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Removal of nickel(II) ions during water purification with ferrous sulfate. Part 1. Mechanism and efficiency of the process

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Abstract: The purification of natural water and wastewater from nickel ions is critically important for both environmental protection and human health due to their high toxicity. This study aimed to investigate the removal of nickel ions from contaminated aqueous solutions using the coagulant $FeSO_4$. The results demonstrate that the removal of nickel ions via an iron(III) hydroxide precipitate, formed during coagulation at pH 7 and pH 8, can be accurately described by classical adsorption isotherms, including the Langmuir, Freundlich and Dubinin–Radushkevich models. The calculated free energy of adsorption, based on the Dubinin–Radushkevich equation, does not exceed 8 kJ mol^{-1}, indicating the physical nature of the adsorption process and ruling out ion-exchange interactions between nickel ions and iron(III) hydroxide. The sorption capacity of the resulting iron(III) hydroxide precipitate for nickel ions at pH 8 is 0.727 mg (mg Fe)$^{-1}$ of added Fe to the solution. At pH 7, the sorption capacity depends on the initial coagulant concentration and ranges from 0.105 to 0.730 mg (mg Fe)$^{-1}$. A comparison between the coagulants $FeSO_4$ and the previously studied $FeCl_3$ reveals that $FeSO_4$ is more effective for nickel ion removal when the initial iron ion concentration is below 70 mg L^{-1}. However, at higher initial concentrations of iron, $FeCl_3$ demonstrates greater efficacy.

Keywords: coagulation; iron(III) hydroxide; adsorption isotherms; ferrous sulphate; removal of nickel ions; water treatment.

INTRODUCTION

Due to the high toxicity of nickel ions, the purification of natural water and wastewater from nickel ions is critically important for both human health and environmental protection.[1,2] Various international standards have set stringent maximum permissible concentrations for nickel ions in purified water. For instance, the allowable concentration in drinking water ranges from 0.02 to 0.1 mg L^{-1},[3] while Russian regulations mandate that the concentration of nickel ions in

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purified water discharged into natural reservoirs must not exceed 0.01 mg L^{-1}. Achieving such low residual concentrations of nickel ions during water treatment is therefore a significant challenge.

In most industrial settings, wastewater is treated with to remove nickel ions and other heavy metals. This process increases the solution's pH to 8–10, causing many heavy metals to precipitate as hydroxides. However, due to the relatively high solubility of nickel hydroxide, this method is insufficient for reducing nickel ion concentrations to levels that meet regulatory standards. One approach to address this limitation is to apply an additional purification step using sorption methods.

Currently, numerous studies[3–13] have demonstrated the potential for nickel ion sorption using various carbon, coal, and mineral sorbents. However, their industrial application is often hindered by challenges related to the disposal of spent sorbents. Over time, the sorption capacity of these materials decreases, even with regeneration, necessitating their eventual replacement. This creates concerns regarding the safe disposal or burial of used sorbents, which is not always straightforward.

In light of these challenges, there is ongoing research to identify new, efficient sorbents that can be easily disposed of or repurposed after use. Metal oxides and hydroxides, particularly those of iron, show promise as effective sorbents. These materials offer several advantages, including their compactness, small particle size, high specific surface area and the potential for recycling in metallurgical processes after use. Metal hydroxides can be precipitated directly during the water purification process using inorganic coagulants. Aluminum and iron salts are commonly used as coagulants, and alongside the removal of insoluble coarse and colloidal impurities, these coagulants have been shown to also remove dissolved heavy metal ions.[14]

Ferric chloride is one of the most widely used coagulants in water treatment. Several studies have documented its effectiveness in removing arsenic oxyanions,[15] antimony[16] and other heavy metals.[14,17,18] Recently, we conducted a comprehensive study on the use of $FeCl_3$ as a coagulant for removing nickel ions from contaminated solutions.[19] The hydrolysis of $FeCl_3$ during coagulation leads to the formation of an iron(III) hydroxide precipitate, identified as two-line ferrihydrite with the general (gross) formula $Fe_2O_3 \cdot 3H_2O$. This precipitate adsorbs nickel ions onto its surface during the coagulation process. The sorption of nickel ions by the forming iron(III) hydroxide precipitate at pH 7 and 8 is accurately described by classical adsorption isotherms, including the Freundlich, Langmuir and Dubinin–Radushkevich models. The sorption capacity of the precipitate for nickel ions is 60.5 mg g^{-1} at pH 7 and 141.9 mg g^{-1} at pH 8 – nearly an order of magnitude higher than the capacities reported for many mineral, carbon and coal sorbents.[3–13]

In this study, we investigated another commonly used iron salt coagulant, iron(II) sulfate, for the same purpose. When $FeSO_4$ is used, the formation and precipitation of iron(III) hydroxide occur due to the oxidation of Fe^{2+} by dissolved atmospheric oxygen in the solution. At low concentrations of Fe^{2+}, this process can be summarized by the following reaction:

$$4Fe^{2+} + O_2 + 2H_2O + 8OH^- \rightarrow 4Fe(OH)_3\downarrow$$

According to the literature, the iron(III) hydroxide precipitate formed in this process is reported to have varying general (gross) formulas.[20–23] Consequently, its sorption properties with respect to nickel ions are likely to differ from those of the previously studied iron(III) hydroxide precipitate derived from the hydrolysis of iron(III) chloride.[19] Furthermore, no data have been found in the literature regarding the use of $FeSO_4$ as a coagulant for the removal of nickel ions from contaminated solutions. In this context, the objective of this study is to investigate the potential of $FeSO_4$ as a coagulant for purifying contaminated solutions containing nickel ions. Additionally, the composition and structure of the iron(III) hydroxide precipitate formed from an $FeSO_4$ solution under the conditions of our experiments are of interest, as is a comparison of the effectiveness of $FeSO_4$ and $FeCl_3$ coagulants in nickel ion removal.

Given the extensive experimental data obtained, this study is presented in two parts. The first part explores the sorption of nickel ions by iron(III) hydroxide formed during the hydrolysis of $FeSO_4$ at pH 7 and 8. The second part focuses on the structure, composition and physicochemical properties of the resulting iron(III) hydroxide precipitate.

EXPERIMENTAL

Materials and devices

All studies were conducted under laboratory conditions at room temperature (25±2 °C). The temperature during the experiments was measured using a thermometer. A sodium sulfate solution with a concentration of 400 mg L^{-1} was used as a model solution. This solution simulated natural sulfate mine waters and some types of industrial pickling wastewater. The concentration of nickel ions in the model solution varied from 3.13 to 20 mg L^{-1}. Russian-made reagents were used to prepare the solutions: pure-grade $FeSO_4$ (the content of the main substance was 98 %, GOST 4148-78, supplier CJSC "KHIMREAKTIVSNAB"), chemically pure NaOH (the content of the main substance was 99.1 %, GOST 4328-77, supplier of JSC "ECOS-1"), chemically pure Na_2SO_4 (the content of the main substance was 99 %, GOST 4166-76, supplier JSC "VEKTON"), and analytical-grade $NiSO_4$ (the content of the main substance was 98 %, GOST 4465-74, supplier JSC "REAKHIM"). The solutions were mixed using a magnetic stirrer MR Hei-Tec mixer (Heidolph Instruments GmbH & Co. KG) at a speed of 650 rpm. This allowed the system to keep the iron(III) hydroxide precipitate formed in the solution in a suspended state. An ANION 4100 pH meter (Russia) was used to control the pH. During the experiments, the pH meter electrodes were constantly immersed in the model solution.

Preliminary coagulation experiments

Preliminary experiments were conducted to examine the effect of coagulation duration on the residual concentration of nickel ions in the model solution. In these experiments, a calculated amount of $FeSO_4$ solution (13.57 g L^{-1}) was added to a specified volume of the model solution containing 6.25 mg L^{-1} of nickel ions, ensuring that the concentration of Fe^{2+} reached 50 mg L^{-1}. The pH of the solution was then adjusted to either 7 or 8 using a NaOH solution (10 g L^{-1}). After the addition of alkali, the solution was continuously stirred for 30, 60 and 120 min. The precipitate of iron(III) hydroxide formed during coagulation was separated from the solution by filtration using blue ribbon filter paper (Russia), with the filtration process lasting 15 min. The residual concentration of nickel ions in the filtrate was subsequently measured. After filtration, the iron(III) hydroxide precipitate was rinsed multiple times with distilled water and dried at room temperature for further analysis. Additionally, a series of similar experiments was performed with aeration of the solution. In these experiments, air was bubbled through the model solution at a rate of 60 L h^{-1} to evaluate the effect of aeration on the removal of nickel ions by the $FeSO_4$ coagulant. The results were compared to determine the influence of air aeration on nickel ion removal efficiency.

Serial coagulation experiments

The effect of the resulting iron(III) hydroxide precipitate on the removal of nickel ions was studied in a series of experiments with different initial concentrations of iron(II) ions (12.5, 25, 50 and 100 mg L^{-1}) and nickel ions (3.13, 6.25, 10 and 20 mg L^{-1}) in the model solution. The experimental technique was the same as in the preliminary runs. Aeration of the solution was not carried out during these experiments.

The concentration of nickel ions in the solutions was determined on a KFK-2 photocolorimeter (Russia) by the photocolorimetric method with dimethylglyoxime.[24] In each experiment, three parallel measurements of the concentration of nickel ions in the solution were carried out. The results were averaged.

RESULTS AND DISCUSSION

Effect of the coagulation duration on the residual concentration of nickel ions in the solution

Fig. 1 illustrates the effect of coagulation duration on the residual concentration of nickel ions in the model solution. At pH 7, the formation of an iron(III) hydroxide precipitate reduces the nickel ion concentration by approximately threefold, from 6.25 to 1.56–2.17 mg L^{-1}. At pH 8, the reduction is even more significant, with the nickel ion concentration decreasing nearly 20-fold, from 6.25 to 0.19–0.35 mg L^{-1}. Aeration has no observable impact on the removal of nickel ions, as the experimental data for runs with and without aeration align closely on the same curve for both pH 7 and 8 (Fig. 1). After 30 min of coagulation, the residual concentration of nickel ions at both pH levels reaches a near-equilibrium value and changes minimally thereafter. This indicates that the removal process of nickel ions, as well as the nucleation and formation of the iron(III) hydroxide precipitate, were complete within the studied time intervals at the given pH values. Based on these observations, the coagulation duration was set to 30 min for all subsequent experiments.

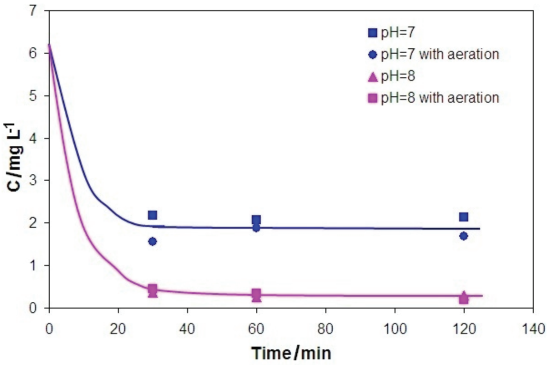

Fig. 1. Effect of the coagulation duration and pH on the residual concentration of nickel ions (C) in the model solution. The initial concentrations of iron(II) and nickel ions in the solution were 50 and 6.25 mg L^{-1}, respectively.

Coagulation removal of nickel ions at pH 7

Fig. 2a illustrates the changes in the residual concentrations of nickel ions in the model solution during the coagulation process using FeSO$_4$ at pH 7. It can be observed that as the initial concentration of iron(II) ions introduced into the solution increases, the residual concentration of nickel ions gradually decreases. For example, at the initial concentration of iron(II) in a solution of 100 mg L$^{–1}$, the concentration of nickel ions in it decreases from 10 to 3.12–4.03 mg L$^{–1}$, from 6.25 to 1.57–2.17 mg L$^{–1}$ and from 3.13 to 0.69–0.89 mg L$^{–1}$ (Fig. 2a).

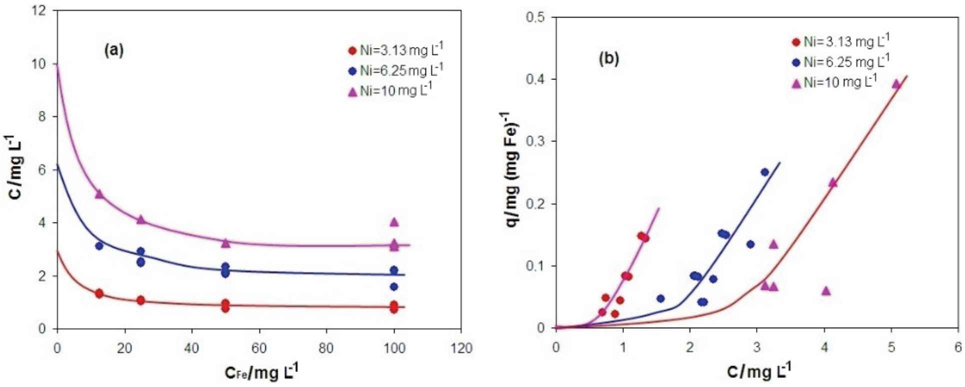

Fig. 2. Effect of the initial concentration of iron(II) ions ($C_{\rm Fe}$) in the model solution on the residual concentration of nickel ions at pH 7 (a) and sorption isotherms of nickel ions on the iron(III) hydroxide precipitate formed in the solution during coagulation at pH 7 (b).

Fig. 2b presents the sorption isotherms of nickel ions on the iron(III) hydroxide precipitate formed during coagulation at pH 7. It is important to note that the sorption value, q, in this figure is expressed in units of mg (mg Fe)$^{–1}$, indicating that the calculation is based on the initial concentration of iron(II) ions in the solution rather than on the concentration of the iron(III) hydroxide precipitate formed, which serves as the sorbent in this case:

$$q = \frac{C_{\text{in}} - C}{C_{\text{Fe}}} \tag{1}$$

where C_{in} is the initial concentration of nickel ions in the solution (mg L^{-1}). This definition of q was adopted for convenience and to facilitate the subsequent possible use of the obtained results in practice in technological calculations.

As shown in Fig. 2b, instead of a single generalized curve, three separate sorption isotherms are observed. This unusual behavior, similar to what was previously reported[25] can be explained by assuming that the iron(III) hydroxide precipitates formed at different initial concentrations of iron(II) ions in the model solution have varying specific surface areas. In other words, there is no direct proportionality between the initial concentration of iron(II) ions in the solution and the total surface area of the resulting iron(III) hydroxide precipitates. This assumption is supported by Fig. 3, which shows the sorption isotherms recalculated from Fig. 2a for identical initial concentrations of iron(II) ions introduced into the model soluteion at the start of the experiment.

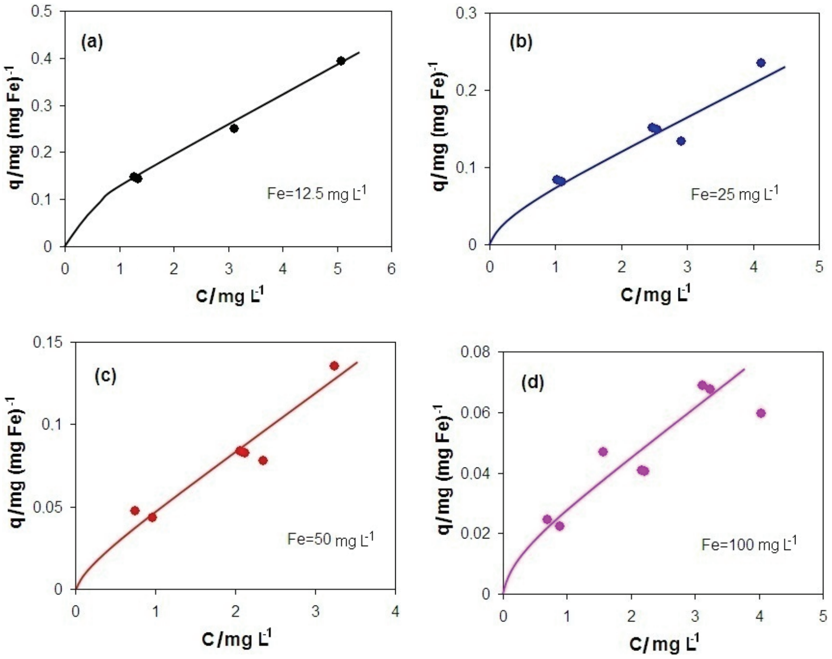

Fig. 3. Sorption isotherms of nickel ions on iron(III) hydroxide formed during coagulation process at pH 7 and different initial concentrations of iron(II) ions in solution.

As demonstrated by this calculation of sorption isotherms, they can be classified as typical L-type isotherms,[26] which are well described by the classical Langmuir equation for monomolecular adsorption:

$$q = q_\infty \frac{K_\mathrm{L} C}{1 + K_\mathrm{L} C} \tag{2}$$

and the empirical Freundlich equation:

$$q = K_\mathrm{F} C^{1/n} \tag{3}$$

where q_∞ is the monolayer adsorption capacity of the sorbent, mg (mg Fe)$^{-1}$; K_L is the constant of adsorption equilibrium, L mg^{-1}; K_F is the proportionality factor; and n is the exponent ($n > 1$).

In linear form, Eqs. (2) and (3) have the following forms, respectively:

$$\frac{1}{q} = \frac{1}{q_\infty} + \frac{1}{q_\infty K_\mathrm{L}} \frac{1}{C} \tag{4}$$

$$\log q = \log K_\mathrm{F} + \frac{1}{n} \log C \tag{5}$$

To estimate the interaction energy of the adsorbed substance with the sorbent, the Dubinin–Radushkevich equation was used:[5,12]

$$q = q_\infty \exp(-k\varepsilon^2) \tag{6}$$

or in linear form (after taking the logarithm):

$$\ln q = \ln q_\infty - k\varepsilon^2 \tag{7}$$

where k is a constant related to the average adsorption energy; ε is the Polanyi potential, calculated as:

$$\varepsilon = RT \ln(1 + 1/C) \tag{8}$$

The free energy of adsorption (E) can be found using the equation:

$$E = \frac{1}{\sqrt{2k}} \tag{9}$$

It is known that if E lies in the range of 8–16 kJ mol^{-1}, then the adsorption process proceeds by ion exchange. At $E < 8$ kJ mol^{-1}, physical adsorption takes place.[5,12]

The results of processing the experimental data in the coordinates of Eqs. (4), (5) and (7) are presented in Fig. 4. As can be seen, all the obtained experimental points can be approximated by straight lines. This indicates that the sorption of nickel ions by the iron(III) hydroxide precipitate formed in the model solution can be described with satisfactory accuracy by the classical Langmuir, Freundlich and

Dubinin–Radushkevich isotherms. The parameters of Eqs. (2), (3) and (6) calculated from the experimental data are given in Table I.

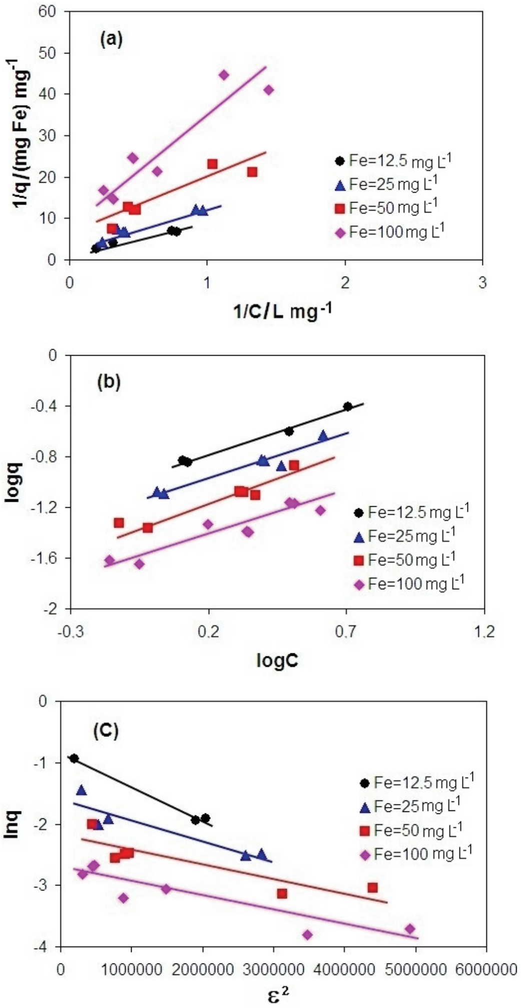

Fig. 4. Experimental data on the sorption of nickel ions by the precipitate of iron(III) hydroxide forming in the solution during the coagulation process at pH 7 in the coordinates of Eqs.: a – (4); b – (5); c – (7).

A comparison of the correlation coefficients of equations (2), (3) and (6) (see Table I) shows that they are very close to each other and have relatively high values. In general, all three classical isotherms describe with satisfactory accuracy the sorption of nickel ions by the formed precipitate of iron(III) hydroxide during its precipitation from an $FeSO_4$ solution. From a comparison of the sorption capacities of iron(III) hydroxide precipitates with respect to nickel ions calculated using the Langmuir and Dubinin–Radushkevich equations, it can be seen that calculations using the Dubinin–Radushkevich isotherm give approximately twofold lower values. With an increase in the initial concentration of iron(II) ions in the solution, the sorption capacity of the resulting iron(III) hydroxide precipitates changes. This indirectly confirms the previously made conclusion about the dependence of the specific surface area of the precipitates on the initial concentration of iron(II) ions in the solution. In this case, there is a decrease in the specific surface area of the precipitates due, apparently, to the aggregation (coagulation) of their particles. It is clear that in this case, the surfaces of the primary iron(III) hydroxide particles overlap internally in the aggregates and part of their surface inside the aggregates becomes inaccessible to the solution. This leads to a decrease in the specific surface area of such an aggregated precipitate.

TABLE I. Parameters of the Langmuir, Freundlich and Dubinin–Radushkevich equations for the sorption of nickel ions on the forming precipitate of iron(III) hydroxide at pH 7 and different initial concentrations of iron(II) ions in the model solution. *R* is the correlation coefficient

Initial concentrations of iron(II) ions, mg L^{-1}	12.5	25	50	100
Langmuir constants				
q_∞ / mg (mg Fe)$^{-1}$	0.730	0.352	0.181	0.105
K_L / L mg^{-1}	0.189	0.289	0.407	0.383
R	0.990	0.971	0.928	0.920
Freundlich constants				
K_F	0.119	0.078	0.050	0.028
n	1.407	1.455	1.433	1.452
R	0.994	0.962	0.948	0.933
Dubinin–Radushkevich constants				
q_∞ / mg (mg Fe)$^{-1}$	0.438	0.199	0.109	0.065
E / kJ mol^{-1}	0.913	1.291	1.581	1.581
R	0.995	0.913	0.874	0.915

In addition to a decrease in q_∞ with an increase in C_{Fe}, there is also a change in the value of the adsorption equilibrium constant K_L, namely, its growth. This may be due to a change in the surface state of the iron(III) hydroxide precipitate during coagulation (aggregation) of its particles.

The values of the free energy of adsorption (E) calculated by the Dubinin–Radushkevich equation do not exceed 8 kJ mol^{-1} (see Table I). This indicates the physical nature of adsorption and excludes ion-exchange interaction of nickel ions with iron(III) hydroxide.

Coagulation removal of nickel ions at pH 8

The changes in the residual concentrations of nickel ions in the model solution during the coagulation process using $FeSO_4$ at pH 8 are shown in Fig. 5a. As can be seen, in this case, as at pH 7, a regular decrease in the residual concentration of nickel ions in the solution is observed with an increase in the concentration of iron(II) ions introduced into the solution at the beginning of the experiment. In other words, the concentration of nickel ions in the solution decreases as the concentration of the formed iron(III) hydroxide precipitate increases. In this case, a deeper purification of the solution from nickel ions occurs. For example, if at pH 7 and an initial concentration of nickel ions in the solution of 10 mg L^{-1}, the residual concentration of its ions in the solution at C_{Fe} = 100 mg L^{-1} was 3.12–4.02 mg L^{-1} (Fig. 2a), then at pH 8 under the same experimental conditions C = 0.24–0.25 mg L^{-1} (Fig. 5a). Similarly, if at pH 7, C_{Fe} = 100 mg L^{-1} and an initial concentration of nickel ions in the solution of 6.25 mg L^{-1}, the residual concentration of nickel ions in the solution was 1.57–2.17 mg L^{-1} (Fig. 2a), then at pH 8 under the same experimental conditions, C = 0.15 mg L^{-1} (Fig. 5a).

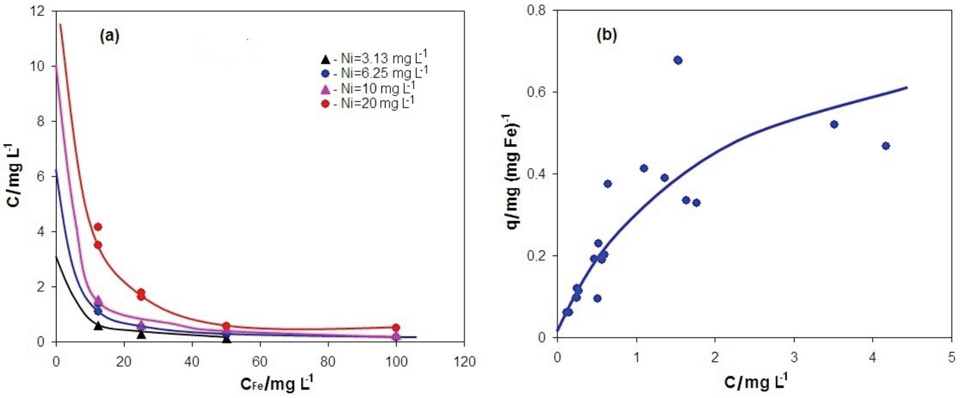

Fig. 5. Effect of the initial concentration of iron(II) ions in the model solution on the residual concentration of nickel ions in it at pH 8 (a) and the sorption isotherm of nickel ions on the formed precipitate of iron(III) hydroxide at pH 8 (b).

The sorption isotherm for nickel ions on the iron(III) hydroxide precipitate formed at pH 8, derived from the data in Fig. 5a, is shown in Fig. 5b. It is evident that there is a significant spread of experimental points; however, they all align along the same curve, which can be classified as a typical L-type isotherm.[26] Notably, there is no stratification of the sorption isotherm into multiple independent curves, as observed at pH 7 (Fig. 2b). This is likely because, at pH 8, the coagulation of iron(III) hydroxide particles is less pronounced and remains relatively consistent across all values of C_{Fe}. Consequently, the resulting precipitates exhibit nearly the same specific surface area.

The results of processing the experimental data in the coordinates of Eqs. (4), (5) and (7) are shown in Fig. 6. The corresponding parameters of Eqs. (2), (3) and (6) calculated from the experimental data are given in Table II.

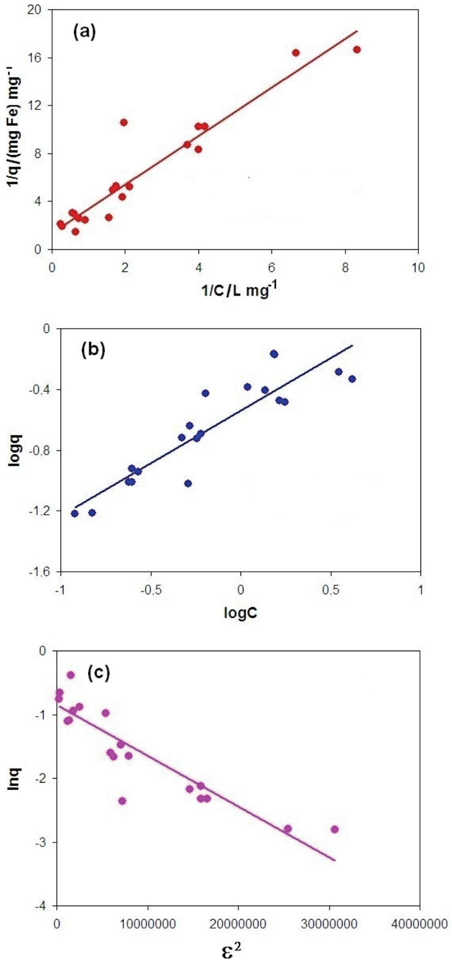

Fig. 6. Experimental data on the sorption of nickel ions by the precipitate of iron(III) hydroxide forming in the solution during the coagulation process at pH 8 in the coordinates of Eqs.: a – (4); b – (5); c – (7).

TABLE II. Parameters of the Langmuir, Freundlich and Dubinin–Radushkevich equations for the sorption of nickel ions on the forming precipitate of iron(III) hydroxide at pH 8

Langmuir constants	
q_∞ / mg (mg Fe)$^{-1}$	0.727
K_L / L mg^{-1}	0.680
R	0.948
Freundlich constants	
K_F	0.288
n	1.439
R	0.905
Dubinin–Radushkevich constants	
q_∞ / mg (mg Fe)$^{-1}$	0.438
E / kJ mol^{-1}	0.913
R	0.995

Analysis of the results presented in Table II shows that the same patterns are observed here as in the sorption at pH 7 (see Table I). At the same time, all three classical isotherms (Langmuir, Freundlich and Dubinin–Radushkevich) describe with satisfactory accuracy the sorption of nickel ions by the resulting precipitate of iron(III) hydroxide during its precipitation from an $FeSO_4$ solution. This is evidenced by the fairly high correlation coefficients. Comparison of the sorption capacities of iron(III) hydroxide precipitates with respect to nickel ions, calculated using the Langmuir and Dubinin–Radushkevich equations, shows that here, as at pH 7, calculation using the Dubinin–Radushkevich isotherm yields approximately twofold smaller q_∞ values. The value of the free energy of adsorption (E) calculated by the Dubinin–Radushkevich equation, as well as at pH 7, does not exceed 8 kJ mol^{-1} (Table II). This indicates that in this case, adsorption also has a physical nature.

It is interesting to compare these results with the findings from the study in reference,[19] which also investigated the sorption of nickel ions by the precipitate of iron(III) hydroxide formed during precipitation from $FeCl_3$ solutions at pH 7 and 8. A key difference from the previous work is that no stratification of sorption isotherms was observed at either pH 7 or 8, unlike the results found in this study at pH 7. This suggests that the specific surface area of the formed iron(III) hydroxide precipitates in reference[19] did not depend on the initial concentration of iron(III) ions in the solution.

The exponents of the Freundlich equation found in[19] are close to those determined in this work (Tables I and II). The values of K_F also have similar magnitudes. A comparison of the parameters of the Langmuir equation shows that the adsorption equilibrium constants defined in[19] exceed the similar values found in this work (Tables I and II), whereas the sorption capacities, on the contrary, have lower values. All this may indicate differences in the structure of the formed iron(III) hydroxide precipitates and their different general (gross) formulas.

Thus, the data obtained indicate that the iron(III) hydroxide precipitate formed in the solution during hydrolysis of the $FeSO_4$ coagulant is a highly effective sorbent for removing toxic nickel ions from a contaminated solution. Its sorption capacity for nickel ions at pH 8 is 0.727 mg per 1 mg of iron(II) ions introduced into the solution (0.727 mg (mg Fe)$^{-1}$), and at pH 7 it depends on the initial concentration of the coagulant in the solution and is in the range of 0.105–0.730 mg (mg Fe)$^{-1}$. This is about an order of magnitude higher than the same value for many mineral, carbon and coal sorbents.[3–13]

As noted above, a similar study was previously conducted with the coagulant $FeCl_3$.[19] A high sorption capacity of the formed iron(III) hydroxide precipitate with respect to nickel ions was also found there. In this regard, it is unclear which coagulant ($FeSO_4$ or $FeCl_3$) is preferable for the purification of contaminated solutions from nickel ions. A simple comparison of adsorption capacities does not allow one to make such a choice, since it is also necessary to take into account the values of the adsorption equilibrium constants. For such a comparative assessment, the Langmuir equation may be useful, which, after transformations, takes the form:[25]

$$C = \frac{1}{2K_{\mathrm{L}}}\left(-b + \sqrt{b^2 + 4K_{\mathrm{L}}C_{\mathrm{in}}}\right) \qquad (10)$$

where $b = 1 - K_{\mathrm{L}}C_{\mathrm{in}} + q_{\infty}K_{\mathrm{L}}C_{\mathrm{Fe}}$.

Formula (10) allows one to calculate the residual concentration of the adsorbed substance (in this case, nickel ions) in the solution depending on the initial concentration of iron ions in it and the parameters of the Langmuir equation. The results of comparative calculations using this equation for pH 7 and 8 and an initial concentration of nickel ions in the solution of 10 mg L^{-1}, according to Tables I and II, as well as the works,[19] are graphically presented in Fig. 7.

Fig. 7 shows that at both pH 7 and pH 8, the use of iron(II) sulfate as a coagulant at its initial concentration in the solution (in terms of iron ions) of 0–70 mg L^{-1} leads to a deeper removal of nickel ions from the model solution compared with previously studied $FeCl_3$ coagulant. However, with an increase in the concentration of $FeSO_4$ in the solution above 70 mg L^{-1} (in terms of iron ions), the effectiveness of this coagulant decreases, and in this case the $FeCl_3$ coagulant already removes nickel ions from the solution more effectively.

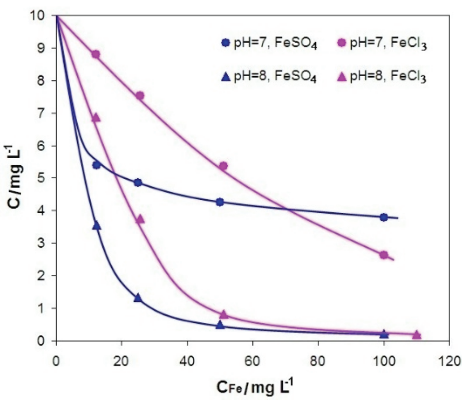

Fig. 7. Calculated change in the residual concentration of nickel ions in the model solution during its adsorption on iron(III) hydroxide precipitates formed at pH 7 and 8 using $FeSO_4$ and $FeCl_3$ coagulants.

CONCLUSION

The use of iron(II) sulfate ($FeSO_4$) as a coagulant enables the removal of not only insoluble impurities from contaminated solutions, but also toxic nickel ions. The removal of nickel ions by the iron(III) hydroxide precipitate formed during coagulation is most effective at pH 8. The sorption of nickel ions onto this precipitate is accurately described by the classical Langmuir, Freundlich and Dubinin–Radushkevich isotherms. The free energy of adsorption, calculated using the

Dubinin–Radushkevich equation, does not exceed 8 kJ mol^{-1}, indicating a physical nature of the adsorption process and ruling out ion–exchange interactions between nickel ions and iron(III) hydroxide. At pH 8, the sorption capacity of the resulting iron(III) hydroxide precipitate for nickel ions is 0.727 mg per 1 mg of Fe^{2+} introduced into the solution (0.727 mg (mg $Fe)^{-1}$). At pH 7, the sorption capacity depends on the coagulant concentration in the solution and ranges from 0.105 to 0.730 mg (mg $Fe)^{-1}$. A comparison between $FeSO_4$ and the previously studied $FeCl_3$ coagulant shows that $FeSO_4$ is more effective at removing nickel ions when the initial concentration of iron ions in the solution is below 70 mg L^{-1}. However, at higher initial concentrations of iron, $FeCl_3$ demonstrates greater removal efficiency.

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ИЗВОД

УКЛАЊАЊЕ НИКЛА(II) ЈОНА ТОКОМ ПРЕЧИШЋАВАЊА ВОДЕ ГВОЖЂЕ(II)--СУЛФАТОМ. 1. ДЕО. МЕХАНИЗАМ И ЕФИКАСНОСТ ПРОЦЕСА

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Пречишћавање природних и отпадних вода уклањањем јона никла је од велике важности за животну средину и здравље људи због њихове високе токсичности. Циљ овог рада био је испитивање могућности уклањања јона никла из контаминираних водених раствора помоћу коагуланта $FeSO_4$. Показано је да се уклањање јона никла из воденог раствора путем преципитата са гвожђе(III) хидроксидом, који настаје коагулацијом на pH 7 и 8, може успешно описати класичним адсорпционим изотермама, и то Ленгмир, Фројндлих и Дубинин–Радушкевич моделима. Вредности слободне енергије адсорпције израчунате на основу Дубинин–Радушкевичеве једначине не прелазе 8 kJ mol^{-1}, што указује на физичку природу адсорпције и искључује јоноизмењивачку интеракцију између јона никла и гвожђе(III)-хидроксида. Капацитет сорпције добијеног преципитата гвожђе(III)-хидроксида за јоне никла на pH 8 је 0,727 mg по 1 mg гвожђе(II) јона додатих у раствор, а на pH 7 зависи од почетне концентрације коагуланта у раствору и налази се у опсегу 0,105-0,730 mg (mg $Fe)^{-1}$. Поређење коагуланата $FeSO_4$ и раније испитиваног коагуланта $FeCl_3$ показује да при почетној концентрацији јона гвожђа у раствору мањој од 70 mg L^{-1}, $FeSO_4$ коагулант ефикасније уклања јоне никла. Међутим, при већим полазним концентрацијама гвожђа ефикаснији је $FeCl_3$.

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