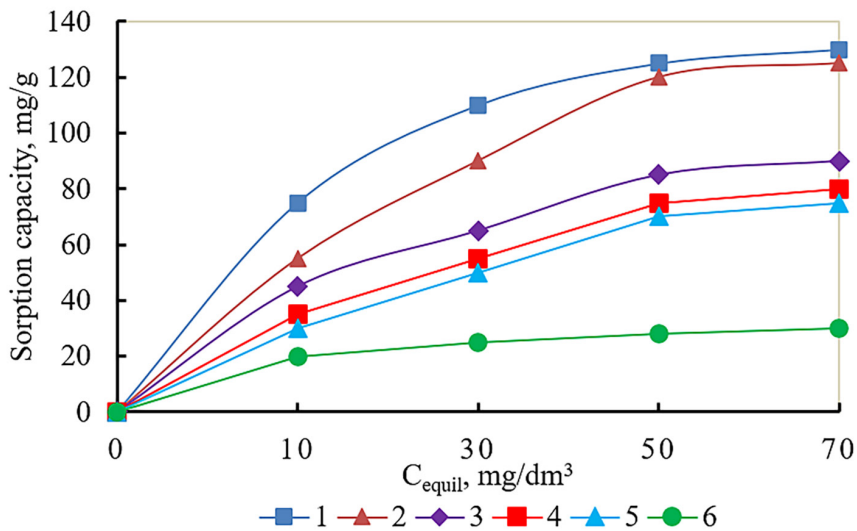


Figure 14. Dependence of the sorption capacity of magnetite samples on the equilibrium concentration of chromates at $\text{pH} = 8$, $t = 25 \text{ }^\circ\text{C}$ and different K : 1 – 2.6; 2 – 2.2; 3 – 1.8; 4 – 1.4; 5 – 1.0; 6 – 0.5

with an increase in the equilibrium concentration. At the same time, the amount of surface Fe^{2+} ions in magnetite particles remains constant. It is obvious that other mechanisms are additionally included in the process, and the sorption capacity must be understood as the totality of all mechanisms involved in chromate extraction. With excess chromates in the solution, all surface ions of magnetite particles are represented by Fe^{3+} ions. Various sparingly soluble chemical compounds can be formed in the $\text{Fe}_2\text{O}_3 - \text{CrO}_3 - \text{H}_2\text{O}$ system, the most common of which are FeOHCrO_4 and $\text{Fe}_2(\text{CrO}_4)_3$ (Honcharuk et al., 2003). In the presence of Na^+ , NH_4^+ , K^+ , Ti^{3+} (Me), double chromates $\text{MeFe}_3(\text{OH})_6(\text{CrO}_4)_2$, $\text{MeFe}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{MeFe}(\text{CrO}_4)_2$ and other compounds can crystallize. In substantiating the chemical concept of chromate sorption on iron (III) hydroxide, a linear dependence of the sorption capacity of $\text{Fe}(\text{OH})_3$ hydroxide on the equilibrium concentration of chromates was noted. In our case, in addition to the process of reduction of chromates and sorption of hydroxide, the formation of poorly soluble chemical compounds

with the participation of chromates and sorption of chromates by surface particles of $\text{Fe}(\text{OH})_3$ will take place. We found that the sorption capacity of magnetite increases with increasing temperature (Fig. 15). This can be considered a confirmation of a sorption mechanism for chromate removal. Under normal conditions, OH^- ions located on the surface of particles can exchange for anions. As the temperature increases, the kinetic energy of the particles increases to such an extent that the exchange of OH^- for chromate anions becomes possible. However, the use of significant equilibrium concentrations in wastewater treatment is unacceptable due to substantial residual concentrations of chromates in treated water, which prevents its discharge into the sewer, and poorly soluble chromates in sediments, which require additional treatment for their recovery.

Therefore, in practical technologies, it is necessary to proceed from the condition of recovery of all chromates by magnetite particles. A variant of the technological scheme of such a process is presented in Figure 16.

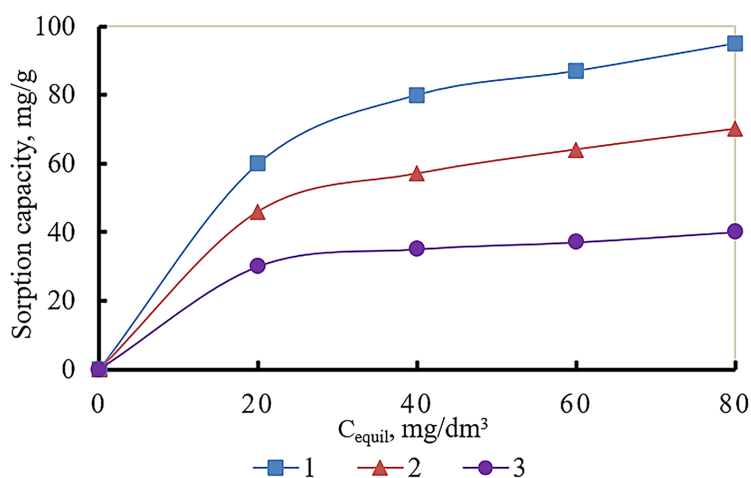


Figure 15. Dependence of the sorption capacity of magnetite samples with $K = 1.0$ on the equilibrium concentration of chromates at $\text{pH}=8$ and different temperatures, $^{\circ}\text{C}$: 1 – 80, 2 – 60, 3 – 40

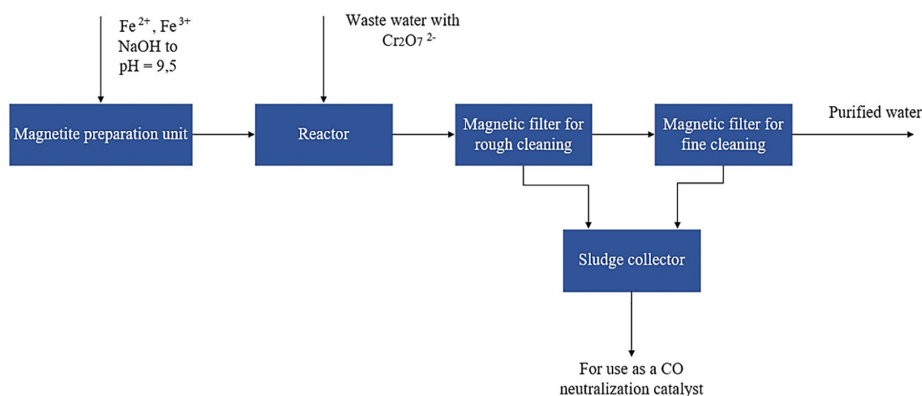


Figure 16. Technological scheme of water purification from chromates with magnetite

A mixture of Fe^{2+} and Fe^{3+} ions in appropriate ratios or Fe^{2+} with subsequent oxidation of part of it to Fe^{3+} is fed into the magnetite preparation unit. In the presence of NaOH in the mixture treated in this way, magnetite particles are formed. The resulting suspension is dosed into the reactor, where wastewater containing chromates is simultaneously fed. Since, in most cases, chromate-containing wastewaters have an acidic reaction, their neutralization co-occurs. During the contact of magnetite particles with wastewater, chromates are reduced, and the surface of the particles sorbs the formed compounds. Particles of spent sorbent are separated from water on magnetic filters. Sludge can be used in metallurgy to neutralize carbon monoxide in flue gases (Ivanenko et al., 2020; Ivanenko et al., 2021).

CONCLUSIONS

Thus, summarizing the above results, we can conclude that the possibility of optimizing the conditions of magnetite deposition can be used to obtain particles of magnetic sorbents of different dispersions. At the same time, securing magnetite under certain conditions ($\text{pH} > 9$, temperature more than 25–30 °C, $K = 0.5\text{--}2.8$, total concentration of iron ions in the initial solutions more than one g/dm^3) is not accompanied by significant changes in dispersion particles.

As a result of studies on the extraction of iron ions using highly dispersed sorbents with magnetic properties, it was established that hydrolyzed forms of iron ions (III) are better absorbed from sulphate-containing solutions. At the same time, the extraction efficiency of Fe^{3+} ions increases with increasing pH, and the maximum efficiency of the process corresponds to the pH of complete hydrolysis of Fe^{3+} ions. The process of sorption of hydrolyzed forms of iron (III) by synthetic magnetite particles takes place in full if the magnetite particles are in contact with the solution for 2 minutes. In acidic solutions with an increase in $(\text{Fe}^{2+}):(\text{Fe}^{3+})$, the efficiency of removal of iron ions decreases since, with an increase in the ratio of iron ions, the defectiveness of the structure increases. At $\text{pH} \leq 3$, magnetite begins to dissolve. As the studies have shown, using magnetite with $(\text{Fe}^{2+}):(\text{Fe}^{3+}) = 0.5$ when applying the magnetic absorption method is most suitable. Therefore, considering the established optimal conditions for removing iron ions, the proposed technological

scheme of water purification from iron ions with the repeated use of magnetite particles ensures the maximum standards for the discharge of purified water into the sewer network. During the decontamination of chromate-containing waters with magnetite formed from iron sulphate-containing, I spent steel pickling solutions, in addition to the processes of reduction of chromate ions, oxidation of surface ions Fe^{2+} to Fe^{3+} , sorption of ions Cr^{3+} or hydroxides $\text{Cr}(\text{OH})_3$, the restoration of its particles of chromate anions, in the basis which can be both the formation of chemical compounds and the sorption mechanism. The optimal conditions for the removal of chromium(VI) compounds from model solutions with the help of highly dispersed magnetite particles obtained from an iron sulphate-containing solution with a concentration ratio of $K = (\text{Fe}^{2+}):(\text{Fe}^{3+}) = 2$ are to carry out the process at an elevated temperature and use magnetite with a consumption of 20 mg per 1 mg of Cr^{6+} .

REFERENCES

1. Karpenko, M.V., Radovenchyk Ya.V., Ivanenko O.I. 2023. Removal of iron compounds from mechanical filters household reverse osmotic systems water purification. *Energy: Economics, Technology, Ecology*, 2, 127–132. DOI 10.20535/1813-5420.2.2023.279720 (in Ukrainian)
2. Frolova, L.A. 2018. Using spent etching solution to obtain yellow ferric oxide pigments. *Modern problems of Metallurgy*, 21(1), 82–86. DOI: 10.34185/1991-7848.2018.01.013 (in Ukrainian)
3. Ivanenko, O.I., Nosachova, Yu.V., Ovsiankina, V.O., Vember, V.V. 2022. *Technoecology*. Publishing House “Condor,” Kyiv, Ukraine, 388.
4. Statistical publication «Environment of Ukraine 2020». 2021. State Statistics Service of Ukraine. https://ukrstat.gov.ua/druk/publicat/kat_u/2021/zb/11/Dovk_20.pdf
5. Natsionalna dopovid pro stan navkolyshnoho pryrodnoho seredovyscha v Ukrayini u 2021 rotsi. 2021. Ministry of Environmental Protection and Natural Resources of Ukraine. <https://mepr.gov.ua/wp-content/uploads/2023/01/Natsdopovid-2021-n.pdf> (in Ukrainian)
6. Dvostoronnye spivrobitnytstvo u sferi upravlinnya vodnymy resursamy. 2017. State Water Resources Agency of Ukraine. <https://davr.gov.ua/transkordonne-spivrobitnictvo> (in Ukrainian)
7. Donchenko, M.I., Frolenkova, S.V., Motronyuk, T.I. 2018. *Ekologichna bezpeka galvanotekhniky. Stichni vody. Mekhanichna ta sorbtsiyina ochystka*, 202. <https://ela.kpi.ua/>

- bitstream/123456789/24936/3/Ekologichna_bezpeka_galvanotekhniky.doc (in Ukrainian)
8. Trus, I., Radovenchyk, I., Halysh, V., Skiba, M., Vasylenko, I., Vorobyova, V., Hlushko, O., Sirenko, L. 2019. Innovative Approach in Creation of Integrated Technology of Desalination of Mineralized Water. *Journal of Ecological Engineering*, 20(8), 107–113. <https://doi.org/10.12911/22998993/110767>
 9. Gomelya, M., Hrabitchenko, V., Trokhymenko, A., Shablii, T. 2016. Research into ion exchange softening of highly mineralized waters. *Easten-Europen Journal of Enterprise Technologies*, 4/10(82), 4–9. DOI: <https://doi.org/10.15587/1729-4061.2016.75338>
 10. Radovenchyk, V.M., Ivanenko, O.I., Radovenchyk, Ya.V., Krysenko, T.V. 2020. Zastosuvannya ferytynykh materialiv v protsesakh ochyshchennya vody: monohrafiya. Vydavnytstvo O. V. Pshonkivskyy, Bila Tserkva, Ukraine, 215. https://ecopaper.kpi.ua/CONTENT/literatyr/ferity_mono.pdf (in Ukrainian)
 11. Khokhotva, O., Butchenko, L., Gomelya, N. 2018. The use of modified and composite ferritic sorbents for selective extraction of Cu^{2+} . *Technical sciences and technologies*, 1, 264–272. <http://tst.stu.cn.ua/article/view/134785>
 12. Vozniuk, M., Shablii, T., Gomelya, M., Sirenko, L., Sidorov, D. 2023. Magnetosorption Purification of Water from Petroleum Products. *Journal of Ecological Engineering*, 24(11), 155–162. <https://doi.org/10.12911/22998993/170290>
 13. Samchenko, D., Kochetov, H., Vasylyev, O., Derecha, D., Skyrtva, Y., Lastivka, O. 2022. Enerhooshchadna tekhnolohiya pererobky vidpratsovanykh travlynykh rozchyniv z oderzhannyam feromahnitnykh spoluk. *Environmental Safety and Natural Resources*, 43(3), 22–34. <https://doi.org/10.32347/2411-4049.2022.3.22-34>
 14. Dudchenko, N.O. 2011. Magnetic properties of nanomagnetite, synthesized in the temperature range of 40–90 °C. *Mineralogical journal (Ukraine)*, 33(2), 38–41. <http://dspace.nbu.gov.ua/xmlui/handle/123456789/63463>
 15. Bukliv, R.L., Yaremko, Z.M. 2008. Analysis of the correlation dependence between the type of hydration of the cations of the second group of the main subgroup and singly, doubly, and triply charged anions and the formation of crystal hydrates. *Bulletin of the Lviv Polytechnic National University. Chemistry, Technology, and Application of Substances*, 609, 39–42. <https://ena.lpnu.ua/items/a1d6d7f2-88c0-4229-9cbe-b16809df910e>
 16. Ivanenko, O., Radovenchyk, V., Overchenko, T., Radovenchyk I. 2020. Integrated use of magnetite in environmental protection measures. *ScienceRise*, 5, 57–65. <http://doi.org/10.21303/2313-8416.2020.001462>
 17. Nabivanets, B.Y., Osadchii, V.I., Osadcha, N.M., Nabivanets, Yu.B. 2007. *Analychna khimiya poverkhnevnykh vod: monohrafiya*. Naukova dumka, Kyiv, Ukraine, 456. <https://www.nas.gov.ua/UA/Book/Pages/default.aspx?BookID=000002073> (in Ukrainian)
 18. Honcharuk, V. V., Radovenchyk, V. M., Homelya, M. D. 2003. Otrymannya ta vykorystannya vysokodispersnykh sorbentiv z mahnitnyimi vlastyvostyamy: monohrafiya. Hrafika, Kyiv, Ukraine, 264. (in Ukrainian)
 19. Ivanenko, O., Radovenchyk, V., Radovenchyk, I. 2020. Neutralizing carbon monoxide by magnetite-based catalysts. *Technology Audit and Production Reserves*, 5/3(55), 24–28. DOI: 10.15587/2706-5448.2020.214432
 20. Ivanenko, O., Gomelya, N., Shablii, T., Trypolskyi, A., Nosachova, Yu., Leleka, S., Trus, I., Strizhak, P. 2021. Use of metal oxide-modified aerated concrete for cleaning flue gases from carbon monoxide. *Journal of Ecological Engineering*, 22(5), 104–113. <https://doi.org/10.12911/22998993/135873>