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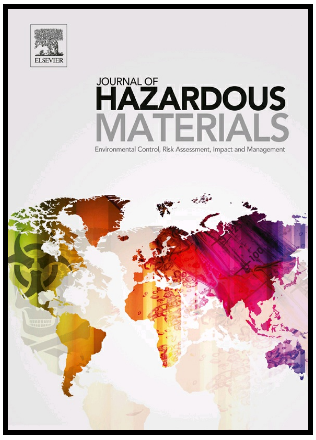

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Effect of Mg^{2+} ions on competitive metal ions adsorption/desorption on magnesium ferrite: mechanism, reusability and stability studies

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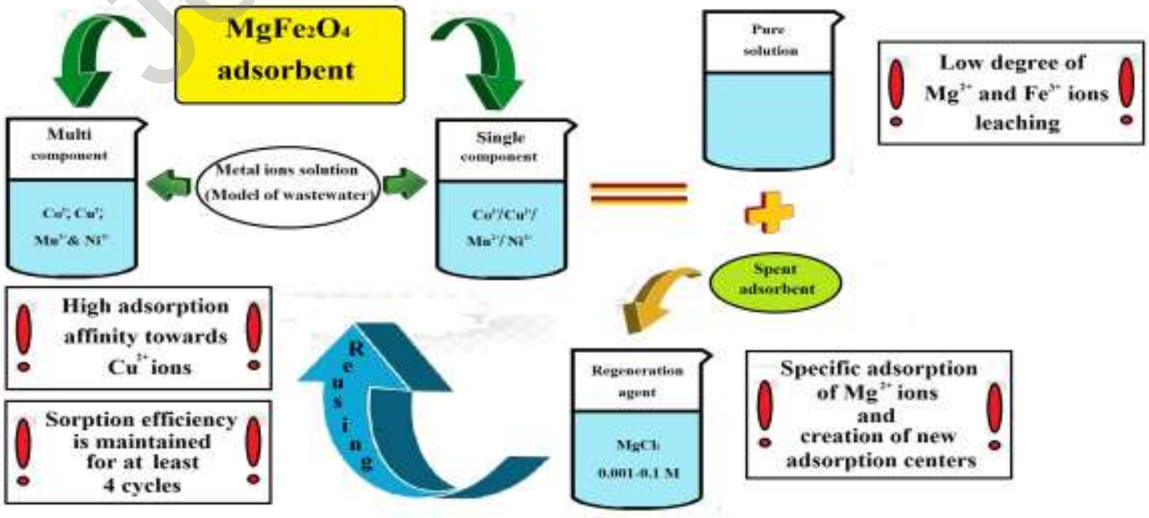
Abstract

The adsorption behavior of magnesium ferrite in single- and multicomponent metal ions solutions in the presence of Mg^{2+} ions were studied. A dramatic decrease in the adsorption capacity of magnesium ferrite towards Mn^{2+}, Co^{2+}, and Ni^{2+} ions for comparison study of single- and multicomponent solutions was established. The affinity of the sorbent in accordance with the maximum sorption capacities increases in the following order $Cu^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}$. High efficiency of magnesium ferrite regeneration (~100%) with aqueous solutions of magnesium chloride in the concentration range of 0.001-0.1 M was shown. The low degree of toxic metal ions desorption combined with XRD, IR spectroscopy, and EDX analysis data indicate the key role of Mg^{2+} ion adsorption in the magnesium ferrite adsorbent regeneration. The positive effect of the introduction of Mg^{2+} ions into multicomponent solutions on metal ions adsorption was established, which is accompanied by an increase in the maximum sorption capacity for all metal ions and especially significant increase in the selectivity towards Cu^{2+} ions (2.41 mmol/g). The stability of the crystal structure of magnesium ferrite and a low degree of Mg^{2+} and Fe^{3+} ions leaching during multiple cycles of adsorption and regeneration of the adsorbent were observed.

Graphical abstract



Keywords: Magnesium ferrite; Competitive adsorption; Mechanism adsorption; Regeneration; Stability.

1 Introduction

The development of nanotechnology has a significant impact on science and technology (Ramsden, 2016). The use of green and environmentally friendly technologies based on nanomaterials is widely used to solve the problem of water purification from toxic pollutants (Grumezescu, 2017; Yaqoob et al., 2020; Nasrollahzadeh et al., 2021). This is primarily due to the creation of nanostructured hybrid (organomineral) membranes (Wang et al., 2018; Li et al., 2020), catalysts for Advanced Oxidation Processes (Zhang, 2020; Hodges et al., 2018) and effective nanoscale adsorbents (Dhillon and Kumar, 2018; Rasheed et al., 2020).

A large number of publications describe the production of new adsorbents based on nanostructured metal oxides/hydroxides, which is due to their efficiency in the removal of cationic (toxic metal ions, pharmaceutically active compounds, cationic dyes) and anionic(Cr (VI), As (III, V) salts, surfactants, anionic dyes) pollutants (Pathania and Singh, 2014; Awad et al., 2020; Goh et al., 2008). To increase the effectiveness of metal oxide sorbents, various techniques are used: formation of composite core/shell sorbents, modification with magnetic and carbon nanoparticles, grafting of various functional groups (Raval and Kumar, 2021; Anuradha et al., 2018; Dontsova et al., 2018; Liu et al., 2020). Despite significant advances in this field, in practice, the described adsorbents are used much less frequently on an industrial scale than traditional adsorbents based on natural clay minerals, zeolites, activated carbons, aluminum oxide, and silicon oxides (Singh et al., 2018; Godage and Gionfriddo, 2020).

The main factors limiting the widespread use of nanostructured adsorbents for water purification are: (i) low selectivity to toxic pollutants in the treatment of multicomponent real wastewater; (ii) reduced sorption capacity in multiple adsorption-desorption cycles, which is associated with low stability of the crystalline and porous structure of materials; (iii) the complexity of using nanoparticles in a dynamic sorption mode; (iv) the need to use an additional technological stage to separate spent sorbents from solutions; (v) high cost compared to natural sorbents and activated carbon.

Metal ferrites with spinel structure are promising adsorbents for water treatment (Reddy and Yun, 2016). Compared with iron oxides (α-Fe_2O_3, γ-Fe_2O_3, Fe_3O_4), metal ferrites are characterized by higher chemical stability in acidic environments (pH 2.0-6.0), improved magnetic characteristics and the absence of phase transitions in a wide temperature range. The crystal structure of spinel ferrites has cubic symmetry and belongs to the Fd3m group. At the same time, depending on the distribution of iron and divalent metal cations in tetrahedral and octahedral positions, metal ferrites belong to normal (M^{2+} - tetrahedral positions, Fe^{3+} - octahedral positions), reversed (M^{2+} - octahedral positions, Fe^{3+} - tetrahedral positions) and mixed (M^{2+} and Fe^{3+} are both in octahedral and tetrahedral positions) spinels. The structure, specific surface area, particle morphology and size, and number of surface Fe-OH and M-OH groups are the main factors influencing the sorption properties of metal ferrites (Kefeni et al., 2017).

Magnesium ferrite ($MgFe_2O_4$) has a predominantly reversed spinel structure (inversion degree of 0.9) (Heidari and Masoudpanah, 2020). Despite significantly less pronounced magnetic characteristics compared to transition metal ferrites ($CoFe_2O_4$, $CuFe_2O_4$, $MnFe_2O_4$, etc.) (Pacakova et al., 2016), magnesium ferrite has high sorption and catalytic activity and extremely low toxicity (Tang et al., 2013; Ivanets et al., 2018; Amiri et al., 2019; Ivanets et al., 2019a). This leads to the absence of environmental risks when using adsorbents and catalysts based on magnesium ferrite, which can be related with both leaching of iron and magnesium ions in the solution when used in adsorption-desorption cycles, and the possibility of nanoparticles entering the environment if they are not effectively separated from the treated aqueous solutions.

Ivanets et al. (2018; 2019a) described the synthesis, physicalchemical, sorption, and catalytic properties of magnesium ferrite obtained by glycine-nitrate methods using NaCl as a protective inert agent that prevents aggregation of nanoparticles. Along with traditional regeneration agents (aqueous solutions of acids and alkalis, organic alcohols and solvents), high efficiency of magnesium chloride was demonstrated in the regeneration of magnesium ferrite after sorption of methylene blue (Ivanets et al., 2019b). The investigation of the mechanism of adsorbent regeneration showed a fundamental difference between the use of acid solutions and magnesium chloride as regenerate agents. It was found that the process of Mg^{2+} ions specific adsorption causes effective regeneration of magnesium ferrite after dye sorption. High efficiency of sorption capacity reduction in four adsorption-desorption cycles using dilute $MgCl_2$ solutions was also established.

Taking into account the high affinity of magnesium ferrite towards Mg^{2+} ions, the current work is devoted to the study of the following important aspects: (i) study of the adsorption efficiency and desorption mechanism of toxic metal ions when using $MgCl_2$ solutions (0.001-0.1 M) for regeneration, (ii) determination of sorption-selective properties of magnesium ferrite towards heavy metal ions for multicomponent solutions, (iii) study of the effect of the $MgCl_2$ presence in model solutions on the sorption properties of magnesium ferrite, (iv) evaluation of the adsorbent stability during multicycle application.

2 Materials and Methods

2.1 Chemicals

$Mg(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 6H_2O$, $C_2H_5NO_2$ (glycine), NaCl, $MgCl_2 \cdot 6H_2O$ reagents were obtained from Five Ocean Company, Ltd, Belarus. During the experiments, all reagents were analytically pure and the solutions were prepared in ultra-pure water (18.2 MΩ·cm).

2.2 Adsorbent preparation and characterization

The magnesium ferrite adsorbent was synthesized by a self-combustion glycine-nitrate technique. Magnesium nitrate, ferrous nitrate, glycine, and sodium chloride as an inert additive were dissolved in deionized water in molar ration 1:2:4.5:10, respectively. The prepared mixture was vaporized at 80 °C under vigorous stirring before preparing a thick gel. Further, heating of the gel mass resulted in its spontaneous combustion. The obtained mixture of magnesium ferrite, coal, and sodium chloride was heated at 300 °C for 5 h. Magnesium ferrite nanoparticles were washed by deionized water and removed by a magnet. The detailed procedure was described in our previous paper (Ivanets et al. 2018; Ivanets et al. 2019a). The synthesized magnesium ferrite nanoparticles characterized by mesoporous structure (BET specific area of 14 m^2 g^{-1}, sorption volume of 0.030 cm^3 g^{-1} and average pore size of 11 nm). The initial magnesium ferrite nanoparticles and samples after adsorption and regeneration experiments were characterized by X-ray diffraction (XRD) analysis (D8 ADVANCE (Bruker, Germany) with CoKα (λ = 0.1789 nm) irradiation, Fourier-transform infrared (FTIR) spectroscopy (IR Affinity-1, Shimadzu, Japan), Scanning electron microscopy JSM-5610 LV (JEOL, Japan), and Energy dispersive X-ray prefix JED-2201 (JEOL, Japan).

2.3 Adsorption experiments

The study of metal ions (Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) adsorption isotherms was performed using single component model solutions with an initial concentration of metal chloride of 0.001-0.01 M at a pH of 5.0 and a contact time of 120 min. The adsorption kinetics was studied on 0.01 M single component model solutions at pH 5.0 in the time range of up to 120 min. The concentration of magnesium ferrite in all experiments was 40.0 mg/10.0 mL that is the optimal value (Ivanets et al., 2018). Mathematical processing of the obtained experimental data was performed using well-known Langmuir (Eq. 1), Freundlich (Eq. 2), Sips (Eq. 3), and Redlich-Peterson (Eq. 4) models of adsorption isotherms and pseudo-first (Eq. 5) and pseudo-second order (Eq. 6) models for adsorption kinetics (Tran et al., 2017).

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \qquad (1)$$

Where$q_e$is the sorption capacity (mmolg^{-1}), C_e – equilibrium concentration (mmol L^{-1}), q_m – maximum sorption capacity (mmolg^{-1}), K_L – coefficient describing affinity of the adsorbate to the adsorbent, (L mmol^{-1}).

$$q_e = K_F C_e^{1/n_F} \qquad (2)$$

Where K_F ((mmol g^{-1})/(L mmol^{-1})$^{n}{}_{F}$) is Freundlich constant; n_F – Freundlich exponent.

$$q_e = \frac{K_S q_m C_e{}^{1/n_S}}{1+K_S C_e{}^{1/n_S}} \qquad (3)$$

Where is K_S – Sips constant ((mmol L^{-1})$^{-1/n}{}_{S}$); n_S – Sips exponent ($0 < n_S \leq 1$).

$$q_e = \frac{K_{RP} C_e}{1+a_{RP} C_e{}^{g}} \qquad (4)$$

Where isK_{RP} – Redlich-Peterson constant (L mmol^{-1}); a_{RP} – Redlich-Peterson constant ((mmol L^{-1})$^{-g}$); g – Redlich-Peterson constant ($0 < g \leq 1$).

$$ln(q_e - q_t) = lnq_e - k_1 t \qquad (5)$$

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e)t \qquad (6)$$

where q_e and q_t (mmol·g^{-1}) are adsorption capacity at the equilibrium and time t, k_1 (min^{-1}) is the pseudo-first order rate constant, k_2 (g·mmol^{-1}·min^{-1}) is the pseudo-second order rate constant.

Competitive adsorption was studied using multicomponent model solution, containing Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} ions with 0.01 M concentration of each cation (pH=5.0, contact time of

120 min). The concentration of magnesium ferrite in the model solution was 80.0 mg /20.0 mL. To assess the effect of Mg^{2+} ions on the adsorption efficiency of metal ions, $MgCl_2$ was introduced into the model solution in the concentration range of 0.001-0.10 M (pH=5.0, contact time of 120 min).

Regeneration of magnesium ferrite after adsorption of metal ions was performed using $MgCl_2$ solutions with concentrations of 0.001, 0.01, and 0.1 M. Adsorbent of 20.0 mg was kept on 10.0 mL of the regeneration solution for 120 minutes.

In all experiments, model solutions were mixed at a speed of 300 rpm by the rotary shaker ST15 (Cat, M. Zipperer GmbH, Staufen, Germany). The pH of the initial solutions was estimated by pH meter of 340i (±0.02) (Mettler Toledo, USA). The temperature of the model solutions was 20 °C. The concentration of metal ions in solutions was measured on inductively coupled plasma optical emission spectrometer (ICP-OES) using ICAP 6300 (Thermo Electron Corporation, USA). Aliquots for ICP-OES analysis were separated from the adsorbent by centrifugation at 5000 rpm for 3 min.

The adsorption capacity of magnesium ferrite (q_e, mmol/g) was calculated from equation (1):

$$q_e = \left(\frac{C_i - C_e}{m}\right) \cdot V \tag{7}$$

where: m (mg) is the mass of the adsorbent; V (L) is the volume of model solution; and C_i and C_e (mol/L) are the initial and equilibrium concentrations of metal ions, respectively.

The desorption efficiency (α_{des}, %) was calculated using the following equations:

$$\alpha_{des} = \left(\frac{C_{des}}{C_i - C_e}\right) \cdot 100 \tag{8}$$

where: C_{des}, C_i and C_e (mol/L) are the after desorption, initial and equilibrium concentrations of metal ions, respectively.

3 Results and Discussion

3.1 Isotherms and kinetics modeling

The study of isotherms and kinetics adsorption of magnesium ferrite from single component model solutions allows evaluating the effectiveness of the prepared sorbent. Isotherms of Mn^{2+}, Co^{2+}, and Ni^{2+} ions adsorption belong to type L according to the Giles classification (Giles et al. 1960), which are typical for cases of low affinity of the adsorbent towards the adsorbate. The isotherm of Cu^{2+} ions adsorption had differ form and characterized by a pronounced vertical course at the initial adsorption site and belongs to type H, which indicates a high affinity of the adsorbent to the adsorbate (Fig. 1).

Also, it is important to note that only in the case of Cu^{2+} ions adsorption there was a pronounced plateau on the adsorption isotherms. The differences in affinity to toxic metal ions were also confirmed by the data of mathematical processing of adsorption isotherms. The Sips model most reliably describes the adsorption of Mn^{2+}, Co^{2+}, and Ni^{2+} ions. While the Redlich-Peterson model was well applicable in the case of Cu^{2+} ions adsorption (Fig. 1). Both models are a combination of Langmuir and Freundlich models, which indicates a similar mechanism of metal ion adsorption on the surface of magnesium ferrite. Isotherms modeling results in detail was described previously (Ivanets et al., 2018).

Magnesium ferrite showed the highest adsorption capacity in relation to Co^{2+} ions, and lower values were obtained for Mn^{2+} and Ni^{2+} ions adsorption. At the same time, despite the high affinity of Cu^{2+} ions to the adsorbent, the adsorption capacity in relation to this cation is very low. This may be due to the presence of several types of sorption centers (Fe-OH and Mg-OH) with different affinities to toxic metal ions. During the adsorption of Cu^{2+} ions, it seems that only one type of adsorption centers was filled (as will be shown below, this is Mg-OH), as evidenced by a decrease in the sorption capacity by 3-4 times compared to Mn^{2+}, Co^{2+}, and Ni^{2+} ions adsorption.

The analysis of kinetic data shows that the adsorption of metal ions proceeded rapidly and equilibrium was established within 10 min (Fig. 2). The pseudo-second-order model described the adsorption kinetics well, which is typical for processes with a controlled stage of chemical adsorption. At the same time, as in the case of adsorption capacity, the highest adsorption rate constant (k_2=5.69 g/(mmol·min)) was observed for Co^{2+} ions, and the lowest was for Cu^{2+} ions (k_2=0.026 g/(mmol·min)).

3.2 Regeneration study

The study of the regeneration of spent adsorbents after the adsorption of toxic metal ions from single-component solutions shows the complete regeneration of adsorption capacity for magnesium ferrite by using 0.001-0.10 M $MgCl_2$ regeneration solutions (Table 1). Rather unexpected result was a more than 5-times increase in the adsorption capacity of magnesium ferrite towards Cu^{2+} ions, which was the first time described by Ivanets et al. (2018). Probably, this was due to the Mg^{2+} ions adsorption during regeneration, which leads to the formation of additional Mg-OH adsorption centers with increased affinity towards Cu^{2+} ions. Concerning magnesium ferrite regeneration after Co^{2+}, Cu^{2+}, and Ni^{2+} ions adsorption, the content of these ions in regenerated solutions was 0.002-0.031 mmol/L and did not exceed 1% of the adsorbed amount. In the case of adsorbent regeneration after Mn^{2+} adsorption, the concentration of manganese ions in the regenerated solutions was higher and reached 0.418 mmol/L, which corresponds to 6.7% degree of metal desorption.

The estimation of the ion exchange contribution in adsorption process was calculated from the values of the ratio $q_{des}(Mg^{2+})$ / $q_{ads}(M^{2+})$ during model solution analysis after the second adsorption cycle. The obtained data indicated that the adsorbed Mg^{2+} ions were strongly bound to the surface of magnesium ferrite during the adsorbent regeneration. The degree of magnesium ions desorption did not exceed 0.1% for low concentrations (0.001 and 0.01 M) of $MgCl_2$ and was 2-9% when using 0.10 M regeneration solution.

The use of 0.01 M $MgCl_2$ solution provided a high efficiency of reducing the sorption capacity of magnesium ferrite towards studied metal ions (Fig.3). At the same time, the increased adsorption capacity of magnesium ferrite towards Cu^{2+} ions, achieved after adsorbent regeneration preserved in subsequent adsorption-desorption cycles.

The unusual behavior of magnesium ferrite during regeneration could be due to different mechanisms of heavy metal ions and Mg^{2+} ions adsorption: (i) for Co^{2+}, Cu^{2+}, Mn^{2+} and Ni^{2+} ions adsorption the main process was the non-specific adsorption in a diffusion layer due to electrostatic forces (Lyklema 1995); (ii) in the case of Mg^{2+}, there was specific adsorption due to the completion of a crystal lattice of magnesium ferrite nanoparticles by Mg^{2+} ions (according to the rules of Fayans-Pannet) with the formation of new Mg-OH adsorption sites and the super-equivalent adsorption of Mg^{2+} ions (according to DLVO theory) accompanied by a recharge of the magnesium ferrite surface (Park & Seo 2011). These phenomena of magnesium ferrite regeneration using Mg^{2+} ions must be taken into account in the theory and practice of adsorption.

3.3 Competitive adsorption

In real conditions, when toxic metal ions and hardness salts (Mg^{2+} and Ca^{2+}) are present together, these patterns have different trends. This was confirmed by the results, which are shown in Table 2. During adsorption from a multicomponent solution containing Co^{2+}, Cu^{2+}, Ni^{2+}, and Cu^{2+} ions, a sharp decrease in adsorption capacity was observed towards all metals except Cu^{2+} ions. In the case of competitive adsorption, this result was due to the different affinity of the adsorbent to metal ions and confirmed the high affinity of magnesium ferrite towards Cu^{2+} ions. In this case, the total adsorption capacity relative to all ions for a multicomponent solution was significantly less than the adsorption capacity towards Co^{2+}, Mn^{2+}, and Ni^{2+} ions during adsorption from single-component solution. This indicated an additive negative effect of toxic metal ions on their adsorption from multicomponent solution.

Introduction of $MgCl_2$ background electrolyte into a multicomponent model solution lead to a significant increase in the adsorption capacity of magnesium ferrite towards metal ions in comparison with multicomponent solutions containing only toxic metal ions. Adsorption capacity of Co^{2+}, Mn^{2+}, Ni^{2+} ions did not reach the values that was obtained during adsorption from single-component solutions. As for Cu^{2+} ions adsorption, the values of the adsorption capacity of magnesium ferrite before and after its regeneration were approximately the same – 2.41 and 2.40-2.49 mmol/g, respectively. This indicated a positive effect of Mg^{2+} ions on the efficiency of Cu^{2+} ion adsorption. In the range from 0.001 to 0.10 M $MgCl_2$, the background electrolyte concentration did not effect on the adsorption capacity of toxic metals. At the same time, the adsorption of Mg^{2+} ions with an increase in the concentration of $MgCl_2$ from 0.001 to 0.10 M increased from 0.75 to 4.05 mmol/g, respectively.

A comparative study of sorption capacity of $MgFe_2O_4$ and other magnetic adsorbents was shown in Table 3. The synthesized nanoparticles had significant adsorption capacity for Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} ions from multicomponent solutions and can be efficiently used for the water treatment.

3.4 Stability study

Elemental analysis data of adsorbents (Table 4) indicate that the composition of the initial magnesium ferrite included iron, magnesium and oxygen. Given that the EDX method allows analyzing the surface layer of the material at a depth of up to 5 µm, this indicated about increase content of iron atoms on the magnesium ferrite surface. This was evidenced by the excess of the molar ratio Fe:Mg = 4.3:1 over a stoichiometric value of 2:1.

After metal ions adsorption from a multicomponent solution, the corresponding metal atoms and chlorine atoms were detected in the adsorbent. This confirmed the fact of metal ion adsorption. The presence of chlorine was due to the use of metal chlorides for the preparation of the model solution. The metal content of the adsorbent was fully consistent with the data on its adsorption capacity obtained for a multicomponent solution: $Cu^{2+} >> Ni^{2+} > Co^{2+} > Mn^{2+}$. At the same time, there was a decrease in the content of iron, magnesium and oxygen atoms due to their adsorption.

During regeneration, the concentration of magnesium ions increased significantly, which was due to the adsorption of these cations. A significant increase in the content of chlorine atoms was also explained by the adsorption of Mg^{2+} ions. The insignificant desorption of toxic metal ions during the regeneration of the adsorbent was confirmed by the relatively high content of corresponding atoms on the surface of magnesium ferrite after regeneration.

According to Fig. 4, regardless of the nature of Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} ions, their uniform distribution on the surface of the adsorbent was observed during the adsorption process. This indicated the unified nature of the adsorption centers, which were characterized by different affinities to heavy metal ions.

SEM images of the magnesium ferrite surface allow evaluating the morphology of the initial, spent and regenerated adsorbent (Fig. 5). Initial adsorbent (Fig. 5a) practically did not undergo morphological changes after adsorption (Fig. 5b). Its surface was represented by large aggregates (10-20 µm) of highly dispersed particles with a size significantly less than 1 µm. During regeneration these aggregates were destroyed and a highly porous sponge structure was formed (Fig. 5c), which was probably due to the adsorption of Mg^{2+} ions.

The results of XRD and IR spectroscopy (Fig. 6) indicated that during the metal ions adsorption, magnesium ferrite practically did not change its structure. On the diffractograms of the initial magnesium ferrite, peaks were corresponding to the reflexes (311), (400), (202), (404), and (511). IR spectra contain weak absorption bands related to –COOH (1640 cm^{-1}), –OH (1544 cm^{-1}), and NO_3^- (1393 cm^{-1}) groups. The intense peak at 550 cm^{-1} refers to fluctuations in the Fe-O bond characteristic of ferrites (Pradeep et al., 2008). At the same time, after regeneration, the adsorbent contains magnesium chloride hexahydrate along with a well-crystallized phase of magnesium ferrite. This confirms the process of adsorption of magnesium ions during the adsorbent regeneration.

4 Conclusion

Magnesium ferrite nanoparticles were prepared by glycine-nitrate self-combustion technique. Their adsorption performance towards Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} ions from single- and multicomponent solutions was studied. The high adsorption affinity of magnesium ferrite adsorbent towards Cu^{2+} ion was established, which was supported by high adsorption capacity that was shown from single and multicomponent metal ions solutions, as well as in presence of Mg^{2+} ions background. The high efficiency of $MgCl_2$ solution as a regeneration agent was demonstrated. Firstly, the insignificant desorption of previously adsorbed heavy metal ions was established. The role of specific adsorption of Mg^{2+} ions on spent magnesium ferrite adsorbent as the main process contributing to effective adsorbent regeneration was shown. The peculiarities of competitive adsorption in presence of $MgCl_2$ were established. The desorption process and metal ions leaching during regeneration of magnesium ferrite was studied and a possible mechanism of adsorbent regeneration was proposed. The adsorbent stability was confirmed by XRD, FTIR and SEM-EDX analysis during four regeneration cycles. The presented results are important for understanding the adsorption-desorption processes, regeneration mechanism and for magnesium ferrite application for wastewater treatment.

CRediT (Contributor Roles Taxonomy) author statement

Andrei Ivanets: Conceptualization, Methodology, Writing-Original Draft, **Vladimir Prozorovich:** Investigation, Visualization, Data Curation; **Tatyana Kouznetsova:** Results discussion, Editing; **Tetiana Dontsova:** Writing-Review & Editing, Formal analysis; **Olena Yanushevska:** Writing-Review & Editing, Formal analysis; **Ahmad Hosseini-**

Bandegharaei: Data discussion, Data Curation; **Varsha Srivastava:** Project administration, Investigation, Editing; **Mika Sillanpää:** Project administration, Funding acquisition, Resources.

Declaration of Competing Interest

No conflict of interest.

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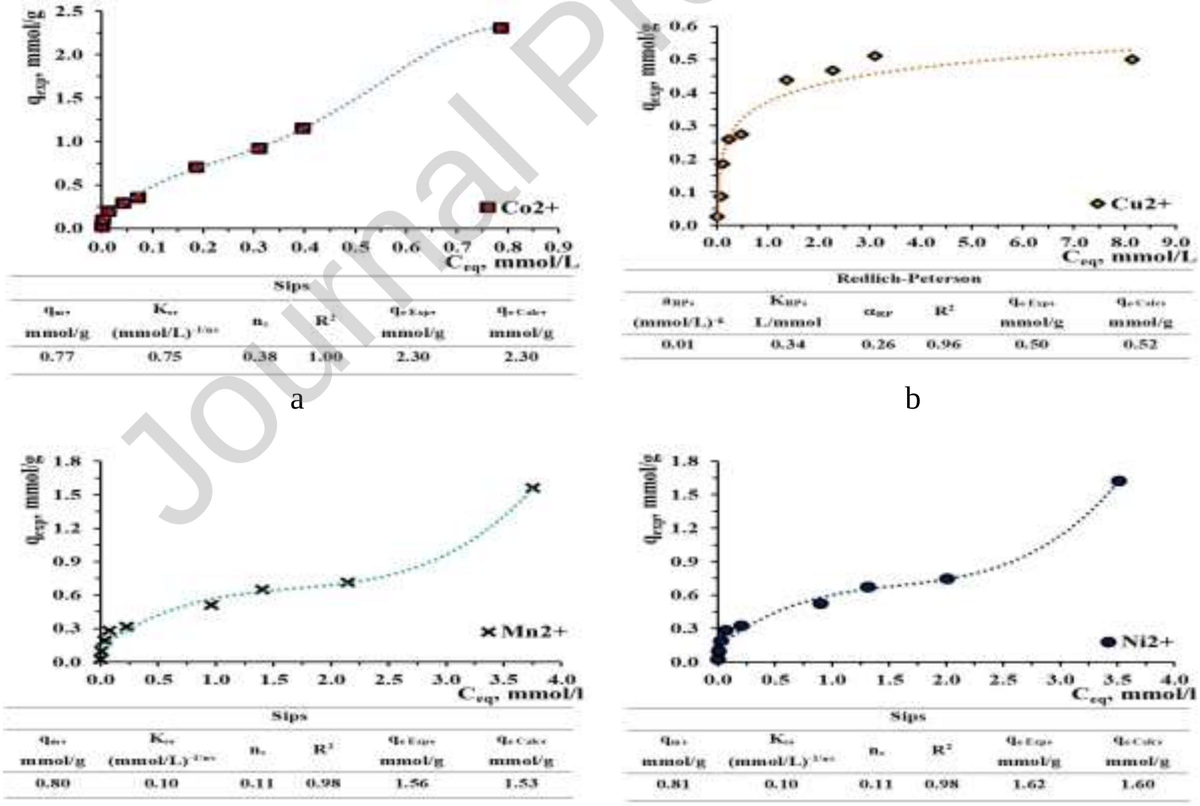
Figures



Sips					
q_{ms}, mmol/g	K_{ss}, $(mmol/L)^{-1/ns}$	n_s	R^2	$q_{e\,Exp}$, mmol/g	$q_{e\,Calc}$, mmol/g
0.77	0.75	0.38	1.00	2.30	2.30

a

Redlich-Peterson					
a_{RP}, $(mmol/L)^{-\beta}$	K_{RP}, L/mmol	α_{RP}	R^2	$q_{e\,Exp}$, mmol/g	$q_{e\,Calc}$, mmol/g
0.01	0.34	0.26	0.96	0.50	0.52

b

Sips					
q_{ms}, mmol/g	K_{ss}, $(mmol/L)^{-1/ns}$	n_s	R^2	$q_{e\,Exp}$, mmol/g	$q_{e\,Calc}$, mmol/g
0.80	0.10	0.11	0.98	1.56	1.53

c

Sips					
q_{ms}, mmol/g	K_{ss}, $(mmol/L)^{-1/ns}$	n_s	R^2	$q_{e\,Exp}$, mmol/g	$q_{e\,Calc}$, mmol/g
0.81	0.10	0.11	0.98	1.62	1.60

d

Fig. 1. Isotherms adsorption and calculated parameters of isotherm models for Co^{2+}(a), Cu^{2+}(b), Mn^{2+}(c) and Ni^{2+}(d) ions adsorption on magnesium ferrite.

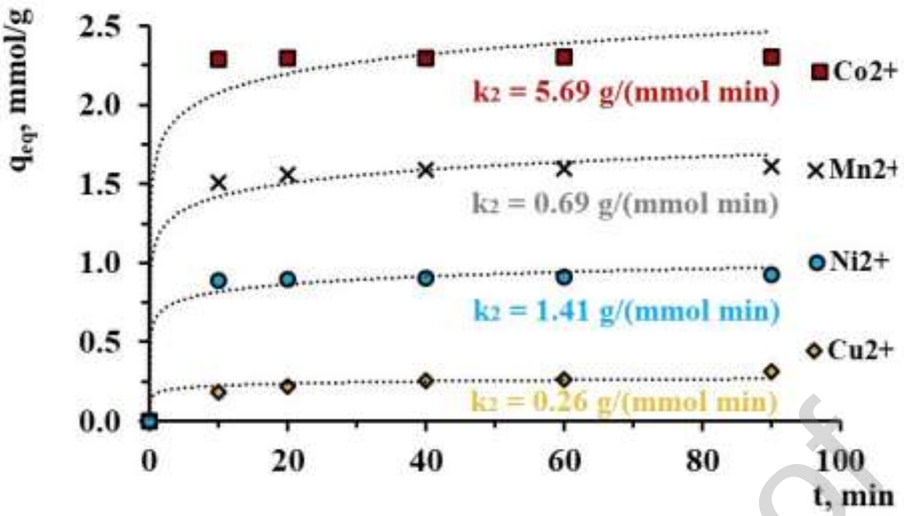


Fig. 2. Kinetics adsorption and calculated parameters of pseudo-second kinetic model for metal ions adsorption on magnesium ferrite.

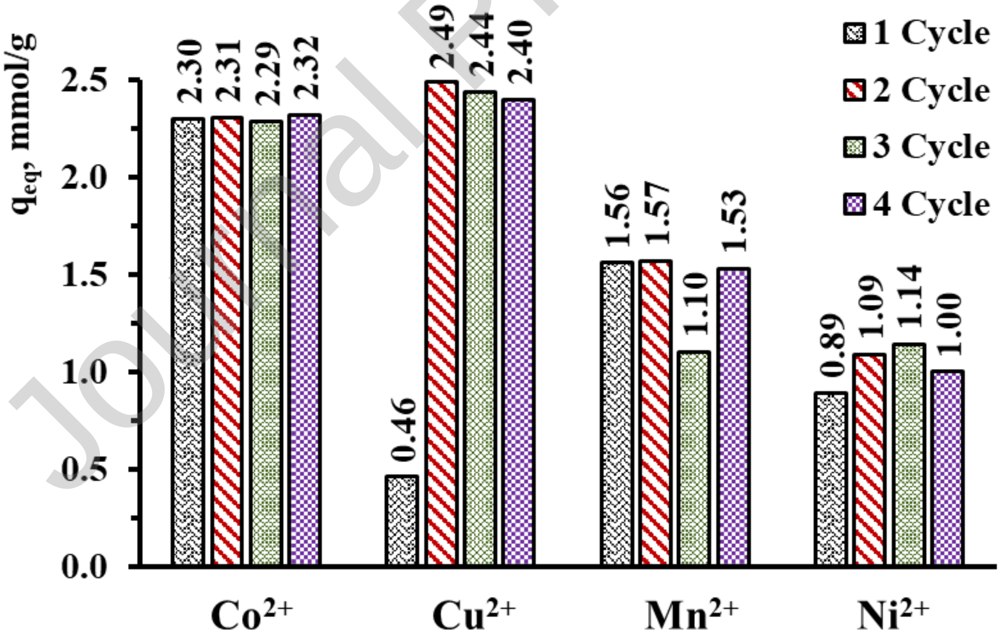
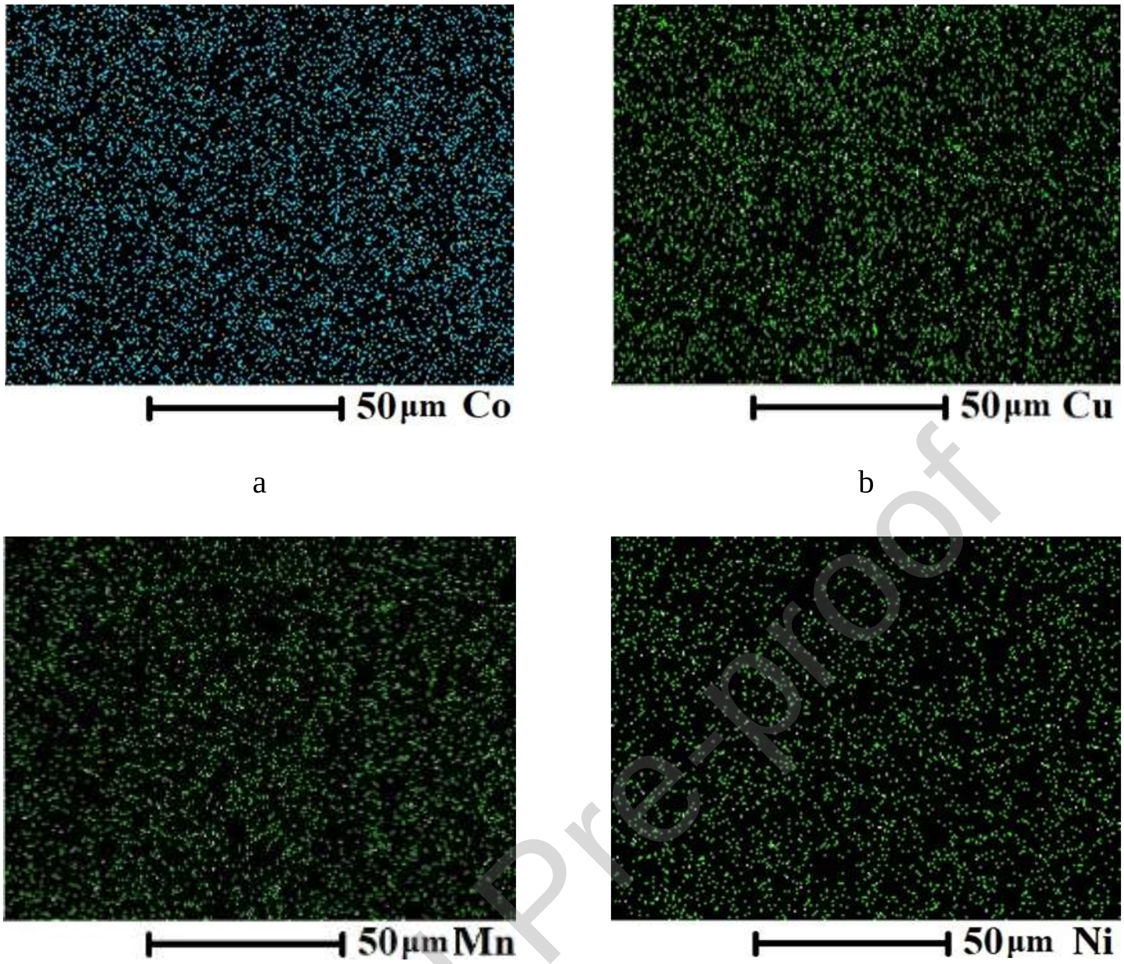


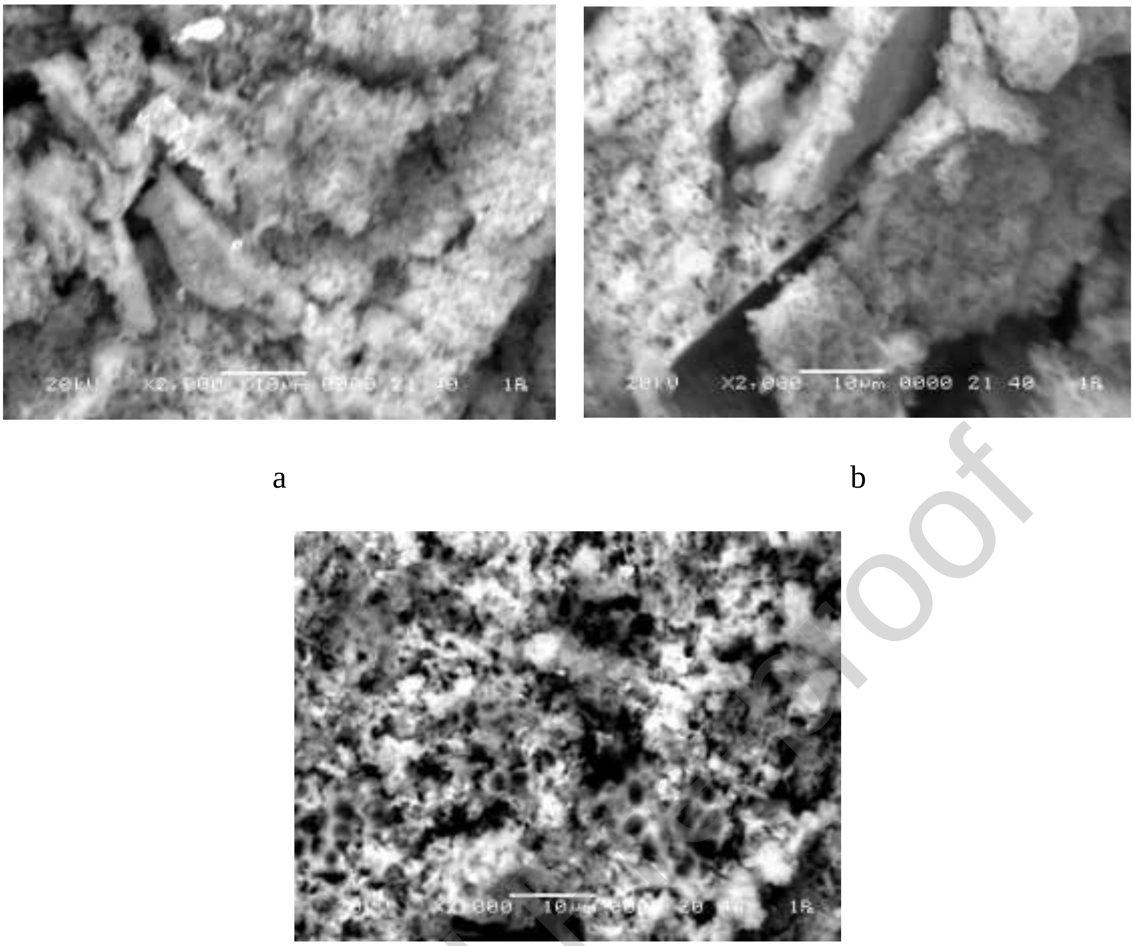
Fig. 3. Adsorption capacity during adsorption/desorption cycles by 0.01 M $MgCl_2$ (pH 5.0, contact time of 120 min).



a b

c d

Fig 4. Distribution of (a) Co, (b) Cu, (c) Mn and (d) Ni atoms on the surface of spent sorbent.

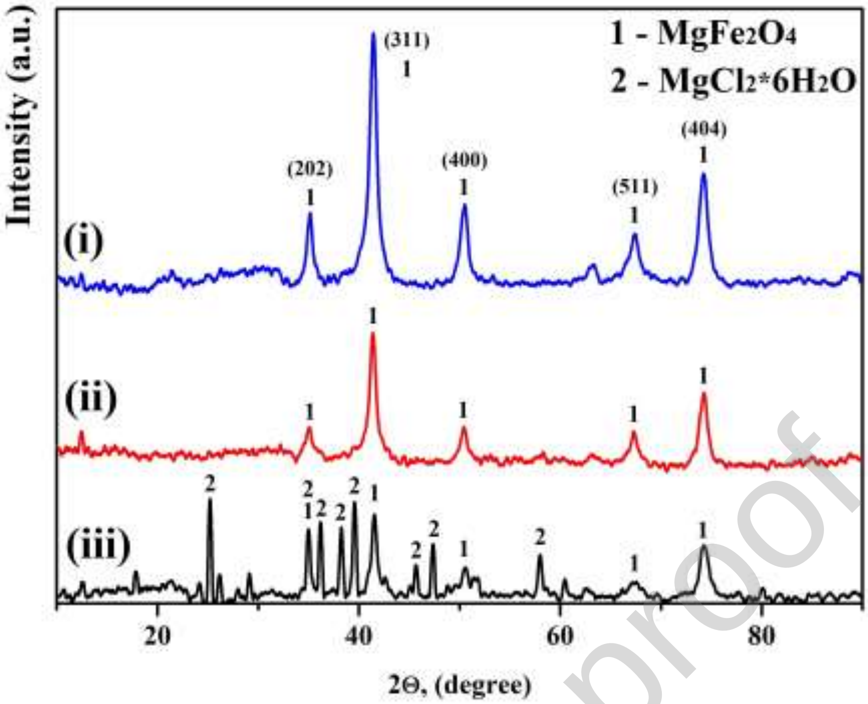


a

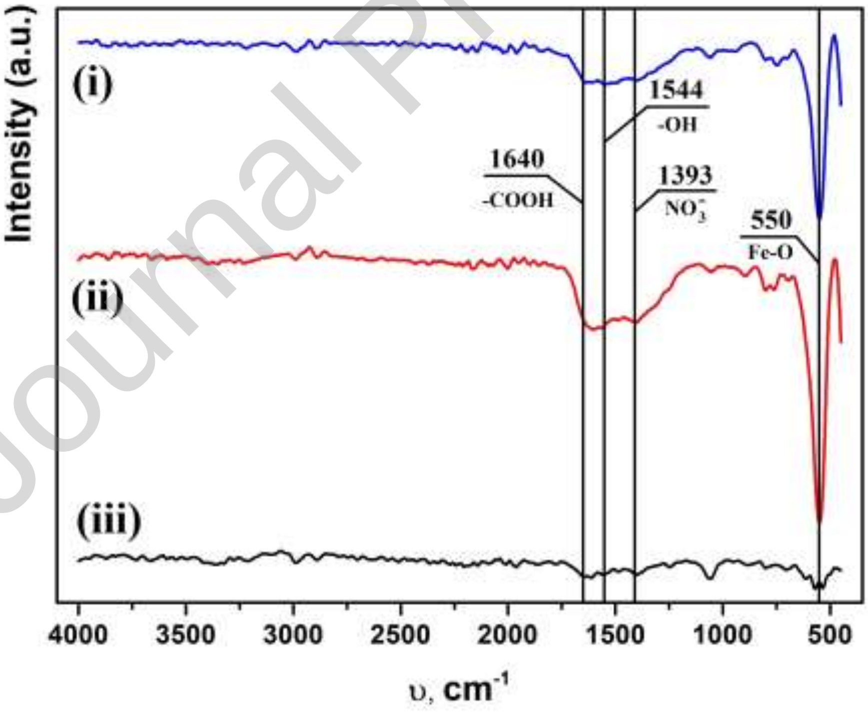
b

c

Fig 5. SEM images of (a) initial sorbent, (b) after metal ions adsorption and (c) after regeneration (×2000).



a



b

Fig 6. (a) XRD patterns and (b) FTIR spectra of (i) initial, (ii) spent and (iii) regenerated sorbents.

Tables

Table 1. Parameters of the sorbent regeneration process by $MgCl_2$ solutions.

	$q_{reg}/q_{initial}$	$C_{des}(M^{2+})$, mmol L^{-1}	$\alpha_{des}(M^{2+})$, %	$q_{des}(Mg^{2+})$ / $q_{ads}(M^{2+})$, %
		Co^{2+}		
0.001 M $MgCl_2$	1.01	0.002	0.02	0.0
0.01 M $MgCl_2$	1.00	0.000	> 0.01	0.06
0.1 M $MgCl_2$	1.00	0.009	0.10	1.83
		Cu^{2+}		
0.001 M $MgCl_2$	5.42	0.011	0.58	0.00
0.01 M $MgCl_2$	5.41	0.008	0.43	0.32
0.1 M $MgCl_2$	5.39	0.012	0.67	9.15
		Mn^{2+}		
0.001 M $MgCl_2$	1.06	0.180	2.88	0.00
0.01 M $MgCl_2$	1.00	0.157	2.52	0.09
0.1 M $MgCl_2$	1.02	0.418	6.70	2.71
		Ni^{2+}		
0.001 M $MgCl_2$	1.36	0.012	0.33	0.00
0.01 M $MgCl_2$	1.22	0.012	0.33	0.16
0.1 M $MgCl_2$	1.19	0.031	0.86	4.72

Table 2. Adsorption capacity of magnesium ferrite from single- and multicomponent solutions (pH = 5.0, contact time of 120 min).

Adsorption capacity, mmol/g	Co^{2+}	Cu^{2+}	Mn^{2+}	Ni^{2+}	Mg^{2+}
single-component 0.01M M^{2+}	2.30	0.46	1.56	0.89	-
multi-component 0.01M M^{2+}	0.18	**0.62**	0.008	0.025	-
multi+background 0.001M $MgCl_2$	0.50±0.02	**2.41±0.05**	0,44±0,04	0.56±0.02	0.75
multi+background 0,01M $MgCl_2$					1.20
multi+background 0.1M $MgCl_2$					4.05

Table.3. Adsorption capacity of toxic metal ions on magnetic adsorbents.

Adsorbent	Pollutant	q_e, mmol/g	Reference
Fe_3O_4 nanoparticles	Cu^{2+}	1.97	(Liu et al., 2019)
Cobalt Ferrite Nanoparticles	Cu^{2+}	2.58	(Vamvakidis et al., 2020)
Magnesium ferrite nanoparticles	Co^{2+}	1.10	(Srivastava et al., 2015)
Fe_3O_4	Mn^{2+}	0.14	(Hou et al., 2011)
	Cu^{2}	0.17	
γ-Fe_2O_3	Cd^{2+}	0.30	(Roy et al., 2013)
	Ni^{2+}	0.78	
	Co^{2+}	0.80	
Magnesium ferrite nanoparticles	Mn^{2+}	0.44	This work
	Co^{2+}	0.50	
	Ni^{2+}	0.56	
	Cu^{2+}	2.41	

Table.4. Composition of magnesium ferrite sorbents according to EDX analysis.

Magnesium ferrite sorbent	Content of element, at. %							
	Fe	Mg	O	Cl	Mn	Co	Ni	Cu
Initial	63.86	14.95	21.19	-	-	-	-	-
After sorption from multi component	53.60	8.11	16.16	4.96	1.52	1.91	3.76	9.97
After regeneration by 0.01 M $MgCl_2$	36.09	16.95	22.10	16.53	0.69	0.48	1.23	5.83

CRediT (Contributor Roles Taxonomy) author statement

Andrei Ivanets: Conceptualization, Methodology, Writing-Original Draft, **Vladimir Prozorovich:** Investigation, Visualization, Data Curation; **Tatyana Kouznetsova:** Results discussion, Editing; **Tetiana Dontsova:** Writing-Review & Editing, Formal analysis; **Olena Yanushevska:** Writing-Review & Editing, Formal analysis; **Ahmad Hosseini-Bandegharaei:** Data discussion, Data Curation; **Varsha Srivastava:** Project administration, Investigation, Editing; **Mika Sillanpää:** Project administration, Funding acquisition, Resources.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- The adsorption of metal ions from single- and multicomponent solutions was studied
- The high efficiency of $MgCl_2$ solution as a regeneration agent was shown
- The peculiarities of competitive adsorption in presence of $MgCl_2$ was established
- The mechanism of $MgFe_2O_4$ regeneration and their stability were carried out