Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.11439

64 (2017) 437–446
February

Application of PEUF to competitive separation of Cu(II) and Cr(VI) from aqueous solutions containing chloride or sulphate ions

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Received 13 May 2016; Accepted 7 September 2016

ABSTRACT

The paper addresses the separation of Cu(II) and Cr(VI) ions from their binary mixtures by polymer enhanced ultrafiltration (PEUF). The tests were performed with solutions containing two types of anions: chlorides and sulphates. Polyethyleneimine (PEI), a water-soluble polymer containing amino groups, was used to aid the ultrafiltration separation of metal ions. The main parameters affecting the process effectiveness investigated herein included the composition of bi-ionic Cu(II)/Cr(VI) mixture, pH, polymer–metal molar ratio C_{PEI}/C_M and the presence of chloride or sulphate anions. The rejection coefficients of the metals in various process conditions were analysed, and the possibility of simultaneous separation of Cu(II) and Cr(VI) ions from the solutions as well as selective separation of one metal from the bi-ionic mixture was discussed.

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

1. Introduction

Recently, membrane separation techniques have become increasingly important in the environmental protection area. Membranes are used in gas separation processes, in water purification technologies and in municipal and industrial wastewater treatments. Many hazardous contaminants, heavy metal ions among them, can be removed from the aqueous environment using membrane processes.

Some membrane techniques, such as electrodialysis [1,2], Donnan dialysis [3], nanofiltration and reverse osmosis [4] or liquid membranes [5,6], give an opportunity for direct separation of heavy metals from aqueous solutions. Some other techniques need an enhancement by another process to be an effective separation method for these contaminants. Polymer enhanced ultrafiltration (PEUF) is one of the most important ones. This method (also known as: liquid-phase polymer-based retention (LPR), polymer-assisted ultrafiltration (PAUF) or complexation-ultrafiltration) uses water-soluble polymers with appropriate functional groups to bind heavy metal ions and form macromolecular complexes, which can be rejected on an ultrafiltration membrane. PEUF applied to the separation of heavy metals uses a wide variety of polymers with different functional groups, the amino, amide, hydroxyl, carboxyl and sulphonic groups being the most common.

Polyethyleneimine (PEI) is a water-soluble polymer containing primary, secondary and tertiary amino groups. It is widely used for the separation of heavy metals, such as: Cu(II), Ni(II), Pb(II), Cd(II), Zn(II), Cr(III) [7–10], with which it forms coordinate bonds. Due to its week anion-exchanging properties, PEI can also be applied to enhance the UF separation of Cr(VI) ions [9,11,12].

The effectiveness of the PEUF process is influenced by many factors, such as: type and amount of polymer, type and concentration of metal ions, pH, the presence of other ions in the solution and separation ability of an ultrafiltration membrane used in the process.

In some research works, binary mixtures of heavy metals have been investigated toward simultaneous separation of both metals, as well as selective separation of one metal from the other [13–16]. PEI was used to enhance the

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Presented at the conference on Membranes and Membrane Processes in Environmental Protection (MEMPEP 2016) Zakopane, Poland, 15–19 June 2016.

1944-3994/1944-3986

ultrafiltration removal of Cu(II) and Ni(II) from their bi-ionic solutions [13,14]. Adjustments to the pH and the amount of polymer enabled preferential copper removal or simultaneous removal of the metals to obtain metal-free water. The effectiveness of selective separation of heavy metals from binary solutions can also be affected by the ionic strength and the type of counter-ions. It was found that an addition of $NaNO_3$ improved the selective separation of Ni(II) from Ni(II)/Cd(II) binary solutions in the PEUF enhanced by PEI [15].

Due to previously proven ability to bind both cationic and anionic forms of heavy metals, PEI was used in the PEUF separation of Ni(II)/Cr(VI) bi-ionic mixtures [16]. Depending on the process conditions, a possibility of simultaneous or selective separation of metal ions was discussed.

In this work, the PEUF enhanced by PEI was employed to separate Cu(II) and Cr(VI) ions from binary mixtures containing chloride or sulphate anions. The impact of pH, the bi-ionic mixture composition, the polymer/metals molar ratio and the type of anion on the Cu(II) and Cr(VI) rejection coefficients was investigated.

2. Materials and methods

Inorganic salts $Cu(NO_3)_2{\cdot}3H_2O$ and $K_2Cr_2O_7$ (POCH SA, Poland) were used to prepare the solutions containing bi-ionic mixtures of Cu(II) and Cr(VI) ions. Appropriate sodium salts (NaCl and Na_2SO_4 [POCH SA, Poland]) constituted the source of chloride and sulphate ions. PEI with average molecular weight ca. 750 kDa (Sigma-Aldrich Sp. z o.o., Poland) enhanced the ultrafiltration process. pH adjustments were carried out by means of NaOH and HNO_3 solutions.

The research involved three series of solutions with various molar ratios of Cu(II) and Cr(VI) ions. The composition of bi-ionic mixture was expressed by the molar fraction of Cu(II) ions (X_{Cu}), which was adjusted as 0.1; 0.5 and 0.9. The total molar concentration of both metals (C_M) was constant and equalled 1 mmol dm^{-3}. The solutions were prepared with the addition of chloride or sulphate ions with the concentration of 10 mmol dm^{-3}. The metal ions were bound with PEI polymer, which was added to the solutions in four different amounts. The polymer to metals molar ratios C_{PEI}/C_M (with respect to the repeat unit of the polymer) was adjusted to: 0.5; 1; 5; 10. The solution pH in the ultrafiltration tests was maintained at: 2; 4; 6; 8 and 10. Table 1 gives a full description of the composition of the solutions.

The ultrafiltration tests enhanced with PEI were conducted using a stirred membrane cell Amicon 8400 (Merck Millipore, Merck Sp. z o.o., Poland). An UltraFilic MW membrane (molecular weight cutoff 50 kDa, effective area 38.5 cm^2) was supplied by GE Osmonics (Sterlitech Co.). The transmembrane pressure of 0.1 MPa was generated by compressed nitrogen. As the membrane cell worked in the dead-end mode, the volume of collected permeate amounted to 10% of the feed volume to enable both metals analyses and to avoid a significant concentration of the solution during the PEUF process.

The concentrations of the metals in the feed solutions and the permeates were analysed using atomic absorption spectrometry (SpectrAA 880, Varian, Candela Sp. z o.o., Poland) with atomisation in the air-acetylene flame. Prior to analysis, samples were acidified with concentrated nitric acid, at a volume ratio acid:sample equal to 1:10. The error of measurement did not exceed 2%, and the detection limit was 0.005 mg dm^{-3} for both analysed metals.

The process effectiveness was evaluated on the basis of the rejection coefficients (R_{Cu} and R_{Cr}):

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

and the selectivity coefficient $\alpha_{Cr/Cu}$:

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

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

The results have been discussed in relation to the effectiveness of the simultaneous separation of both metals as well as selective separation of one metal type from the bi-ionic mixture.

For both types of the solutions (containing Cl^- and SO_4^{2-} ions), Spearman's rank correlation coefficients between the process parameters (pH, molar ratio C_{PEI}/C_M, bi-ionic mixture composition [X_{Cu}]) and retention coefficients R_{Cu} and R_{Cr} were determined. Spearman's rank correlation is a convenient statistical technique that allows to determine whether a monotonic (even if nonlinear) relationship between two variables exists. It is a nonparametric method and can be used at any probability distribution of the analysed variables. The values of Spearman's rank correlation coefficient can change from –1 (perfect negative monotone relationship) to +1 (perfect positive monotone relationship). The statistical analysis was performed using STATISTICA 10 software (StatSoft Polska Sp. z o.o., Poland).

3. Results and discussion

Figs. 1–4 present the metal rejection coefficients R_{Cu} and R_{Cr} as well as the selectivity coefficient $\alpha_{Cr/Cu}$ achieved during

Table 1
Characteristics of the solutions containing bi-ionic mixture of Cu(II) and Cr(VI) ions

Type of solution	C_M mmol dm^{-3} (mg dm^{-3})	X_{Cu}	C_{Cl} or C_{SO4} mmol dm^{-3}	C_{PEI}:C_M	pH
I	Cu(II) – 0.9 (57.2) Cr(VI) – 0.1 (5.2)	0.9	10	0.5; 1; 5; 10	2; 4; 6; 8; 10
II	Cu(II) – 0.5 (31.8) Cr(VI) – 0.5 (26.0)	0.5	10	0.5; 1; 5; 10	2; 4; 6; 8; 10
III	Cu(II) – 0.1 (6.4) Cr(VI) – 0.9 (46.8)	0.1	10	0.5; 1; 5; 10	2; 4; 6; 8; 10

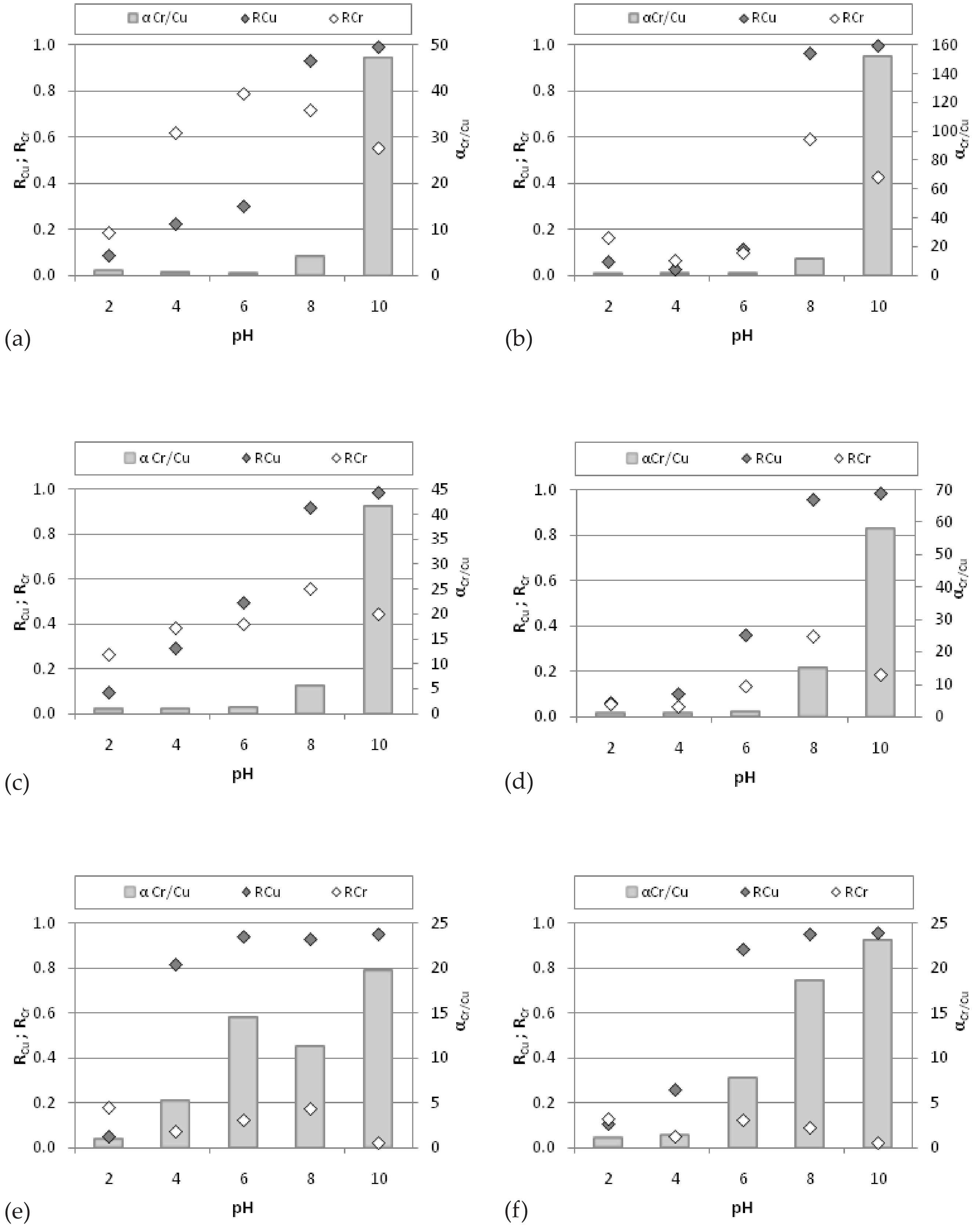

Fig. 1. R_{Cu}, R_{Cr} and $\alpha_{Cr/Cu}$ vs. pH. $C_{PEI}/C_M = 0.5$: (a) $X_{Cu} = 0.9$, $X_{Cr} = 0.1$, Cl^- ions; (b) $X_{Cu} = 0.9$, $X_{Cr} = 0.1$, SO_4^{2-} ions; (c) $X_{Cu} = 0.5$, $X_{Cr} = 0.5$, Cl^- ions; (d) $X_{Cu} = 0.5$, $X_{Cr} = 0.5$, SO_4^{2-} ions; (e) $X_{Cu} = 0.1$, $X_{Cr} = 0.9$, Cl^- ions; and (f) $X_{Cu} = 0.1$, $X_{Cr} = 0.9$, SO_4^{2-} ions.

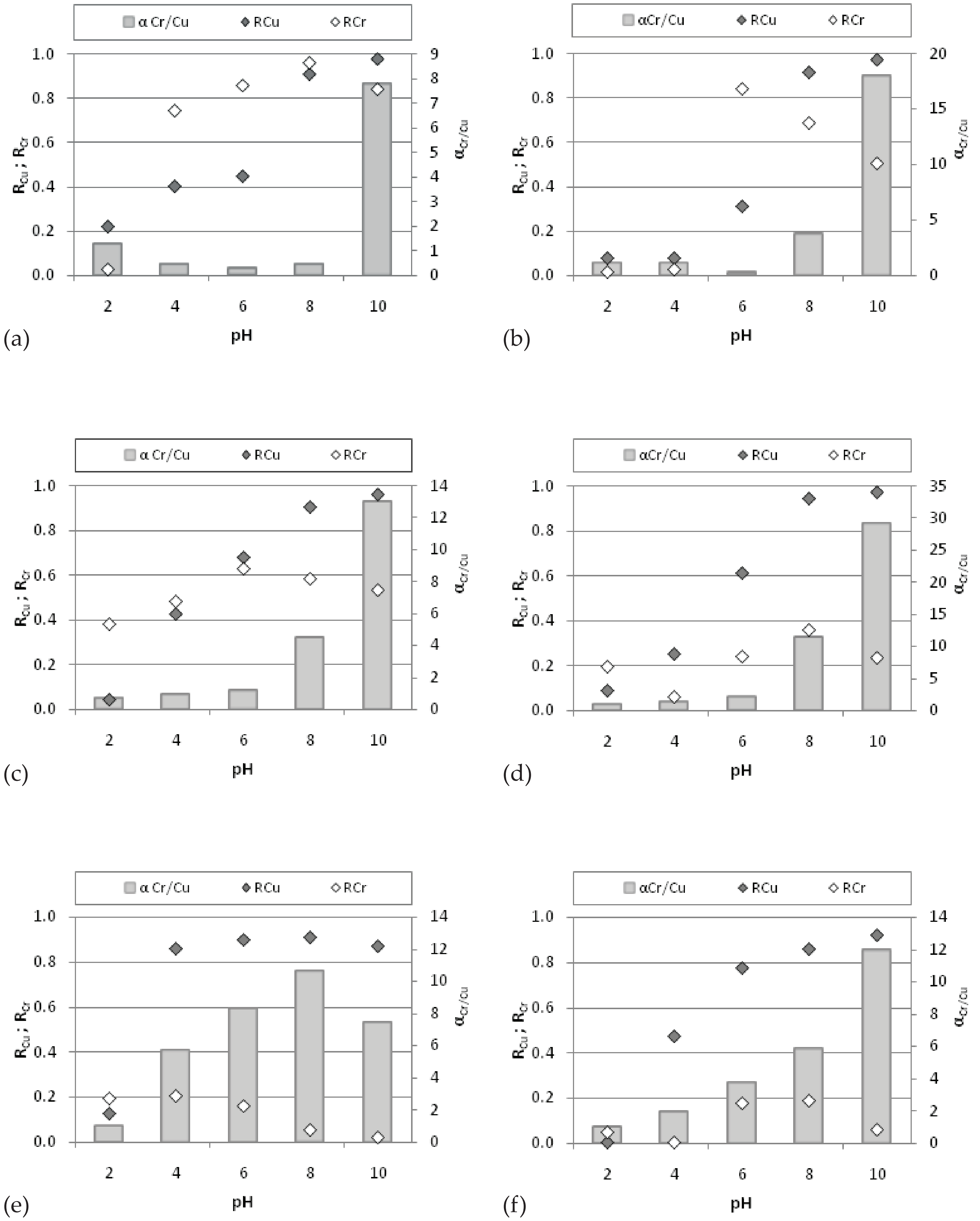

Fig. 2. R_{Cu}, R_{Cr} and $\alpha_{Cr/Cu}$ vs. pH. $C_{PEI}/C_M = 1$: (a) $X_{Cu} = 0.9$, $X_{Cr} = 0.1$, Cl^- ions; (b) $X_{Cu} = 0.9$, $X_{Cr} = 0.1$, SO_4^{2-} ions; (c) $X_{Cu} = 0.5$, $X_{Cr} = 0.5$, Cl^- ions; (d) $X_{Cu} = 0.5$, $X_{Cr} = 0.5$, SO_4^{2-} ions; (e) $X_{Cu} = 0.1$, $X_{Cr} = 0.9$, Cl^- ions; and (f) $X_{Cu} = 0.1$, $X_{Cr} = 0.9$, SO_4^{2-} ions.

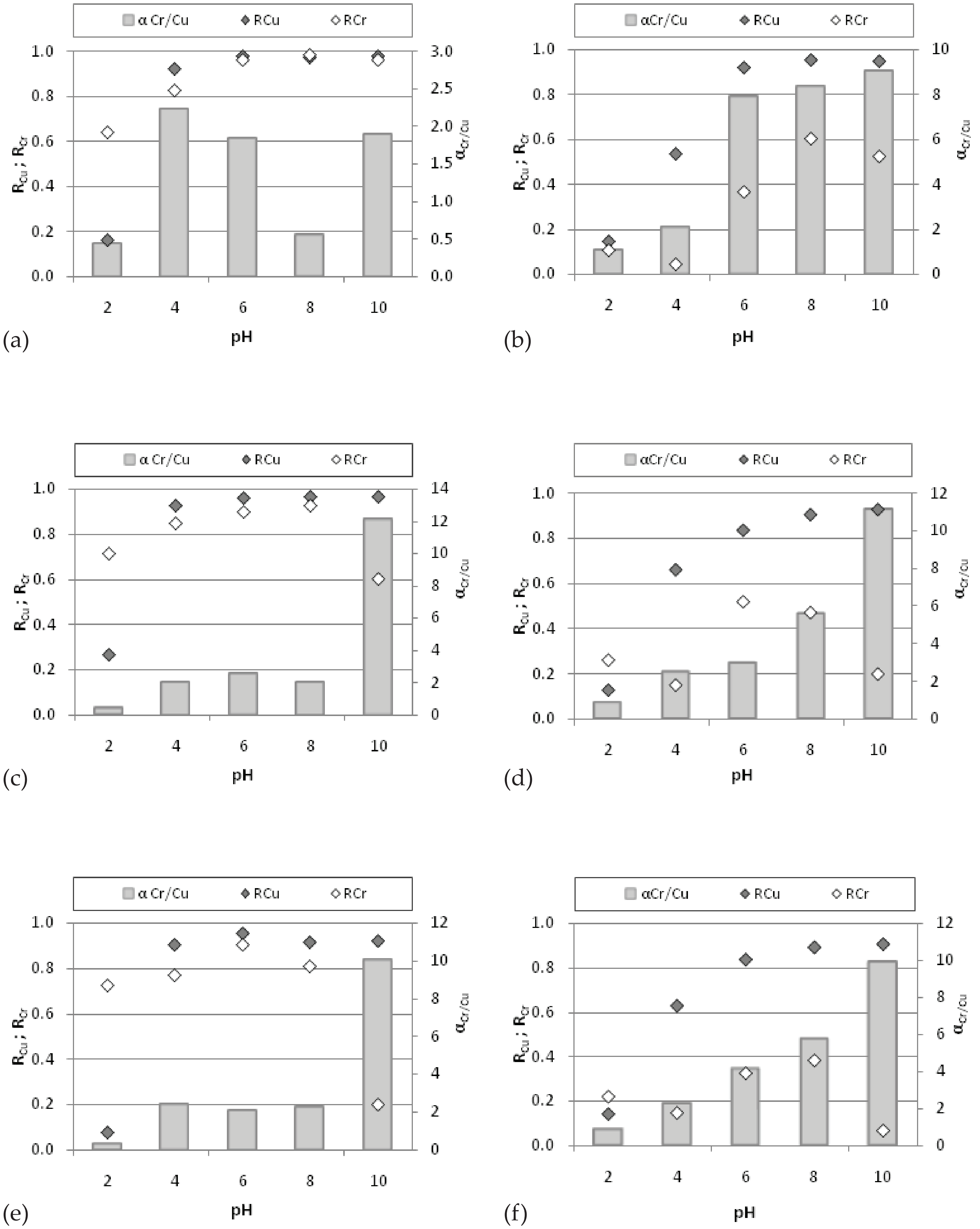

Fig. 3. R_{Cu}, R_{Cr} and $\alpha_{Cr/Cu}$ vs. pH. $C_{PEI}/C_M = 5$: (a) $X_{Cu} = 0.9$, $X_{Cr} = 0.1$, Cl^- ions; (b) $X_{Cu} = 0.9$, $X_{Cr} = 0.1$, SO_4^{2-} ions; (c) $X_{Cu} = 0.5$, $X_{Cr} = 0.5$, Cl^- ions; (d) $X_{Cu} = 0.5$, $X_{Cr} = 0.5$, SO_4^{2-} ions; (e) $X_{Cu} = 0.1$, $X_{Cr} = 0.9$, Cl^- ions; and (f) $X_{Cu} = 0.1$, $X_{Cr} = 0.9$, SO_4^{2-} ions.

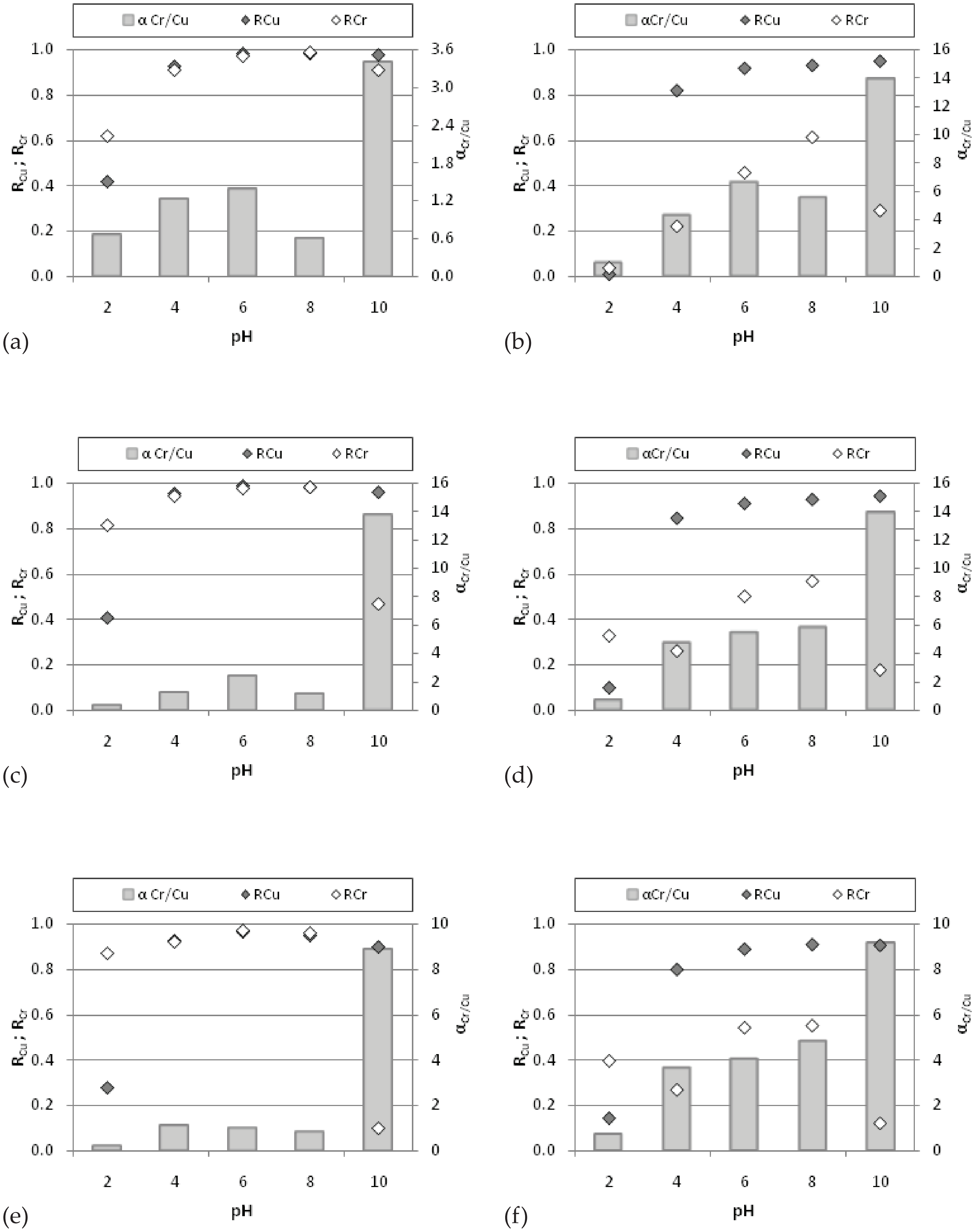

Fig. 4. R_{Cu}, R_{Cr} and $\alpha_{Cr/Cu}$ vs. pH. $C_{PEI}/C_M = 10$: (a) $X_{Cu} = 0.9$, $X_{Cr} = 0.1$, Cl^- ions; (b) $X_{Cu} = 0.9$, $X_{Cr} = 0.1$, SO_4^{2-} ions; (c) $X_{Cu} = 0.5$, $X_{Cr} = 0.5$, Cl^- ions; (d) $X_{Cu} = 0.5$, $X_{Cr} = 0.5$, SO_4^{2-} ions; (e) $X_{Cu} = 0.1$, $X_{Cr} = 0.9$, Cl^- ions; and (f) $X_{Cu} = 0.1$, $X_{Cr} = 0.9$, SO_4^{2-} ions.

the PEUF process of the binary Cu/Cr solutions of various compositions (various copper molar fractions X_{Cu}) and different molar C_{PEI}/C_M ratio. Each figure shows a direct comparison of the process results for the solutions containing Cl^- and $\mathrm{SO_4}^{2-}$ ions.

Analysing results on Figs. 1–4, it can be concluded that copper and chromium rejection coefficients depend on pH, the amount of PEI aiding the ultrafiltration process, the composition of the bi-ionic Cu/Cr mixture and the presence of Cl^- or $\mathrm{SO_4}^{2-}$ ions.

In all the solutions tested in the PEUF process, the effectiveness of Cu(II) separation increased with increasing basicity of the solutions. Generally, the lowest R_{Cu} values in each series of the solutions tested were achieved at pH = 2, which was due to the protonation of polymer functional (amine) groups. The effectiveness of copper separation in such acidic conditions changed from several percentages to ca. 40% in the solutions containing Cl^- ions and the largest polymer dose (Fig. 4). It needs to be emphasised that under similar conditions (pH = 2, $C_{\mathrm{PEI}}/C_M = 10$) the copper rejection coefficient was much lower in the solutions containing $\mathrm{SO_4}^{2-}$ ions. It can be explained by the anion-exchange properties of the polymer used and the presence of sulphate ions competing with Cu and Cr in the separation process.

The increase in pH caused a substantial increase in the copper rejection coefficient, and high R_{Cu} values (over 0.8–0.9) were observed in the pH ranges of 8–10 and 4–10, depending on the polymer amount and composition of the bi-ionic solution. Generally, the higher C_{PEI}/C_M ratio and the lower Cu(II) molar fraction in the binary mixture, the wider the pH range of effective copper separation. Comparing both types of anions (Cl^- and $\mathrm{SO_4}^{2-}$), at medium pH values (particularly at pH = 4), a slightly lower rejection of copper was achieved in the solution containing sulphate ions.

The effectiveness of Cr(VI) separation also depended significantly on the PEUF process conditions. Relatively low chromium rejection coefficients R_{Cr} were observed in the series of solutions with lower polymer doses ($C_{\mathrm{PEI}}/C_M = 0.5$, $C_{\mathrm{PEI}}/C_M = 1$) and higher chromium concentrations ($X_{\mathrm{Cu}} = 0.1$, $X_{\mathrm{Cr}} = 0.9$). Regardless of the pH, R_{Cr} did not exceed 0.2 under these conditions, while R_{Cu} at the pH range of 4–10 (Cl^- ions present in the solutions) or 6–10 ($\mathrm{SO_4}^{2-}$ ions in the solutions) was very high (Figs. 1(e) and (f) and Figs. 2(e) and (f)). This indicates that the amount of polymer was insufficient to enhance the separation of both metals present in the solution and copper(II) was preferentially bound by the functional groups of PEI. A similar phenomenon was reported during the PEI enhanced ultrafiltration of binary Cu(II)/Ni(II) mixture carried out in a diafiltration mode with a relatively small amount of polymer applied [13]. It was observed that copper is selectively complexed by the polymer and retained in the retentate and nickel was gradually leached into permeate.

Effective Cr(VI) separation took place in chloride-containing solutions when the PEUF process was carried out with a greater amount of PEI ($C_{\mathrm{PEI}}/C_M = 5$, $C_{\mathrm{PEI}}/C_M = 10$). The most satisfactory results were achieved at the pH range of 4–8 and $C_{\mathrm{PEI}}/C_M = 10$, where chromium rejection coefficients of 0.92–0.99 were observed (Figs. 4(a), (c), and (e)). These conditions also resulted in high R_{Cu} levels, which indicates a sufficient quantity of polymer to bind the two metals effectively. When $\mathrm{SO_4}^{2-}$ ions were present in the solution (instead of Cl^-), significantly lower chromium rejection coefficients were recorded, which is visible in Figs. 4(b), (d), and (f). In this series of the solutions, the highest R_{Cr} values within the range of 0.55–0.61 (depending on the solution composition, X_{Cu}) were noted at pH = 8. The comparison of the effectiveness of Cr(VI) separation from the solutions containing Cl^- or $\mathrm{SO_4}^{2-}$ ions proves that the presence of sulphate anions lowers the removal of metal ions (especially Cr(VI)), which may be due to the competitive interaction of $\mathrm{SO_4}^{2-}$ ions with the polymer that is a weak anion exchanger.

The dependence of R_{Cr} on pH indicates lower rejection coefficients under the most acidic (pH = 2) and the most basic (pH = 10) conditions. Most likely, in the acidic solutions protonation of Cr(VI) anionic forms occurs, which makes them less dissociated. In the basic solutions, hydroxide OH^- ions compete with Cr(VI), obstructing chromium separation. The decrease of Cr(VI) rejection values at pH > 9 was also observed during ultrafiltration of Cr(VI) model solutions aided by PEI [9].

The selectivity coefficients $\alpha_{\mathrm{Cr/Cu}}$ observed in the PEUF of bi-ionic Cu(II)/Cr(VI) mixtures differed significantly depending on the process conditions. Comparing the two types of anions (chlorides and sulphates), it can be concluded that $\alpha_{\mathrm{Cr/Cu}}$ values were generally higher when the solutions contained $\mathrm{SO_4}^{2-}$ ions. As mentioned before, the presence of sulphate ions in the solution lowered the effectiveness of Cr(VI) separation (and raised the $\alpha_{\mathrm{Cr/Cu}}$ coefficient). The lowest value of the $\alpha_{\mathrm{Cr/Cu}}$ coefficient was observed in the solution containing chlorides and a significant amount of Cr(VI) ions ($X_{\mathrm{Cr}} = 0.9$; $X_{\mathrm{Cu}} = 0.1$), when the PEUF process was conducted using the highest C_{PEI}/C_M ratio, at pH = 2. In these conditions, $\alpha_{\mathrm{Cr/Cu}}$ amounted to 0.18, and the rejection coefficients were $R_{\mathrm{Cu}} = 0.28$ and $R_{\mathrm{Cr}} = 0.87$. The highest $\alpha_{\mathrm{Cr/Cu}}$ value was found in the solution containing sulphates, and the prevailing amount of Cu(II) ions when the lowest C_{PEI}/C_M ratio ($C_{\mathrm{PEI}}/C_M = 0.5$) was used, and the pH was equal to 10 ($\alpha_{\mathrm{Cr/Cu}} = 151$, and $R_{\mathrm{Cu}} = 0.996$, $R_{\mathrm{Cr}} = 0.43$). To sum up, it has been found that for all three series of the solutions the highest selectivity coefficients were observed when the smallest tested polymer dose was applied in the process (Fig. 1). A similar impact of the polymer content on the selectivity coefficient was stated during the Cu(II)/Zn(II) binary mixture ultrafiltration process enhanced by partially ethoxylated polyethyleneimine (PEPEI) [17].

The results indicate that the PEUF separation process assisted by PEI enables partial selective separation of Cu(II) and Cr(VI) from their bi-ionic solutions containing chlorides or sulphates, which is confirmed by significant differences in the rejection coefficients of both metals. Effective simultaneous separation of both metals is feasible in the solutions containing chlorides when sufficient amount of polymer is used and the solution pH ranges between 4 and 8.

Tables 2–4 present Spearman's rank correlation coefficients determined on the basis of different grouping variables: pH (Table 2), the molar fraction of Cu(II) in the bi-ionic mixture X_{Cu} (Table 3) and the polymer to metals molar ratio C_{PEI}/C_M (Table 4). The statistically significant coefficients at the significance level of 0.05 are presented in bold.

The solutions containing chloride ions exhibited statistically significant positive correlations between the copper molar fraction X_{Cu} and the metal rejection coefficients R_{Cr} and

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

	R_{Cu}		R_{Cr}	
	Cl^-	SO_4^{2-}	Cl^-	SO_4^{2-}
	pH = 2			
X_{Cu}	0.296	–0.266	–0.148	–0.443
C_{PEI}/C_M	**0.691**	0.389	**0.864**	0.389
	pH = 4			
X_{Cu}	–0.059	–0.237	0.237	–0.089
C_{PEI}/C_M	**0.907**	**0.907**	**0.907**	**0.713**
	pH = 6			
X_{Cu}	–0.089	–0.089	0.296	0.148
C_{PEI}/C_M	**0.864**	**0.734**	**0.907**	**0.734**
	pH = 8			
X_{Cu}	0.325	0.532	**0.591**	**0.798**
C_{PEI}/C_M	**0.605**	–0.475	**0.756**	0.453
	pH = 10			
X_{Cu}	**0.857**	**0.591**	**0.917**	**0.946**
C_{PEI}/C_M	–0.346	**–0.691**	0.259	0.043

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

	R_{Cu}		R_{Cr}	
	Cl^-	SO_4^{2-}	Cl^-	SO_4^{2-}
	X_{Cu} = 0.9			
C_{PEI}/C_M	0.357	0.101	**0.605**	0.062
pH	**0.803**	**0.877**	**0.546**	**0.699**
	X_{Cu} = 0.5			
C_{PEI}/C_M	0.403	0.078	**0.768**	**0.535**
pH	**0.779**	**0.914**	0.080	0.227
	X_{Cu} = 0.1			
C_{PEI}/C_M	0.186	0.023	**0.721**	**0.682**
pH	**0.576**	**0.932**	–0.374	–0.141

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

	R_{Cu}		R_{Cr}	
	Cl^-	SO_4^{2-}	Cl^-	SO_4^{2-}
	C_{PEI}/C_M = 0.5			
X_{Cu}	–0.113	–0.094	**0.832**	0.472
pH	**0.927**	**0.917**	0.164	0.327
	C_{PEI}/C_M = 1			
X_{Cu}	0.000	–0.057	**0.850**	0.416
pH	**0.906**	**0.938**	0.153	**0.546**
	C_{PEI}/C_M = 5			
X_{Cu}	0.510	0.246	0.435	0.189
pH	**0.698**	**0.906**	0.229	0.393
	C_{PEI}/C_M = 10			
X_{Cu}	0.340	0.265	0.151	–0.094
pH	**0.556**	**0.884**	0.131	0.164

R_{Cu} at high pH values (pH 10, correlation $X_{Cu} - R_{Cu}$, pH 8–10, correlation $X_{Cu} - R_{Cr}$). Similar statistically significant relationships were found in the solutions containing sulphate ions with lower $X_{Cu} - R_{Cu}$ and higher $X_{Cu} - R_{Cr}$ correlation coefficients. Previous studies of bi-ionic mixtures of Cu(II)/Cr(VI) with no chlorides or sulphates additives revealed similar statistically significant correlations in a wider pH range (pH 8–10, correlation $X_{Cu} - R_{Cu}$, pH 6–10, correlation $X_{Cu} - R_{Cr}$) [18]. It can be concluded that the presence of additional anions in the solutions (especially sulphates) diminished the impact of the bi-ionic mixture composition on the separation effectiveness in the neutral and weakly basic range of pH values. It may be explained by the competitive interaction of anions with PEI functional groups.

The solutions containing chloride ions showed a positive correlation between the C_{PEI}/C_M concentration ratio and the retention coefficients R_{Cu} and R_{Cr} in the pH range 2–8, wherein the highest strength of this correlation is at pH 4–6. A similar correlation was observed in the pH range of 4–6 in the solutions containing sulphate ions.

Thus, it can be concluded that when chloride ions were present in the solutions, the amount of PEI used in the process was the main parameter affecting Cu(II) and Cr(VI) rejection coefficients at the lower and medium pH values. At higher pH values, the composition of the binary mixture constituted the important parameter affecting Cu(II) and Cr(VI) separation.

A similar dependence was observed in the solutions containing sulphates; however, there was no significant effect of the PEI concentration on Cu(II) and Cr(VI) separation at pH = 2, which may be due to an interaction of sulphate ions with protonated PEI amino groups.

Analysing the composition of the bi-ionic mixture (grouping variable X_{Cu}, Table 3), a significant positive correlation between the copper retention ratio R_{Cu} and pH was determined for both types of solutions containing chlorides and sulphates. In the case of solutions containing Cl^-, the correlation coefficients decreased with decreasing copper content in the bi-ionic mixture, while when SO_4^{2-} anions were present in solutions the pH – R_{Cu} correlation coefficients increased and had generally higher values. This indicates that an increase in pH leads to an increase in copper rejection coefficients mainly in the solutions with a greater amount of copper and chlorides, as well as in the solutions containing greater amounts of chromium and sulphates.

The solutions containing chloride or sulphate anions and a prevailing amount of copper in the bi-ionic mixture revealed a significant positive correlation of medium strength between pH and R_{Cr}. However, the correlation was not found in the solutions with a greater chromium molar fraction. When the solutions contained an equimolar Cu(II)/Cr(VI) mixture or a predominant Cr(VI) quantity, a significant positive correlation between the C_{PEI}/C_M ratio and R_{Cr} was observed. It was valid for both types of solutions containing Cl^- or SO_4^{2-}, wherein the strength of this correlation was higher in the chloride-containing solutions. The analysis of R_{Cr} changes leads to the conclusion that pH primarily affects the chromium rejection coefficient in the solutions with a predominant quantity of copper while in the remaining bi-ionic mixtures R_{Cr} was affected by the amount of PEI used in the PEUF process.

Spearman's rank correlation coefficients determined using C_{PEI}/C_M grouping variable indicate the existence of a significant positive correlation between pH and the copper rejection coefficient in the whole C_{PEI}/C_M range and for both types of solutions. In the chloride-containing solutions, the influence of pH on R_{Cu} becomes weaker with an increasing amount of PEI aiding ultrafiltration. pH is an important parameter affecting the efficiency of Cu(II) complexation by polymer functional groups. At lower pH values, due to the protonation of some part of amino groups, copper separation might be less effective. As the amount of polymer in the solution increases, the process becomes less sensitive to pH changes. In the solutions containing sulphates, the dependence between pH and R_{Cu} is strong, regardless of the C_{PEI}/C_M value (in the analysed range). This may confirm the competitive effect of sulphate ions. Even if the PEI concentration is relatively high, the copper separation in the PEUF process is strongly dependent on pH because a part of the polymer interacts with SO_4^{2-} ions and is not capable of binding Cu(II).

A significant and strong correlation of X_{Cu} and R_{Cr} was found in the chloride-containing solutions when lower C_{PEI}/C_M concentration ratios of 0.5 and 1 were used. In the case of low polymer concentration and the presence of Cl^- ions, the separation of Cr(VI) depends on the bi-ionic mixture composition, which is also visible in Figs. 1(a), (c), and (e) and Figs. 2(a), (c), and (d). A similar relationship was found in the Cu(II)/Cr(VI) solutions without the addition of chlorides but the correlation coefficients were statistically significant in the whole range of C_{PEI}/C_M [18].

4. Conclusions

PEI proved to be an effective polymer aiding the ultrafiltration removal of Cu(II) and Cr(VI) from their binary solutions containing chloride or sulphate ions.

The effectiveness of the PEUF process was influenced by several parameters, such as pH, the quantity of polymer in relation to the amount of metals, the bi-ionic Cu(II)/Cr(VI) mixture composition and the type of accompanying anions. Variable process conditions produced diversified rejection coefficients of both metals. Simultaneous effective separation of Cu(II) and Cr(VI) was possible in the solutions containing chlorides and a sufficient amount of PEI ($C_{PEI}/C_M = 10$), at the pH range of 4–8. In such conditions, 91%–99% of chromium and 92%–99% of copper was removed from the solution in the ultrafiltration process. Significant differences between Cu(II) and Cr(VI) retention coefficients were found during treatment of the solutions with the prevailing amount of chromium at pH = 10 (high R_{Cu} and low R_{Cr} were observed). The greatest differences were found when the smallest amount of PEI was used in the PEUF process, that is, $R_{Cr} = 0.02$ and R_{Cu} 0.95 or 0.96 for chlorides or sulphates present in the solution, respectively. Such significant differences in the rejection coefficients for both metals indicate the possibility of selective removal of one metal from the bi-ionic mixture.

A comparison of both types of anions indicates that the presence of sulphate ions in the solutions diminishes the separation effectiveness of the metals, especially the rejection of Cr(VI) ions, due to the competitive interaction of SO_4^{2-} ions with the polymer functional groups.

Spearman's rank correlation analysis enabled the assessment of the effect of the process parameters on the Cu(II) and Cr(VI) rejection coefficients. It indicated a relationship between metal rejection coefficients R_M (R_{Cu} and R_{Cr}) and C_{PEI}/C_M ratio at the pH ranges 2–8 (chloride-containing solutions) and 4–6 (sulphate-containing solutions), as well as the relationship between R_M and X_{Cu} at the pH = 10, which is particularly strong in the case of R_{Cr}. Regardless of the bi-ionic mixture composition, R_{Cu} correlated well with pH, while R_{Cr} was mainly influenced by the C_{PEI}/C_M ratio. When the PEUF process was carried out with low PEI quantity and chloride anions were present in the solutions, Cr(VI) rejection was affected by the bi-ionic mixture composition.

Acknowledgement

This work was supported by the Silesian University of Technology (Project No. BK- 270/RIE4/2015).

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