

Separation of chosen heavy metals from multi-component mixtures and galvanic wastewater in adsorption on unmodified and modified magnetite

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ABSTRACT

Adsorption is often proposed for the separation of heavy metals from aqueous solutions. The composition of the solution and the presence of the competing ions can strongly affect the process efficiency. To improve the effectiveness of adsorbents, various modifications are applied, including the functionalization of adsorbents with appropriate chemical compounds. This work aimed to investigate and compare two nanoadsorbents – unmodified magnetite and magnetite modified with poly(sodium acrylate) (PSA) – in the separation of heavy metal ions from multi-component mixtures and galvanic wastewater. The effect of the type and dose of adsorbent on the separation efficiency of heavy metals from two multi-component mixtures containing Cu(II), Zn(II), Cd(II), Ni(II), Pb(II), Cr(III), and Cr(VI) were investigated. The process effectiveness depends on the type and the dose of the adsorbent and the type of metal ion, and was higher using the PSA-modified magnetite, especially towards Zn(II), Ni(II) and Cd(II) ions. With the adsorbent to metals mass ratio $m_{\text{NPs}}/m_{\text{Ms}} = 50$, magnetite modified with poly(sodium acrylate) enabled the separation of 93.2%–94.7% of the total amount of metals, while for non-modified magnetite these values were 55.7%–59.9%. In addition, both adsorbents were used to remove heavy metal ions from five types of galvanic wastewater, containing Cu(II), Zn(II), Ni(II), Cr(VI) and a mixture of Zn(II) and Cr(III), respectively. PSA-modified adsorbent was especially effective towards Cu(II) and Cr(III) (over 90% removal) and Ni(II) and Zn(II) (approx. 70% separation). Separation of Cr(III) ions occurred with good efficiency (about 98%) on both types of magnetite.

Keywords: Magnetic iron oxides; Poly(sodium acrylate); Heavy metals; Competitive adsorption

1. Introduction

The presence of heavy metals in the environment constitutes a serious problem due to their toxicity, non-degradability, and easy bioaccumulation. Among heavy metals and metalloids, Cr, Cd, Pb, Ni, Cu, Zn, Hg, and As are considered to be the most toxic and dangerous in environmental terms. Cr, Cd, Pb, Ni, Cu and Zn are also listed among the heavy metals most commonly found in the environment [1]. The increasing presence of heavy metals in the environment, mainly of anthropogenic origin, requires new and improved solutions for their separation from wastewater

and industrial effluents, reuse, as well as rational resource management.

Many techniques provide effective separation of heavy metal ions, the most important of which are: precipitation of metal hydroxides or sulphides, ion exchange, membrane techniques such as nanofiltration, reverse osmosis, electrodialysis or liquid membranes, membrane processes assisted by other methods (e.g., polymer-enhanced ultrafiltration – PEUF, micellar-enhanced ultrafiltration – MEUF), as well as coagulation/flocculation, flotation, photocatalysis, hydrogels, electrochemical processes and adsorption [2–7]. However, these processes have also some drawbacks limiting

their use. For example, chemical precipitation is widely used for heavy metal separation due to simplicity and low operating costs. But the method has some disadvantages, such as a large amount of sludge, the need for disposal, and the danger of secondary contamination. Sometimes additional treatment is also necessary to reach the concentration of metals acceptable for discharge [7]. Similarly, the need to use chemicals and sludge disposal are the main disadvantages of the coagulation and flocculation method. Although this method is considered relatively economical, heavy metal separation is often incomplete, and other separation techniques should also be involved [3,7,8]. Ion exchangers are effective in the removal of many heavy metals, especially from diluted solutions, the process is fast, and the ion-exchange resins can be regenerated and reused. However, regeneration requires the use of chemicals and can generate additional costs. It also can be a source of secondary pollution [2]. Various membrane techniques are promising in heavy metal separation because they generally do not need additional chemicals or high temperatures and are easy to operate, control, and scale up. The main drawbacks of these processes are an elevated investment and operating costs, membrane fouling, and limited mechanical and chemical membrane resistance [7,8].

Adsorption is considered a promising separation technique due to its simplicity, flexibility in operation, high separation efficiency, and the large variety of adsorbents available, including many low-cost adsorbents efficient toward heavy metal ions. However, the existing disadvantages of the adsorption process should also be noted, among them the limited pH range, the extended time to reach equilibrium, low selectivity (some adsorbents), difficulties in adsorbent separation and regeneration, loss of adsorbent quality with work cycles, waste disposal [3,4,6,7]. Many different materials are considered to be effective adsorbents towards heavy metal ions. These include various types of activated carbons, carbon nanotubes and graphene-based materials [9–14], clays and their minerals [12,15], chitosan and chitosan-based composites [16], metal oxide-based nanomaterials [17], bioadsorbents and low-cost adsorbents, mainly waste products of natural origin [18] but also industrial wastes [19].

A group of attractive adsorbents that have aroused wide-ranging scientific interest are magnetic iron oxides and various composite sorbents prepared on their basis. They are cheap, easy to prepare and modify, and, thanks to their magnetic properties, they can be effectively separated after the process in the magnetic field. Magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), hematite ($\alpha\text{-Fe}_2\text{O}_3$) and mixed iron oxide-based nanoparticles have proven to be efficient adsorbents of various heavy metal ions from aqueous solutions [13,14,20–22]. These promising nano-sized adsorbents can be applied in several morphological forms as nanoovals, nanobelts, nanorings, nanotubes or nanorods [13,23,24]. Magnetic iron oxides are often functionalized by various chemical compounds or combined with other materials into composite structures [13,25]. This enables the introduction of selected functional groups (mainly amino $-\text{NH}_2$, hydroxyl $-\text{OH}$, carboxyl $-\text{COOH}$, thiol $-\text{SH}$, silica SiO_2) into these sorbents to increase the adsorption efficiency, modify the surface charge and improve their stability in aqueous

solutions while maintaining the magnetic properties of the base material. Various chemical compounds are used for the functionalization of nanoadsorbents, including silica, surfactants, synthetic polymers, biopolymers (e.g., alginate, chitosan, humic acids), carboxylic acids, compounds containing multiple amino groups (e.g., diethylenetriamine DETA, triethylenetetramine TETA), and others [13,26].

Many research works have been devoted to the adsorption of single metals from model aqueous solutions. An important aspect of research seems to be the removal of heavy metals from their multi-component mixtures and from real industrial effluents and wastewater. For the separation of metals from their multi-component mixtures, various adsorbents, such as activated carbon [27], carbon nanotubes [28], clay [29], biopolymers, biosorbents, and bio-polysaccharide hydrogels [30–33], as well as magnetic iron oxide-based materials [34–38], are proposed.

Among magnetic iron oxides, magnetite is of great interest. Magnetite is an inexpensive, effective, easy to manufacture and recycle, low-toxic, and chemically inert material. When used in the form of nanoparticles, it has a large specific surface area. Its superparamagnetic properties enable fast separation of nanoparticles in a magnetic field. These features make magnetite nanoparticles a promising adsorbent of many pollutants, both organic and inorganic, including heavy metal ions. Additional modification of the magnetite surface with appropriate functional groups (e.g., carboxyl groups) may increase the sorption capacity of magnetite [39,40].

In our previous work, two types of adsorbents, unmodified magnetite (M NPs) and magnetite modified with poly(sodium acrylate) (PSA/M NPs) were synthesized, characterized, and applied to the separation of heavy metals from single-metal-containing solutions [41]. In the present work, the research was focused on the separation of heavy metal ions from model multi-component mixtures using unmodified magnetite and PSA-modified magnetite as adsorbents. The effect of adsorbent dose on metal separation effectiveness, magnetite adsorption capacity and the composition of the post-sorption solutions were investigated. The two types of adsorbents were also used for the removal of heavy metals from the five types of galvanic wastewater.

2. Materials and methods

2.1. Separation of heavy metals from multi-component mixtures

The adsorption of heavy metals (Cu(II), Zn(II), Ni(II), Cd(II), Pb(II), Cr(III) and Cr(VI)) from multi-component mixtures on magnetic iron oxides nanoparticles was investigated. Because of the two different forms of chromium ions, two multi-component heavy metal mixtures were considered. Solution I contains Cu(II), Zn(II), Cd(II), Ni(II), Pb(II) and Cr(III) ions, each of them at the concentration of 10 mg/L, the total metal concentration in the solution $C_{\text{Ms}} = 60$ mg/L. Solution II contains Cu(II), Zn(II), Cd(II), Ni(II) and Cr(VI) ions, each of them at the concentration of 10 mg/L, the total metal concentration in the solution $C_{\text{Ms}} = 50$ mg/L. Mixture II was prepared without Pb(II) ions due to the possibility of lead(II) chromate precipitation in the solution. Nitrate salts $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ (POCH S.A.,

Poland), and potassium dichromate $K_2Cr_2O_7$ (Merck, Poland) were used as a source of heavy metal ions, and deionized water (resistivity $> 5 M\Omega/cm$) as a solvent.

For the adsorbent, two types of magnetite nanoparticles synthesized in a laboratory by a co-precipitation method from Fe(II) and Fe(III) salts were used: unmodified magnetite (M NPs) and magnetite modified with poly(sodium acrylate) PSA (PSA/M NPs). The adsorbents were synthesized according to the method described in the previous works [41,42], using $Fe_2SO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ (StanLab, Poland) (4.2 and 6.1 g, respectively) dissolved in 100 mL of distilled water. The synthesis was performed at $30^\circ C$, and magnetites were precipitated at intensive stirring by adding 20 mL of ammonia ($NH_3 \cdot H_2O$, 25 wt.%, StanLab, Poland) and 50 mL of deionized water or 50 mL of 1% PSA solution for M NPs or PSA/M NPs, respectively. Poly(sodium acrylate) PSA was purchased from Sigma-Aldrich, (Poland), as a 40% aqueous solution. A more comprehensive characterization of the two adsorbents is presented in a previous paper [41].

An appropriate dose of an adsorbent (M NPs or PSA/M NPs) was mixed with the 40 mL of a metal-containing solution (type I or II), and the pH was adjusted at the value of 5 using NaOH or HNO_3 0.1 M solutions (POCH S.A., Poland). The mixture was then shaken for 8 h (orbital shaker SK-O330-Pro, ChemLand, Poland), and the supernatant was separated on neodymium magnet (N38 type, ring-shaped, dimensions: outer diameter/inner diameter/thickness 64/42/25 mm, remanence 1,220–1,260 T, coercivity 860–915 kA/m, energy density 287–303 kJ/m³). The adsorption process was conducted at various ratios of the mass of adsorbent and the total amount of heavy metals m_{NPs}/m_{Ms} equal to 0.5, 3, 5, 30 and 50.

Metal concentrations in supernatants and feed solutions were determined by means of a SpectrAA-880 Atomic Absorption Spectrometer (Varian, Candela Sp. z o.o., Poland). All adsorption experiments were carried out in triplicate.

To characterize the effectiveness of the separation process towards each metal ion and the magnetite adsorption capacity under experimental conditions, Eqs. (1) and (2) were used:

$$\eta = \frac{C_i - C_e}{C_i} \times 100\% \quad (1)$$

$$q_e = \frac{(C_i - C_e)V}{m} \quad (2)$$

where η – separation effectiveness, %, C_i and C_e – initial and equilibrium concentration of a given heavy metal ion (in feed solution and in the supernatant, respectively), mg/L, q_e – adsorption capacity of magnetite, mg/g; m – mass of adsorbent, g; V – volume of metal solution, L.

2.2. Removal of heavy metal from galvanic wastewater

Five examples of heavy metal-containing wastewater were obtained from metal-finishing factories. Four of them (wastewater I, II, III and IV) each contained one heavy metal

(Ni(II), Cu(II), Cr(VI), Zn(II), respectively) and originated from rinsing processes. The fifth (wastewater V) contained two heavy metals (Zn(II) and Cr(III)) and resulted from the passivation process. Due to the content of the suspension (ca. 42 mg/L), the wastewater from the passivation process was subjected to preliminary filtration through filter paper with a medium-fast flow rate. The four types of rinse water from the remaining galvanic processes were decanted and used without any further pre-treatment. The basic characteristics of the galvanic wastewater is given in Table 4.

The wastewater's pH and conductivity was measured using the inoLab Level 3 system (WTW GmbH & Co., Germany) with SenTix 81 pH-electrode and WTW TetraCon® 325 conductivity cell. The concentration of anions in the wastewater was analyzed using ion chromatography (Chromatograph Dionex DX-120, A.G.A. Analytical, Poland). The total solid content, the residue on ignition, and the loss on ignition were determined according to PN-78/C-04541 standard. All analyses were performed in triplicate.

The adsorption of heavy metals from galvanic wastewater was conducted according to the method described above. The two types of magnetites, M NPs and PSA/M NPs, were applied. 50 mL of wastewater was placed in a 100 mL bottle and 300 mg of magnetite (in the form of a suspension with a concentration of 6 g/L) was introduced. After 8 h of shaking (at pH 5), the supernatant was separated using a neodymium magnet and the content of heavy metal was analyzed. Each of the experiments was performed three times.

3. Results and discussion

3.1. Separation of heavy metals from multi-component mixtures

The effectiveness of the separation of investigated heavy metals from solution I using unmodified and PSA-modified magnetites is shown in Fig. 1. Table 1 presents the average values of adsorption capacity for both types of magnetites achieved in the experimental conditions.

Type I feed solution was a mixture of 6 heavy metal cations with equal representation of each by mass. The effectiveness of the separation of individual heavy metals from the mixture in the adsorption process was diverse and depended on the type of heavy metal ion, the type of magnetite and the mass of the adsorbent used in the process. An increase in m_{NPs}/m_{Ms} ratio caused a significant increase in adsorption efficiency for both tested adsorbents. Together with the improvement in heavy metal removal with the increasing dose of iron oxide nanoparticles in the solution, the decrease in the amount of metal adsorbed by 1 g of magnetite can be observed (Table 1). The adsorption capacity q_e was different for individual metals and magnetites and varied with m_{NPs}/m_{Ms} ratio. At the lowest amount of unmodified magnetite used in the process, the total amount of metals adsorbed from solution I was 133 mg/g, while PSA-modified magnetite adsorbed 210 mg/g under such conditions.

Generally, the application of magnetite modified with PSA resulted in higher separation effectiveness of all heavy metals tested. The exceptions are Zn(II) and Ni(II) ions at low adsorbent-to-metal mass ratios, which were insufficient to ensure the effective removal of all heavy metals from the

mixture. The differences between M NPs and PSA/M NPs adsorbents were particularly visible for Zn(II), Cd(II) and Ni(II) ions at higher values of $m_{\text{NPs}}/m_{\text{Ms}}$ of 30 and 50. In such experimental conditions, it was possible to remove 61%–97% of these metals with the use of PSA-modified adsorbent, and only 6%–46% when using unmodified magnetite.

Among the metals present in solution I, Cr(III), Pb(II) and Cu(II) were separated to the greatest extent with the use of

the M NPs adsorbent. At $m_{\text{NPs}}/m_{\text{Ms}}$ ratio of 50, the removal effectiveness for these metals exceeded 90%. The removal of three other metals from solution I (Zn(II), Cd(II) and Ni(II)) was much less effective, and the efficiency obtained for these metals at $m_{\text{NPs}}/m_{\text{Ms}} = 50$ was below 50%. The lowest value of η (η ca. 12%) was recorded for Ni(II) ions. Considering the highest dose of unmodified magnetite used, the removal efficiency of metal ions from the mixture I decreased in the following order:

$$\text{Cr(III)} \geq \text{Pb(II)} > \text{Cu(II)} \gg \text{Zn(II)} > \text{Cd(II)} > \text{Ni(II)} \quad (\text{I})$$

Significant differences in the η values, observed between metals, indicate the possibility of selective separation of solution components, for example, the separation of Cr(III) from Ni(II) ions.

The use of PSA-modified magnetite ensured high removal degrees of Cr(III), Pb(II) and Cu(II) ions, but also enabled a significant increase in the separation coefficients of other metals, components of solution I. At the highest dose of the PSA/M NPs adsorbent, copper ions were removed at almost 100%, Cr(III), Pb(II), Cd(II) and Zn(II) ions in over 90%, and Ni(II) ions in over 85%. The order of metal separation was as follows:

$$\text{Cu(II)} > \text{Cr(III)} > \text{Cd(II)} \approx \text{Pb(II)} > \text{Zn(II)} > \text{Ni(II)} \quad (\text{II})$$

High η coefficients, obtained for all components of solution I at a sufficiently high amount of modified magnetite, testify to the possibility of simultaneous separation of metal ions from the solution. Selective separation of components of mixture I is possible with a reduced amount of PSA/M NPs adsorbent. For instance, at $m_{\text{NPs}}/m_{\text{Ms}} = 5$, high values of η for Cr(III) and Pb(II) ions and relatively low values of η for Zn(II), Cd(II) and Ni(II) ions may be obtained.

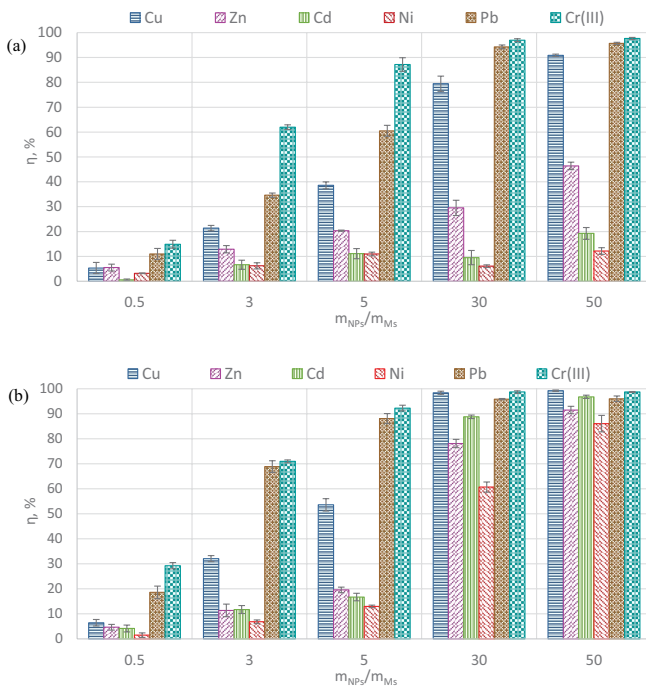


Fig. 1. Effect of $m_{\text{NPs}}/m_{\text{Ms}}$ on the effectiveness of heavy metals separation from the multi-component mixture I. (a) M NPs magnetite and (b) PSA/M NPs magnetite.

Table 1

Average amounts ($q_{e,av}$) of heavy metals adsorbed from the multi-component mixture I using M NPs and PSA/M NPs magnetites at various $m_{\text{NPs}}/m_{\text{Ms}}$ ratios

$m_{\text{NPs}}/m_{\text{Ms}}$	Cu(II)		Zn(II)		Cd(II)		Ni(II)		Pb(II)		Cr(III)	
	$q_{e,av}$ (mg/g)	STD (mg/g)	$q_{e,av}$ (mg/g)	STD (mg/g)	$q_{e,av}$ (mg/g)	STD (mg/g)	$q_{e,av}$ (mg/g)	STD (mg/g)	$q_{e,av}$ (mg/g)	STD (mg/g)	$q_{e,av}$ (mg/g)	STD (mg/g)
M NPs												
0.5	18.08	7.57	19.02	4.76	1.89	1.10	10.80	0.41	36.34	7.30	46.79	5.00
3	12.76	0.65	7.85	0.89	3.85	1.06	3.67	0.73	20.18	0.50	34.32	0.52
5	14.41	0.52	7.76	0.09	4.04	0.74	4.06	0.28	22.07	0.80	30.20	0.95
30	4.74	0.18	1.80	0.19	0.55	0.17	0.36	0.03	5.49	0.04	5.37	0.03
50	3.40	0.02	1.77	0.06	0.70	0.09	0.45	0.05	3.49	0.02	3.38	0.01
PSA/M NPs												
0.5	22.23	4.47	15.88	3.89	14.72	4.87	5.08	3.07	62.94	8.49	89.08	3.80
3	19.49	0.73	6.86	1.52	7.34	1.00	4.09	0.44	41.16	1.39	38.15	0.31
5	20.40	0.94	7.39	0.42	6.56	0.59	4.88	0.19	32.98	0.76	31.09	0.39
30	5.98	0.04	4.70	0.10	5.55	0.04	3.64	0.12	5.73	0.01	5.30	0.03
50	3.78	0.01	3.45	0.06	3.79	0.03	3.23	0.12	3.60	0.04	3.33	0.01

The varied sorption capacity of the magnetites with respect to the components of mixture I means that the mass fractions of individual metals in supernatants differ from the equal shares in the initial solution (Fig. 2). Fig. 2 also shows a reduction in the total metal concentration in the supernatants compared to the starting solution, particularly evident with PSA-modified magnetite.

When using M NPs adsorbent (Fig. 2a), with the increasing $m_{\text{NPs}}/m_{\text{Ms}}$, an increase in the mass fraction of Zn(II), Cd(II), and Ni(II) and a decrease in the mass fraction of Cu(II), Pb(II), and Cr(III) can be observed in supernatants. The application of PSA-modified magnetite (Fig. 2b) gave similar results, however, the mass fraction of Cd(II) in the post-adsorption solution was reduced compared to the feed solution, due to the high efficiency of this adsorbent towards cadmium ions. These results show that some components of a multi-component mixture may be partially fractionated as a result of the adsorption process.

The second investigated mixture – solution II – contained four metal cations (Cu(II), Zn(II), Cd(II), Ni(II)) and an anionic form of Cr(VI). The adsorbent-to-metal mass ratios and the pH value during the adsorption process were the same as in the tests of solution I. The effectiveness of heavy

metal removal and the sorbents capacity toward separated ions were presented in Fig. 3 and Table 2, respectively.

Unmodified magnetite showed the highest separation efficiency towards Cr(VI) ions. The second ion which was effectively separated from mixture II was copper(II). The efficiency of Cr(VI) and Cu(II) removal from the multi-component solution II at $m_{\text{NPs}}/m_{\text{Ms}} = 50$ was over 98% and over 94%, respectively. The affinity of the M NPs adsorbent for Zn(II), and especially Cd(II) and Ni(II) cations, was significantly lower, and the separation efficiency of the last two components from mixture II did not exceed 20% at the highest adsorbent dose applied. The following order describes the effectiveness of the separation of components from the multi-component solution II using the greatest dose of unmodified magnetite:

$$\text{Cr(VI)} \approx \text{Cu(II)} > \text{Zn(II)} > \text{Ni(II)} \approx \text{Cd(II)} \quad (\text{III})$$

PSA-modified magnetite was a particularly efficient adsorbent of Cu(II) ions. This is evidenced by both high Cu(II) ion separation coefficients from mixture II ($\eta > 98\%$ at $m_{\text{NPs}}/m_{\text{Ms}} = 50$), as well as high values of sorption capacity of magnetite ($q_{e,av} > 45 \text{ mg/g}$ at $m_{\text{NPs}}/m_{\text{Ms}} = 0.5$). The use of PSA/M NPs magnetite also facilitated high values of Cr(VI) ion removal from the solution in which the adsorbent dose was sufficiently high. At the $m_{\text{NPs}}/m_{\text{Ms}}$ ratio of 50 the effectiveness of heavy metal separation reached values in the range of 84.7%–98.1% and the order of metal removal can be written as follows:

$$\text{Cu(II)} \approx \text{Cr(VI)} \approx \text{Cd(II)} > \text{Zn(II)} > \text{Ni(II)} \quad (\text{IV})$$

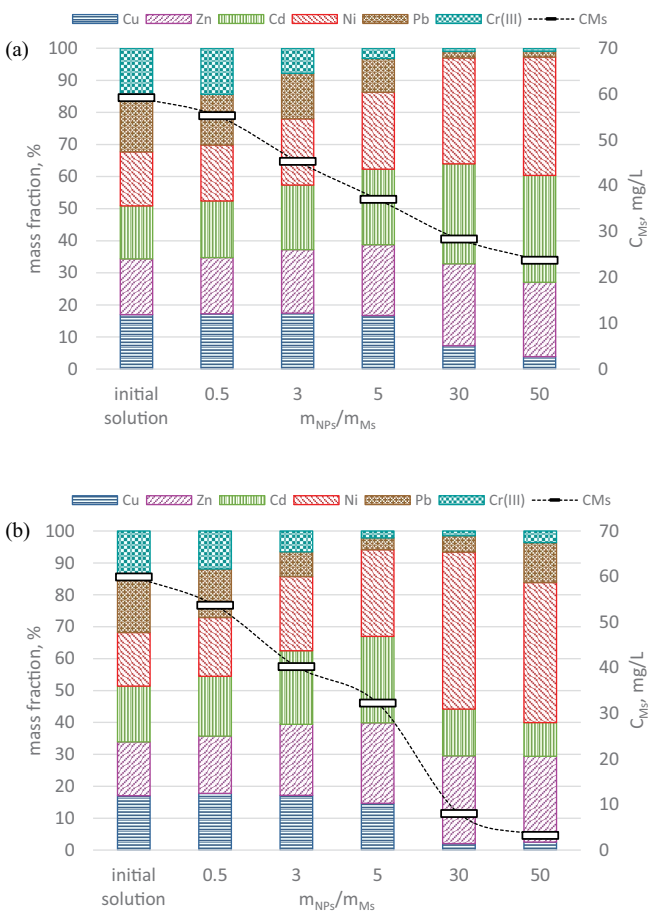


Fig. 2. Total metal concentration C_{Ms} (secondary vertical axis) and composition of the initial solution (mixture I) and supernatants (primary vertical axis) at various $m_{\text{NPs}}/m_{\text{Ms}}$ ratios. (a) M NPs magnetite and (b) PSA/M NPs magnetite.

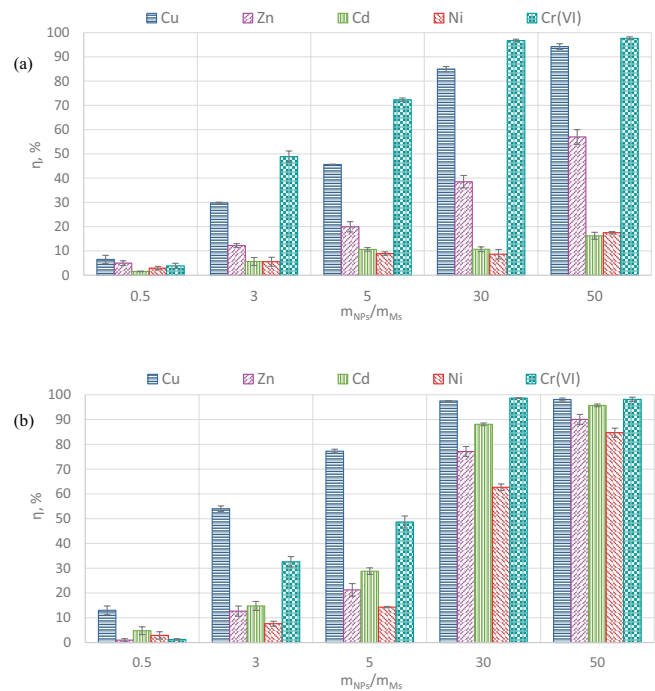


Fig. 3. Effect of $m_{\text{NPs}}/m_{\text{Ms}}$ on the effectiveness of heavy metals separation from the multi-component mixture II. (a) M NPs magnetite and (b) PSA/M NPs magnetite.

Table 2

Average amounts ($q_{e,av}$) of heavy metals adsorbed from multi-component mixture II using M NPs and PSA/M NPs magnetites at various m_{NPs}/m_{Ms} ratios

m_{NPs}/m_{Ms}	Cu(II)		Zn(II)		Cd(II)		Ni(II)		Cr(VI)	
	$q_{e,av}$ (mg/g)	STD (mg/g)	$q_{e,av}$ (mg/g)	STD (mg/g)	$q_{e,av}$ (mg/g)	STD (mg/g)	$q_{e,av}$ (mg/g)	STD (mg/g)	$q_{e,av}$ (mg/g)	STD (mg/g)
M NPs										
0.5	22.01	5.84	17.25	3.42	5.05	0.46	9.86	2.53	11.22	3.18
3	17.68	0.19	7.39	0.50	3.22	0.93	3.30	1.09	25.11	1.19
5	16.85	0.04	7.52	0.80	3.76	0.26	3.29	0.26	23.10	0.23
30	5.04	0.06	2.34	0.16	0.61	0.06	0.51	0.12	4.97	0.03
50	3.48	0.04	2.15	0.11	0.57	0.05	0.65	0.02	3.12	0.02
PSA/M NPs										
0.5	45.56	6.17	3.22	2.01	16.96	5.60	9.93	5.15	3.71	0.85
3	33.06	0.69	7.39	1.21	9.14	1.12	4.58	0.60	16.84	1.07
5	29.44	0.29	7.71	0.93	11.09	0.51	5.37	0.10	15.63	0.78
30	5.97	0.01	4.49	0.12	5.44	0.03	3.78	0.08	5.09	0.01
50	3.74	0.02	3.27	0.07	3.68	0.02	3.18	0.07	3.15	0.03

Varied metal separation coefficients indicate that some particular metals contained in the multi-component mixture II can be selectively separated from others using magnetite adsorbents. This was especially visible in the process with unmodified magnetite when the high η coefficients of Cr(VI) and Cu(II) prove the possibility of separation of these metals from Ni(II) and Cd(II), which were characterized with low values of η .

The diversified magnetite capacity for the separation of various metal ions is confirmed by the analysis of the mass fraction of heavy metals in post-adsorption solutions. Fig. 4 presents mass fractions of individual metals in the multi-component mixture II, supernatants achieved at different doses of magnetite, and the total metal concentration C_{Ms} in these samples.

Using unmodified magnetite, a clear decrease in the mass fraction of Cr(VI) and Cu(II) and an increase in the percentage of Cd(II) and Ni(II) ions in the supernatant in comparison to the starting solution are visible. The use of PSA-modified magnetite caused similar changes in the composition of the supernatant, but in this case a decrease in the mass fraction of Cd(II) is also visible due to the higher affinity of PSA-modified adsorbents for Cd(II) ions.

The results of the separation of heavy metal ions from multi-component mixtures were analyzed using one-way analysis of variance at the significance level of $p = 0.05$. There was no statistically significant difference between mixtures I and II ($F = 1.47 < F_{critical} = 3.87$; $p = 0.23 > 0.05$). However, the analysis confirmed statistically significant differences between the types of magnetite ($F = 20.09 > F_{critical} = 3.87$; $p = 1.02 \times 10^{-5} < 0.05$), the types of separated metal ions ($F = 18.93 > F_{critical} = 2.13$; $p = 6.89 \times 10^{-19} < 0.05$), and the adsorbent doses applied ($F = 80.60 > F_{critical} = 2.40$; $p = 1.90 \times 10^{-47} < 0.05$), thus confirming the impact of these parameters on process efficiency.

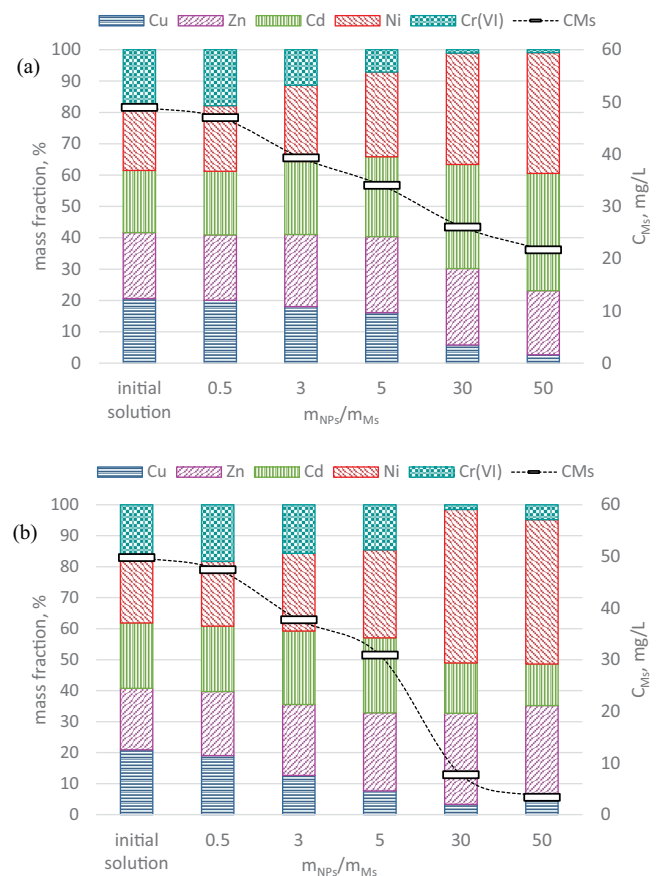


Fig. 4. Total metal concentration C_{Ms} (secondary vertical axis) and composition of the initial solution (mixture II) and supernatants at various m_{NPs}/m_{Ms} ratios. (a) M NPs magnetite and (b) PSA/M NPs magnetite.

3.2. Discussion and comparison of the results with the results of other authors obtained for multi-component mixtures of heavy metals and similar adsorbents

In general, the mechanism of heavy metal separation combines physical and chemical adsorption, including pore filling, intramolecular diffusion, ion exchange, coordination, and electrostatic interaction [36].

In aqueous solutions, the surface of the hydrated magnetite nanoparticles is covered with hydroxyl groups ($\text{\{Fe-OH}}$), which in turn undergo protonation/deprotonation, depending on the acid-base nature of the solution, and form positively ($\text{\{Fe-OH}_2^+$) or negatively ($\text{\{Fe-O}^-$) charged surface groups. PSA-modified magnetite additionally contains dissociation-capable carboxyl groups (-COO^-), which increase its surface negative charge and lower the pH of the adsorbent isoelectric point. The pH values of the isoelectric point (pH_{iep}) for M NPs and PSA/M NPs magnetites were determined in our team's previous work and amounted to 6.34 and 3.17 for unmodified and PSA-modified magnetite, respectively [41]. In solutions with $\text{pH} < \text{pH}_{\text{iep}}$, the positive charge predominates on the surface of the adsorbent, facilitating the separation of contaminants containing negative groups (among them Cr(VI) anions, as was visible in experiments with M NPs). On the other hand, at $\text{pH} > \text{pH}_{\text{iep}}$, the resultant adsorbent surface charge is negative, enhancing the separation of cationic contaminants (including heavy metal cations). Due to the large difference in the determined pH_{iep} values of the tested adsorbents, in order to demonstrate the differences between them, a pH of 5 was chosen for the study in this work. This relatively low value was also intended to protect the ions of the tested metals from the precipitation of their hydroxides. Visible differences in the separation of metal ions from mixtures, obtained for both tested adsorbents at $\text{pH} = 5$, such as greater removal of Cr(VI) ions compared to the cations of other metals of mixture II, on unmodified magnetite, or generally higher separation efficiency of metal cations on magnetite modified compared to the unmodified adsorbent, can be explained by the difference in the resultant surface charge of adsorbents (its sign and magnitude).

Our previous studies have shown that for both adsorbents, chemisorption was the dominant mechanism of separation of the investigated metals from single ion-containing solutions [41]. Some features of the separated metals, such as hydrated ion radius or electronegativity, hard/soft character according to the HASB theory, and the ability to form complexes, may significantly affect the efficiency of metal ion separation [43]. In the adsorption of metal ions from multi-component mixtures (in competing conditions), it is often difficult to indicate the dominant factor determining the order of ion separation. Nevertheless, analyzing the results of this work, some similarities to other cases of metal adsorption from multi-ionic mixtures using similar adsorbents described in the literature can be seen.

The separation efficiency of individual metals observed in the tests with unmodified magnetite is consistent with the results achieved by Fato et al. [44] during the separation of Pb, Cd, Cu, and Ni from river water, from single-metal-containing solutions and a four-component solution, using ultrafine mesoporous magnetite nanoparticles.

The separation efficiency decreased in the series of Pb, Cu, Cd, Ni, both in single-component and multi-component solutions of these metals, with lower removal coefficients in the latter case. The same trend ($\text{Pb} > \text{Cu} > \text{Cd} > \text{Ni}$) in adsorption capacity was also found for mesoporous magnetic polymer beads (the adsorbent containing hydroxyl, carboxyl, Si-O-, and Al-O- groups) used to adsorb a quaternary metal mixture [38].

An investigation conducted by Wang et al. [36] on the competitive adsorption of Pb(II) and Cr(III) on magnetite nanoparticles showed higher Pb(II) removal (compared to Cr(III)) and a significant decrease in the Pb(II) adsorption at the presence of Cr(III) in the two-metal system. The proposed mechanism of adsorption of Pb(II) includes the electrostatic interaction and surface complexation, while the adsorption of Cr(III) can be complemented by a possible substitution of Cr(III) for Fe(III) in $\text{Cr-Fe}_3\text{O}_4$ through ion exchanges. In the presented work, Cr(III) removal using unmodified magnetite was higher than Pb(II) separation, especially at lower $m_{\text{NPs}}/m_{\text{Ms}}$ ratios. This observation may indicate the competing effects of other divalent ions present in the solution, lowering the separation of Pb(II) ions. Higher adsorption of Cr(III) ions than of coexisting divalent ions, decreasing in the order of $\text{Cu(III)} > \text{Ni(II)} > \text{Cu(II)} > \text{Cd(II)}$, was also found by Siddiqui et al. [45], who examined the separation of heavy metals from multi-ion systems on magnetic carbon nanocomposites.

The separation of heavy metal mixtures on PSA-modified magnetite also leads to some general observations which are in good agreement with the results of other researchers who investigated magnetic iron oxide-based adsorbents functionalized with carboxylic groups.

Poly(NIPAM-co-AA)/silica-coated MNP composite, when used for the competitive adsorption Cu(II), Mn(II), Co(II), and Ni(II) ions, revealed significantly higher affinity towards Cu(II), compared with other metal ions present in the solution [46]. The tendency is in line with the results of this study, reporting higher adsorption capacity of PSA-modified magnetite for Cu(II) than for Ni(II) and Zn(II) (and also Cd(II)) in both tested mixtures, which may be explained by the higher value of poly(acrylic acid)-Cu complex stability constant [46,47].

PSA-modified magnetite was also more effective towards Pb(II) than Cd(II) and Ni(II) (solution I), which is consistent with the observations of other authors. A similar arrangement of metals in the direction of decreasing sorption capacity was obtained by Badruddoza et al. [43] in the study of simultaneous adsorption of these metals on Fe_3O_4 /cyclodextrin polymer nanocomposites, which, according to the authors, can be explained by the hard and soft acids and bases theory. A slightly different adsorbent affinity of $\text{Pb(II)} > \text{Ni(II)} > \text{Cd(II)}$ was reported by Kothavale et al. [48] during the simultaneous removal of these metals from a tertiary solution using carboxyl- and thiol-functionalized magnetic nanoparticles. The sequence is in line with the increase in the metals' hydration radius and the decrease in their electronegativity.

In another work, Xu et al. [35] found that magnetite with grafted carboxyl groups showed high affinity towards Cd(II) ions present in the multi-heavy metal ion mixture, with the adsorption priority decreasing in the order $\text{Cd(II)} > \text{Cu(II)} > \text{P}$

b(II) > Ni(II). Moreover, this order does not correspond to the sorption capacity order of these metals in single-component systems and solutions with higher ionic strength. According to the authors, this order results from the different metal tendency to form inner-sphere and outer-sphere complexes, of which the former dominated in the case of Cd(II) and the latter in the case of Ni(II). The smallest affinity of the PSA-modified magnetite to Ni(II) (significantly smaller than to Cd(II)) was also found in both tested mixtures in this work.

The separation of Zn(II), Pb(II), and Cd(II) from their tertiary system using the Fe₃O₄-Si-COOH magnetic silica gel adsorbent studied by Guo et al. [49] showed the following order of metal adsorption Pb(II) > Zn(II) > Cd(II), which, according to the authors, was due to the higher electronegativity and smaller hydrated ionic radius of Pb(II) compared to Zn(II) and Cd(II), and the higher stability constant of oxalic acid complexes with Zn(II) compared to Cd(II). In this work, the adsorption of these three metals on PSA-modified magnetite decreased in the order Pb(II) > Cd(II) > Zn(II), which is consistent with decreasing electronegativity (2.33 > 1.69 > 1.65) and increasing hydrated ionic radii (4.01 Å < 4.26 Å < 4.30 Å) of the metals [49]. However, the results confirmed the predominant adsorption of Pb(II) ions.

An investigation of the adsorption of Cu(II), Co(II), and Zn(II) from binary and tertiary systems using citric acid-coated magnetic olive wood sawdust (cit-MO), performed by El-Sheikh et al. [50], showed that bioadsorbent revealed higher adsorption capacity towards Cu(II) than Zn(II) and Co(II) and the presence of Cu(II) significantly decreases the adsorption of Zn(II) and Co(II). The priority of Cu(II) adsorption over Zn(II) was also visible in both types of magnetites tested in this work.

Wang et al. [51] synthesized an amino-salicylic acid-modified amino-hyperbranched functionalized magnetite (Fe₃O₄-HBPA-ASA) – an adsorbent with a high density of multifunctional groups, which was used (among others) for the separation of Pb(II), Cd(II), and Zn(II) from the binary and tertiary systems. Compared to single metal solutions, a strong competitive effect and a significant decrease in adsorption capacity were found in multiple systems, being in the order Pb(II) > Cu(II) > Cd(II), which is in line with the results obtained for mixture I and PSA-modified magnetite in the present work.

Adsorption capacities of some magnetic iron oxide-based adsorbents (without and with carboxylic groups) for selected heavy metals in multi-component solutions are given in Table 3.

The studied magnetites (M NPs and PSA/M NPs) exhibit good adsorption capacity of metal ions from multi-component mixtures, comparable to or higher than similar adsorbents described in the literature. The total adsorption capacity for all metals of mixture I reached a value of 132.9 mg/g for unmodified magnetite and 209.9 mg/g for PSA/M NPs, which exceeds other values summarized in Table 3 for unmodified magnetites and adsorbents functionalized with carboxyl groups.

3.3. Removal of heavy metals from galvanic wastewater

The basic characteristics of various types of galvanic wastewater are presented in Table 4.

The five types of wastewater used in the work differed in the type and the concentration of heavy metals, pH, conductivity, as well as the content of mineral substances, including inorganic anions. The same dose of magnetite was introduced into each type of wastewater and the adsorption process was carried out. The separation effectiveness of heavy metal ions obtained using unmodified and PSA-modified magnetite is shown in Fig. 5. Table 5 presents the average values of adsorption capacity for both types of adsorbents observed during the tests with galvanic wastewater.

Unmodified magnetite, as a heavy metal adsorbent, enabled moderate levels of Ni(II) and Zn(II) separation in the experimental conditions. More effective removal of Cu(II) and Cr(VI) ions were observed, despite the fact that the concentrations of these ions in the wastewater were higher. It was also visible by comparing adsorbent capacity towards Cr(VI) and Cu(II) with other metal ions (Table 5). The highest separation effectiveness was recorded towards Cr(III) ions in wastewater V (over 84%), although the wastewater contained coexisting Zn(II) ions, competing with chromium ions in the adsorption process. The comparison of the efficiency of individual metal separation from galvanic wastewater is consistent with the observations regarding metal removal from multi-component mixtures, proving that unmodified magnetite has a greater ability to remove Cr(VI), Cr(III) and Cu(II) ions than Zn(II) and Ni(II).

The use of PSA-modified magnetite resulted in a two-fold increase in the efficiency of heavy metal separation in the case of wastewater containing Ni(II) and Zn(II), as well as a 1.9-fold increase in the removal coefficient of Zn(II) ions from wastewater containing Zn and Cr. In addition, the efficiency of Cu(II) ion separation increased significantly (by approx. 50%) after using PSA/M NPs magnetite. In turn, the efficiency of Cr(III) ion separation was comparable for both magnetites used, while Cr(VI) ions were removed less effectively (by approx. 10%) using PSA-modified magnetite, which was due to the presence of carboxyl groups and a negative surface charge of the adsorbent.

One-way analysis of variance confirmed (at the 0.05 significance level) a statistically significant difference between the results obtained for the two types of adsorbents ($F = 8.300 > F_{\text{critical}} = 4.13$; $p = 0.006818 < 0.5$).

The conducted research demonstrated that magnetic iron oxide-based materials are promising adsorbents of heavy metal ions from wastewater and industrial effluents, which has also been confirmed in studies by other authors.

Magnetite particles, tested as an adsorbent of contaminants from samples collected at different stages of the wastewater treatment plants (WTP) [52], showed better removal efficiency towards chromium and copper (up to 73.2% and 87.1%, respectively) than to nickel (up to 42.1%), which is in line with the results achieved for M NPs in this work.

Wei et al. [53] applied magnetic iron-nickel oxide particles to the selective separation of Cr(VI) from simulated Cr(VI)-Ni(II) bi-ionic wastewater, achieving the maximum adsorption capacity of 30 mg Cr(VI)/g at pH of 5. The value is consistent with the average q_e determined in this work for M NPs and PSA/M NPs (about 37 and 33 mg/g, respectively).

Baseri et al. applied citric acid-modified magnetite to remove Ni(II) from contaminated water. The high separation

Table 3

Comparison of adsorption capacities reported for some magnetic iron oxide-based adsorbents towards selected heavy metals in multi-component solutions

Order and the value of adsorption capacity	Adsorbent	Conditions	References
Pb(II) > Cu(II) > Cd(II) > Ni(II) 21.41, 21.10, 20.08, 13.55 mg/g	Ultrafine mesoporous magnetite nanoparticles (UFMNPs)	Metal concentration 50 mg/L, adsorbent dose 100 mg/50 mL, pH 6.5, temp. 25°C	[44]
Pb(II) > Cr(III) 3.44, 2.77 mg/g	Magnetite nanoparticles (NCM)	Metal concentration 10–100 mg/L, adsorbent dose 0.100 g, pH 3.8, temp. 20°C	[36]
Cr(III) > Ni(II) > Cu(II) > Cd(II) 31.55, 29.1, 26.31, 19.21 mg/g	Magnetic carbon nanocomposite (MCNC-GH)	Metal concentration 100 mg/L, adsorbent dose 2.5 g/L, pH 7.5	[45]
Pb(II) > Cu(II) > Cd(II) > Ni(II) 21.09, 15.54, 2.47, 2.68 mg/g	Mesoporous alginate/ β -cyclodextrin polymer beads (HNTs-FeNPs@Alg/ β -CD)	Metal concentration 0.5–80 mg/L, adsorbent dose 3 g/L, pH 6.10	[38]
Cu(II) >> Mn(II), Co(II), Ni(II) 0.511 mmol/g (32.47 mg/g)	Poly(NIPAM-co-AA) immobilized on silica-coated magnetite (poly(4:1)-Si(450)-MNP)	Metal concentration 0.25–2.5 mmol/L, adsorbent dose 50 mg/20 mL, pH 5, temp. 50°C	[46]
Pb(II) \geq Cd(II) > Ni(II)	Fe ₃ O ₄ /cyclodextrin polymer nanocomposite (CDpoly-MNPs)	Metal concentration 100 mg/L, adsorbent dose 120 mg/10 mL, pH 5.5, 25°C	[43]
Pb(II) > Ni(II) > Cd(II) 64.5, 53.9, 27.18 mg/g	Carboxyl and thiol-functionalized magnetic nanoadsorbent (MNP-DMSA)	Metal concentration 5–70 mg/L, adsorbent dose = 0.14 g/L, pH = 7	[48]
Cd(II) > Cu(II) > Pb(II) > Ni(II)	Carboxylated magnetic iron oxide nanoparticles (MNPs-COOH)	Metal concentration 1.0 mmol/L, adsorbent dose 0.1–1 g/100 mL pH 5.5, 25°C	[35]
Pb(II) > Zn(II) > Cd(II)	Magnetic silica gel (Fe ₃ O ₄ -Si-COOH)	Metal concentration 210 mg/L, adsorbent dose 100 mg/100 mL, pH 6, 25°C	[49]
Cu(II) > Co(II) > Zn(II) 14.0, 5.1, 5.0 mg/g	Citric acid-coated magnetic olive wood sawdust (cit-MOW)	Adsorbent dose 25 mg/25 mL, pH 5.6, 30°C	[50]
Pb(II) > Cu(II) > Cd(II) 52.05, 45.35, 35.18 mg/g	Amino-salicylic acid-modified amino-hyperbranched functionalized magnetite (Fe ₃ O ₄ -HBPA-ASA)	Metal concentration 2–150 mg/L, adsorbent dose 0.8 mg/L, pH 7, 25°C	[51]
Cr(III) > Pb(II) > Zn(II) > Cu(II) > Ni(II) > Cd(II) 46.79, 36.34, 19.02, 18.08, 10.80, 1.89 mg/g	Magnetite nanoparticles (M NPs) – mixture I	$m_{\text{NPs}}/m_{\text{Ms}} = 0.5$, pH = 5, CM = 10 mg/L (CMs = 60 mg/L)	This work
Cu(II) > Zn(II) > Cr(VI) > Ni(II) > Cd(II) 22.01, 17.25, 11.22, 9.86, 5.05 mg/g	Magnetite nanoparticles (M NPs) – mixture II	$m_{\text{NPs}}/m_{\text{Ms}} = 0.5$, pH = 5, CM = 10 mg/L (CMs = 50 mg/L)	This work
Cr(III) > Pb(II) > Cu(II) > Zn(II) > Cd(II) > Ni(II) 89.08, 62.94, 22.23, 15.88, 14.72, 5.08 mg/g	Poly(sodium acrylate)-modified magnetite nanoparticles (PSA/M NPs) – mixture I	$m_{\text{NPs}}/m_{\text{Ms}} = 0.5$, pH = 5, CM = 10 mg/L (CMs = 60 mg/L)	This work
Cu(II) > Cd(II) > Ni(II) > Cr(VI) > Zn(II) 45.56, 16.96, 9.93, 3.71, 3.22 mg/g	Poly(sodium acrylate)-modified magnetite nanoparticles (PSA/M NPs) – mixture II	$m_{\text{NPs}}/m_{\text{Ms}} = 0.5$, pH = 5, CM = 10 mg/L (CMs = 50 mg/L)	This work

efficiency (98%), obtained with an initial Ni(II) concentration of 25 mg/L, adsorbent dose of 0.2 g, pH of 8 and temperature of 313 K, decreased significantly (to approx. 60%) with a reduction in temperature to 293 K or pH to 5, or adsorbent dose to 0.1 g [54]. Considering the real wastewater, the 70% Ni(II) separation achieved in this work for PSA/M NPs at relatively low pH and temperature and high metal concentration is promising.

The high dependence of adsorption efficiency on pH was confirmed during the separation of Cu, Ni, Mn, Cd(II), and Cr(VI) from acid mine drainage (AMD) from the copper mine with the use of maghemite nanoparticles γ -Fe₂O₃ [55]. The highest removal of these metals was observed at different pH (2.6 for Cr(VI), 6.5 for Cu, 10 for Ni and Mn, and 11 for Cd(II)), with the noticeable precipitation of Ni and Mn at a pH of 9.5. Experiments conducted with model single-metal

Table 4
Characteristics of galvanic wastewater

Wastewater parameter	Wastewater and metal ion				
	I Ni(II)	II Cu(II)	III Cr(VI)	IV Zn(II)	V Zn/Cr
Average heavy metal concentration, mg/L	106.5 ± 2.0	240.4 ± 0.9	415.8 ± 9.0	133.6 ± 0.8	171.9 ± 1.4 (Zn) 116.3 ± 3.5 (Cr)
pH	6.33	2.84	2.46	3.82	3.62
Conductivity, µS/cm	558 ± 0.0	1,412.0 ± 1.0	2,523.3 ± 5.8	1,334.0 ± 1.7	3,593.3 ± 5.8
Cl ⁻ , mg/L	35.7 ± 0.6	3.2 ± 0.8	9.3 ± 2.1	513.3 ± 41.7	918.0 ± 54.6.5
NO ₃ ⁻ , mg/L	5.4 ± 1.2	nd.	nd	7.3 ± 1.8	310.0 ± 25.9
PO ₄ ³⁻ , mg/L	5.1 ± 1.2	nd	nd	nd	17.7 ± 4.7
SO ₄ ²⁻ , mg/L	246.7 ± 4.0	670.8 ± 27.5	25.3 ± 7.6	36.5 ± 0.5	281.7 ± 3.5
Total solids content (105°C), mg/L	501.8 ± 2.3	918.6 ± 6.5	834 ± 4.8	787.3 ± 6.3	1,866.0 ± 6.5
Residue on ignition (550°C), mg/L	399.6 ± 1.1	667.2 ± 8.2	654.5 ± 3.4	533.2 ± 5.6	526.9 ± 2.9
Loss on ignition (550°C), mg/L	102.2 ± 3.1	251.4 ± 8.9	179.7 ± 5.1	254.1 ± 3.4	1,339.1 ± 7.5

nd – not detected

Table 5
Average amounts ($q_{e,av}$) of heavy metals adsorbed from different types of wastewater using M NPs and PSA/M NPs magnetites

Wastewater – metal ion	$q_{e,av}$ (mg/g)	STD (mg/g)	
		M NPs	PSA/M NPs
I – Ni(II)	6.00	0.15	12.37
II – Cu(II)	24.61	0.53	37.34
III – Cr(VI)	36.65	0.46	32.85
IV – Zn(II)	8.06	0.22	16.27
V – Zn(II) in Zn(II)/Cr(III)	8.25	0.42	15.89
V – Cr(III) in Zn(II)/Cr(III)	19.04	0.15	18.98

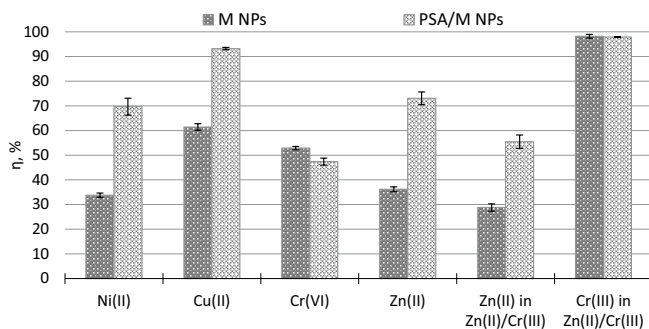


Fig. 5. Effectiveness of heavy metal separation from different types of wastewater.

and mixed-metal solutions showed that the effectiveness of metal removal significantly increases with temperature and a decrease in initial metal concentration. At pH = 6, the following sequence of the metal separation efficiency was observed: Cu > Cr > Mn > Ni > Cd, which is consistent with

the order (Cu(II) > Cr(VI) > Ni(II)) achieved in this work for wastewater treatment using M NPs. The selective adsorption of Cr(VI) from wastewater using maghemite nanoparticles was also confirmed by Hu et al. [56], with the maghemite adsorption capacity of 19.2 mg/g achieved at pH of 2.5 (favorable for Cr(VI) anion separation). The values recorded in this work for Cr(VI) separation using unmodified or PSA-modified magnetites were significantly higher.

A magnetoactive compound based on humic acid and magnetite was selected as an adsorbent of heavy metals (Pb(II), Cu(II), Al(III), Zn(II), Sr(II), and Fe(III)) from tail solutions after flotation of circulating water from a lead–zinc ore enrichment plant [57]. At pH = 6.5, the highest adsorption capacity (and removal efficiency) was observed, amounting to 0.01 mg/g (83.1% removal) and 0.12 mg/g (78.1% removal) for Cu(II) and Zn(II), respectively. The effectiveness of Cu(II) and Zn(II) separation using PSA/M NPs was comparable (or better – in the case of Cu(II) containing wastewater), but the PSA-modified adsorbent showed a significantly higher adsorption capacity at lower pH and higher metal concentration.

4. Conclusions

Two types of magnetic iron oxide-based adsorbents, unmodified magnetite (M NPs) and magnetite modified with poly(sodium acrylate) (PSA/M NPs) were synthesized and used for the competitive separation of heavy metals from multi-component mixtures and galvanic wastewater.

Both magnetites were suitable for use as adsorbents of heavy metals from multi-component mixtures, and (at pH of 5) the effectiveness of metal separation depended significantly on the type of adsorbent, type of metal ions, and the adsorbent to metals mass ratio $m_{\text{NPs}}/m_{\text{Ms}}$. The total heavy metal removal efficiency was higher for PSA/M NPs than for M NPs, due to the presence of carboxyl groups and the negative surface charge of the PSA-modified adsorbent. The differences between the two adsorbents were particularly visible in the adsorption of Cd(II), Ni(II), and Zn(II) ions. Significant differences between individual metal removal ratios, visible at lower $m_{\text{NPs}}/m_{\text{Ms}}$ ratios, indicate the possibility of selective metal separation from multi-component mixtures.

Both types of magnetites were also suitable for the adsorption of heavy metals from different types of galvanic wastewater. The PSA-modified magnetite exhibited higher separation effectiveness towards heavy metal cations. The removal of Cr(VI) from wastewater was slightly less effective using the PSA-modified magnetite due to the dissociated carboxyl groups, which lowered the surface charge of the adsorbent and hindered the adsorption of chromate anions.

The magnetite functionalization with carboxyl groups is a promising way to improve the separation efficiency of heavy metal cations.

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