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# Modeling of Cu(II) and Cr(VI) ions PEUF separation from the bi-ionic mixtures containing sulfates

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**ABSTRACT**

Application of nonlinear regression methods for modeling of the polymer enhanced ultrafiltration (PEUF) effectiveness was proposed. Separation of Cu(II) and Cr(VI) ions (bi-ionic mixtures) in the sulfates environment was experimentally tested. Polyethyleneimine (PEI) was chosen as a polymer aiding the ultrafiltration process. Selection of PEI resulted of the amine groups presence within its structure. In effect, the polymer is well water soluble, demonstrates the ability of binding metal cations, as well as it has weak anion exchange properties. Experimental analysis of the PEUF process covered 3 bi-ionic Cu(II)/Cr(VI) mixtures of different metals mole fractions, pH within 2–10 range and polymer/metals molar ratio $C_{PEI}/C_M$ from 0.5 to 10. Based on measurement data, the nonlinear empirical models were elaborated for prediction of Cu(II) and Cr(VI) retention coefficients, as well as their selective separation effectiveness. The largest differences in retention coefficients of chromium(VI) and copper(II) were reported for their bi-ionic mixtures with prevailing chromium molar fraction, at high pH and relatively small PEI dose. Concentration of the bi-ionic mixture initially of 0.9 mmol dm$^{-3}$ Cr(VI) and 0.1 mmol dm$^{-3}$ Cu(II) at pH 10 with molar ratio $C_{PEI}/C_M = 0.5$ resulted in 9.5-time growth of copper concentration in retentate and 1.5-time chromium concentration raise.

*Keywords:* Polymer enhanced ultrafiltration (PEUF); Bi-ionic mixture; Cu(II); Cr(VI); Polyethyleneimine (PEI); Empirical nonlinear model

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## 1. Introduction

Membrane techniques are commonly used in environmental engineering as efficient methods of gas components separation, water purification and wastewater treatment. These techniques are also combined with other separation methods, thus forming integrated or hybrid membrane systems. One of such hybrid methods, enabling efficient separation of heavy metal ions from the solutions, is the polymer enhanced ultrafiltration (PEUF).

The method is based on application of soluble polymers containing functional groups capable of binding the selected heavy metal ions. Produced macromolecular structures can be more effectively separated with classical ultrafiltration method. As the ultrafiltration enhancement agents, the chelating polymers, which form coordination bonds with the metal ions, can be used. Some polyelectrolytes of ion-exchange properties are found to be useful, as well. Polymers such as chitosane [1], polyethyleneimine (PEI), ethoxylated polyethyleneimine (EPEI), poly(vinyl alcohol) (PVA) [2,3], poly(acrylic acid) (PAA) [4], poly(acrylic acid-co-maleic acid) (PACMA) [2,5], poly(diallyldimethylammonium chloride) (PDDAC) [6], poly(sodium 4-styrenesulfonate) (PSS) [7] are the most often used.

PEI is a soluble polymer containing primary, secondary and tertiary amine groups. In many works, its efficiency as an agent complexing the copper(II) ions and enhancing their ultrafiltration separation from simulated solutions [8], industrial wastewaters [9], as well as from the binary systems in

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which these ions competed with different other heavy metal ions [10,11] or alkaline earths metal cations [12], was demonstrated. Due to the presence of weak-alkaline amine groups in the polymer structure, PEI demonstrates also anion exchange properties. Thus, it can be used for the Cr(VI) ions separation enhancement [13–15].

Heavy metals are usually present in multicomponent mixtures, what makes their separation and reusing difficult. Many research works reported removal of heavy metal ions from binary systems with the PEUF method, where both metal ions competed in the separation process. The effectiveness of simultaneous separation of both metals from solutions [16–18] was especially studied; however, the possibility of their selective separation was also evaluated [10,11,19–21]. The most advantageous conditions defined mainly by polymer/metal ratio and pH were reported. Moreover, many authors point on other essential factors responsible for the efficiency of the heavy metals separation in a PEUF process and for their separation selectivity from the bi-ionic mixtures, that is, ionic strength of the solution and presence of some anions, like nitrates, chlorides or sulfates [20,21].

Because of the process complexity, for investigation and characterization of the membrane techniques some numerical approaches or empirical models are often used. These are useful tools enabling predictions of the process effects under various conditions. For this purpose, the response surface methodology (RSM) [15,22–24] and artificial neural networks (ANNs) [15,25] are especially valuable.

In the present work, several empirical regression models were derived for the modeling of the effectiveness of the polymer (here: PEI) enhanced ultrafiltration (PEUF) applied for separation of coexisting Cu(II) and Cr(VI) ions in the presence of sulfate anions. The models, derived as the function of PEI dose and pH, were intended for the prediction of individual retention coefficients of these metals in each from the three bi-ionic mixtures (different Cu(II) and Cr(VI) molar fractions). Moreover, identification of process conditions corresponding to the demanded (e.g., the highest) efficiency of selective separation of single metal ions from the Cu(II)/Cr(VI) mixture was thus possible.

## 2. Materials and methods

### 2.1. Reagents

Simulated aqueous solutions of Cu(II) and Cr(VI) were prepared on the basis of $Cu(NO_3)_2 \times 3H_2O$ and $K_2Cr_2O_7$ (POCH S.A., Gliwice, Poland), whereas sulfate anions were introduced into the solution as sodium sulfate (POCH S.A., Gliwice, Poland). All salts were of analytical grade. PEI of average molecular weight $M_w = 750$ kDa was used in a form of commercial solution of concentration $50\%_{w/v}$ (Sigma-Aldrich).

The pH adjustment was done with NaOH and $HNO_3$ solutions, of concentrations 1 or 0.1 mol dm$^{-3}$ (POCH S.A., Gliwice, Poland).

Deionized water with resistivity > 5 MΩ·cm (water purification system Elix 10, Millipore) was used in PEUF experiments.

### 2.2. Ultrafiltration

Preliminary ultrafiltration tests were done in a stirred membrane cell Amicon 8400 (Millipore) of working volume 400 cm$^3$ with membrane surface 38.5 cm$^2$, using transmembrane pressure of 0.1 MPa. UltraFilic MW membrane of cut-off 50 kDa, made of modified polyacrylonitrile (GE Osmonics), was used in the process. Permeate in the amount not exceeding 10% of the initial feed volume was collected, what prevented considerable concentration of solution.

The solutions of constant total concentration of both metals ions $C_M = 1$ mmol dm$^{-3}$ and 10-time higher concentration of sulfate anions $C_{SO4} = 10$ mmol dm$^{-3}$ were tested. Ultrafiltration tests were done for series of three solutions differing in mole fractions of both metals ($X_{Cu}$, $X_{Cr}$) in bi-ionic mixture. First series was represented by solutions of prevailing copper fraction: $C_{Cu} = 0.9$ mmol dm$^{-3}$, $C_{Cr} = 0.1$ mmol dm$^{-3}$ ($X_{Cu} = 0.9$; $X_{Cr} = 0.1$), second – solutions of equimolar representation of both metals ions: $C_{Cu} = 0.5$ mmol dm$^{-3}$, $C_{Cr} = 0.5$ mmol dm$^{-3}$ ($X_{Cu} = 0.5$; $X_{Cr} = 0.5$), whereas in third series the prevailing metal in solution was chromium: $C_{Cu} = 0.1$ mmol dm$^{-3}$, $C_{Cr} = 0.9$ mmol dm$^{-3}$ ($X_{Cu} = 0.1$; $X_{Cr} = 0.9$). For each series ultrafiltration tests with different polymer/metals molar ratio $C_{PEI}/C_M$ in the range of 0.5–10 were done. Various pH from acidic (pH 2) to basic (pH 10) was applied during the tests. Concentrations of Cu(II) and Cr(VI) were determined twice: in a feed and in permeate (atomic absorption spectrometer SpectrAA 880, Varian). On this basis, calculation of each metal's retention coefficient ($R_{Cu}$, $R_{Cr}$) (Eq. (1)) and the absolute relative difference parameter (separation selectivity) denoted as ARD (Eq. (2)) were done:

$$R_{Cu} = 1 - \frac{C_{Cu_P}}{C_{Cu_F}} \qquad R_{Cr} = 1 - \frac{C_{Cr_P}}{C_{Cr_F}} \tag{1}$$

$$\mathrm{ARD} = \frac{\left|R_{Cu} - R_{Cr}\right|}{\left|R_{Cu} - R_{Cr}\right|_{MAX}} = \frac{\left|R_{Cu} - R_{Cr}\right|}{1} = \left|R_{Cu} - R_{Cr}\right| \tag{2}$$

where $C_{Cu}$ and $C_{Cr}$ denote copper and chromium concentrations, in permeate (index $P$) and in a feed (index $F$), appropriately.

In general, 60 sets of experimental data of identical structure were obtained ($X_{Cu}$, $X_{Cr}$, $C_{PEI}/C_M$, pH → $R_{Cu}$ or $R_{Cr}$ or ARD), covering: three combinations of $X_{Cu}$, $X_{Cr}$, four combinations of $C_{PEI}/C_M$ and 5 pH values.

At the selected process conditions (composition of bi-ionic mixture, $C_{PEI}/C_M$ ratio, pH), UF concentration of solution was done and changes in concentrations of both metals in retentate and permeate were analyzed. Process was conducted till volume reduction factor (VRF) coefficient reached the value of 20. This coefficient was defined as the ratio of initial feed volume to the remaining retentate volume (VRF = $V_F/V_R$). Modification of retentate and permeate compositions during the process course was evaluated, as well.

### 2.3. Models

The acquired data were analyzed with nonlinear regression methods. In particular, for proper modeling of the complex $R_{Cu} = f(C_{PEI}/C_M, \mathrm{pH})$, $R_{Cr} = f(C_{PEI}/C_M, \mathrm{pH})$ and $\mathrm{ARD} = f(C_{PEI}/C_M, \mathrm{pH})$ dependencies, hierarchical nonlinear regression was proposed. The method was based on preliminary identification of the most suitable form of 1-variable function, for example, $R_{\mathrm{Cu}} = f(\mathrm{pH})$ ("external function"), which had to be identical in form for all $C_{\mathrm{PEI}}/C_{\mathrm{M}}$ values. Then, the resulting parameters of each $R_{\mathrm{Cu}} = f(\mathrm{pH})$ function were independently correlated with $C_{\mathrm{PEI}}/C_{\mathrm{M}}$ values, producing other 1-variable "internal functions". In result, after inserting "internal functions" instead of the "external function" parameters a more complex $R_{\mathrm{Cu}} = f(C_{\mathrm{PEI}}/C_{\mathrm{M}}, \mathrm{pH})$ 2-variable "hierarchical model" was derived. The nine empirical "hierarchical models" were elaborated with ORIGIN 6.2 software. On their basis, graphical projections of these 2-variable dependencies were done (see Figs. 1 and 2), after statistical validation with experimental data ($R^2$, see Fig. 3).

The following final "hierarchical models" Eqs. (3)–(11) were derived, for:

$R_{\mathrm{Cu}}$ ($X_{\mathrm{Cu}} = 0.9$, $X_{\mathrm{Cr}} = 0.1$)

$$\begin{aligned} R_{Cu} &= 0.986 + 0.0036(C_{PEI}/C_M) - 0.00086(C_{PEI}/C_M)^2 \\ &\times \exp\left\{-\exp\left[\frac{0.778 - 0.198(C_{PEI}/C_M) + 0.018(C_{PEI}/C_M)^2 \cdot 2.718}{0.986 + 0.0036(C_{PEI}/C_M) - 0.00086(C_{PEI}/C_M)^2}(6.772 - 1.589(C_{PEI}/C_M) + 0.114(C_{PEI}/C_M)^2 - pH) + 1\right]\right\} \end{aligned} \tag{3}$$

$R_{\mathrm{Cu}}$ ($X_{\mathrm{Cu}} = 0.5$, $X_{\mathrm{Cr}} = 0.5$)

$$\begin{aligned} R_{Cu} &= 1.068 - 0.042\left(C_{PEI}/C_M\right) + 0.0028\left(C_{PEI}/C_M\right)^2 \times \\ &\times \exp\left\{-\exp\left[\frac{0.026 \cdot 7.43^{\left(1/\left(C_{PEI}/C_M\right)\right)} \cdot \left(C_{PEI}/C_M\right)^{1.215} \cdot 2.718}{1.068 - 0.042\left(C_{PEI}/C_M\right) + 0.0028\left(C_{PEI}/C_M\right)^2}\left(2.252 \cdot \left(C_{PEI}/C_M\right)^{\left(-0.638/\left(C_{PEI}/C_M\right)\right)} - pH\right) + 1\right]\right\} \end{aligned} \tag{4}$$

$R_{\mathrm{Cu}}$ ($X_{\mathrm{Cu}} = 0.1$, $X_{\mathrm{Cr}} = 0.9$)

$$\begin{aligned} R_{Cu} &= \frac{0.903}{1 - 2.18\exp(-7.315(C_{PEI}/C_M))_{\max}} \\ &\times \exp\left\{-\exp\left[\frac{0.455 - 0.082(C_{PEI}/C_M) + 0.008(C_{PEI}/C_M)^2 \cdot 2.718}{\dfrac{0.903}{1 - 2.18\exp(-7.315(C_{PEI}/C_M))}}\left(\frac{1.83 \cdot 10^8 + 1.64 \cdot 10^8 (C_{PEI}/C_M)}{1 + 1.55 \cdot 10^8 (C_{PEI}/C_M) - 4.67 \cdot 10^6 (C_{PEI}/C_M)^2} - pH\right) + 1\right]\right\} \end{aligned} \tag{5}$$

$R_{\mathrm{Cr}}$ ($X_{\mathrm{Cu}} = 0.9$, $X_{\mathrm{Cr}} = 0.1$)

$$\begin{aligned} R_{Cr} &= \left(2.082 - 0.215\left(C_{PEI}/C_M\right) - \frac{0.862}{\left(C_{PEI}/C_M\right)^2}\right) + \left(-1.829 + 0.192\left(C_{PEI}/C_M\right) + \frac{0.863}{\left(C_{PEI}/C_M\right)^2}\right)pH \\ &+ \left(0.496 - 0.052\left(C_{PEI}/C_M\right) - \frac{0.269}{\left(C_{PEI}/C_M\right)^2}\right)pH^2 + \left(-0.050 + 0.0057\left(C_{PEI}/C_M\right) + \frac{0.032}{\left(C_{PEI}/C_M\right)^2}\right)pH^3 \\ &+ \left(0.0017 - 0.0002\left(C_{PEI}/C_M\right) - \frac{0.0013}{\left(C_{PEI}/C_M\right)^2}\right)pH^4 \end{aligned} \tag{6}$$

$R_{\mathrm{Cr}}$ ($X_{\mathrm{Cu}} = 0.5$, $X_{\mathrm{Cr}} = 0.5$)

$$\begin{aligned} R_{Cr} &= \left(\frac{-9.61 \cdot 10^6 + 5.98 \cdot 10^7\left(C_{PEI}/C_M\right)}{1 + 6.51 \cdot 10^7\left(C_{PEI}/C_M\right) - 6.85 \cdot 10^5\left(C_{PEI}/C_M\right)^2}\right) + \left(\frac{1.93 \cdot 10^9 - 1.96 \cdot 10^{10}\left(C_{PEI}/C_M\right)}{1 + 3.64 \cdot 10^{10}\left(C_{PEI}/C_M\right) - 2.39 \cdot 10^8\left(C_{PEI}/C_M\right)^2}\right)pH \\ &+ \left(0.1007 + 0.012\ln\left(C_{PEI}/C_M\right)\right)pH^2 + \left(-0.0058 - 0.00093\ln\left(C_{PEI}/C_M\right)\right)pH^3 \end{aligned} \tag{7}$$

$R_{\mathrm{Cr}}$ ($X_{\mathrm{Cu}} = 0.1$, $X_{\mathrm{Cr}} = 0.9$)

$$\begin{aligned} R_{Cr} &= \left(\frac{1.408}{1 + 3.473\exp\left(-0.303\left(C_{PEI}/C_M\right)\right)}\right) + \left(\frac{1}{-3.83 + 1.0088\ln\left(C_{PEI}/C_M\right)}\right)pH \\ &+ \left(0.0549\left(C_{PEI}/C_M\right)^{0.411}\right)pH^2 + \left(-0.0035 - 0.0021\ln\left(C_{PEI}/C_M\right)\right)pH^3 \end{aligned} \tag{8}$$

ARD ($X_{Cu} = 0.9$, $X_{Cr} = 0.1$)

$$ARD = \left(-0.0817 - 0.743\ln\left(C_{PEI}/C_M\right)\right) + \left(0.0924 + 0.5256\ln\left(C_{PEI}/C_M\right)\right)pH \\ + \left(-0.0108 - 0.091\ln\left(C_{PEI}/C_M\right)\right)pH^2 + \left(0.00074 + 0.0046\ln\left(C_{PEI}/C_M\right)\right)pH^3 \tag{9}$$

ARD ($X_{Cu} = 0.5$, $X_{Cr} = 0.5$)

$$ARD = \left(-0.0688 + 0.0526\left(C_{PEI}/C_M\right) - 0.0013\left(C_{PEI}/C_M\right)^2\right) + \left(0.0624 - 0.0068\left(C_{PEI}/C_M\right) - \frac{0.015}{\left(C_{PEI}/C_M\right)^2}\right)pH \\ + \left(0.0011 + 0.00028\left(C_{PEI}/C_M\right) + \frac{0.00197}{\left(C_{PEI}/C_M\right)^2}\right)pH^2 \tag{10}$$

ARD ($X_{Cu} = 0.1$, $X_{Cr} = 0.9$)

$$ARD = \left(-0.479 + 0.0897\left(C_{PEI}/C_M\right)\right) + \left(0.263 - 0.032\left(C_{PEI}/C_M\right)\right)pH \\ + \left(-0.0125 + 0.0021\left(C_{PEI}/C_M\right)\right)pH^2 \tag{11}$$

Using the validated models, the advantageous conditions for selective separation of the single metal ions were proposed.

## 3. Results and discussion

In Fig. 1, the response surfaces of $R_{Cu} = f(C_{PEI}/C_M, \text{pH})$ (Eqs. (3)–(5)) and $R_{Cr} = f(C_{PEI}/C_M, \text{pH})$ (Eqs. (6)–(8)) "hierarchical model" dependencies are shown, individually for each from the three bi-ionic Cu(II)/Cr(VI) mixtures of different metals molar fractions.

Model surfaces presenting the copper retention coefficients demonstrate sigmoid character and partly steep course of the "cross-sectional" $R_{Cu} = f(\text{pH})$ relations (for a given $C_{PEI}/C_M$ value). It confirms distinct growth of copper retention coefficient with the pH rise followed by its final stabilization, observed in a whole range of PEI doses tested, independent of the bi-ionic mixture type. In solutions containing prevailing fraction of copper, within the small $C_{PEI}/C_M$ molar ratio (below 2), the increase in copper separation effectiveness with higher solution alkalinity was observed only for pH > 3–4. In a more acidic environment, protonation of PEI amine groups occurs, what makes, that at relatively small polymer content in solution and for prevailing of copper ions the sufficient number of functional groups in polymer capable to effective binding of Cu(II) ions is not attained. In the solutions characterized by lower copper mole fraction, this effect was less visible, and growth of copper retention coefficient with the pH rise could be here observed in the whole pH range. From the $R_{Cu} = f(C_{PEI}/C_M)_{pH}$ relation, it was noticed that increase of the copper separation effectiveness resulted also of the growth of PEI dose. This effect was the most distinct in bi-ionic mixtures containing prevailing fraction of copper(II), whereas the lowest effects corresponded to the highest chromium(VI) concentration. Effect of the polymer additive dose on the copper(II) retention in each from the three bi-ionic mixtures was the largest in this pH range, where partly protonation of the polymer functional groups occurred, and where clear influence of solution's pH on this metal separation was observed (especially within pH 3–7 range).

The character of $R_{Cr} = f(C_{PEI}/C_M, \text{pH})$ response surface projected (Eqs. (6)–(8)) was significantly different from the shapes characteristic for $R_{Cu}$ based on Eqs. (3)–(5). Minima and maxima were present, and were probably connected with the competitive interaction of Cu(II) cations with PEI, strongly bonded by the polymer functional groups, and sulfate anions effect. The $R_{Cr} = f(\text{pH})$ dependency (for a given $C_{PEI}/C_M$) showed minimum within the pH of ca. 3–4, what could be attributed to competitive binding of sulfate anions by partly protonated PEI functional groups, as well as coordination interaction of non-protonated groups with copper(II) cations present in the solution. Maximal values of Cr(VI) retention coefficient corresponded to pH 7–8, and in the solution with prevailing Cr(VI) it distinctly increased with the growth of PEI dose. Generally, one should emphasize, that the model predicted maximal $R_{Cr}$ values for ultrafiltration in Cu(II)/Cr(VI) bi-ionic mixtures containing sulfates was clearly lower compared with the data reported in similar tests, however, concerning Cu(II)/Cr(VI) mixtures with chlorides [26] and Cr(VI) solutions [14] without $SO_4^{2-}$ anions. It suggests, that presence of sulfate anions in solution, especially in significant concentration ($C_{SO4}/C_M = 10$), clearly decreases the chromium(VI) separation effectiveness.

Fig. 2 presents the ARD = $f(C_{PEI}/C_M; \text{pH})$ "hierarchical model" response surfaces (according to Eqs. (9)–(11)) – as a 3-D projections and in a form of 2-D ARD contour maps. In all three bi-ionic mixture types, of different metals mole fractions, some effect of pH on the absolute relative difference (ARD) values for copper(II) and chromium(VI) retention was observed. In solutions, where Cu prevailed, the ARD reached maximal values mainly within the pH 4–7, especially for higher PEI doses (Figs. 2(a) and (b)). Within this pH range, increase in $C_{PEI}/C_M$ produced significant raise of $R_{Cu}$ (Fig. 1(a)) with less intensive $R_{Cr}$ raise (Fig. 1(b)), resulting thus in the observed ARD values.

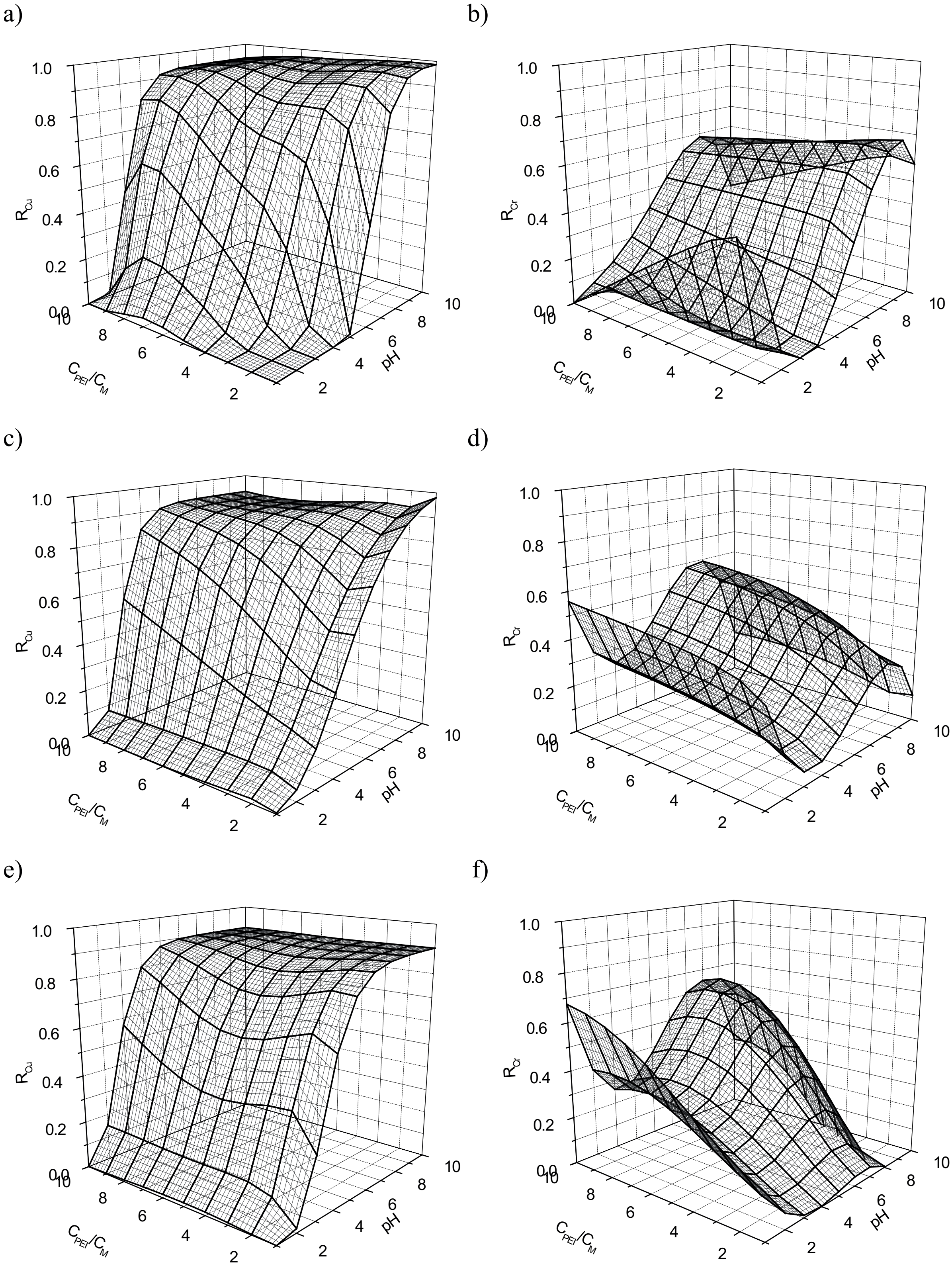

Fig. 1. Model-based predictions of $R_{Cu}$ and $R_{Cr}$ in bi-ionic solutions of different compositions: (a) $R_{Cu}$; (b) $R_{Cr}$; $X_{Cu} = 0.9$, $X_{Cr} = 0.1$; (c) $R_{Cu}$; (d) $R_{Cr}$, $X_{Cu} = 0.5$, $X_{Cr} = 0.5$; (e) $R_{Cu}$; (f) $R_{Cr}$, $X_{Cu} = 0.1$, $X_{Cr} = 0.9$.

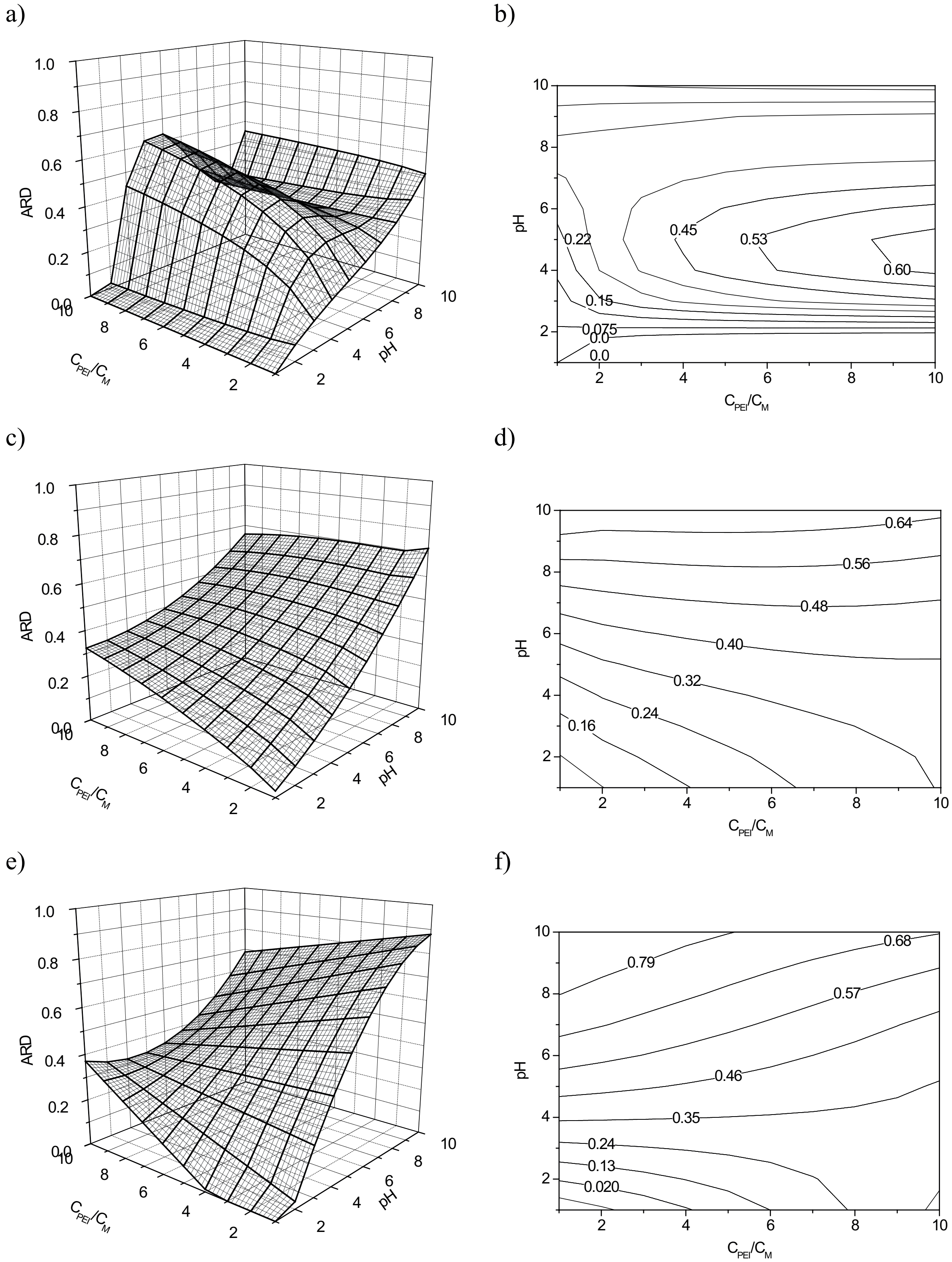

Fig. 2. Model-based projections of ARD (3-D and 2-D) for bi-ionic solutions of different compositions: (a) ARD = $f(C_{PEI}/C_M, \text{pH})$; (b) ARD contour lines, $X_{Cu} = 0.9$, $X_{Cr} = 0.1$; (c) ARD = $f(C_{PEI}/C_M, \text{pH})$; (d) ARD contour lines, $X_{Cu} = 0.5$, $X_{Cr} = 0.5$; (e) ARD = $f(C_{PEI}/C_M, \text{pH})$; (f) ARD contour lines, $X_{Cu} = 0.1$, $X_{Cr} = 0.9$.

In solutions of equal metals fractions, as well as in these with chromium(VI) domination, for low pH (<4), the ARD values grew with the growth of $C_{PEI}/C_M$ molar ratio. Moreover, in the mixtures where chromium(VI) prevailed, at pH > 4 one could observe lowering of ARD value with the PEI dosage increase. The largest ARD values corresponded to solutions with dominating chromium(VI), low $C_{PEI}/C_M$ molar ratio range and high pH values (Figs. 2(e) and (f)). Such process conditions favor separation of one metal (copper) only from the Cu(II)/Cr(VI) bi-ionic mixture.

Fig. 3 presents graphical verification of the "hierarchical models" prediction quality in respect to the experimentally determined metal retention coefficients $R_{Cu}$ and $R_{Cr}$, as well as ARD values. High values of determination coefficients $R^2$ reveal good compatibility between the experimental and predicted values, as well as point on the possibility of practical application of these "hierarchical models" in design or suggesting of optimal process conditions for PEUF separation technology.

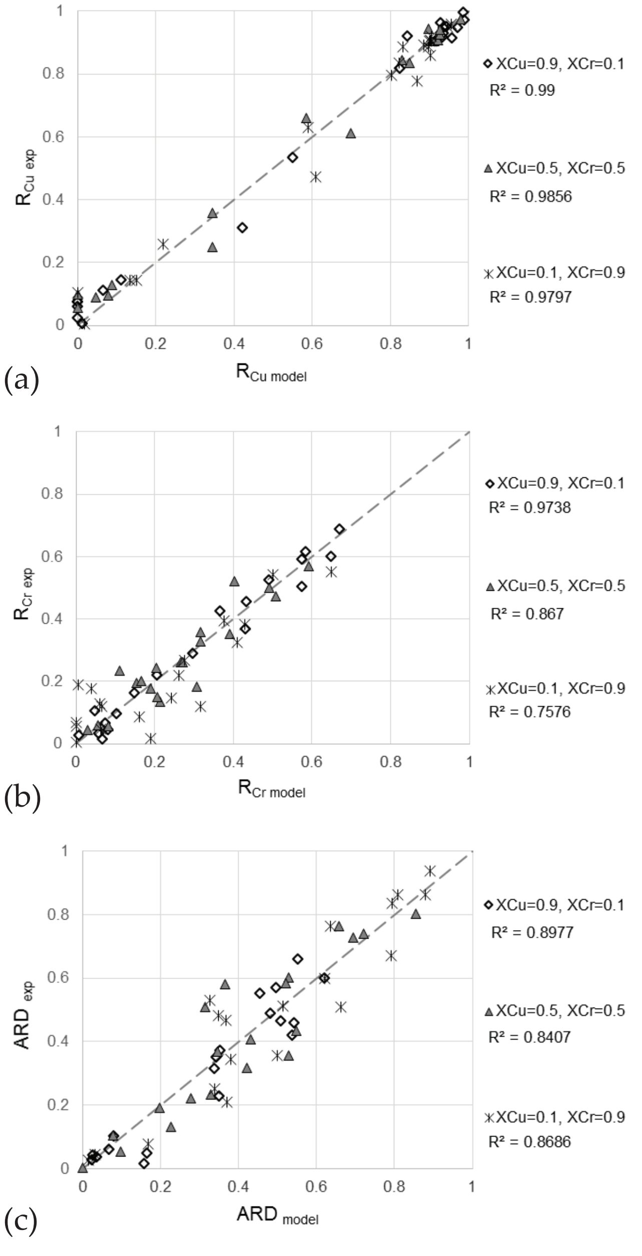

Fig. 3. The $R_{Cu}$ (a), $R_{Cr}$ (b) and ARD (c) – experimental values vs. (Eqs. (3)–(11)) "hierarchical models" predictions.

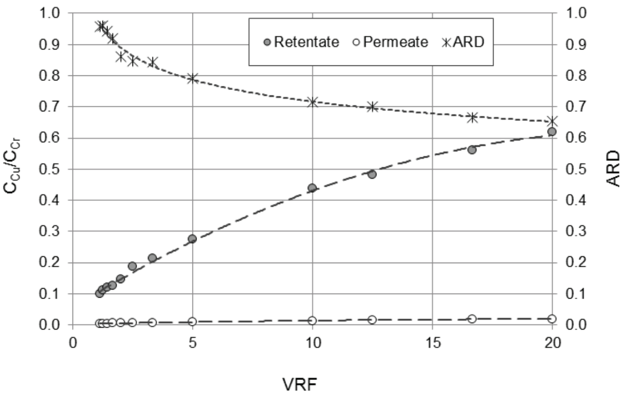

Fig. 4. Changes in $C_{Cu}/C_{Cr}$ concentration ratio in retentate and permeate, as well as absolute relative difference ARD during ultrafiltration of solution with prevailing of Cr(VI) ($C_{Cu}$ = 0.1 mmol dm$^{-3}$, $C_{Cr}$ = 0.9 mmol dm$^{-3}$, $C_{PEI}/C_M$ = 0.5, $C_{SO4}$ = 10 mmol dm$^{-3}$).

The modeling results enabled one to identify the PEUF process conditions favoring selective separation of one metal only from the binary Cu(II)/Cr(VI) mixture. To verify these conclusions, the PEUF process was carried out for bi-ionic mixture containing 0.9 mmol dm$^{-3}$ Cr(VI) and 0.1 mmol dm$^{-3}$ Cu(II), for pH = 10 and molar ratio $C_{PEI}/C_M$ = 0.5. Process results are presented in Fig. 4, demonstrating variation of concentration ratio $C_{Cr}/C_{Cu}$ in both ultrafiltration streams (retentate and permeate), as well as the corresponding ARD values observed during the progress of concentration process.

In result of the solution concentration, ca. 9.5-time increase in Cu(II) concentration and only ca. 1.5-time raise of Cr(VI) concentration were confirmed in the final retentate compared with the initial feed. Separation of Cr(VI) ran with low efficiency, resulting in removal from several % (in initial process stage) up to 32% of the metal present in the solution. In the same time, retention coefficient of copper(II) stabilized on very high level, insignificantly varying within the 0.96–0.98 range. Diversified effectiveness of both metals ions separation resulted in successive growth of the concentration ratio $C_{Cu}/C_{Cr}$ in retentate during the process from 0.095 up to 0.62. Absolute relative difference ARD values were relatively high; however, during the process course and raise of volume reduction factor VRF, these decreased from 0.96 down to 0.66. Hence, in averaged permeate 96.7% of Cr(VI) and only 7.6% of Cu(II) remained in respect to the initial feed solution.

## 4. Conclusions

Empirical nonlinear "hierarchical models" were used for successful prediction of separation effectiveness in the bi-ionic Cu(II)/Cr(VI) mixtures in a polymer (represented by PEI) enhanced ultrafiltration (PEUF) process. Prediction of copper(II) and chromium(VI) retention coefficients $R_{Cu}$, $R_{Cr}$, as well as absolute relative difference ARD characterizing both *R* deviations, made determination of process conditions favoring, for example, selective separation of one metal from the bi-ionic mixture, possible. It was concluded, that the largest differences in copper(II) and chromium(VI) separation efficiency were identified in binary mixtures with prevailing chromium(VI) fraction, at high pH and for relatively small PEI addition, unsatisfactory for effective binding of both metal ions together. High values of copper(II) retention coefficient at relatively low chromium(VI) retention coefficients were thus identified, what made fractional separation of both metals possible. Moreover, it was concluded, that presence of sulfate anions influenced the PEI enhanced ultrafiltration process effectiveness, particularly lowering the Cr(VI) separation efficiency.

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## Symbols

$C_{\mathrm{Cr\ F}}$ — Molar concentration of Cr(VI) in a feed, mmol dm$^{-3}$
$C_{\mathrm{Cr\ P}}$ — Molar concentration of Cr(VI) in permeate, mmol dm$^{-3}$
$C_{\mathrm{Cr}}$ — Molar concentration of Cr(VI), mmol dm$^{-3}$
$C_{\mathrm{Cu\ F}}$ — Molar concentration of Cu(II) in a feed, mmol dm$^{-3}$
$C_{\mathrm{Cu\ P}}$ — Molar concentration of Cu(II) in permeate, mmol dm$^{-3}$
$C_{\mathrm{Cu}}$ — Molar concentration of Cu(II), mmol dm$^{-3}$
$C_{\mathrm{M}}$ — Molar concentration of both metals (here: Cu(II) + Cr(VI)), mmol dm$^{-3}$
$C_{\mathrm{PEI}}$ — Molar concentration of polymer (PEI), mmol dm$^{-3}$
$C_{\mathrm{SO4}}$ — Molar concentration of $SO_4^{2-}$ anions, mmol dm$^{-3}$
$M_w$ — Weight-average molecular mass, kDa
$R^2$ — Determination coefficient
$R_{\mathrm{Cr}}$ — Retention coefficient of Cr
$R_{\mathrm{Cu}}$ — Retention coefficient of Cu
$V_{\mathrm{F}}$ — Initial feed volume, dm$^3$
$V_{\mathrm{R}}$ — Remaining retentate volume, dm$^3$
$X_{\mathrm{Cr}}$ — Mole fraction of Cr
$X_{\mathrm{Cu}}$ — Mole fraction of Cu
ANN — Artificial neural network
ARD — Absolute relative difference (parameter)
EPEI — Ethoxylated polyethyleneimine
exp — Experimental value
model — Model-predicted value
PAA — Poly(acrylic acid)
PACMA — Poly(acrylic acid-co-maleic acid)
PDDAC — Poly(diallyldimethylammonium chloride)
PEI — Polyethyleneimine
PEUF — Polymer enhanced ultrafiltration
PSS — Poly(sodium 4-styrenesulfonate)
PVA — Poly(vinyl alcohol)
RSM — Response surface methodology
UF — Ultrafiltration
VRF — Volume reduction factor

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