



Influence of ionic environment on the process of adsorption of heavy metal ions on magnetic iron oxides

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ABSTRACT

Magnetic iron oxides, mainly magnetite Fe_3O_4 and maghemite $\gamma\text{-Fe}_2\text{O}_3$, are seen as cheap, effective and convenient to use adsorbent of impurities such as heavy metals or dyes. The paper presents the influence of selected ions: inorganic monovalent and multivalent anions (NO_3^- , Cl^- , SO_4^{2-} , PO_4^{3-}), organic anions, including complexing agents (CH_3COO^- , EDTA) and monovalent and bivalent metal cations (Ca^{2+} , Na^+) on the separation of Cu(II) , Zn(II) , Ni(II) , Cd(II) , Pb(II) , Cr(III) and Cr(VI) ions from solutions, using unmodified magnetite nanoparticles (M_NPs) and magnetite modified with poly(sodium acrylate) (M/PSA_NPs). The adsorption process was carried out at two pH values (5 and 6 for Cu(II) , Zn(II) , Ni(II) , Cd(II) and 4 and 5 for Pb(II) , Cr(III) and Cr(VI) ions) and at the concentration of the accompanying ion 10 times higher than the metal concentration. The reference test was carried out without the addition of accompanying salts. It was found that the increase in pH and the use of M/PSA_NPs adsorbent containing dissociated carboxylate groups -COO^- contributed to the increase in the degree of separation of all tested metals except for the anionic Cr(VI) form. Under the experimental conditions, inorganic monovalent anions did not show any significant effect on the process efficiency, whereas multivalent anions, especially PO_4^{3-} , increased the degree of separation of Cu(II) , Zn(II) , Ni(II) and Cd(II) , which suggests that these anions may participate in the process of bonding metal cations with magnetite. A similar effect was observed for Pb(II) and Cr(III) cations using unmodified magnetite and lower pH value. The presence of a strong complexing agent (EDTA) significantly decreased the efficiency of cationic metal forms separation. The degree of this decrease depended on the type of metal and the conditions of adsorption. Cr(VI) anions were separated to a greater extent using unmodified magnetite. The presence of versenate (EDTA), phosphate and sulfate ions caused a decrease in the efficiency of the process, which may be explained by the fact that these multivalent anions compete with chromate ions in the adsorption process.

Keywords: Magnetic iron oxides; Adsorption; Heavy metals; Coexisting ions

1. Introduction

The widespread use of heavy metals, which grows with the development of civilization, poses a serious threat to the natural environment. Heavy metals are toxic, they bioaccumulate in tissues of living organisms and are not biodegradable, which makes it necessary to develop separation

techniques enabling effective elimination of these pollutants from water, sewage, post-process streams and solid waste. An additional aspect that increases this need is the economic factor and the possibility of recovering and reusing heavy metals.

Among the techniques used for the separation of heavy metal ions, the most important are: precipitation (usually

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in the form of hydroxides or sulfides), ion exchange, membrane techniques (mainly nanofiltration, reverse osmosis, electro dialysis, as well as ultrafiltration combined with other methods - polymer enhanced ultrafiltration or micellar enhanced ultrafiltration), coagulation/flocculation, flotation, electrochemical processes and adsorption [1–4]. The separation of metal ions is hindered by the presence of other impurities, ions or organic compounds, including complexing agents. In the case of heavy metals in the chelated form, the previously mentioned techniques can be extended by such methods as replacement-coprecipitation, TiO_2 photocatalysis, and Fenton-like oxidation [3].

Adsorption is one of the most frequently studied techniques for the separation of heavy metal ions. The advantages of this process include ease of operation, a wide range of adsorbents, low-cost of operation (low cost adsorbents) and high efficiency in relation to various metals. On the other hand, the process disadvantages may include difficulties with sorbent regeneration, desorption, long time to reach equilibrium and limited pH range [2,3]. Many potential adsorbents are tested for their applicability to various heavy metals and the effectiveness of the adsorption process. These are, among others, various types of active carbon, both commercial [5,6] and especially produced from waste products [7,8], carbon nanotubes [1,2,9], mineral adsorbents (kaolinite, montmorillonite and bentonite) [9], bioadsorbents (non-living biomass, algal biomass, microbial biomass) and low-cost adsorbents, mainly waste products of natural origin [1,2].

In recent years, adsorbents prepared on the basis of magnetic iron oxides, mainly magnetite Fe_3O_4 and maghemite $\gamma\text{-Fe}_2\text{O}_3$, are of great interest. They enable the preparation of non-toxic sorbents, characterized by a large specific surface area, showing good sorption abilities towards various substances in a wide range of pH (including heavy metal ions and metalloids) and easily separable in a magnetic field. These adsorbents are usually used as nanoparticles or nanotubes and have been successfully applied to separate Cu(II), Zn(II), Pb(II), As(III), As(V), Cr(VI), Mn(II) [10–14]. Often, in order to produce effective adsorbents, magnetic iron oxides are combined with carbon, graphene or graphene oxide [15,16]. Another modification method is the functionalization of adsorbents with compounds containing functional groups capable of binding heavy metal ions, e.g. amino, carboxyl or sulfonic groups. The use of iron oxides-based adsorbents modified with chitosan [17,18], 1,4-hexadiazine [19], polyaniline [20], poly(acrylic acid) [21] or DOWEX 50WX4 resin [22], can be given as an example.

Heavy metal ions in real solutions are usually accompanied by other ionic compounds, while the concentration of accompanying ions often exceeds the concentration of heavy metal ions. The ionic environment is one of the important factors that may influence the efficiency of heavy metal ion adsorption. The ions present in the solution may compete with the heavy metals for active sites of the sorbent, may change the surface charge of the adsorbent and reduce its sorption capacity, or may interact with the metal ions forming insoluble or chelated compounds, thus decreasing the efficiency of the separation process.

The aim of the study was to determine the effect of selected ions on the separation process of Cu(II), Zn(II),

Cd(II), Ni(II), Pb(II), Cr(III) and Cr(VI) ions using unmodified magnetite nanoparticles (M_NPs) and nanoparticles modified with poly(sodium acrylate) (M/PSA_NPs) as adsorbents. As ions accompanying the adsorption process, the following ions were selected: inorganic monovalent (NO_3^- , Cl^-) and multivalent (SO_4^{2-} , PO_4^{3-}) anions, organic anions, including a strong complexing agent (CH_3COO^- , EDTA), as well as metal cations (Ca^{2+} , Na^+).

2. Materials and methods

Iron(II) and iron(III) salts: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, as well as ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25 wt.%) were used to synthesize magnetite (Stanlab, Poland). PSA ($M_w = 30000$, 40 % aqueous solution, Sigma Aldrich, USA) was used as a magnetite modifier. Heavy metal ion solutions were prepared from suitable metal salts: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (POCH S.A., Poland) and $\text{K}_2\text{Cr}_2\text{O}_7$ (Merck, Germany). The following salts were used as the source of accompanying ions (NO_3^- , Cl^- , SO_4^{2-} , PO_4^{3-} , CH_3COO^- , EDTA, Ca^{2+} , Na^+): NaNO_3 , NaCl , Na_2SO_4 , $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ (EDTA), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, NaNO_3 (POCH S.A., Poland). NaOH and HNO_3 (POCH S.A., Poland) solutions of variable concentration were used for pH correction.

Magnetite was synthesized by co-precipitation from iron(II) and iron(III) salts, according to the methodology described earlier [23,24]. 6.1 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 4.2 g of $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ and 100 mL of deionized water were introduced into a conical flask placed in a water bath at temp. 30°C . After dissolving and heating the solution to a suitable temperature, 20 mL of ammonia solution 25 wt.% and 50 mL of deionized water were added to the flask at intensive stirring. In the case of PSA modified magnetite synthesis, 50 mL of 1% polymer solution was added instead of 50 mL of water. After precipitation of iron oxides, the mixture was stirred for 30 min. and then the magnetite obtained was separated using a neodymium magnet and washed three times with 50 mL of deionized water. Magnetite was introduced into the adsorption process in the form of a 10 g/L suspension. The pH of the isoelectric point (pH_{IEP}) was determined for both types of synthesized magnetites by recording the zeta potential in the range of $\text{pH} = 3\text{--}10$ (M_NPs) and $\text{pH} = 2.8\text{--}10$ (M/PSA_NPs) (Zetasizer Nano-ZS ZEN 3600, Malvern Instruments Ltd.). The measurements were made in deionized water and the pH was adjusted with NaOH and HCl solutions (Chempur, Poland) at 0.5 mol/L concentrations.

For each heavy metal ion, a series of model solutions containing 50 mg/L of heavy metal ions and a salt introducing the analyzed accompanying ions at a concentration 10 times higher (500 mg/L) were prepared. Heavy metal solutions of the same concentration (50 mg/L) without additional salts were used as a reference.

Adsorption tests of heavy metal ions from the prepared solutions were carried out using two types of adsorbents: unmodified magnetite (M_NPs) and magnetite modified with PSA (M/PSA_NPs). The volume of the solution used for adsorption was 20 mL and the mass of the adsorbent amounted to 50 mg. The process was carried out at two pH values of 5 and 6 for Cu(II), Zn(II), Ni(II) and Cd(II) and 4 and 5 for adsorption of Pb(II), Cr(III) and Cr(VI) ions.

Solutions with magnetite were shaken for 8 h (260 rpm) at 22°C (orbital shaker SK-O330-Pro, ChemLand Poland) and then supernatant and adsorbent were separated using a neodymium magnet. In supernatants, as well as in initial solutions, the content of heavy metals was analyzed using a SpectrAA 880 atomic absorption spectrometer (Varian, Candela Sp. z o.o., Poland). All adsorption experiments were conducted in triplicate.

The efficiency of the separation process was determined from Eq. (1), while Eq. (2) was used to calculate the sorption capacity of magnetites under experimental conditions.

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

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

where η – adsorption efficiency, %, C_i and C_e – respectively, initial and equilibrium concentration of metal ions (before and after adsorption process), mg/L, q_e – adsorption capacity of magnetite, mg/g; m – mass of adsorbent, g; V – volume of metal solution, L.

3. Results and discussion

Figs. 1–7 show the effectiveness of the process of separation of individual heavy metal ions in the presence of the

analyzed accompanying ions and in the reference sample without additional salts, while Tables 1 and 2 show the mean amounts of metals adsorbed on unmodified and modified magnetites under experimental conditions.

The adsorption of Cu(II), Zn(II), Cd(II) and Ni(II) cations on unmodified magnetite at pH = 5 proceeded at moderate efficiency. Depending on the ionic environment, 15%–97% of these metal cations could be removed under experimental conditions, which corresponds to the sorption capacity of magnetite in the range of 3.42–24.5 mg/g. Among these four metals, the highest efficiency was recorded for copper cations and the lowest for nickel ions. The use of magnetite modified with PSA at the same pH value of 5 resulted in better metal separation (Figs. 1b–4b). The efficiency of the process changed then in the range of 17.5%–99%, which means adsorption of 4.61–26.16 mg of the metal per 1 g of magnetite. Higher efficiency of the process resulted from the presence of carboxyl groups capable of binding metal cations, introduced into the structure of the adsorbent in the form of polymer used to modify magnetite. In the case of both magnetites, the process efficiency increased with an increase in pH from 5 to 6. The determined values of isoelectric points of magnetites (pH_{IEP}) were 6.34 and 3.18, respectively, for unmodified magnetite and magnetite modified with PSA polymer. At lower pH values, the resultant surface charge of the adsorbent is positive, which makes it difficult to bind metal cations. As pH increases above pH_{IEP} the resultant surface charge of the sorbent takes on a negative sign, which favors the binding of metal cations. An increase

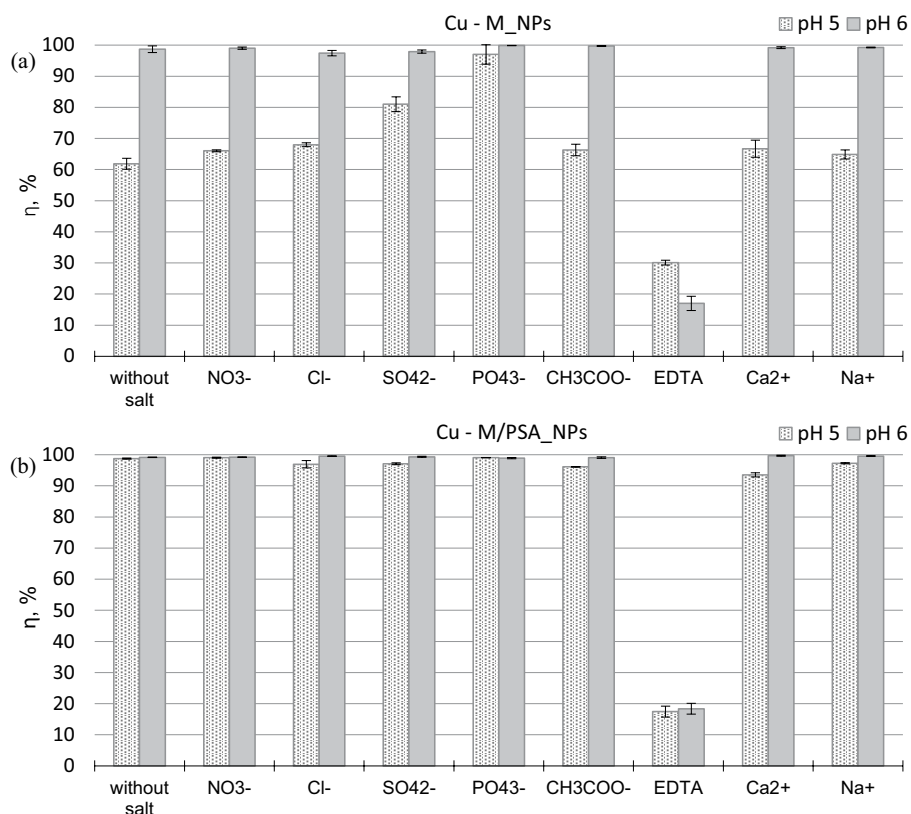


Fig. 1. Effect of coexisting ion type on the effectiveness of Cu(II) separation. (a) M_NPs and (b) M/PSA_NPs.

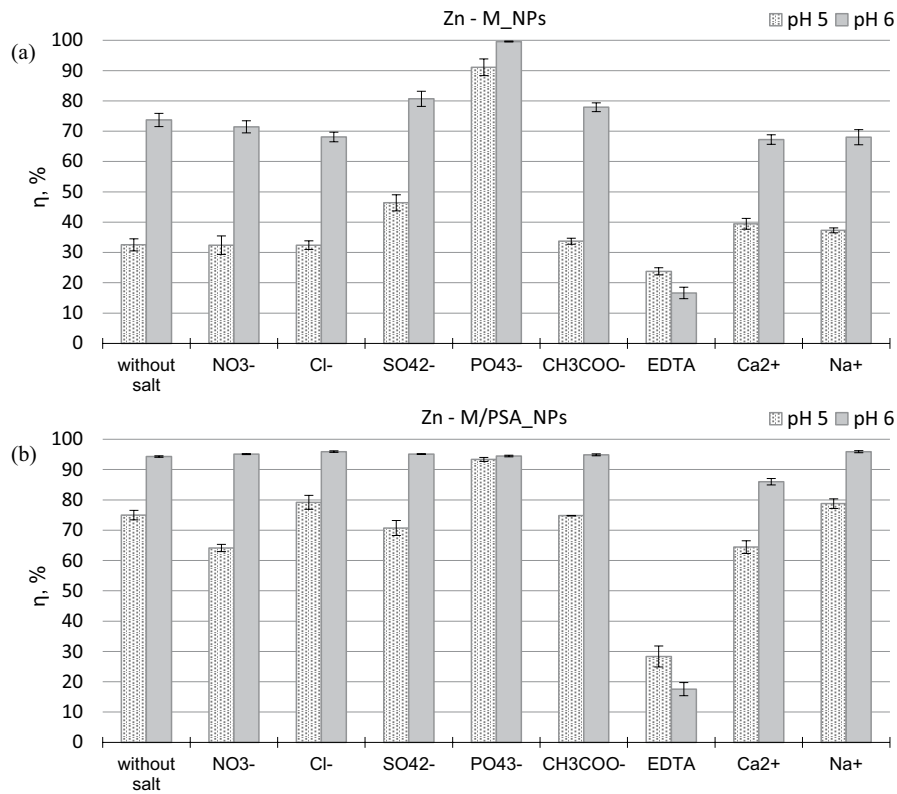


Fig. 2. Effect of coexisting ion type on the effectiveness of Zn(II) separation. (a) M_NPs and (b) M/PSA_NPs.

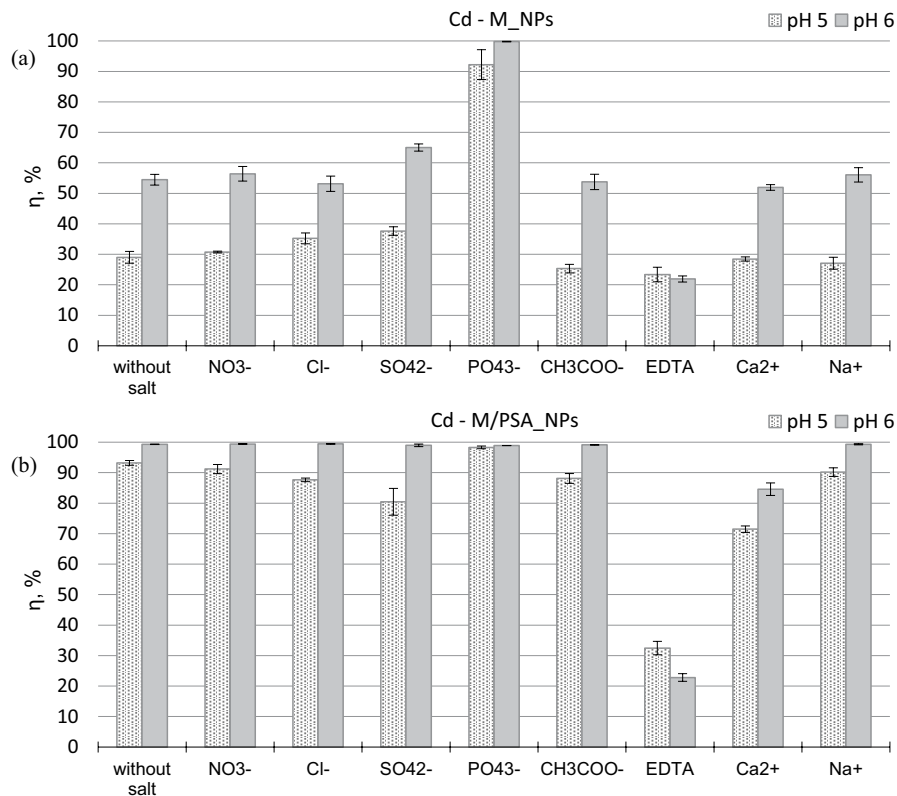


Fig. 3. Effect of coexisting ion type on the effectiveness of Cd(II) separation. (a) M_NPs and (b) M/PSA_NPs.

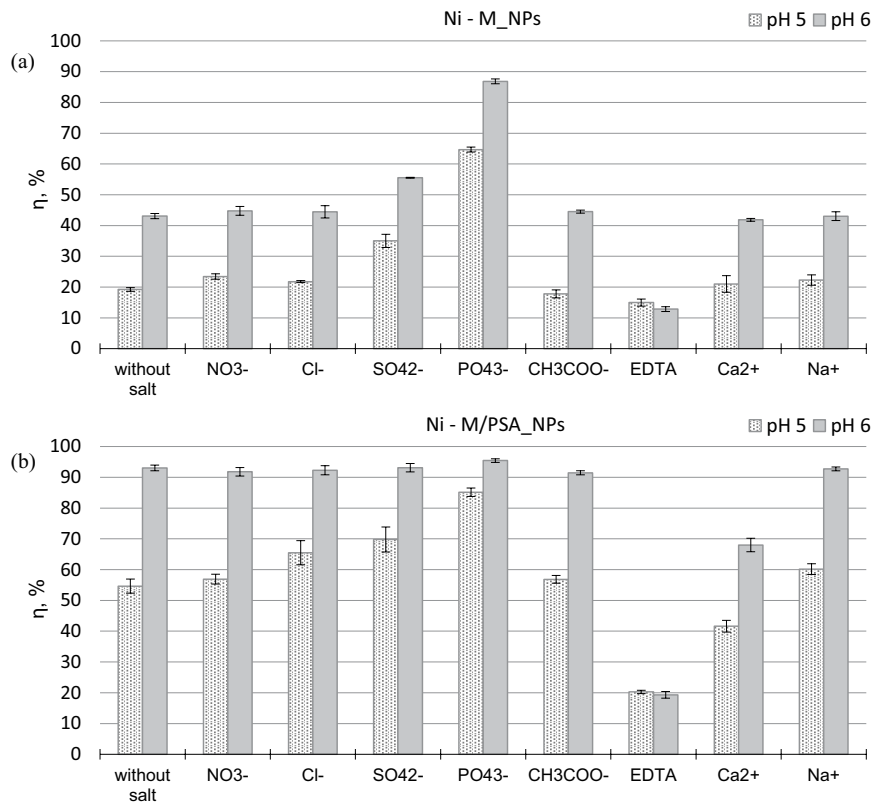


Fig. 4. Effect of coexisting ion type on the effectiveness of Ni(II) separation. (a) M_NPs and (b) M/PSA_NPs.

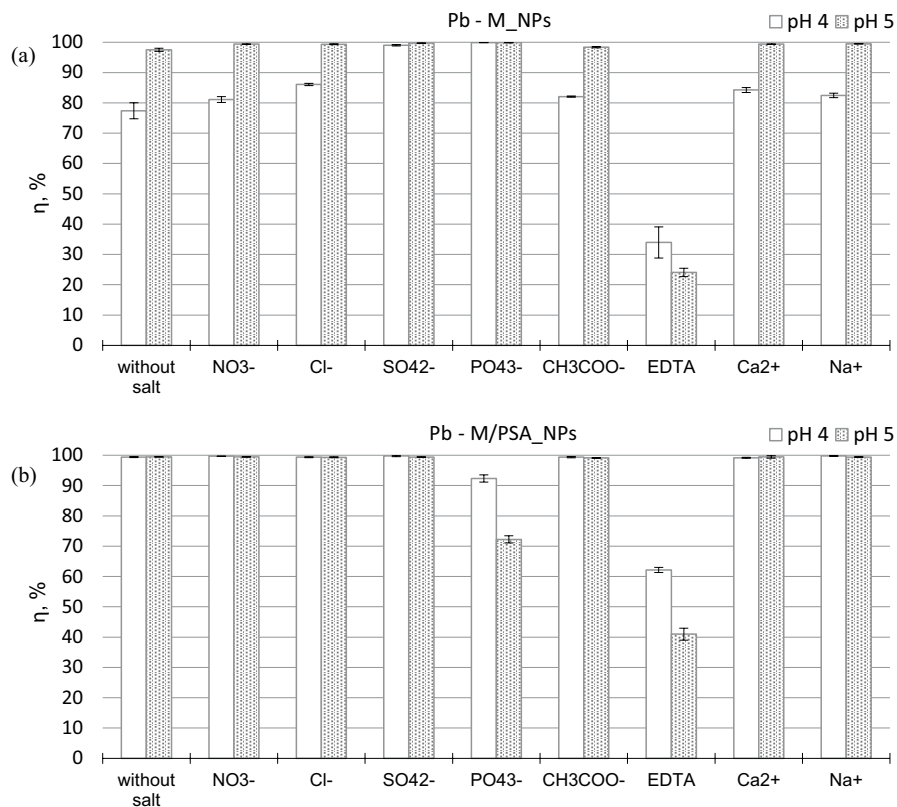


Fig. 5. Effect of coexisting ion type on the effectiveness of Pb(II) separation. (a) M_NPs and (b) M/PSA_NPs.

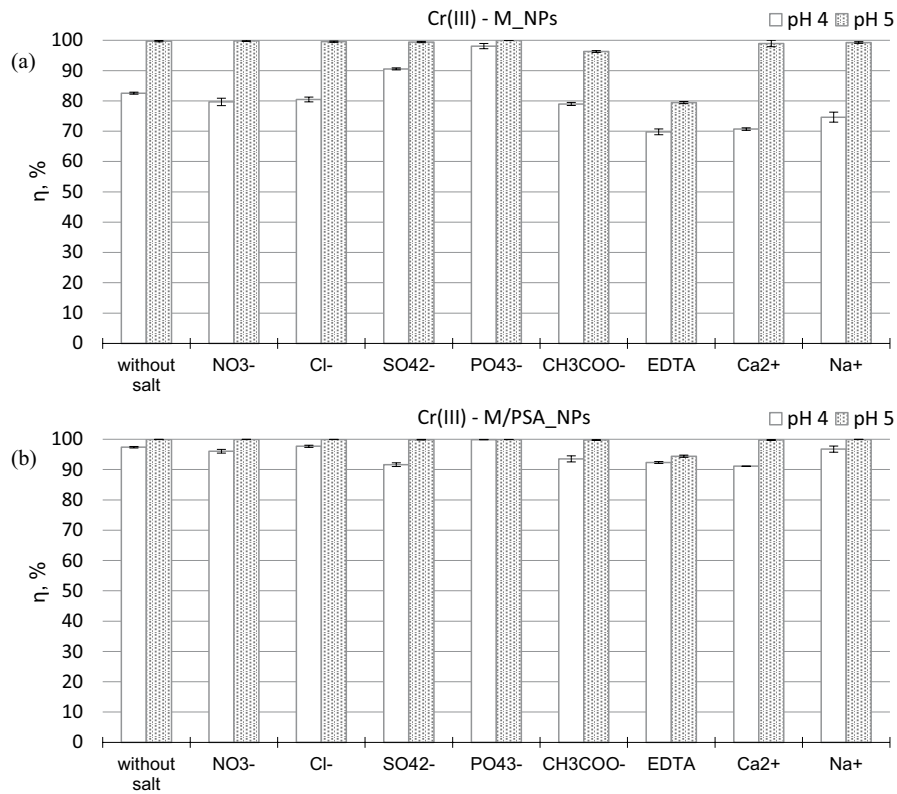


Fig. 6. Effect of coexisting ion type on the effectiveness of Cr(III) separation. (a) M_NPs and (b) M/PSA_NPs.

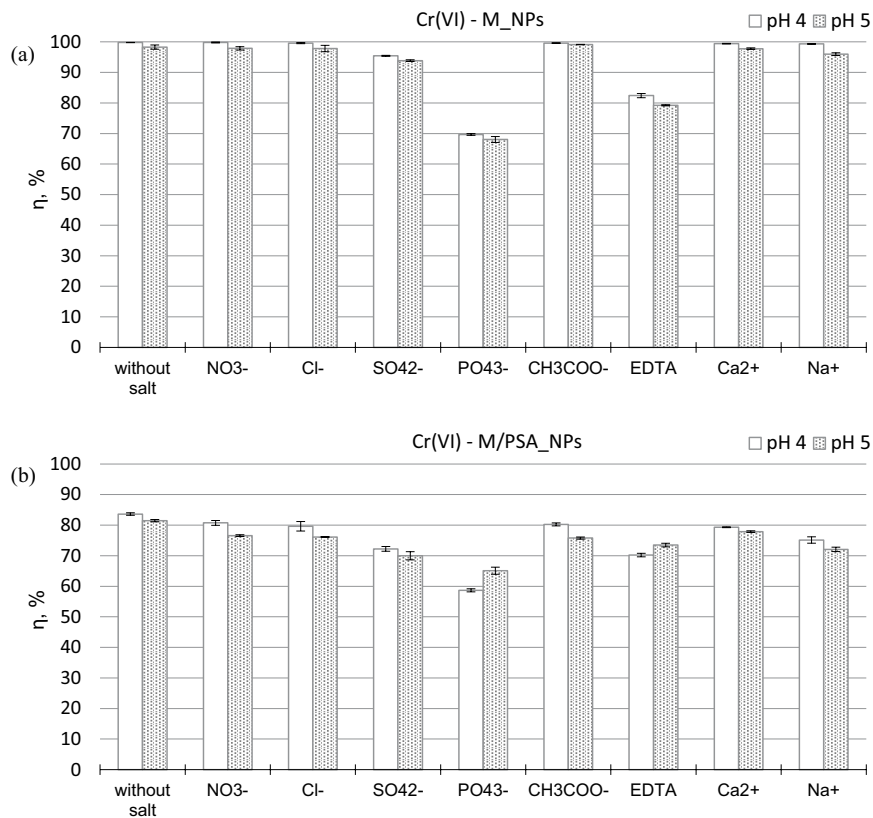


Fig. 7. Effect of coexisting ion type on the effectiveness of Cr(VI) separation. (a) M_NPs and (b) M/PSA_NPs.

Table 1

Average amounts of Cu(II), Zn(II), Cd(II) and Ni(II) ($q_{e,av}$) adsorbed on M_NPs and M/PSA_NPs at pH 5 and 6 in solutions containing no additional salt and in solutions with added test salts

	$q_{e,av}$ mg/g	SD mg/g	$q_{e,av}$ mg/g	SD mg/g	$q_{e,av}$ mg/g	SD mg/g	$q_{e,av}$ mg/g	SD mg/g
	M_NPs, pH 5		M_NPs, pH 6		M/PSA_NPs, pH 5		M/PSA_NPs, pH 6	
Cu(II)								
Without salt	15.67	0.44	23.69	0.26	26.09	0.04	25.89	0.02
NaNO ₃	16.73	0.07	23.77	0.09	26.16	0.04	25.89	0.02
NaCl	17.22	0.16	23.39	0.21	25.61	0.31	25.98	0.02
Na ₂ SO ₄	20.52	0.60	23.51	0.13	25.64	0.07	25.93	0.04
Na ₃ PO ₄	24.57	0.79	23.98	0.01	26.16	0.01	25.81	0.05
CH ₃ COONa	16.80	0.47	23.94	0.02	25.39	0.03	25.86	0.06
Na-EDTA	7.63	0.20	4.08	0.55	4.61	0.46	4.80	0.45
Ca(NO ₃) ₂	16.90	0.69	23.81	0.07	24.71	0.18	26.02	0.04
NaNO ₃	16.43	0.37	23.83	0.03	25.69	0.05	25.99	0.02
Zn(II)								
Without salt	7.13	0.44	15.28	0.45	18.18	0.38	22.19	0.05
NaNO ₃	7.11	0.67	14.81	0.41	15.55	0.29	22.38	0.04
NaCl	7.10	0.32	14.12	0.33	19.20	0.56	22.57	0.05
Na ₂ SO ₄	10.17	0.58	16.73	0.52	17.15	0.60	22.38	0.01
Na ₃ PO ₄	19.97	0.60	20.65	0.03	22.63	0.16	22.23	0.06
CH ₃ COONa	7.39	0.22	16.15	0.30	18.13	0.02	22.32	0.07
Na-EDTA	5.22	0.26	3.45	0.39	6.87	0.84	4.13	0.51
Ca(NO ₃) ₂	8.65	0.39	13.94	0.33	15.62	0.51	20.24	0.25
NaNO ₃	8.18	0.18	14.10	0.52	19.09	0.38	22.56	0.08
Cd(II)								
Without salt	6.51	0.43	12.04	0.39	23.22	0.20	24.21	0.02
NaNO ₃	6.89	0.07	12.47	0.53	22.72	0.37	24.23	0.01
NaCl	7.90	0.40	11.74	0.55	21.84	0.15	24.24	0.02
Na ₂ SO ₄	8.44	0.31	14.37	0.26	20.04	1.09	24.12	0.10
Na ₃ PO ₄	20.67	1.10	22.05	0.02	24.49	0.11	24.11	0.01
CH ₃ COONa	5.67	0.31	11.88	0.56	21.95	0.40	24.16	0.02
Na-EDTA	5.24	0.54	4.84	0.22	8.09	0.55	5.56	0.31
Ca(NO ₃) ₂	6.38	0.15	11.47	0.20	17.81	0.26	20.62	0.50
NaNO ₃	6.07	0.44	12.39	0.52	22.47	0.35	24.21	0.04
Ni(II)								
Without salt	4.39	0.14	9.34	0.18	13.17	0.55	22.84	0.23
NaNO ₃	5.36	0.20	9.71	0.31	13.71	0.38	22.53	0.34
NaCl	4.98	0.07	9.65	0.43	15.78	0.95	22.65	0.36
Na ₂ SO ₄	8.19	0.50	12.94	0.03	16.82	0.98	22.85	0.34
Na ₃ PO ₄	14.97	0.43	20.23	0.18	20.52	0.33	23.42	0.14
CH ₃ COONa	4.07	0.30	9.66	0.11	13.70	0.30	22.45	0.16
Na-EDTA	3.42	0.26	2.79	0.17	4.88	0.13	4.74	0.27
Ca(NO ₃) ₂	4.80	0.62	9.08	0.10	10.03	0.46	16.69	0.54
NaNO ₃	5.09	0.38	9.34	0.31	14.50	0.42	22.76	0.15

in alkalinity of the solution also intensifies the dissociation of carboxylic groups of PSA-modified magnetite, increasing the efficiency of metal cation separation.

The removal efficiency of Cu(II), Zn(II), Cd(II) and Ni(II) from the solutions also depended on the presence of some accompanying ions, which was particularly evident in the

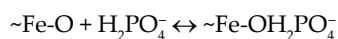
adsorption on unmodified magnetite at pH = 5. While the monovalent anions NO₃⁻, Cl⁻, CH₃COO⁻, generally did not show a significant effect on the process efficiency (within the range of tested concentrations), the multivalent anions, sulfate anions and especially phosphate anions caused that the removal effectiveness of Cu(II), Zn(II), Cd(II) and Ni(II)

Table 2

Average amounts of Pb(II), Cr(III) and Cr(VI) ($q_{e,av.}$) adsorbed on M_NPs and M/PSA_NPs at pH 4 and 5 in solutions containing no additional salt and in solutions with added test salts

	$q_{e,av.}$ mg/g	SD mg/g	$q_{e,av.}$ mg/g	SD mg/g	$q_{e,av.}$ mg/g	SD mg/g	$q_{e,av.}$ mg/g	SD mg/g
	M_NPs, pH 5		M_NPs, pH 4		M/PSA_NPs, pH 5		M/PSA_NPs, pH 4	
Pb(II)								
Without salt	25.11	0.13	19.82	0.68	24.68	0.01	24.75	0.04
NaNO ₃	25.59	0.01	20.77	0.25	24.67	0.01	24.82	0.01
NaCl	25.58	0.03	22.04	0.09	24.64	0.03	24.73	0.04
Na ₂ SO ₄	25.67	0.01	25.36	0.06	24.66	0.03	24.83	0.05
Na ₃ PO ₄	25.71	0.02	25.59	0.01	17.92	0.29	22.99	0.30
CH ₃ COONa	25.33	0.06	21.02	0.05	24.58	0.02	24.74	0.05
Na-EDTA	6.20	0.35	8.70	1.32	10.16	0.49	15.47	0.21
Ca(NO ₃) ₂	25.58	0.01	21.57	0.21	24.67	0.10	24.69	0.04
NaNO ₃	25.62	0.01	21.12	0.19	24.66	0.01	24.84	0.01
Cr(III)								
Without salt	26.35	0.06	20.26	0.08	27.89	0.01	24.67	0.06
NaNO ₃	26.38	0.06	19.55	0.30	27.90	0.00	24.34	0.16
NaCl	26.31	0.06	19.75	0.19	27.89	0.01	24.75	0.09
Na ₂ SO ₄	26.28	0.05	22.22	0.08	27.87	0.03	23.21	0.16
Na ₃ PO ₄	26.43	0.00	24.07	0.21	27.88	0.01	25.31	0.01
CH ₃ COONa	25.45	0.08	19.38	0.13	27.83	0.02	23.70	0.25
Na-EDTA	21.00	0.09	17.13	0.23	26.35	0.10	23.39	0.08
Ca(NO ₃) ₂	26.15	0.28	17.34	0.10	27.84	0.02	23.08	0.02
NaNO ₃	26.23	0.07	18.31	0.40	27.89	0.00	24.51	0.26
Cr(VI)								
Without salt	26.31	0.19	26.65	0.01	22.65	0.10	20.13	0.09
NaNO ₃	26.20	0.15	26.65	0.04	21.28	0.08	19.43	0.19
NaCl	26.19	0.28	26.60	0.05	21.16	0.03	19.16	0.37
Na ₂ SO ₄	25.12	0.07	25.49	0.04	19.46	0.37	17.38	0.19
Na ₃ PO ₄	18.22	0.26	18.61	0.07	18.10	0.32	14.12	0.12
CH ₃ COONa	26.54	0.01	26.60	0.01	21.07	0.09	19.31	0.12
Na-EDTA	21.21	0.05	22.01	0.18	20.43	0.16	16.90	0.14
Ca(NO ₃) ₂	26.17	0.06	26.55	0.03	21.65	0.07	19.08	0.03
NaNO ₃	25.70	0.12	26.52	0.02	20.04	0.20	18.08	0.25

increased. This effect was also visible during the adsorption of these metals on unmodified magnetite at pH = 6, however, due to generally higher values of the process efficiency, it was less pronounced. This suggests that multivalent anions (especially phosphate anions) can take part in the binding of metal cations with magnetite. The influence of phosphate anions was also observed in the case of the use of PSA-modified magnetite. At pH = 5, the presence of phosphates increased the adsorption efficiency of Cd(II), Zn(II) and Ni(II) cations in relation to reference solutions (without additional salts), in which adsorption took place with moderate efficiency. These results are consistent with the studies of other authors, who prove that phosphate anions are adsorbed on magnetite, mainly in the form of H₂PO₄⁻ ions, according to the reaction:



which causes the reduction of the magnetite zeta potential [25]. Lowering the surface charge of the adsorbent may cause the observed increase in the adsorption of heavy metal cations, which is connected with the increasing number of available active sites with a negative charge.

The introduction of a strong complexing agent (EDTA) into the solutions caused a significant decrease in the separation efficiency of Cu(II), Zn(II), Cd(II) and Ni(II) cations. It was particularly visible in the conditions in which high metal removal effectiveness was obtained, that is, using unmodified magnetite and pH 6 and during adsorption on magnetite modified with PSA. The highest decrease in the efficiency of the process conducted with EDTA was observed for Cu(II) cations (M_NPs, pH 6 and M/PSA_NP, pH 5 and 6) as well as for Zn(II), Cd(II) and Ni(II) cations (M/PSA_NPs, pH 6). The efficiency of metal ion separation in these conditions was even 80% lower than that of the separation of

ions from solutions without additional salts. This effect can be explained by the ability of EDTA to form complexes with metal cations, especially at higher pH values. Moreover, EDTA molecules could be adsorbed on magnetite [26,27], thus taking up the available active sites of the adsorbent and reducing the efficiency of metal ion separation. In the solutions containing EDTA the lowest values of magnetite sorption capacity in relation to Cu(II), Zn(II), Cd(II) and Ni(II) cations were observed, remaining in the range of 2.79–8.09 mg/g.

The presence of Ca^{2+} and Na^{+} cations in the solutions did not cause a significant change in the adsorption efficiency of Cu(II), Zn(II), Cd(II) and Ni(II) ions on the magnetites studied. Compared with the reference solutions, a moderate increase in the separation efficiency of the Cu(II), Ni(II) and Zn(II) cations were observed (in the range of 9.3%–21.4%) at pH 5 for unmodified magnetite. Using modified magnetite and pH = 5, solutions containing calcium cations showed a decrease of Zn(II), Cd(II) and Ni(II) separation efficiency by about 14%–24% in comparison to the tests carried out without additional salts. A similar effect was observed for Cd(II) and Ni(II) cations at pH = 6 – the adsorption efficiency decreased by 14.8% and 26.9% respectively. These effects may be caused by the interaction of calcium cations present in the solution with functional groups of magnetite and the resulting increase in the adsorbent surface charge, which is confirmed by the work of other authors [28]. Similar conclusions were reached by Potapova et al. [29], stating an increase in the zeta potential of hematite (Fe_2O_3) caused by the presence of CaCl_2 in the solution and explaining it by interaction of calcium cations with the negatively charged hematite surface.

The process of separation of Pb(II) and Cr(III) cations using unmodified magnetite at pH 5, in solutions without additional salts and in solutions with addition of most of the studied ions (except EDTA) was characterized by high efficiency exceeding 96% (Fig. 5a) and the sorption capacity of magnetite in relation to these metals was about 25–26 mg/g. The efficiency of separation of Pb(II) and Cr(III) cations with M_NPs magnetite decreased when pH was lowered to 4. A similar effect was observed for Cr(III) ions and PSA-modified magnetite, although in this case the decrease in the efficiency of the process was smaller when the acidity of the solution increased. A clear effect of added ion on the separation of Pb(II) and Cr(III) cations was observed in the case of EDTA, for which a decrease in process efficiency was observed for both magnetites used and pH values tested in comparison with solutions without additional salts. This reduction was in the range of 5.17%–20.32% and 37.47%–75.32% for Cr(III) and Pb(II) respectively, reaching the highest values for M_NPs magnetite and pH 5 and the lowest values for M/PSA_NPs and pH 4. At pH 4, an increase in the separation efficiency of Pb(II) and Cr(III) cations due to the presence of sulfate and, especially, phosphate anions was observed when using unmodified magnetite, similarly to the Cu(II), Zn(II), Cd(II) and Ni(II) cations.

Cr(VI) anions removal (Fig. 7), regardless of the ionic environment, was performed with higher efficiency on unmodified magnetite than on nanoparticles modified with PSA, which resulted from the presence of anionic functional groups in the modified magnetite structure, reducing the

surface charge of the sorbent. Within the range of tested pH values, no significant differences in the efficiency of chromate ion separation were found. When analyzing the effect of the type of ions present in the solution on the adsorption process, the decrease in the efficiency of Cr(VI) anion separation caused by the presence of versenate (EDTA), phosphate and sulfate anions should be emphasized. This effect can be explained by the fact that multivalent anions compete with chromate anions for the active sites of magnetite, resulting in a decrease of Cr(VI) adsorption. Reduced efficiency of Cr(VI) adsorption caused by the presence of phosphate or sulfate anions is also confirmed by other authors. An example is the negative effect of phosphates on the arsenic and Cr(VI) ion adsorption on magnetite-maghemite nanoparticles [11] and on the adsorption of Cr(VI) on a composite adsorbent prepared on the basis of polyaniline and humic acids [30]. Likewise, the presence of sulfate anions decreased the efficiency of chromate anion separation with the use of adsorbent being a composite of magnetite, polyethyleneimine and steam-exploded rice straw SERS [31].

4. Conclusions

Two types of magnetic iron oxide-based adsorbents were synthesized in the laboratory conditions and the separation of heavy metal ions: Cu(II), Zn(II), Cd(II), Ni(II), Pb(II), Cr(III) and Cr(VI) from the solution was performed. The impact of an adsorbent type, pH value and a type of accompanying ion on the separation effectiveness was evaluated. The synthesized magnetites, unmodified (M_NPs) and modified with PSA (M/PSA_NPs), were effective adsorbents of analyzed heavy metal ions. The adsorption of metal cations took place with higher efficiency on the PSA-modified adsorbent, which was particularly visible in the case of Cu(II), Zn(II), Ni(II), Cd(II) ions and the lower of the two pH values tested, and resulted from the presence of dissociated $-\text{COO}^-$ groups in the structure of the adsorbent. Cr(VI) anion separation was more effective with unmodified magnetite, which did not contain carboxylate groups. Inorganic monovalent anions co-existing with separated heavy metal ions generally did not show a significant influence on the efficiency of the process under the experimental conditions. Multivalent anions, especially PO_4^{3-} , supported the separation of Cu(II), Zn(II), Ni(II) and Cd(II), as well as Pb(II) and Cr(III) ions adsorbed on unmodified magnetite at lower pH value, which may indicate their participation in the process of metal cations adsorption. Strong complexing agent (EDTA) decreased the efficiency of metal cations adsorption, while the degree of this decrease depended on the process conditions. The separation of Cr(VI) was negatively affected by the presence of versenate, phosphate and sulfate anions competing with chromate anions in the adsorption process and reducing the effectiveness of their removal from the solution.

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