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Separation of heavy metal ions from multi-component solutions using ultrafiltration enhanced with complexing polymer

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ABSTRACT

Polymer-enhanced ultrafiltration (PEUF) is a new, attractive membrane technique enabling the separation of low molecular weight compounds from aqueous solutions. PEUF is especially interesting in terms of heavy metal ions removal from industrial effluents. In the presented work, the technique was applied for the separation of heavy metal ions (Cu(II), Cd(II), Zn(II), Ni(II), and Cr(III)) from their equimolar five-component solution. Polyethyleneimine (PEI), a water-soluble polymer containing amine groups, was chosen to enhance metal ions separation in the ultrafiltration. The effect of pH, polymer-to-total metals molar ratio C_{PEI}/C_{Ms}, and the presence of the accompanying ions (NO_3^-, Cl^-, SO_4^{2-}, PO_4^{3-}, CH_3COO^-, EDTA, Ca^{2+}) on the separation efficiency of the heavy metal ions was investigated. Then, ultrafiltration concentration of the heavy metal ions was conducted at selected process parameters followed by the decomposition of polymer-metal complexes (pH = 2) and recovery of metal ion concentrates. Both C_{PEI}/C_{Ms} and pH strongly influenced the PEUF effectiveness. At a moderate pH (pH = 5) and lower PEI dose ($C_{PEI}/C_{Ms} = 1$), the preferential Cu(II) separation from the multi-component mixture was observed. Applying a higher PEI dose ($C_{PEI}/C_{Ms} = 7$), very high rejection coefficients (0.98–1.00) of all heavy metal ions can be achieved. At a lower polymer dose, the tested accompanying ions diminished permeate flux and metal ion retention coefficients. The effect was much less visible at a higher C_{PEI}/C_{Ms} value. Ultrafiltration concentration of polymer-metal complexes with subsequent decomplexation–ultrafiltration step (pH = 2) enabled recovery of 67%–91% of concentrated metal ions.

Keywords: Polymer-enhanced ultrafiltration; Heavy metal ions; Multi-component mixtures; Competitive separation; Polyethyleneimine

1. Introduction

Progressive development and industrialization, as well as the associated growing anthropogenic impact, mean that we should pay increasing attention to environmental aspects. Among the various micropollutants in soil, air, and aquatic environment, heavy metals and metalloids constitute a crucial threat due to their lack of biodegradability, ability for bioaccumulation, and potential toxic, mutagenic, and carcinogenic effects [1,2]. The main sources of heavy metals in the environment are industries and activities such as metal plating and electroplating, mining, metal smelting, petroleum refinery, tanneries, the textile industry, paper manufacturing, batteries, pesticides, etc. [3,4]. Due to the widespread threat caused by heavy metals and increasingly strict regulations related to their emission into the environment, great attention is being paid to effective methods of heavy metal separation from aqueous solutions and industrial effluents. In addition to conventional heavy metal separation methods (chemical precipitation, ion exchange, flotation, coagulation and flocculation, adsorption, electrochemical processes, solvent extraction), newly proposed alternative separation methods are of great interest. They include the application of nanoadsorbents, graphene, carbon

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nanotubes, hydrogels, multifunctional materials, metal–organic frameworks (MOFs), bioadsorbents, and membrane processes, mainly high-pressure driven processes of reverse osmosis (RO) and nanofiltration (NF), electro-membrane processes of electrodialysis (ED) and electrodeionization (EDI), and liquid membranes (LM) [5–10]. Also, some novel membrane-based techniques are considered interesting in terms of heavy metal ions separation, among them polymer inclusion membranes (PIM), adsorptive ultrafiltration mixed matrix membranes (MMMs), micellar-enhanced ultrafiltration (MEUF) and polymer-enhanced ultrafiltration (PEUF) [9,10]. The latter, also known as complexation–ultrafiltration, polymer-assisted ultrafiltration (PAUF) or liquid-phase polymer-based retention (LPR), combines the binding of metal ions with a water-soluble polymer containing the appropriate functional (binding) groups and the ultrafiltration (UF) removal of the resulting macromolecular polymer-metal complexes. As the reaction between metal ions and the complexing polymer is an equilibrium process, the separated complexes can then be decomposed, allowing the metal ions and polymer to be recovered. Compared to other pressure-driven membrane processes, such as NF or RO, PEUF does not require high transmembrane pressures and, due to the specific bonds between the polymer and metal ions, heavy metal ions can be selectively separated from multi-component mixtures containing different chemical species.

In general, two groups of polymers are used to assist the UF separation, polyelectrolytes and polychelatogens. Polyelectrolytes are macromolecular compounds containing ionic or ionizable functional groups that can be negatively or positively charged depending on the type of polymer (mainly sulfonic, carboxylic or phosphonic acids and salts, or quaternary ammonium salts). In chelating polymers (polychelatogens) complexing functional groups occur, predominantly N-donors or O-donors, like amines, amides, alcohols, or crown ethers [11–13]. Another interesting macromolecular compounds supporting ultrafiltration separation of metal ions are biopolymers, among them chitosan, starch, pectin, carboxymethylcellulose, alginic acid, or sodium alginate [14–16].

One of the most useful polymer functionalities is the amine group containing N-donor atom with a free electron pair. Reacting with such polymers, heavy metal cations can act as acceptors of the electron pair. Due to the coordination character of polymer-metal bonds, such polymers are selective towards heavy metal cations, even in solutions containing other cationic species [12,17]. One of the most frequently used N-donor chelating polymers is polyethyleneimine (PEI). PEI is a water-soluble macromolecular compound that can be used in the linear or, more commonly, branched form, containing primary, secondary, and tertiary amine groups. Due to its complex-forming abilities, the polymer is applied to enhance the ultrafiltration separation of many heavy metal cations: Cu(II), Cd(II), Ni(II), Zn(II), Co(II), Pb(II), Cr(III), Hg(II) [18–24]. The process is pH-sensitive – at acidic conditions, amine groups are protonated and are unable to form complexes, so PEI-metal bonds can be easily decomposed. On the other hand, because of the possible protonation of amine groups, the polymer reveals weak anion exchange properties and can be used in PEUF separation of anionic forms, like Cr(VI) [24,25] or Sb(V) [26]. PEI was also effective as a process-enhancing agent in the UF separation of heavy metal–organic complexes, such as Cu(II)–citric acid [27,28] or Cu(II)– and Ni(II)–polyaminocarboxylate complexes [29].

The real aqueous systems and industrial effluents often contain a mixture of heavy metal ions in the form of diluted solutions. Therefore, besides the application of the PEUF method to single heavy metal containing solutions, the important aspect is the separation of heavy metal ions from multi-component systems (in competitive conditions). PEI was applied by Molinari et al. [30] for the selective separation of metal ions from binary Cu(II)/Ni(II) aqueous solutions using ultrafiltration membranes. At optimal pH and polymer amount for both separated metal ions, the simultaneous separation of the two metals was possible. To achieve the preferential Cu(II) separation, it was necessary to reduce both the PEI dose and the solution pH to the values favorable only for copper ions. Partially ethoxylated polyethyleneimine (PEPEI) was an effective polymer for preferential separation of Cu(II) from Cu(II)/Zn(II) bionic solutions at optimal pH and metal-to-polymer molar ratio (loading ratio) [31]. Separation of heavy metal ions from the binary Cd(II)/Ni(II) solution using the PEUF method assisted with PEI revealed that another important parameter that can affect separation selectivity is ionic strength [32]. In the studied case, the presence of a 0.5 N $NaNO_3$ solution increased the Ni(II) and decreased Cd(II) rejection coefficients, changing the preferentially retained metal ion and influencing the selectivity. The effect of the PEI dose, pH, and the presence of additional salt on the metal ion mixture separation in the PEUF process was also investigated towards binary Cd(II)/Ni(II), Zn(II)/Cd(II), Ni(II)/Zn(II) and tertiary Cd(II)/Ni(II)/Zn(II) solutions [33]. Three types of PEI polymers (hyperbranched, modified, and partially ethoxylated) were investigated to assist the ultrafiltration separation of Cu from municipal solid waste incineration fly ash extracts [34]. The investigations were conducted at both the laboratory and pilot plant scale. It was stated that hyperbranched and partially ethoxylated polyethyleneimine were suitable for the selective copper separation from among 16 other metal ions (predominantly Zn, Pb, Ca) at high chloride concentration. The applied three-step procedure (enrichment, purification, and regeneration) enabled the recovery of Cu concentrates from fly ash extracts and the regeneration of the polymer.

In the presented paper, polymer-enhanced ultrafiltration was used for the competitive separation of heavy metal ions from their multi-component mixture. The heavy metal ion mixture was prepared as a model solution containing an equimolar partition of most typical heavy metal ions for industrial wastewater: Cu(II), Ni(II), Zn(II), Cd(II), and Cr(III), at the concentration of 0.2 mmol/dm^3 each. The total concentration of metal ions in the solution was 1 mmol/dm^3 (*c.a.* 70 mg/dm^3). To enhance the rejection of heavy metal ions on the ultrafiltration membrane, a water-soluble complexing polymer, PEI, was applied. The main process parameters investigated in the research were pH, polymer-to-metals molar ratio C_{PEI}/C_{Ms} (calculated concerning polymer repeat units), and the presence of other ionic forms at much higher concentrations than heavy metal ions. The impact of these parameters on the rejection coefficient of the individual metal ions was discussed. The next step included ultrafiltration concentration of a solution containing five metal ions at selected parameters enabling (i) preferential concentration of some metal ions from the multi-component mixture and (ii) simultaneous concentration of all five metal components. After concentration, the decomplexation of the retentate was performed at pH = 2, and the recovery of the heavy metal ions was evaluated.

2. Materials and methods

The model solution containing five heavy metal ions was prepared using the appropriate nitrates: $Cu(NO_3)_2 \cdot 3H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 9H_2O$, and $Cr(NO_3)_3 \cdot 9H_2O$ (POCH SA, Avantor, Poland). The salts were dissolved in distilled water to achieve an equimolar solution of total heavy metal ion concentration C_{Ms} = 1 mmol/dm^3 (*c.a.* 70 mg/dm^3) and each heavy metal ion concentration of 0.2 mmol/dm^3. To investigate the impact of the coexisting ions, the following salts were selected: $NaNO_3$, NaCl, Na_2SO_4, $Na_3PO_4 \cdot 12H_2O$, $CH_3COONa \cdot 3H_2O$, $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$ (EDTA), $Ca(NO_3)_2 \cdot 4H_2O$ (POCH SA, Avantor, Poland). The salts were introduced to the five-heavy metal ions solution to achieve a concentration of the investigated ion (NO_3^-, Cl^-, SO_4^{2-}, PO_4^{3-}, CH_3COO^-, EDTA, or Ca^{2+}) of 700 mg/dm^3, which is 10-times higher than the total heavy metal amount in the solution. The complexing polymer (PEI), MW ~ 750 kDa, was purchased as a 50% aqueous solution in Sigma-Aldrich (Merck Life Science Sp. z o.o., Poland). Analytical grade NaOH and HNO_3 (POCH SA, Avantor, Poland) were used as pH correctors. Ultrafiltration experiments were conducted in an Amicon 8400 stirred membrane cell (Millipore, Merck Life Science Sp. z o.o., Poland), equipped with the MW-type Ultrafiltration Membrane (GE Osmonics, Minnetonka, MN, USA), provided by Sterlitech Co., (Auburn, WA, USA). Compressed nitrogen was used to achieve an appropriate transmembrane pressure during the process.

Preliminary ultrafiltration tests were conducted at various polymer to total metal ions molar ratios (C_{PEI}/C_{Ms}), changed in the range of 0–10. For each tested value of C_{PEI}/C_{Ms}, five different pH values were applied in the range of 2–7. The feed solutions contain five heavy metal cations and the appropriate dose of PEI. Before the ultrafiltration experiment, the pH of the feed solution was adjusted to the tested value using NaOH or HNO_3 solutions, and the mixture was left for 2 h to ensure the complexation of heavy metal cations with polymer functional groups. Then the feed solution was placed in the Amicon stirred cell (at 360 rpm), and the permeate was collected at transmembrane pressure ΔP of 0.1 MPa. The volume of permeate gathered amounted to 10% of the initial volume (feed solution), to avoid the significant concentration of the retentate (volume reduction factor, VRF = 0.1). The volumetric permeate flux J_v was calculated for each experiment, according to (1). Prior to the ultrafiltration test, the native membrane was conditioned with distilled water (about 3 h at ΔP 0.05–0.2 MPa) and the water permeability of 1,288 ± 23 dm^3/(m^2·h·MPa) was determined. Also, normalized permeate flux J_v/J_w, defined as a ratio of permeate flux to the distilled water flux, was calculated.

$$J_v\left(\text{or } J_w\right) = \frac{V}{S \cdot t} \tag{1}$$

where J_v (J_w) – permeate (or distilled water) volumetric flux (dm^3/(m^2·h)), V – permeate volume (dm^3), S – membrane surface area (3.85 × 10^{-3} m^2), and t – time (h).

Collected samples of feed solutions and permeates were analyzed to determine the concentrations of individual heavy metal ions. To this purpose, an atomic absorption spectrometer SpectrAA 880 (Varian, Candela, Poland) was used. Prior to the analysis, all samples were acidified using 65% nitric acid (J.T. Baker, Avantor, Poland). By comparing individual metal ion concentrations in the feed solution and permeate, the rejection coefficients (R) of each metal ion were calculated according to equation (2). Similarly, rejection coefficients of all metal ions (considering total metals content) (R_{Ms}) were determined.

$$R\left(\text{or } R_{\text{Ms}}\right) = 1 - \frac{C_P}{C_F} \tag{2}$$

where R (or R_{Ms}) – rejection coefficient of individual metal ion (or total metal ions) (–), C_P – individual metal ions (or total metal ions) concentration in permeate (mg/dm^3), C_F – individual metal ions (or total metal ions) concentration in feed solution (mg/dm^3).

Additionally, two sets of ultrafiltration at selected conditions were carried out to investigate the impact of accompanying ions (NO_3^-, Cl^-, SO_4^{2-}, PO_4^{3-}, CH_3COO^-, EDTA, or Ca^{2+}) on individual heavy metal ion rejection. The parameters of the preliminary tests were gathered in Table 1.

Table 1
Preliminary tests parameters

Parameter	Values
Composition of multi-component heavy metal ion solution	0.2 mmol/dm^3 of each heavy metal ion (in mg/dm^3: Cu(II) – 12.7, Zn(II) – 13.1, Ni(II) – 11.7, Cd(II) – 22.5, Cr(III) – 10.4). Total metal ion concentration C_{Ms} = 1 mmol/dm^3 (70.4 mg/dm^3)
Polymer-to-total metals molar ratio, C_{PEI}/C_{Ms}*	0.5, 1, 2, 3, 5, 7
pH	2, 3, 3.5, 4, 4.5, 5, 5.5, 6, 7, 8
Accompanying ion	non, NO_3^-, Cl^-, SO_4^{2-}, PO_4^{3-}, CH_3COO^-, EDTA, Ca^{2+} (700 mg/dm^3) at C_{PEI}/C_{Ms} = 1, pH 5.5, and C_{PEI}/C_{Ms} = 7, pH = 5.5
Ultrafiltration parameters	MW-type membrane, ΔP = 0.1 MPa, VRF = 0.1

*moles of PEI were considered as moles of polymer repeat unit (mers).

The results of preliminary tests were analyzed using a statistical approach (Microsoft Excel Software). One-way analysis of variance (ANOVA), completed with Tukey's post hoc test (honest significant difference) on the significance level $\alpha = 0.05$ was used to assess if differences in R values between 5 analyzed metal ions (groups) were statistically different.

Following preliminary tests, two ultrafiltration-concentration tests of solutions containing five heavy metal ions were conducted at selected parameters. One of the tests was performed at strongly competing conditions (the amount of PEI and pH were not sufficient to achieve high R for all heavy metal ions). The second test was conducted with PEI dose and pH ensuring high effectiveness of separation of all five heavy metal ions. The concentrations of feed solutions were performed up to VRF of 10 (VRF is the ratio of initial solution volume and the remaining retentate volume, V_F/V_R), so the volume of the retentate in the membrane cell was reduced 10 times during the process. One-way ANOVA and Tukey test were used for the statistical assessment of heavy metal ion rejection coefficients achieved at this stage of the investigation. Then the achieved retentates were submitted to the decomposition of PEI-metals complexes at low pH, and the separation of concentrated heavy metal ions from the complexing polymer (decomplexation–ultrafiltration steps). The effectiveness of these tests was determined based on heavy metal ion concentration measurements in the feed solutions, permeates, and retentates. The parameters chosen for these investigations are given in Table 2.

3. Results and discussion

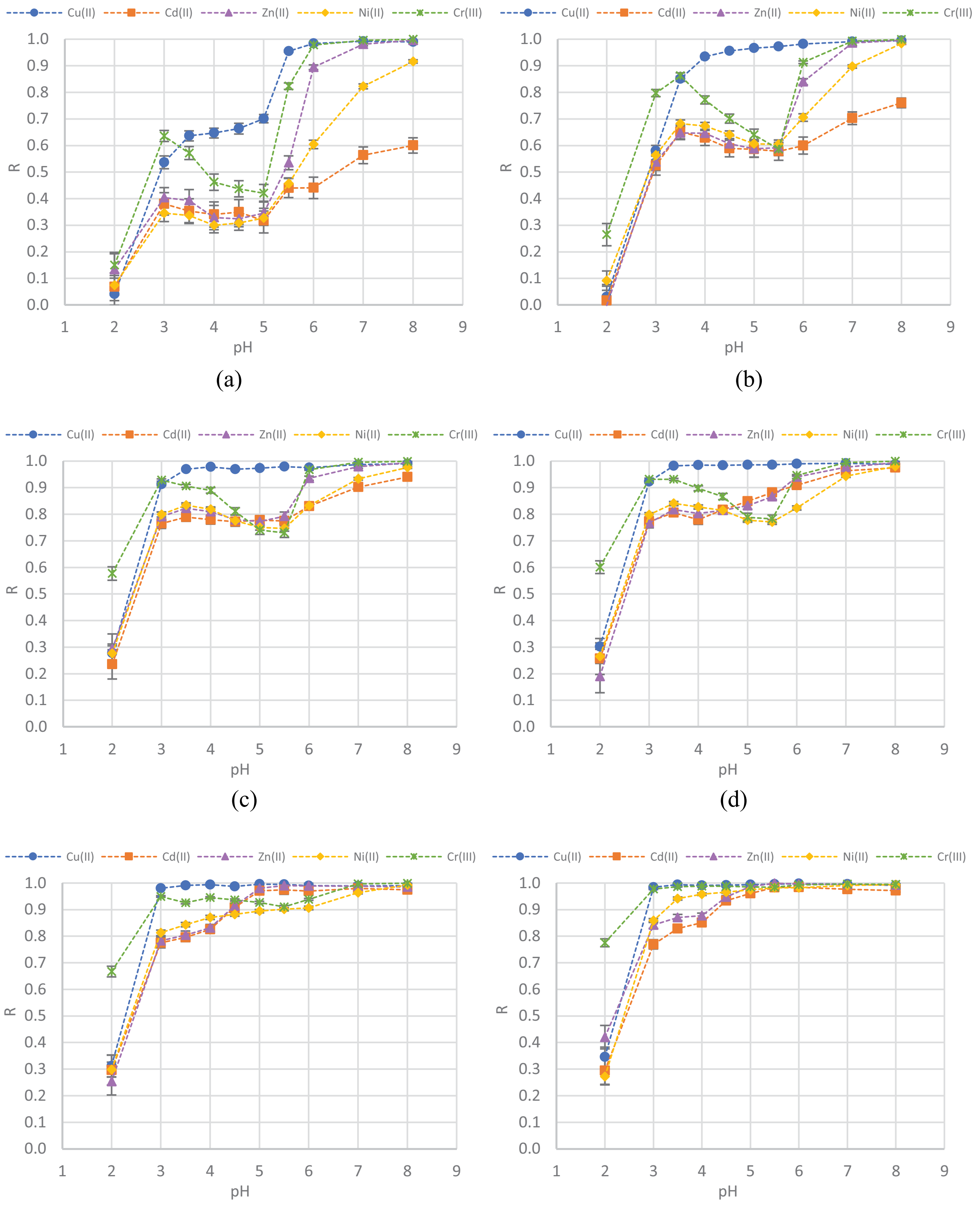
The results of preliminary tests were presented in Figs. 1 and 2. In the Fig. 1 graphs, the effect of pH on individual metal ion retention coefficients (R) for C_{PEI}/C_{Ms} ratio tested were depicted. Fig. 2 shows the total heavy metal ion contents (bars at the graphs) and the compositions of the feed solution and the permeates (mole fractions of particular metal ions) obtained at different process conditions (given pH value at C_{PEI}/C_{Ms} tested).

Analyzing graphs presented in Fig. 1, it can be concluded that both pH and C_{PEI}/C_{Ms} ratio strongly affected the effectiveness of individual heavy metal ion separation. The most diverse values of metal ion rejection coefficients were observed at the smallest PEI dose tested ($C_{PEI}/C_{Ms} = 0.5$), where a strong competition of metal ions in the multi-component mixture was revealed. At pH 2, low rejection coefficients of all heavy metal ions from 0.04 (Cu(II)) to 0.15 (Cr(III)) were observed. This was due to the protonation of amine groups of the polymer in an acidic solution, which caused PEI functional groups to be unable to complex heavy metal ions (this effect was also visible at higher C_{PEI}/C_{Ms} ratios). At higher pH, from pH 3 to pH 5, relatively stable values of R_{Zn}, R_{Ni}, and R_{Cd}, were observed, reporting the separation of 30%–40% of these metal ions with a visible, slightly decreasing tendency. These R values are lower than R_{Cu} and R_{Cr} at such conditions, indicating higher PEI affinity for Cu(II) and Cr(III) than for Zn(II), Ni(II), and Cd(II). At those process conditions, a significant increase of R_{Cu} and simultaneous decrease of R_{Cr} were stated, suggesting a strong competition between the two metals at a limited amount of available complexing groups. At higher pH (pH > 6), opalescence of the feed solution was visible, which may indicate partial metal precipitation and the contribution of this process to metal separation at a limited amount of PEI. The observations of the R vs. pH dependence were similar at $C_{PEI}/C_{Ms} = 1$, with a gradual increase of R_{Cu} (exceeding 0.9 at pH of 4) correlated with a significant decrease of R_{Cr} and a slight decrease of the rejection coefficient of the other three metal ions in the pH range of 3.5–5.5. When a moderate pH value of 4–5 and a limited PEI amount were applied, the affinity for heavy metal ions was in the order Cu(II) > Cr(III) > Ni(II) ≈ Zn(II) ≈ Cd(II). For higher pH of 7–8, the order is as follows: Cu(II) ≈ Cr(III) ≈ Zn(II) > Ni(II) > Cd(II). At C_{PEI}/C_{Ms} of 1 and pH of 5.5, a significant difference in the rejection coefficients of Cu(II) and other analyzed heavy metal ions was visible, indicating the possibility of preferential (partially selective) separation of Cu(II) from the multi-component metal ion mixture. This was consistent with the results achieved

Table 2
Ultrafiltration–concentration and decomplexation–ultrafiltration experiments parameters

Parameter	Values
Ultrafiltration-concentration	
Composition of feed solution	0.2 mmol/dm^3 of each heavy metal ion (in mg/dm^3: Cu(II) – 12.7, Zn(II) – 13.1, Ni(II) – 11.7, Cd(II) – 22.5, Cr(III) – 10.4). Total metal ion concentration C_{Ms} = 1 mmol/dm^3 (70.4 mg/dm^3)
Polymer-to-total metals molar ratio, C_{PEI}/C_{Ms}*	1 (ultrafiltration–concentration I) 7 (ultrafiltration–concentration II)
pH	5.5
Ultrafiltration parameters	MW-type membrane, ΔP = 0.1 MPa, VRF = 10
Decomplexation–ultrafiltration	
Feed solutions	Retentates from ultrafiltration–concentration step
pH	2
Ultrafiltration parameters	MW-type membrane, ΔP = 0.1 MPa, VRF = 0.1

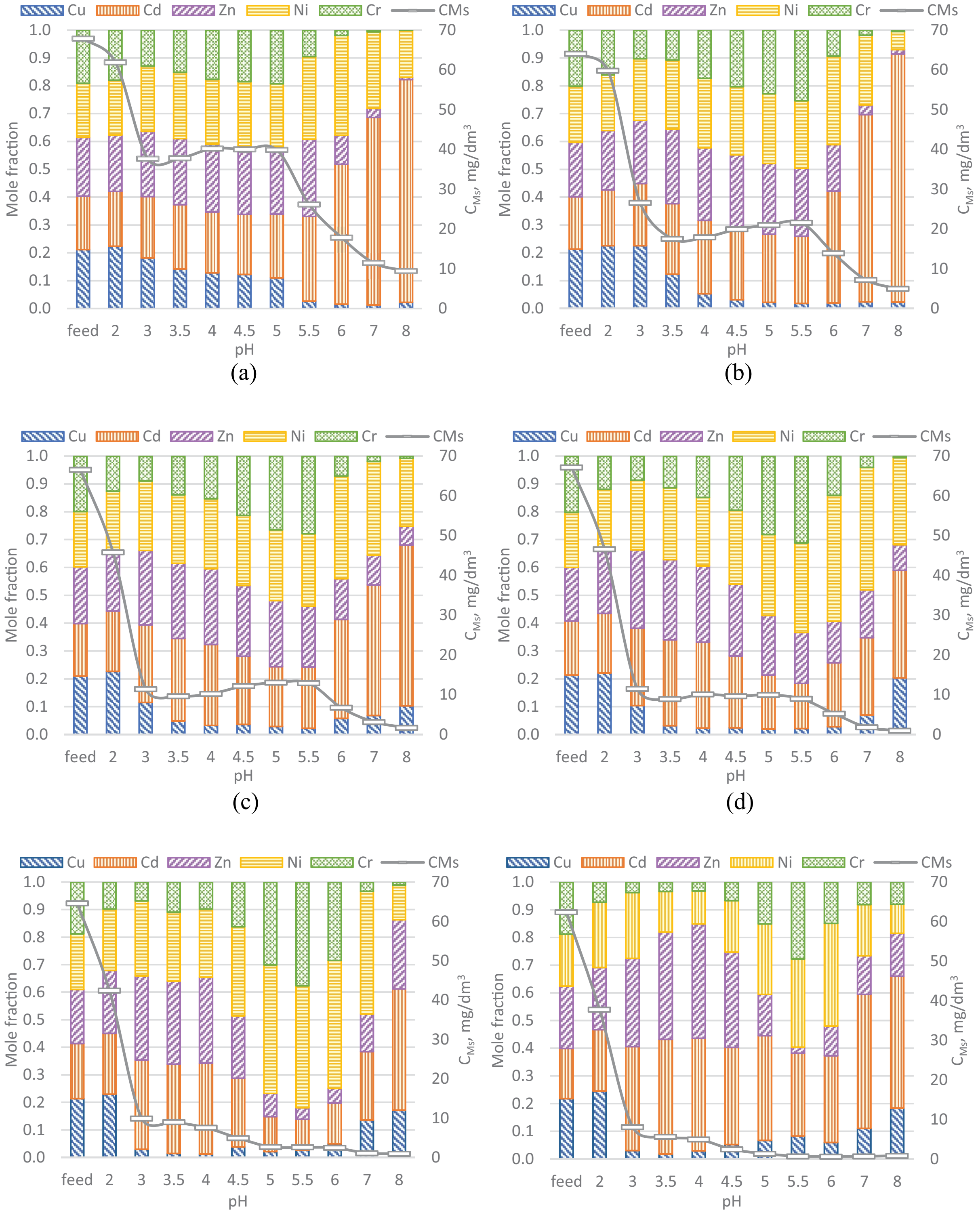
*moles of PEI were considered as moles of polymer repeat unit (mers).



(a) (b) (c) (d) (e) (f)

Fig. 1. Dependence of *R* vs. pH. (a) $C_{PEI}/C_{Ms} = 0.5$, (b) $C_{PEI}/C_{Ms} = 1$, (c) $C_{PEI}/C_{Ms} = 2$, (d) $C_{PEI}/C_{Ms} = 3$, (e) $C_{PEI}/C_{Ms} = 5$, and (f) $C_{PEI}/C_{Ms} = 7$.

by Llanos et al. [31] for partially ethoxylated PEI (PEPEI) in the ultrafiltration of single metal-containing solutions – at a fixed loading ratio (147.37 mmol·metal/mol PEPEI), within pH range of 4–6, the PEPEI affinity towards Cu(II) was much higher than for Ni(II), Cd(II) and Zn(II), but at pH 7 rejection coefficients of Cu(II), Ni(II), and Zn(II) were similar and high compared with significantly lower Cd(II) rejection coefficient.



(a) (b)

(c) (d)

(e) (f)

Fig. 2. Mole fraction of individual metal ions (left *y*-axis) and total heavy metal ion concentrations (right *y*-axis) in feed and permeates at various pH. (a) $C_{PEI}/C_{Ms} = 0.5$, (b) $C_{PEI}/C_{Ms} = 1$, (c) $C_{PEI}/C_{Ms} = 2$, (d) $C_{PEI}/C_{Ms} = 3$, (e) $C_{PEI}/C_{Ms} = 5$, and (f) $C_{PEI}/C_{Ms} = 7$.

For bigger applied doses of PEI, a high copper rejection coefficient, exceeding 0.9 at pH ≥ 3 and reaching up to > 0.99, was noted. A significant decrease of R_{Cr} at pH of 3.3–5.5 was visible up to C_{PEI}/C_{Ms} of 5, then for higher polymer doses disappeared, and very high R_{Cr} values, over 0.98–0.99 were achieved for pH ≥ 3 at $C_{PEI}/C_{Ms} = 7$. Moreover, such a high polymer dose enabled the separation of all investigated heavy metal ions with very high efficiency (≥ 0.98) at the pH of 5.5 or higher.

Comparing the total amount of heavy metal ions in the feed and permeates achieved at smaller C_{PEI}/C_{Ms} ratios (0.5–3) and increasing pH (Fig. 2), a steep decrease of metal ion content can be seen in permeates up to pH 3–3.5, then the C_{Ms} concentration in permeates stabilized in the pH range of 3–5 (C_{PEI}/C_{Ms} = 0.5) or 3.5–5.5 at the level dependent on PEI dose. This indicates that the amine groups of the polymer are partially protonated in this pH range, making the unprotonated functional groups of the polymer too few to bind all the metal ions present in the solution at the limited concentration of PEI. A further increase in pH causes the number of polymer functional groups capable of complexing metal ions to increase, as evidenced by a further reduction in the total concentration of metal ions remaining in the permeate. In addition, as mentioned above, at the lowest applied polymer doses and high pH values, some of the metal ions are precipitated, which also increases their removal efficiency. For a higher amount of polymer used to enhance the UF process (C_{PEI}/C_{Ms} = 5–7), a continuous decrease in total metal ion concentration in permeates with increasing pH is evident throughout the tested pH range, with the most pronounced decrease up to pH 3.

The composition of permeates also fluctuated with C_{PEI}/C_{Ms} and pH, which can be seen comparing mole fractions of particular metal ions in the feed and permeates. It can be seen from the graphs presented in Fig. 2 that with an increase in pH up to 5–5.5, the mole fraction of Cu(II) in permeates decreases with a concomitant increase of mole fraction of Cr(III). This is consistent with $R = f(\text{pH})$ graphs, where competing heavy metal ions revealed higher removal efficiency of Cu(II) over Cr(III). At lower applied PEI doses, the molar fractions of the other three metal ions in this pH range remain similar to each other, testifying to the similar contribution of Ni(II), Zn(II), and Cd(II) in the permeates. This is consistent with the course of the $R = f(\text{pH})$ dependence for these metal ions, which were separated with similar efficiencies in the pH range up to 5–5.5 and C_{PEI}/C_{Ms} up to 3. At higher pH values (and greater availability of functional groups of the polymer), the separation coefficient of Zn(II) and also Ni(II) increases, which results in an increase in the proportion (mole fraction) of Cd(II) in the obtained permeates. A visible increase of mole fractions of Cu(II) and Zn(II) at higher pH (and C_{PEI}/C_{Ms}) values can be caused by both the competing effect of other separated ions and Zn(II) and Cu(II) amphoteric character, although separation efficiency of these metal ions at such conditions remained very high.

ANOVA analysis of different heavy metal ion rejection coefficients revealed statistically significant differences between groups – metal ion types ($F_{\text{value}} = 5.0226 > F_{\text{critical}} = 2.4022$ and $p = 0.0006 < \alpha = 0.05$). The Tukey test showed statistically significant differences between metal ions in pairs R_{Cu} & R_{Cd}, R_{Cu} & R_{Ni}, and R_{Cd} & R_{Cr}, with absolute differences in means, respectively, 0.1658, 0.1371, and 0.1344 (the Tukey critical value 0.1220) at the significance level α = 0.05. According to that test, other pairs of metal ions do not differ statistically significantly, and their absolute differences in means were lower than the Tukey critical value, with the lowest value for the pair R_{Zn} & R_{Ni} (0.0231), and the highest for the pair R_{Cu} & R_{Zn} (0.1140).

Another series of experiments involved ultrafiltration of a heavy metal ions mixture with the addition of tested accompanying ions at selected conditions of C_{PEI}/C_{Ms} = 1, pH = 5.5, and C_{PEI}/C_{Ms} = 7, pH = 5.5. Fig. 3 presents the effect of selected ions on normalized permeate flux J_v/J_w and metal ion separation effectiveness.

The addition of salt reduced permeate flux. That was particularly evident for SO_4^{2-}, PO_4^{3-}, and EDTA ions, both at higher and lower polymer doses. It is known that in the presence of salts with high concentration, PEI molecules reveal a tendency to aggregation [33], which can intensify the transport-limiting phenomena (fouling and polarization concentration). In addition, multivalent anions and EDTA have greater (than monovalent anions) ability to interact with PEI protonated amino groups, enhancing this phenomenon.

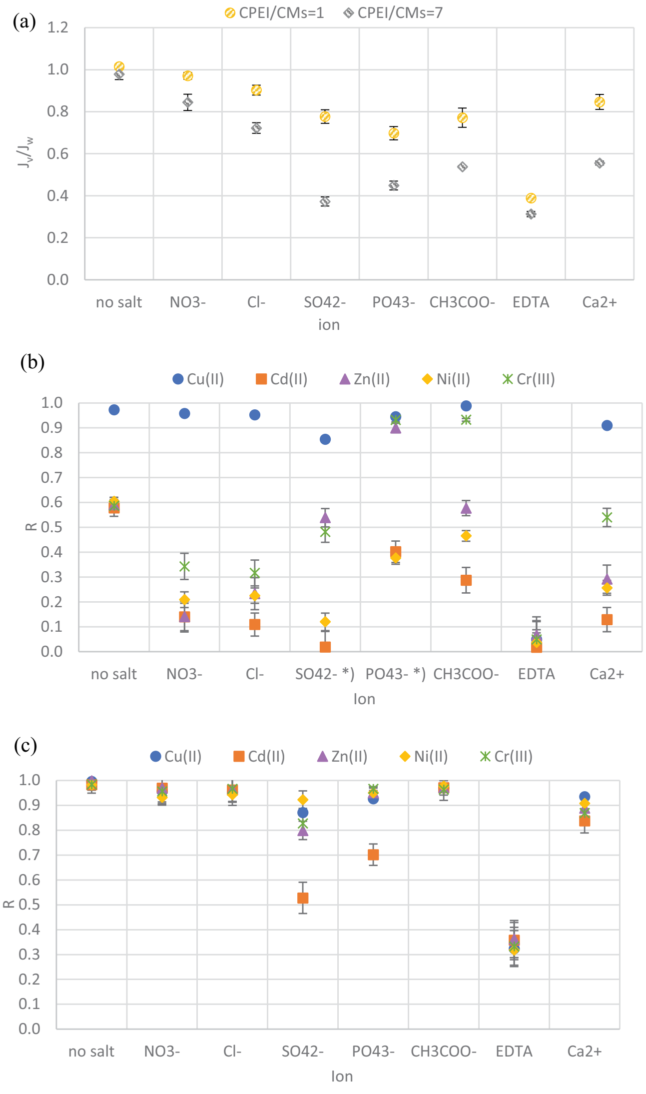


Fig. 3. Impact of selected ions on normalized permeate flux (a), and individual metal ion rejection coefficients at C_{PEI}/C_{Ms} = 1, pH = 5.5 (b), C_{PEI}/C_{Ms} = 7, pH = 5.5 (c). (*) visible opalescence in the solution.

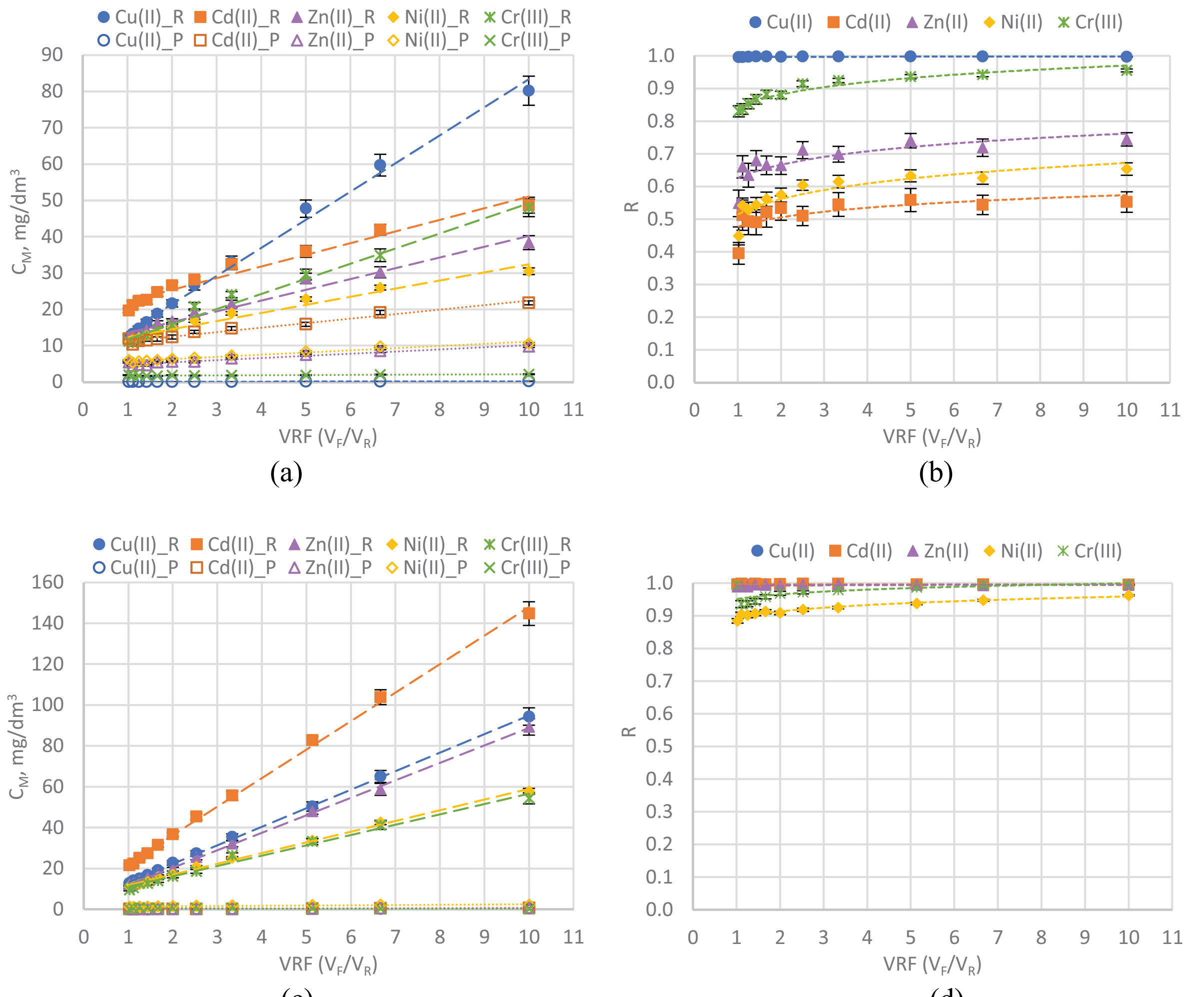
Salt-induced aggregation of PEI results in a more compact polymer molecule and less availability of functional groups for metal ions. This, in turn, can result in lower metal ion retention coefficients (Fig. 3b and c). At a lower PEI dose and the presence of tested accompanying ions, a significant decrease of almost all metal ion rejection coefficients was visible compared to the model solution without an additional salt (reference solution). The exceptions are R_{Cu} and R_{Cr} in the presence of CH_3COO^- and R_{Zn} and R_{Cr} in the presence of PO_4^{3-}, which were higher than for the reference solution, which may be induced by an additional interaction between the anion, metal cation and polymer. Molinari et al. [27] confirmed the possibility of Cu(II) removal in UF enhanced with PEI in the presence of copper-chelating citric acid due to the formation of the ternary Cu-citric acid-PEI complexes. Acetic acid is known for forming 1:1 metal-carboxylate complexes with stability constants higher for Cu(II) than for other divalent metal ions (like Cd(II), Zn(II), Ni(II)) [35], which possibly can enhance Cu(II) separation in the PEUF process. Better separation of Cr(III) and Zn(II) ions from the solution containing PO_4^{3-} can be explained by the partial precipitation of these metal ions (an opalescence of the solution was visible at the smaller applied PEI dose). A significant decrease of metal ion rejection coefficients, especially R_{Ni}, R_{Cd} (and also R_{Cu}, although that rejection coefficient was still the highest of all metals), was visible in the solution containing SO_4^{2-} ions. In that solution, with pH adjustment, turbidity (opalescence) appeared. The reason for this may be the formation of insoluble complexes of PEI with sulfate ions at tested pH [36] and the lower availability of PEI to metal cations, worsening their separation efficiency. The most visible decrease of the metal ion rejection coefficients was registered in the test with an additive of EDTA. EDTA is a strong chelating agent (competing with PEI functional groups) and can form stable low-molecular-weight complexes with many heavy metal cations, which can pass through the UF membranes, decreasing metal ion rejection coefficients. PEI, containing amine groups, can bind heavy metal ions based on two possible mechanisms – an acid–base interaction (coordination bonds) or the electrostatic effect of metal chelates and protonated amine groups [29]. According to Rivas et al. [37] PEI amine groups are protonated to some extent even at a pH of 7, and the degree of protonation strongly increases with lowering pH. At such conditions, the negatively charged metal-EDTA complexes can electrostatically interact with protonated polyamine (PEI). At pH > 10, amine groups are completely deprotonated and metal ion rejection is due to acid–base interaction [29]. As was shown, both Ni-EDTA and Cd-EDTA chelates can be effectively removed by UF enhanced with PEI at low Me-EDTA/PEI molar ratios. With an increasing Cu-EDTA/PEI ratio, Cu concentration in the permeate sharply increased, and the UV-Vis analysis revealed that Cu-EDTA chelates appeared in the permeate [29]. At the higher PEI dose (Fig. 3c), the reduction of metal ion rejection coefficients in solutions containing tested salts was less pronounced but remained significant for EDTA and SO_4^{2-}, and PO_4^{3}- (the case of Cd(II) ion).

ANOVA analysis followed by the Tukey test demonstrated statistically important differences between groups (type of metal ions) at $C_{PEI}/C_{Ms} = 1$ ($F_{value} = 4.7781 > F_{critical} = 2.6896$ and $p = 0.0042 < \alpha = 0.05$). The significant differences accrued between the metal ion R pairs R_{Cu} & R_{Cd} and R_{Cu} & R_{Ni} (absolute differences in means, respectively, 0.5952 and 0.5257, at Tukey critical value 0.4087). Other pairwise differences were statistically insignificant with absolute differences in means from 0.0695 (R_{Cd} & R_{Ni}) to 0.3816 (R_{Cu} & R_{Zn}). At $C_{PEI}/C_{Ms} = 7$, no statistically significant differences appeared between the metal ion R values ($F_{value} = 0.1828 < F_{critical} = 2.6415$ and $p = 0.9458 > \alpha = 0.05$).

For the next ultrafiltration–concentration tests, two sets of process parameters were chosen (Table 2). UF concentration I was conducted at the polymer dose insufficient for complete complexation of all heavy metal ions in the mixture, but without any visible opalescence or precipitants in the solution ($C_{PEI}/C_{Ms} = 1$, pH 5.5). UF concentration II was performed at the same pH (5.5) but with a much higher PEI dose ($C_{PEI}/C_{Ms} = 7$). The comparison of ultrafiltration concentrations I and II for the five-component heavy metal ion solution is given in Fig. 4. The graphs present concentrations of particular metal ions in retentates and permeates and their rejection coefficients as a function of VRF.

At a higher dose of polymer enhancing ultrafiltration, a significantly higher increase of all metal ion concentrations in retentate within the course of the process was observed. It was particularly pronounced in the case of Cd(II), Zn(II), and Ni(II) – the final retentate achieved at $C_{PEI}/C_{Ms} = 7$ contains, respectively, 3-, 1.9-, and 1.8-times higher amounts of these metal ions. Concentration of Cu(II) and Cr(III) also occurred with greater efficiency at a higher PEI dose, but the difference in the case of these metal ions was not so significant (several percent). Heavy metal ion rejection coefficients varied depending on metal type and the process conditions. At $C_{PEI}/C_{Ms} = 7$ and pH = 5.5, all heavy metal ions were separated with more than 90% efficiency, and the rejection coefficient of Cu(II), Cd(II), and Zn(II) exceeded even 99%. At the lower PEI dose ($C_{PEI}/C_{Ms} = 1$, pH = 5.5), only Cu(II) was separated at a very high level (over 99%). Cr(III) separation occurred with an efficiency of 83%–96%, while the other metal ions were removed to a much lower extent (up to 74% of Zn(II), 65% of Ni(II), and 55% of Cd(II)). These results confirm the observations from the preliminary studies indicating a greater affinity of PEI for copper ions than for other metal ions present in the mixture. It can also be concluded that the metal whose separation was most affected by the PEI dose was Cd(II).

Heavy metal ion rejection coefficients were also proceeded using the ANOVA method and the Tukey test. At $C_{PEI}/C_{Ms} = 1$, pH = 5.5, statistically significant differences were stated between the metal ion types ($F_{value} = 222.27 > F_{critical} = 2.5572$ and $p = 3.5 \times 10^{-31} < \alpha = 0.05$) with statistically significant differences between all pairs of metal ions except for R_{Cd} & R_{Ni} (absolute difference in means 0.0611 at Tukey critical value 0.0634). Statistical evaluation of R values of the five metal ions during UF-concentration (II), at $C_{PEI}/C_{Ms} = 7$ and pH = 5.5, indicated significant differences between them ($F_{value} = 56.925 > F_{critical} = 2.5572$ and $p = 5.2 \times 10^{-18} < \alpha = 0.05$) with significant differences pairwise between the metal ions, except for R_{Cu} & R_{Cd}, R_{Cu} & R_{Zn}, and R_{Cd} & R_{Zn} (absolute differences in means, respectively, 0.0002, 0.0029, and 0.0031, at Tukey critical value 0.0201). Statistically significant differences were also stated between



(a) (b)

(c) (d)

Fig. 4. Concentrations of heavy metal ions in retentates and permeates (a,c) and heavy metal ion retention coefficients (b,d) as a function of volume reduction factor in ultrafiltration at $C_{PEI}/C_{Ms} = 1$, pH = 5.5 (a,b) and $C_{PEI}/C_{Ms} = 7$, pH = 5.5 (c,d).

R values achieved for the two sets of all metal ions during UF-concentration I and II ($F_{value} = 85.9364 > F_{critical} = 3.9290$ and $p = 2.12 \times 10^{-15} < \alpha = 0.05$). Moreover, a comparison of *R* values for each of the five metal ion types revealed statistically significant differences between means determined at process condition I and II (F_{value} from 7.9930 for Cu(II) to 1,226.5 for Cd(II), at $F_{critical} = 4.3512$, and p from 0.01401 (Cu(II)) to 2.00×10^{-19} (Cd(II)), at the assumed level of significance of $\alpha = 0.05$).

The final retentates from UF-concentration processes were then subjected to decomplexation at pH = 2, followed by ultrafiltration. Fig. 5 presents the comparison of the initial feed solution, final retentate, and average permeate achieved at the ultrafiltration–concentration step, as well as feed and permeate from the decomplexation–ultrafiltration process, for both PEI doses tested. The graphs depict the total metal ion concentrations (additional *y*-axis) and mole fractions of particular metal ions.

In each of the two concentration cycles, carried out at different PEI doses, a significant increase in the total metal ion concentration in the retentate relative to the feed solution was evident, with the higher PEI dose, $C_{PEI}/C_{Ms} = 7$, making the final concentration almost 1.8 times higher than at $C_{PEI}/C_{Ms} = 1$. Substantial differences were also stated in permeates, with total metal ion concentrations amounting to 28.7 and 2.88 mg/dm³ at, respectively, C_{PEI}/C_{Ms} of 1 and 7. The decomplexation–ultrafiltration process enabled the recovery of 79.7% and 80.0% of the total concentrated metal ions, respectively for lower and higher PEI doses. The efficiency according to individual metal ions amounted to 83.48%, 90.49%, 86.98%, 84.92%, and 54.57%, respectively for Cu(II), Cd(II), Zn(II), Ni(II), and Cr(III) for the solution concentrated at $C_{PEI}/C_{Ms} = 1$, and 77.80%, 79.76%, 87.35%, 91.65%, and 66.91% of the same metal ions for the solution concentrated at higher dose of PEI. In the process conducted at $C_{PEI}/C_{Ms} = 7$, the equimolar composition of the feed solution was more or less maintained in the retentate from the concentration process, as well as in the feed and permeate from the decomplexation–ultrafiltration process. There were only minor changes in the molar contribution of metal ions (a slight increase in the mole fraction of copper, cadmium, and zinc, and a decrease in the mole fraction

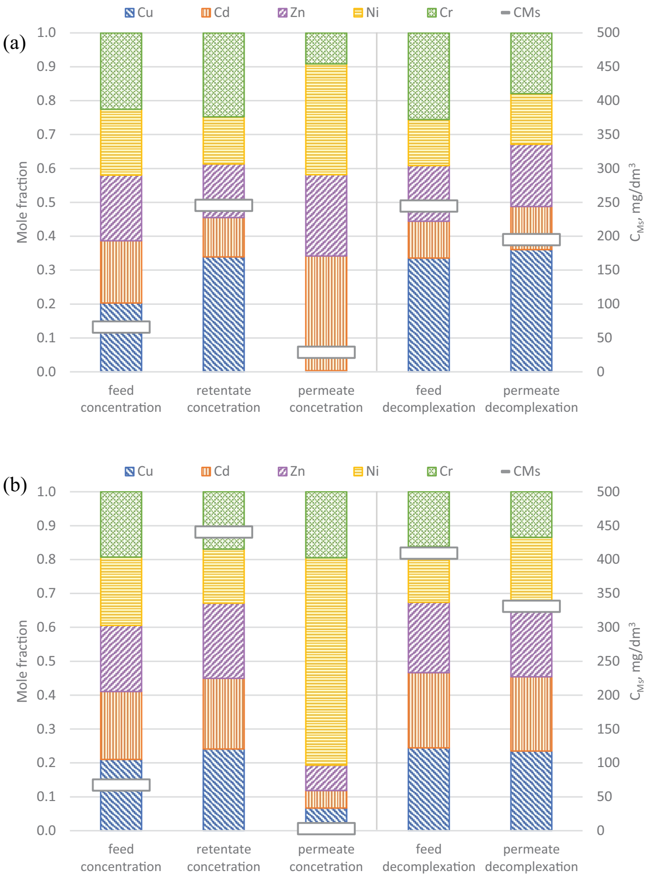


Fig. 5. Mole fractions of heavy metal ions and total heavy metal ion concentration (additional axis) in ultrafiltration streams from concentration and decomplexation processes. (a) Concentration at C_{PEI}/C_{Ms} = 1, pH = 5.5, decomplexation pH = 2 and (b) concentration at C_{PEI}/C_{Ms} = 7, pH = 5.5, decomplexation pH = 2.

of nickel and chromium). In the process carried out with a lower dose of PEI, the competitive separation of the metal ion mixture led to greater differences in the molar composition of the concentrated retentate and the feed and permeate from the decomplexation–ultrafiltration process. Above all, these solutions show an increase in the mole fraction of copper, undergoing retention to a greater extent, and a reduction in the mole fraction of less separated cadmium and nickel. Significant variations were also found in the average permeates from concentration processes at different PEI dosages. There was about a 10-fold difference in total metal ion concentration between the two and significant variations in solution composition. In the process conducted with a lower PEI amount, due to the preferential separation of Cu(II), the permeate was almost completely devoid of copper ions. The mole fraction of chromium ions was also reduced, while the mole fractions of cadmium and nickel ions, the two metals separated less effectively, were significantly increased. The permeate obtained by the process with a higher dose of PEI was characterized by reduced mole fractions of Cu(II), Cd(II), and Zn(II) and a significantly increased ratio of Ni(II) compared to the metal ion fractions in the initial feed. However, the overall concentration of metal ions in the permeate was 23-fold lower than in the feed solution and 153-fold lower than in the final retentate.

4. Conclusion

This work presents the possibility of heavy metal ion removal from a five-component mixture (Cu(II), Zn(II), Cd(II), Ni(II), Cr(III)) using ultrafiltration enhanced with PEI. The impact of pH, polymer-to-metals molar ratio and the presence of additional salts on heavy metal ion separation efficiency have been discussed. Two concentration processes have been conducted – at lower and higher PEI doses, followed by decomplexation (pH = 2) and ultrafiltration to recover concentrated heavy metal ions. The composition of the process streams (mole fractions of particular metal ions) was also evaluated.

To promote PEUF selective separation of heavy metal ions from multi-component systems, both limited polymer amount and proper pH adjustment can be used. At PEI-to-total metals molar ratio of 1 and pH 5.5, preferential Cu(II) separation from other heavy metal ions was achieved, but the completely selective copper separation was not possible at tested process parameters.

The additive to the multi-component heavy metal ion solution of an accompanying ion (NO_3^-, Cl^-, SO_4^{2-}, PO_4^{3-}, CH_3COO^-, EDTA or Ca^{2+}), with significant concentration, lowered permeate flux, which was especially pronounced in the case of ions strongly interacting with the polymer used (EDTA, SO_4^{2-}, PO_4^{3-}). Accompanying ions can also diminish heavy metal ion rejection coefficients, especially in a strongly competitive environment (moderate pH, limited amount of the polymer enhancing ultrafiltration).

The combination of the two processes, ultrafiltration–concentration with the following decomplexation–ultrafiltration, enables the separation of polymer-deprived heavy metal ion concentrates with various mole fractions of copper, depending on the process conditions.

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