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Competitive separation of heavy metals from binary solutions by polymer-enhanced ultrafiltration

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ABSTRACT

The polymer-enhanced ultrafiltration has been proposed for the separation of Zn(II) and Cr(VI) ions from binary mixtures. Polyethyleneimine (PEI), a water-soluble polymer containing primary, secondary and tertiary amino groups, was used to bind both metal ions and enhance the ultrafiltration process. Model solutions containing Zn(II) and Cr(VI) ions with various molar ratios of both metals were used in the investigations. The impact of the main process parameters, that is, pH, the molar ratio of PEI to the total amount of both metals, the composition of the bi-ionic Zn(II)/Cr(VI) mixture and the presence of chlorides and sulphates on process effectiveness was discussed. It had been found that the Zn(II) rejection coefficient increased with increasing pH and its value also depended on the amount of PEI and the composition of the binary solution. The Cr(VI) rejection coefficient reached maximum values in the pH range of 6–8 and significantly decreased with a decrease in the PEI dose, increase in Cr(VI) amount in the bi-ionic mixture and the presence of sulphate anions. An effective simultaneous metal separation was observed at pH 6–8 in the solutions without sulphates, when the amount of PEI was sufficient to bind both metals (molar ratio $C_{PEI}/C_M = 5$). Selective separation of Zn(II) ions from the binary Zn(II)/Cr(VI) mixture was visible at pH = 10, and was favoured by both the reduction of the polymer dose and the presence of sulphate ions in the solution.

Keywords: Polymer-enhanced ultrafiltration; Polyethyleneimine; Heavy metals; Zn(II)/Cr(VI) bi-ionic mixture

1. Introduction

In recent years, much attention has been paid to the development of effective separation techniques of heavy metal removal from industrial wastewater and aqueous solutions. In this field, membrane processes have become an interesting alternative to conventional separation techniques. Some of them, such as nanofiltration, reverse osmosis, electrodialysis, pertraction (liquid membranes) or polymer inclusion membranes can be applied directly to the removal of heavy metal ions from the aqueous environment [1–5]. Some other membrane techniques, known as hybrid or integrated processes, combine membranes with other separation methods to improve process efficiency. Polymer-enhanced ultrafiltration (PEUF) is one of the most promising processes among them and has been intensively investigated as a heavy metal separation technique. The method involves the application of polymeric ligands to bind heavy metal ions and the use of an ultrafiltration membrane to separate macromolecular polymer–metal complexes. The polymers used in PEUF process should exhibit selectivity for separated ions, good water solubility and sufficiently high molecular weight to be retained on the ultrafiltration membrane.

Many water-soluble polymers with different functional groups, such as amino, amide, hydroxyl, carboxyl and sulphonic groups, proved to be useful in enhancing the ultrafiltration separation of heavy metals [2,6–16]. Polyethyleneimine (PEI) is one of the most commonly used

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polymers. Due to the primary, secondary and tertiary amino groups, PEI molecules are capable of not only complexing heavy metal cations but also possess weak anion-exchanging properties. The polymer was applied to the PEUF separation of Ni(II), Cd(II), Co(II), Cu(II), Pb(II), Zn(II), Cr(III) [6–9], Cr(VI) [12,13] and Hg [16].

In real wastewater and solutions, heavy metals are often present in complex mixtures composed of several metal ions. Some works focus on metal separation from such multi-ion mixtures. Molinari et al. [17,18] applied ultrafiltration enhanced by PEI to heavy metal removal from binary Cu(II)/Ni(II) solutions. By the adjustment of pH and the amount of polymer used in the process, both the simultaneous removal of metals and their selective separation (one metal from the other) were possible. The amount of the polymer enhancing UF was also the crucial parameter determining the selective separation of Cu(II) from binary Cu(II)/Zn(II) solutions in ultrafiltration aided by poly(acrylic acid) [19]. Besides pH and polymer concentration, the ionic environment also affected bi-ionic mixture separation [20]. In PEUF enhanced by PEI, the presence (and concentration) of inert salt (e.g., $NaNO_3$) was the decisive factor for the selective separation of Cd(II) and Ni(II) from binary solutions.

In the present work, PEI was applied to UF separation of Zn(II) and Cr(VI) from binary model solutions. The effect of some basic process parameters, such as pH, the amount of PEI, the composition of the binary Zn(II)/Cr(VI) mixture and the presence of chlorides and sulphates on separation effectiveness was investigated, as well as the possibility of simultaneous removal of both metals and their selective separation was discussed.

2. Materials and methods

Stock solutions of Zn(II) and Cr(VI) with metal concentration of 1 mol/L were prepared, using appropriate inorganic salts: $Zn(NO_3)_2{\cdot}6H_2O$ and $K_2Cr_2O_7$, (POCH SA, Poland). Sodium chloride (NaCl) and sodium sulphate (Na_2SO_4) (POCH SA, Poland) were used as a source of $Cl^–$ and $SO_4^{2–}$ ions. PEI of average molecular weight ca. 750 kDa was provided as a 50% aqueous solution by Sigma-Aldrich Sp. z o.o., Poland. Model bi-ionic solutions were prepared by mixing appropriate amounts of metal stock solutions and PEI with or without an addition of chloride or sulphate salts. Aqueous solutions of NaOH and HNO_3 (POCH SA, Poland) were used as pH adjustment substances.

The investigations of three series of bi-ionic solutions with the total concentration of both metals C_M = 1 mmol/L and varying molar ratios of Zn(II) and Cr(VI) have been undertaken. The composition of each type of bi-ionic solution was expressed as the mole fraction of Zn(II) (X_{Zn}) in the binary Zn(II)/Cr(VI) mixture. The values of X_{Zn} were adjusted to: 0.9 (predominant concentration of Zn), 0.5 (equimolar solution), and 0.1 (predominant concentration of Cr), and the mass concentrations of the metals in question were: C_{Zn} = 58.8 mg/L, C_{Cr} = 5.2 mg/L; C_{Zn} = 32.7 mg/L, C_{Cr} = 26.0 mg/L and C_{Zn} = 6.5 mg/L, C_{Cr} = 46.8 mg/L, respectively. Each series of the solution was prepared, using three different amounts of PEI so that the molar ratios of PEI to the total amount of both metals (C_{PEI}/C_M) were 0.5; 1 and 5 (with respect to the repeat unit of the polymer). Five values of the solution pH were tested during the investigations, which were: 2, 4, 6, 8 and 10. The studies were carried out in the solutions supplemented with $Cl^–$ (10 mmol/L) or $SO_4^{2–}$ (10 mmol/L) as well as in the solutions without salt additives as a reference samples. Molar concentrations of investigated anions were set to values 10-times higher than the total concentration of Zn and Cr in order to observe the impact of the salt on the process effectiveness. The compositions of the three types of solutions are characterized in Table 1.

Before UF process, the feed solution was prepared by mixing appropriate volumes of Zn(II) and Cr(VI) stock solutions with water or salt-containing solution to achieve proper composition of binary mixture. Then, PEI is added to the solution to obtain established C_{PEI}/C_M concentration ratio. Subsequently, pH of the feed solution was adjusted to appropriate value, given in Table 1. The solution was stirred for 30 min prior to UF.

An AMICON 8400 stirred membrane cell supplied by Merck Millipore (Merck Sp. z o.o., Poland) was used to perform the ultrafiltration tests. The cell was equipped with an UltraFilic MW membrane with molecular weight cut-off of 50 kDa and effective membrane area of 38.5 cm^2 provided by GE Osmonics (Sterlitech Co., USA). Membrane was characterized experimentally in regard to water permeability: $3.7 \times 10^{–10}$ m^3/m^2 s Pa and contact angle: 37° (sessile drop method, goniometer PG-1, FIBRO System AB, Sweden).

Table 1
Compositions of the solutions containing bi-ionic Zn(II)/Cr(VI) mixture

Type of solution	C_M (mmol/L)	X_{Zn}	C_{PEI}:C_M	pH	C_{Cl} and C_{SO_4} (mmol/L)
I	Zn(II) – 0.9 Cr(VI) – 0.1	0.9	0.5; 1; 5	2; 4; 6; 8; 10	C_{Cl} – 0 and C_{SO_4} – 0 C_{Cl} – 10 and C_{SO_4} – 0 C_{Cl} – 0 and C_{SO_4} – 10
II	Zn(II) – 0.5 Cr(VI) – 0.5	0.5	0.5; 1; 5	2; 4; 6; 8; 10	C_{Cl} – 0 and C_{SO_4} – 0 C_{Cl} – 10 and C_{SO_4} – 0 C_{Cl} – 0 and C_{SO_4} – 10
III	Zn(II) – 0.1 Cr(VI) – 0.9	0.1	0.5; 1; 5	2; 4; 6; 8; 10	C_{Cl} – 0 and C_{SO_4} – 0 C_{Cl} – 10 and C_{SO_4} – 0 C_{Cl} – 0 and C_{SO_4} – 10

The ultrafiltration tests were carried out in a dead-end mode at a transmembrane pressure of 0.1 MPa. During the tests, a relatively small amount of permeate was collected, not exceeding 10% of the initial feed solution volume, to prevent the significant concentration of the solution.

The samples of the feed solutions and the permeates produced were acidified with concentrated nitric acid at a volume ratio acid : sample of 1:10 and then zinc and chromium contents were analysed, using a SpectrAA 880 atomic absorption spectrometer (Varian, Candela Sp. z o.o., Poland) with atomisation in the air–acetylene flame.

The Zn(II) and Cr(VI) concentrations measured were used to characterize process effectiveness by determining metal rejection coefficients R_{Zn}, R_{Cr} and selectivity coefficient $\alpha_{Cr/Zn}$ according to the following formulas:

$$R_{Zn} = 1 - \frac{C_{P_{Zn}}}{C_{F_{Zn}}} \quad \text{and} \quad R_{Cr} = 1 - \frac{C_{P_{Cr}}}{C_{F_{Cr}}} \tag{1}$$

$$\alpha_{Cr/Zn} = \frac{\dfrac{C_{P_{Cr}}}{C_{P_{Zn}}}}{\dfrac{C_{F_{Cr}}}{C_{F_{Zn}}}} \tag{2}$$

where C_F and C_P denote metal concentrations (Zn(II) and Cr(VI)) in the feed and permeate, respectively.

The impact of the process parameters on metal rejection coefficients was analysed, using the statistical nonparametric method. Spearman's rank correlation coefficients between R_{Zn} and R_{Cr} and the process parameters, such as pH, polymer/metal molar ratio C_{PEI}/C_M, composition of binary Zn(II)/Cr(VI) mixture (X_{Zn}) were determined, using STATISTICA 10 software (StatSoft Polska Sp. z o.o., Poland). The analysis was performed for the solutions without salt addition, as well as for the solutions containing chlorides or sulphates.

3. Results and discussion

Figs. 1–3 show the effectiveness of PEUF process of the bi-ionic Zn(II)/Cr(VI) mixtures with various compositions (X_{Zn}) and different molar C_{PEI}/C_M ratios. They depict zinc and chromium rejection coefficients (R_{Zn} and R_{Cr}) at various pH observed in the solutions containing Cl^-, SO_4^{2-}, as well as those without additional salt.

In all the solutions tested, an effect of pH on zinc rejection coefficient R_{Zn} of sigmoid-like character was found. Similar dependence of R_{Zn} on pH was also observed by other authors investigating an ultrafiltration assisted by PEI in separation of Zn(II) from aqueous solutions [21]. Generally, the effectiveness of zinc separation increased with an increase in pH, but there were some visible differences between the three types of the bi-ionic mixtures investigated in the study. In the solutions with the smallest PEI content ($C_{PEI}/C_M = 0.5$) and the predominant or equimolar amount of zinc in the bi-ionic mixture, low values of R_{Zn}, below 0.4, were observed at pH < 6 (Figs. 1(a) and (c)). In such conditions, the PEUF separation of Zn(II) ions was ineffective due to the low concentration of PEI, protonation of some part of amine groups (low pH) and the presence of other competing ions (Cr(VI) and optionally Cl^- or SO_4^{2-}).

In the solutions containing relatively small amounts of PEI (C_{PEI}/C_M of 0.5 and 1), probably insufficient for the effective binding of both metals, chromium retention coefficient R_{Cr} decreased significantly with an increase in chromium mole fraction in the bi-ionic mixture. The highest R_{Cr} values were observed in the pH range of 4–8 in the solutions with the predominant quantity of Zn(II) ($X_{Zn} = 0.9$, $X_{Cr} = 0.1$) and with no addition of Cl^- or SO_4^{2-}. In such conditions, 91% – 97% and 97% – 99% of chromium was separated in the UF process, for C_{PEI}/C_M equal to 0.5 and 1, respectively (Figs. 1(b) and 2(b)). In more acidic conditions (pH = 2), lower R_{Cr} values were observed, which might have been caused by the partial protonation of Cr(VI) anionic forms and lowering of the dissociation degree of chromic acid. In alkaline solution (pH = 10), the main amount of PEI is in the unprotonated form and is unable to bind anionic form of Cr(VI). A similar effect was also reported by Aroua et al. [13] and was observed in our previous works with the single-metal containing solution [12] as well as in the solutions containing bi-ionic Cu(II)/Cr(VI) mixture [22].

The addition of chlorides or sulphates in a molar amount 10-times greater than metal ions diminished significantly the Cr(VI) rejection coefficient. This was particularly visible in the presence of SO_4^{2-} ions when chromium removal effectiveness declined to 2%–14% and 12%–36% for C_{PEI}/C_M 0.5 and 1, respectively, at the pH range of 4–8 and $X_{Cr} = 0.1$.

The greater amount of polymer used in the process ($C_{PEI}/C_M = 5$) resulted in higher chromium rejection coefficients in all the series of solutions with various binary mixture composition, but still R_{Cr} values in the presence of chloride were slightly lower and in the presence of sulphate were significantly lower than those observed in the solution without added salt.

It may be concluded that the effectiveness of PEUF separation of chromium from Zn(II)/Cr(VI) binary mixtures depended on the presence of other anions in the solutions, particularly SO_4^{2-} ones. It was probably caused by the weak anion-exchange properties of PEI used in the process and the competition between the two types of metal ions and added anions in terms of their interaction with polymer amine groups.

The differences in the separation effectiveness of both metals (R_{Zn} and R_{Cr} values) caused a diversification of selectivity coefficient $\alpha_{Cr/Zn}$ values (Fig. 4). The value of $\alpha_{Cr/Zn}$ equal to 1 indicates the same degree of separation of Zn(II) and Cr(VI) ions. In this case, there was no selective separation of one metal from the other, and both metals were separated with high effectiveness (e.g., equimolar mixture of Zn(II) and Cr(VI), $C_{PEI}/C_M = 5$, pH 6 or 8) or both metals were poorly rejected on the UF membrane (e.g., equimolar mixture of Zn(II) and Cr(VI), $C_{PEI}/C_M = 0.5$, in the presence of SO_4^{2-} ions, pH = 2). When chromium rejection was greater than that of zinc, the values of $\alpha_{Cr/Zn}$ below 1 were observed (e.g., solutions with the predominant Zn(II) concentration in the bi-ionic mixture and a small amount of PEI [$C_{PEI}/C_M = 0.5$] at pH range 4–8). The selectivity coefficient $\alpha_{Cr/Zn}$ greater than 1 indicated a better separation of Zn(II) ions than Cr(VI) ones. Generally, high

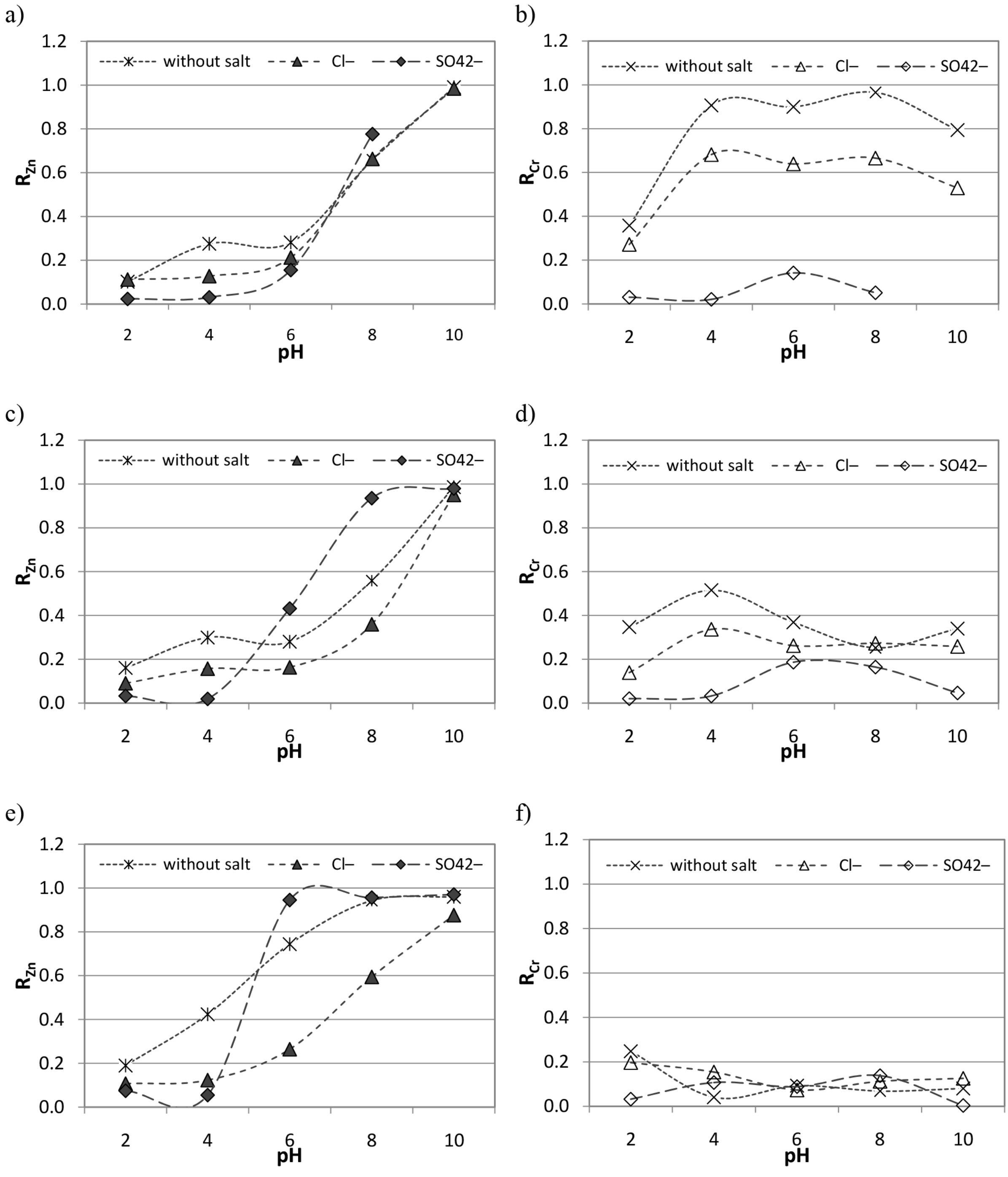

Fig. 1. R_{Zn} vs. pH (a, c, e) and R_{Cr} vs. pH (b, d, f). C_{PEI}/C_M = 0.5. (a) and (b) X_{Zn} = 0.9, X_{Cr} = 0.1, (c) and (d) X_{Zn} = 0.5, X_{Cr} = 0.5, (e) and (f) X_{Zn} = 0.1, X_{Cr}= 0.9.

$\alpha_{Cr/Zn}$ values were observed in each type of the tested bi-ionic mixture at pH = 10. The highest value $\alpha_{Cr/Zn}$ = 147 was found in the solution with molar fractions X_{Zn} = 0.9, X_{Cr} = 0.1 containing SO_4^{2-} anions, at pH = 10. A similar effect of $NaNO_3$ on metal ions separation in ultrafiltration enhanced by PEI was reported for Cd(II)/Ni(II) binary solution, where a decrease of Cd(II) rejection coefficient and an increase of selectivity of Ni(II) over Cd(II) was observed [20]. The importance of the amount of polymer enhancing ultrafiltration separation of heavy metals from binary mixtures was also reported by other authors. The increase of metal/polymer loading ratio improved the selectivity of separation of Zn(II) over Cu(II) in the process aided by partially ethoxylated PEI [23] and Cd(II) over Hg(II) in the process with PEI [24].

Tables 2–4 list the Spearman's rank correlation coefficients r_s determined using different grouping variables: pH (Table 2), bi-ionic mixture composition expressed as X_{Zn} (Table 3) and the polymer to metal molar ratio C_{PEI}/C_M

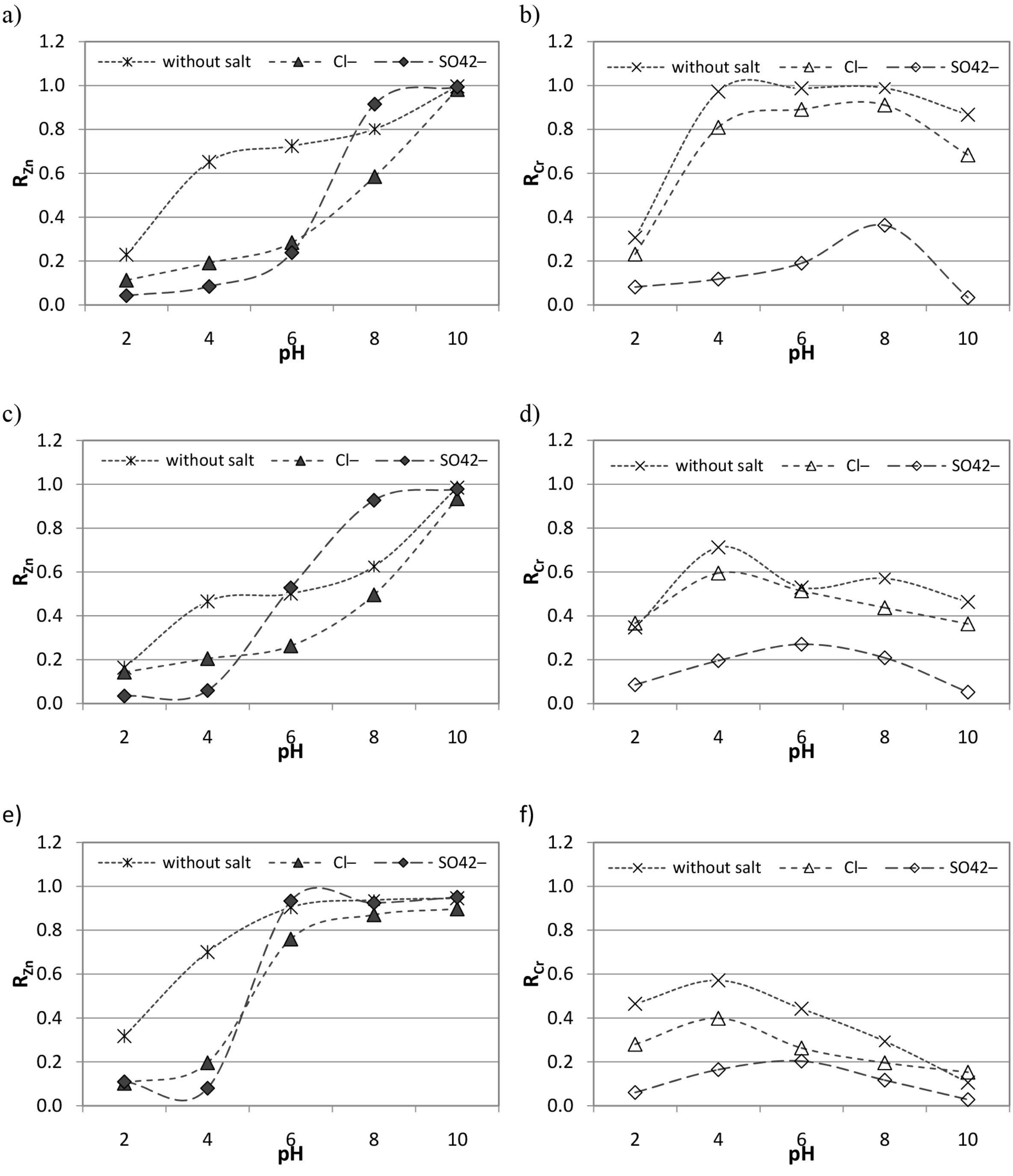

Fig. 2. R_{Zn} vs. pH (a, c, e) and R_{Cr} vs. pH (b, d, f). C_{PEI}/C_M = 1. (a) and (b) X_{Zn} = 0.9, X_{Cr} = 0.1, (c) and (d) X_{Zn} = 0.5, X_{Cr} = 0.5, (e) and (f) X_{Zn} = 0.1, X_{Cr} = 0.9.

(Table 4). The statistically significant coefficients at the significance level of 0.05 are written in bold.

In the solutions without an addition of Cl^- or SO_4^{2-} as well as those containing chlorides, a statistically significant strong positive correlation of both R_{Zn} and R_{Cr} coefficients with C_{PEI}/C_M ratio was observed within the pH range from acidic to weak basic values. This correlation indicates the crucial impact of the amount of polymer enhancing ultrafiltration on the separation effectiveness under such process conditions. The highest values of Spearman's rank correlation coefficients were observed at pH in the range of 4–6, due to the partial protonation of amine groups of PEI and competitive behaviour of both rejected metals.

In basic conditions (pH = 10), R_{Zn} showed a significant correlation with X_{Zn} in all the types of the solutions tested (without salt addition, with Cl^- or SO_4^{2-}). A similar correlation between R_{Cr} and X_{Zn} takes place in the solutions containing no salt additive or in the presence of chlorides. The correlation is positive, which indicates higher values of Zn(II) and Cr(VI) rejection in the solutions containing the greater amount of

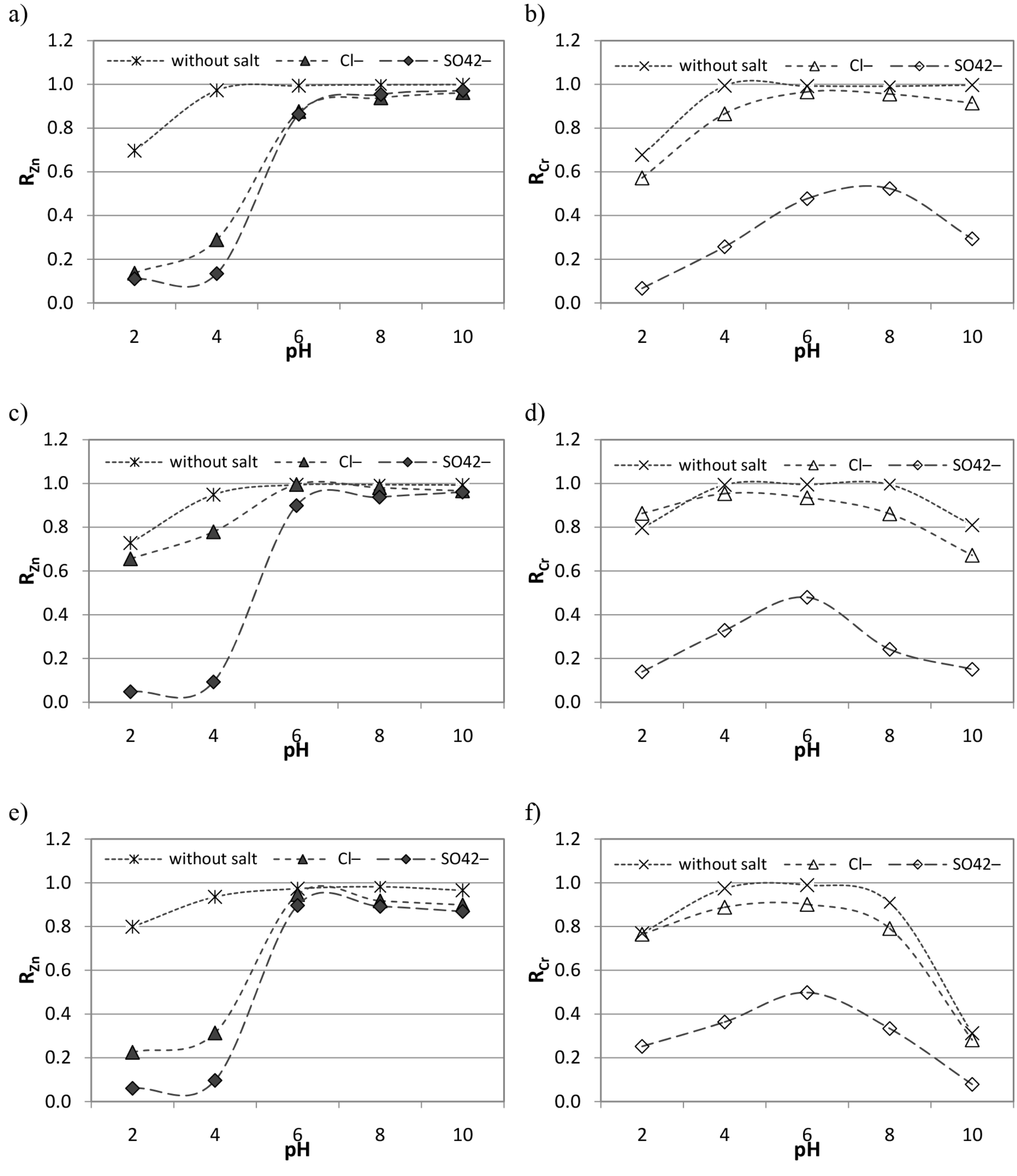

Fig. 3. R_{Zn} vs. pH (a, c, e) and R_{Cr} vs. pH (b, d, f). C_{PEI}/C_M = 5. (a) and (b) X_{Zn} = 0.9, X_{Cr} = 0.1, (c) and (d) X_{Zn} = 0.5, X_{Cr} = 0.5, (e) and (f) X_{Zn} = 0.1, X_{Cr}= 0.9.

Zn(II) in the bi-ionic Zn(II)/Cr(VI) mixture. In the mixtures with a sulphate additive, a strong significant positive correlation between R_{Cr} and C_{PEI}/C_M is visible at the whole pH range tested. In general, the presence of SO_4^{2-} lowers the chromium rejection coefficient so that R_{Cr} becomes more sensitive to the amount of polymer used in the process. A similar correlation between R_{Zn} and C_{PEI}/C_M occurs only when the partial protonation of amino groups is possible (pH = 4).

The Spearman's rank correlation coefficients r_s presented in Table 3 (grouping variable X_{Zn}) indicate a significant, positive correlation between R_{Zn} and pH, valid in all the types of the bi-ionic mixtures tested. The correlation was particularly strong when Zn(II) was the predominant metal in the binary Zn(II)/Cr(VI) system and chlorides or sulphates were added to the solution. A high r_s value was also observed in the equimolar mixture of both metals with the addition of SO_4^{2-}. So it can be concluded that pH is an important parameter affecting zinc separation, especially in Zn(II)-rich multi-ion solutions containing chlorides or sulphates. The amount of the polymer enhancing UF (C_{PEI}/C_M) reveals a significant,

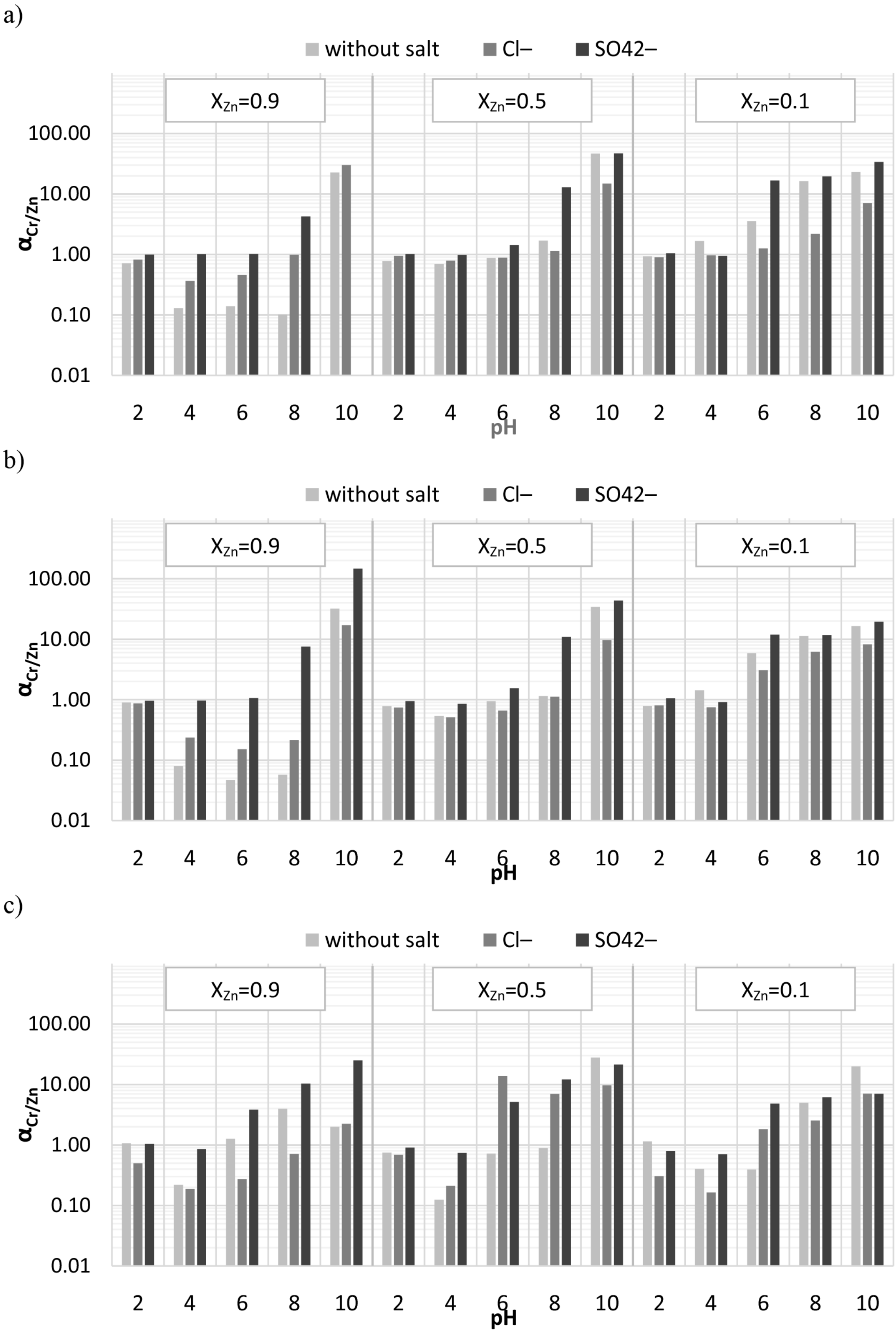

Fig. 4. Selectivity coefficient $\alpha_{Cr/Zn}$ at various pH in the solution without additional ions and in the presence of Cl^- and SO_4^{2-} ions. (a) $C_{PEI}/C_M = 0.5$; (b) $C_{PEI}/C_M = 1$; (c) $C_{PEI}/C_M = 5$.

Table 2
Spearman's rank correlation coefficients r_s, grouping variable: pH

	R_{Zn}			R_{Cr}		
	–	Cl^-	SO_4^{2-}	–	Cl^-	SO_4^{2-}
	pH = 2					
X_{Zn}	–0.1581	0.1054	–0.3689	0.1054	–0.0527	–0.1581
C_{PEI}/C_M	**0.8433**	**0.7906**	0.5270	**0.7379**	**0.8960**	**0.8433**
	pH = 4					
X_{Zn}	–0.0527	–0.0527	0.0527	0.4743	0.3162	–0.2635
C_{PEI}/C_M	**0.9487**	**0.9487**	**0.9487**	**0.8433**	**0.8433**	**0.9487**
	pH = 6					
X_{Zn}	–0.1581	–0.2108	**–0.7906**	0.4216	0.4743	–0.1054
C_{PEI}/C_M	**0.8433**	**0.8960**	0.2635	**0.8433**	**0.8433**	**0.9487**
	pH = 8					
X_{Zn}	–0.1054	–0.0527	–0.1581	0.6325	**0.6852**	0.3162
C_{PEI}/C_M	**0.7379**	**0.7379**	0.0527	**0.6852**	**0.6852**	**0.7379**
	pH = 10					
X_{Zn}	**0.8960**	**0.8960**	**0.7433**	**0.8960**	**0.8433**	0.4662
C_{PEI}/C_M	0.3162	0.0527	–0.4662	0.4216	0.5270	**0.8189**

Table 3
Spearman's rank correlation coefficients r_s, grouping variable: X_{Zn}

	R_{Zn}			R_{Cr}		
	–	Cl^-	SO_4^{2-}	–	Cl^-	SO_4^{2-}
	X_{Zn} = 0.9					
C_{PEI}/C_M	**0.6614**	0.2079	0.4286	**0.7559**	**0.6236**	**0.6756**
pH	**0.6983**	**0.9383**	**0.9139**	0.2400	0.4364	0.3920
	X_{Zn} = 0.5					
C_{PEI}/C_M	**0.6236**	**0.6425**	0.1512	**0.8693**	**0.9449**	**0.5858**
pH	**0.6437**	**0.6437**	**0.9492**	–0.0218	–0.1091	0.0982
	X_{Zn} = 0.1					
C_{PEI}/C_M	0.4725	0.4536	–0.2646	**0.8693**	**0.8693**	**0.6236**
pH	**0.7965**	**0.8074**	**0.7638**	–0.3055	–0.3382	–0.2510

positive, medium-strength correlation with R_{Zn} only in the solution with the highest tested Zn(II) molar fraction containing neither Cl^- nor SO_4^{2-} ions or in the solutions with equimolar ratio of Zn(II) and Cr(VI) in bi-ionic mixture with no addition of other anions or in the presence of chlorides.

Cr(VI) rejection coefficient correlated with C_{PEI}/C_M ratio and significant positive values of r_s were observed. The strength of this correlation was greater in the solutions with a higher chromium content without any additional anions or containing chlorides. Lower correlation coefficients were observed in sulphate-containing solutions, which may indicate that SO_4^{2-} ions decrease the effectiveness of Cr(VI) separation in the UF process enhanced with PEI.

The relationship between zinc rejection coefficient and pH is also confirmed by the data presented in Table 4. A significant positive correlation between R_{Zn} and pH was found in the whole range of PEI doses used in the tests, but the strength of this correlation was greater in the solutions with smaller PEI concentration. Taking into account the grouping variable $C_{PEI}/C_{M,}$ an impact of the bi-ionic mixture composition (X_{Zn}) on R_{Cr} can be observed. A positive significant correlation between those two variables was visible in the solutions without the addition of Cl^- or SO_4^{2-} as well as those containing chlorides and smaller doses of the polymer enhancing ultrafiltration. In such conditions, higher chromium rejection was achieved in the solutions with the lower chromium mole fraction in the binary Zn(II)/Cr(VI) mixture. The strength of this correlation diminished with an increase in C_{PEI}/C_M ratio.

4. Conclusions

PEI was an effective polymer enhancing ultrafiltration separation of Zn(II) and Cr(VI) ions from their binary aqueous solutions.

Table 4
Spearman's rank correlation coefficients r_s, grouping variable: C_{PEI}/C_M

	R_{Zn}			R_{Cr}		
	–	Cl^-	SO_4^{2-}	–	Cl^-	SO_4^{2-}
	$C_{PEI}/C_M = 0.5$					
X_{Zn}	–0.2079	0.0756	–0.4100	**0.9071**	**0.8693**	–0.0280
pH	**0.9165**	**0.9820**	**0.8736**	–0.0327	0.0109	0.3114
	$C_{PEI}/C_M = 1$					
X_{Zn}	–0.0756	–0.0567	–0.1323	**0.6048**	**0.6992**	0.1323
pH	**0.8838**	**0.9602**	**0.9166**	0.0218	0.0218	–0.1200
	$C_{PEI}/C_M = 5$					
X_{Zn}	0.5103	–0.0189	0.2457	**0.5858**	0.3969	0.0000
pH	**0.6983**	**0.7638**	**0.8511**	0.1528	–0.0109	0.1200

Zinc rejection coefficient increased with increasing pH and chromium rejection coefficient reached the highest values in the pH range of 6–8. Both zinc and chromium rejections were strongly affected by the amount of PEI used in the process and the composition of Zn(II)/Cr(VI) bi-ionic mixture. Generally, higher rejection coefficients of a given metal were obtained in the solutions containing larger amounts of the polymer and smaller mole fractions of the metal in question in the bi-ionic mixture. The addition of chlorides or sulphates to the solution diminished the retention coefficients of the analysed metals, which was particularly visible for Cr(VI) ions in the solutions with SO_4^{2-} anions added.

The effective simultaneous separation of the ions of both metals occurred at the pH range of 6–8 when the amount of PEI sufficient to bind the metals was present in the solution (here $C_{PEI}/C_M = 5$). The conditions enhancing the selective separation of Zn(II) ions from Zn(II)/Cr(VI) bi-ionic mixture were as follows: pH = 10, smaller amount of polymer used in the process and the presence of sulphate ions.

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