



Ultrafiltration enhanced with poly(sodium acrylate) as an effective method for separation of heavy metals from multicomponent solutions

Irena Korus

Department of Water and Wastewater Engineering, Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland, Tel. +48 32 2371978; Fax: +48 32 2371047; email: irena.korus@polsl.pl

Received 5 May 2021; Accepted 24 August 2021

ABSTRACT

Polymer-enhanced ultrafiltration was used to separate heavy metal ions from their multicomponent mixtures. Model solutions containing an equimolar mixture of Cu(II), Zn(II), Cd(II), Ni(II), Cr(III) were supplemented with poly(sodium acrylate) PSA (a metal-binding polymer) and the ultrafiltration process was carried out. The separation effectiveness of individual metal ions was studied under various process conditions (amount of PSA, pH, total metal concentration, presence of coexisting ions), and the possibility of simultaneous or selective (competitive) separation of individual ions from a multicomponent mixture was evaluated. Effective simultaneous separation of metal ions occurred in solutions containing a sufficient polymer dosage (polymer/metal molar ratio $C_{PSA}/C_M \geq 7$) and at a sufficiently high pH ($pH \geq 6$). Since the polymer showed differential affinity for the metals tested ($Cr(III) \approx Cu(II) > Cd(II) \gg Zn(II) > Ni(II)$), partially selective separation of ions from the mixture at a decreased pH or lowered C_{PSA}/C_M was possible. In addition, certain co-occurring ions (especially versenate, EDTA) decreased the separation effectiveness of Cu(II), Zn(II), Cd(II) and Ni(II). These preliminary observations were confirmed by the ultrafiltration concentration of the metal mixture, carried out at different values of the process parameters, and the subsequent decomplexation–ultrafiltration process ($pH = 2$), enabling the recovery of concentrated metal solutions of varying composition, depending on the process conditions.

Keywords: Polymer-enhanced ultrafiltration; Poly(sodium acrylate); Heavy metals; Multicomponent mixtures

1. Introduction

Heavy metals are considered dangerous environmental pollutants of increasing impact, as both population and industrialization continue to surge. Their presence in the air, water and soil has serious implications because they are toxic, non-biodegradable and have the ability to accumulate in the tissues of living organisms. Scientists have devoted a great deal of attention to the development of new effective methods for the separation of heavy metals from aqueous solutions, industrial effluents and wastewater. One such method is polymer-enhanced ultrafiltration (PEUF), also known as polymer-assisted ultrafiltration, liquid-phase

polymer-based retention (LPR) or complexation–ultrafiltration. The technique combines the use of a water-soluble polymer with proper functional groups to bind heavy metal ions and a low-pressure membrane process (ultrafiltration) to separate the polymer-metal complexes. Generally, two groups of metal-binding polymers can be distinguished – polychelatogenes and polyelectrolytes. Polychelatogenes are macroligands with uncharged complexing functional groups, mainly O-donors, like alcohols and crown ethers or N-donors, including amines and amides, which can form coordination bonds with metal ions. Polyelectrolytes contain charged (dissociated) functional groups, either acidic (carboxylic, phosphonic, sulfonic acids or their salts)

or basic (quaternary ammonium salts), and reveal ion-exchange properties. Electrostatic interaction is the prevailing metal-bonding mechanism in polyelectrolyte-enhanced ultrafiltration [1,2]. In addition to various synthetic polymers, biopolymers, such as chitosan, carboxymethyl cellulose and starch, are also used to support the ultrafiltration process [3–5]. The membrane used in the PEUF process should be selected according to the applied polymer in terms of separation properties so as to ensure complete retention of polymer-metal complexes. Many parameters affect the efficiency of the separation process, the most important are polymer type and dosage, metal concentration, pH, ionic strength, as well as temperature and transmembrane pressure [2]. Polymer-enhanced ultrafiltration was intensely investigated for the removal of various contaminants from aqueous solutions and wastewater, among them boron [6], dyes [7,8], antibiotics [9,10] and, above all, heavy metals [2,11,12]. In addition to the separation of metals from single-metal-containing solutions, PEUF has been examined for the separation of metals from multicomponent systems. This is a particularly important aspect of the research, as heavy metals often occur as multicomponent mixtures in industrial effluents and wastewater. Chen et al. investigated the competitive separation of Cu(II) and Pb(II) ions from solutions containing naturally occurring mono- and divalent cations. Polyelectrolyte with sulfonate group (poly(sodium 4-styrenesulfonate), PSS) was used as a polymer supporting the PEUF separation. The authors showed that the affinity of the polymer to the cation depends on its valence and ionic radius. A chelating polymer – partially ethoxylated polyethyleneimine (PEPEI) – was used to assist the ultrafiltration separation of Cu(II), Ni(II), Cd(II) and Zn(II) ions [14]. The authors compared PEPEI-metal complex formation constants and assessed that selective separation of Cu(II) and Zn(II) is technically feasible with the process selectivity increasing with pH and the metal/polymer loading ratio. Polyethyleneimine PEI (a polymer containing amino groups and exhibiting both complex formation and weak anion-exchange properties) has proven to be effective in the separation of heavy metals from binary mixtures, such as Cd(II)/Hg(II) [15], Cu(II)/Ni(II) [16], Cu(II)/Cr(VI) [17], Zn(II)/Cr(VI) [18]. With the proper adjustment of pH and the polymer/metal ratio, the simultaneous removal of heavy metals from the binary mixtures or their selective separation (fractionation) was possible. Another important factor that can affect the selectivity of the PEI-enhanced separation process is ionic strength, as was shown by Kadioglu et al. [19] in the tests of Cd(II)/Ni(II) and Ni(II)/Zn(II) binary solutions. Polymers containing carboxyl groups are also proposed to support the ultrafiltration separation of heavy metals in competitive conditions. A commercial copolymer of maleic acid and acrylic acid was investigated towards the selective separation of heavy metals from binary Cu(II)/Zn(II), Zn(II)/Ni(II), and Ni(II)/Mn(II) mixtures [20]. It was found that Cu(II) tendency to form complexes with a copolymer was much greater than the other metals and the order of metal-binding ability with a copolymer was Cu(II) \gg Zn(II) $>$ Ni(II) $>$ Mn(II). A similar effect of higher Cu(II) rejection than Zn(II) was stated in the PEUF enhanced with poly(acrylic acid) in a pH range of 2–10 [21].

The presented work concerns the separation of Cu(II), Cd(II), Zn(II), Ni(II) and Cr(III) ions from multicomponent mixtures with the use of ultrafiltration enhanced by poly(sodium acrylate). These metals are commonly found in galvanic wastewater and industrial effluents from metalworking processes. They often occur in multicomponent mixtures, so their separation under competitive conditions is an essential issue. The influence of the most important parameters (pH, polymer/metal ratio, total metal concentration, presence of selected accompanying ions) on the effectiveness of the removal of individual metals from their equimolar mixture was investigated. The possibility of both simultaneous and selective (fractionated) separation of the mixture components was evaluated. Then, the processes of concentration (complexation-ultrafiltration) of the equimolar metal mixture followed by decomplexation-ultrafiltration of the obtained retentates were conducted, and the composition of the obtained streams was evaluated.

2. Materials and methods

A series of 10 mmol/dm³ stock solutions of heavy metals were prepared from their inorganic salts Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O, Cd(NO₃)₂·4H₂O, Cr(NO₃)₃·9H₂O (POCH SA, Poland). Poly(acrylic acid) sodium salt poly(sodium acrylate) (PSA) (40% aqueous solution, $M_w = 35$ kDa) was purchased at Sigma-Aldrich, (Poland). Two polymer-containing stock solutions were prepared with concentrations of 50 and 5 mmol PSA/dm³. The polymer molar concentration was calculated with the respect to the repeating unit of the polymer. Five-component equimolar mixtures of heavy metals Cu(II), Cd(II), Zn(II), Ni(II) and Cr(III) with a total metal concentration of 0.5–10 mmol/dm³ and an additive of polymer in the range of PSA concentrations 0–10 mmol/dm³ were prepared using individual metal stock solutions and polymer stock solutions. Then, the pH was adjusted to the desired value in the range of 2–9 using HNO₃ or NaOH (POCH SA, Poland), and the solutions were left for 1 h to form polymer-metal bonds before the ultrafiltration process.

The AMICON 8400 stirred ultrafiltration cell (Merck Millipore, Merck Sp. z o.o., Poland) was used to perform the ultrafiltration process. The cell was equipped with the polysulfone ultrafiltration membrane EW type (GE Osmonics) provided by Sterlitech Corporation and compressed nitrogen as a pressure source. The membrane was pre-conditioned in deionized water in the pressure range of 0.05–0.3 MPa for 6 h and then the membrane permeability was characterized experimentally, which was 163.7 ± 4.1 dm³/(m² h MPa).

Four series of the preliminary PEUF tests were carried out at a transmembrane pressure of 0.2 MPa. To prevent the concentration of the solutions, the volume of the received permeate did not exceed 10% of the volume of the feed solution. The basic values of process parameters in the preliminary tests were as follows: total metal concentration $C_M = 1$ mmol/dm³, polymer/metal molar ratio $C_{PSA}/C_M = 5$, pH = 5. To assess the effect of each of these parameters on the separation efficiency, a series of UF tests with different values of one parameter and constant values of the others were carried out. Moreover, a series of tests with the

addition of selected salts was performed to evaluate the effect of certain ions on the removal of metals from the mixture. The process parameters used in the PEUF series were collected in Table 1.

In each test, the concentrations of individual metals were analyzed in the feed and permeate (SpectrAA 880 atomic absorption spectrometer, Varian). The measured values enabled the determination of individual metal rejection coefficients as $R = 1 - (C_p/C_f)$, where C_f is the metal concentration in the feed solution, mg/dm^3 ; C_p is the metal concentration in the permeate, mg/dm^3 .

The error in the determination of the R -value did not exceed 7%. Following the preliminary tests, three PEUF concentration processes at various process parameters were performed to evaluate the possibility of selective or simultaneous concentration of heavy metals in multicomponent solutions. The total initial concentration of heavy metals C_M was $1 \text{ mmol}/\text{dm}^3$ and the solutions contained no additional salt. The other process parameters for the concentration mode were as follows:

- Conc. 1: $C_{\text{PSA}}/C_M = 2$; $\text{pH} = 5$;
- Conc. 2: $C_{\text{PSA}}/C_M = 5$; $\text{pH} = 4$;
- Conc. 3: $C_{\text{PSA}}/C_M = 7$; $\text{pH} = 6$.

The PEUF process was conducted at the transmembrane pressure of 0.2 MPa, until the volume reduction factor (VRF) of 10 was achieved, where $\text{VRF} = V_f/V_r$ and V_f , V_r are the initial feed volume and volume of the retentate,

respectively. The samples of permeate and remaining retentate were collected periodically, metal concentrations were determined, and metal retention coefficients were calculated as $R = 1 - (C_p/C_f)$, where C_r and C_p are concentrations of the metal in, respectively, retentate and permeate at the current stage of the process. Then, the obtained retentates were acidified to $\text{pH} 2$, and an ultrafiltration process was performed to separate the polymer from the concentrated metals. The effectiveness of this decomplexation-ultrafiltration steps were also evaluated. The composition of the process streams (molar fractions of individual metals in the feed, average permeate and final retentate, and permeate from the decomplexation-ultrafiltration step) were compared.

3. Results and discussion

Fig. 1 shows the effect of the polymer/total metal molar ratio C_{PSA}/C_M on the effectiveness of metal ion separation from the multicomponent mixture and the composition of permeates.

Ultrafiltration without the addition of a supporting polymer was ineffective. The removal of individual metals ranged from 3% to 16% (7.3% of total metals) and was most likely caused by the adsorption of metal ions on the membrane. The composition of the permeate was similar to the composition of the feed solution. Generally, the efficiency of PSA-assisted ultrafiltration depended on the amount of polymer added, increasing with the increasing PSA dose

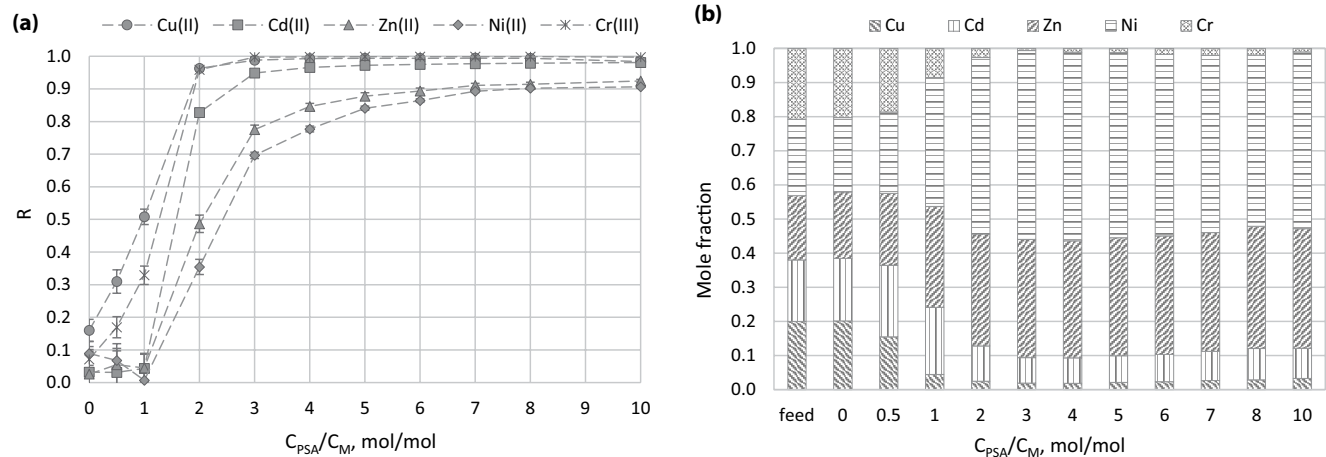


Fig. 1. Effect of the polymer/total metal molar ratio on the individual metal rejection coefficients (a) and the composition of permeates (b). $C_M = 1 \text{ mmol}/\text{dm}^3$; $\text{pH} = 5$.

Table 1
Process parameters in preliminary tests

No.	C_M , mmol/dm^3	C_{PSA}/C_M , mol/mol	pH	Coexisting ion/ C_{ion}/C_M , g/g
I	1	0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 10	5	–/0
II	1	5	2, 3, 3.5, 4, 4.5, 5, 6, 7, 8, 9	–/0
III	0.5, 1, 2, 3, 4, 5, 6, 10	5	5	–/0
IV	1	5	5	$\text{NO}_3^-/10$, $\text{Cl}^-/10$, $\text{SO}_4^{2-}/10$, $\text{PO}_4^{3-}/10$, $\text{CH}_3\text{COO}^-/10$, $\text{EDTA}/10$, $\text{Ca}^{2+}/2.5$, $\text{Fe}^{3+}/2.5$

until a characteristic plateau was obtained, showing the maximum rejection of a given metal at pH = 5, which was 98%–99% for Cu(II) and Cd(II), over 99% for Cr(III) and 91%–93% for Ni(II) and Zn(II). However, the course of the $R = f(C_{PSA}/C_M)$ dependence varied for different metals of the mixture. The steeper increase of R with the amount of PSA was observed for Cu(II) and Cr(III) with the separation effectiveness ca. 96% at $C_{PSA}/C_M = 2$. The lower increase of metal rejection coefficient with the polymer dose was recorded for Zn(II) and Ni(II), and at C_{PSA}/C_M of 2 only 49% and 35% of these metals (respectively) were removed in the process. With an insufficient amount of PSA in the solution, metal ions compete for available active sites – dissociated carboxylic groups of the polymer, which results in various degrees of separation of individual metals. The affinity of the polymer to metals in such conditions can be written as follows: $Cr(III) \approx Cu(II) > Cd(II) \gg Zn(II) > Ni(II)$. These differing behaviors of individual metals in multicomponent solutions resulted in differences in the permeate composition in comparison to the feed solution. As can be seen

from Fig. 1b, with the increase of C_{PSA}/C_M ratio within the range of 0.5–3, the permeate was gradually enriched with Zn(II) and Ni(II) and deprived of Cu(II), Cr(III) and Cd(II). With larger PSA additions, the molar fractions of individual metals in the permeate remained almost constant, but the total concentration of metals decreased. The total metal rejection coefficient reached 96% at $C_{PSA}/C_M = 7$ and did not change with the further increase of the polymer amount.

The retention coefficient of individual metals in the multicomponent mixture and the permeate composition strongly depended on pH (Fig. 2).

In the acidic solution within a pH range of 2–3, a low metal retention was observed. When pH increased (pH > 3), a sharp increase of Cr(III) and Cu(II) rejection coefficient was recorded, leading to the R values of 0.96 and 0.95 (respectively) at pH = 4.5. A similar increase in the separation efficiency of the remaining metals was observed in the pH range of 3–5 (Cd(II)) and 3.5–6 (Zn(II) and Ni(II)). Therefore, the greatest variation in the values of retention

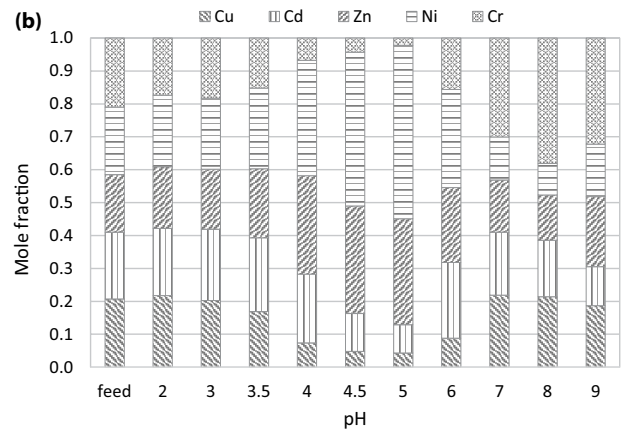
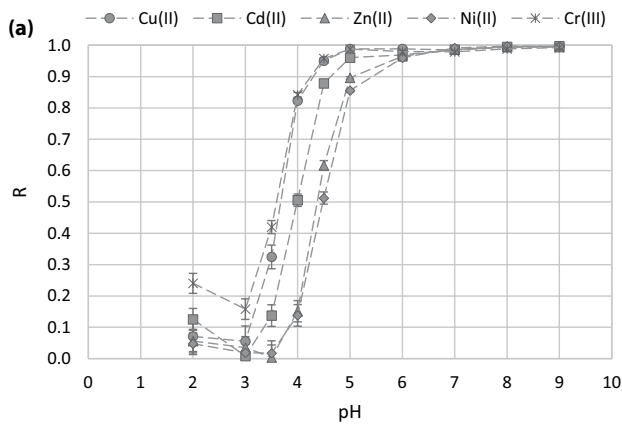


Fig. 2. Effect of pH on the individual metal rejection coefficients (a) and the composition of permeates (b). $C_M = 1 \text{ mmol/dm}^3$; $C_{PSA}/C_M = 5$.

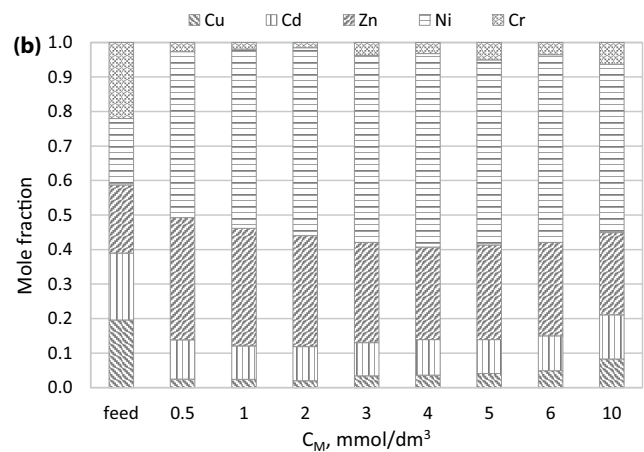
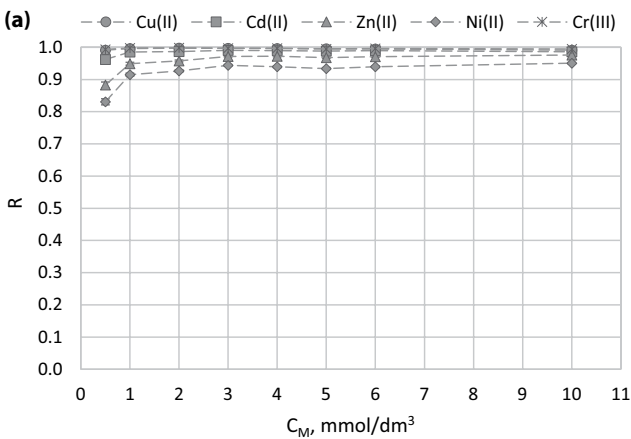


Fig. 3. Effect of total metal concentration C_M on the individual metal rejection coefficients (a) and the composition of permeates (b). $C_{PSA}/C_M = 5$; pH = 5.

factors of individual metals was observed in the pH range 3–6, which resulted in differences in molar proportions of permeate components (Fig. 2b). The acid-base behavior of PSA can be explained by the nature of the functional groups of the polymer. PSA contains carboxylic acid moieties, which are weakly acidic with pK_a c.a. 4–5. At $pH < pK_a$, due to protonation of the carboxyl group, the polymer behaves as a polychelator towards heavy metal ions and forms coordination bonds based on electron-donor oxygen atoms. When the pH of the solutions increases above the pK_a , dissociated carboxyl groups appear and electrostatic interaction between $-COO^-$ groups and heavy metal cations take place. The polymer behaves as a polyelectrolyte [1].

The impact of total metal concentration on individual metal separation and the composition of permeate, at constant values of $C_{PSA}/C_M = 5$ and $pH = 5$, was shown in Fig. 3.

In the range of the total metal concentration tested (C_M from 0.5 to 10 mmol/dm³), at applied process conditions (constant polymer/metal ratio C_{PSA}/C_M of 5 and $pH = 5$), no significant differences in the rejection coefficient of individual metals or permeate composition were observed. The total metal rejection coefficient ranged from 0.94 to 0.98, and was higher for Cu(II), Cr(III) (>0.99) and Cd(II) (0.96–0.99) than for Zn(II) (0.88–0.98) and Ni(II) (0.83–0.95).

The presence of coexisting species (inorganic salts, dissolved organic compounds) in solutions can impact the effectiveness of the PEUF process. The coexisting ions can affect an electrostatic interaction between the target metal ion and the polyelectrolyte used in the process. This decreases the bonding strength between heavy metal and polymer and diminishes the heavy metal rejection coefficient. The co-ions can interact with the polymer competing with the target metal ions and lowering the separation effectiveness. Similarly, the presence of low molecular complexing and chelating species can lead to a decrease in the amount of heavy metal ions available for polymer, making the separation process less effective. Because of that, the PEUF tests with the addition of various ionic species were undertaken. The concentration of the investigated ion was 10 times (by mass) greater than the total metal concentration, except for Ca^{2+} and Fe^{3+} ions, whose

concentrations were 2.5 times greater than C_M . The results were presented in Fig. 4.

The metal whose separation was least influenced by the coexisting ions was Cr(III). The Cr(III) retention coefficient varied in the range of 0.95 – over 0.99, depending on the ionic environment. Also, the separation efficiency of copper and cadmium from all solutions was very high, except for the solution containing a strong complexing agent (EDTA), in which it decreased by 35% and 42%, for Cu(II) and Cd(II) respectively, comparing with the solution without the additional salts. The presence of additional salts, especially sulphate, phosphate and acetate, and above all EDTA, significantly decreased the efficiency of Zn(II) and Ni(II) removal. Calcium ions, competing with heavy metal cations in polymer-metal interactions, can negatively affect their separation. It was particularly visible in the case of Ni(II) ions, due to the lower affinity of the metal-binding polymer to the nickel ions. The highest values of the retention coefficients of all metals in the mixture were obtained in the solution containing Fe^{3+} ions, which may be attributed to the additional coagulation effect.

In order to assess the possibility of selective or simultaneous concentration of heavy metals, three processes of PEUF concentration of equimolar heavy metal mixture of initial total metal concentration $C_M = 1$ mmol/dm³ were carried out at different values of the process parameters. The first concentration process (Conc. 1) was conducted at a lower C_{PSA}/C_M ratio, the second (Conc. 2) at a lower pH, and the third process (Conc. 3) was performed at a higher C_{PSA}/C_M and pH than the basic values in the preliminary tests.

Figs. 5, 7, and 9 present the changes in metal concentrations in the permeate and retentate, as well as rejection coefficients of individual metals observed with the progress of the three concentration processes, Conc. 1, 2 and 3, respectively. In Figs. 6, 8 and 10, the results of decomplexation-ultrafiltration of concentrated retentates achieved at Conc. 1, 2 and 3 are shown, and the metal fractions in different process streams are compared.

The PEUF concentration of the multicomponent mixture with a lowered polymer content allows for a

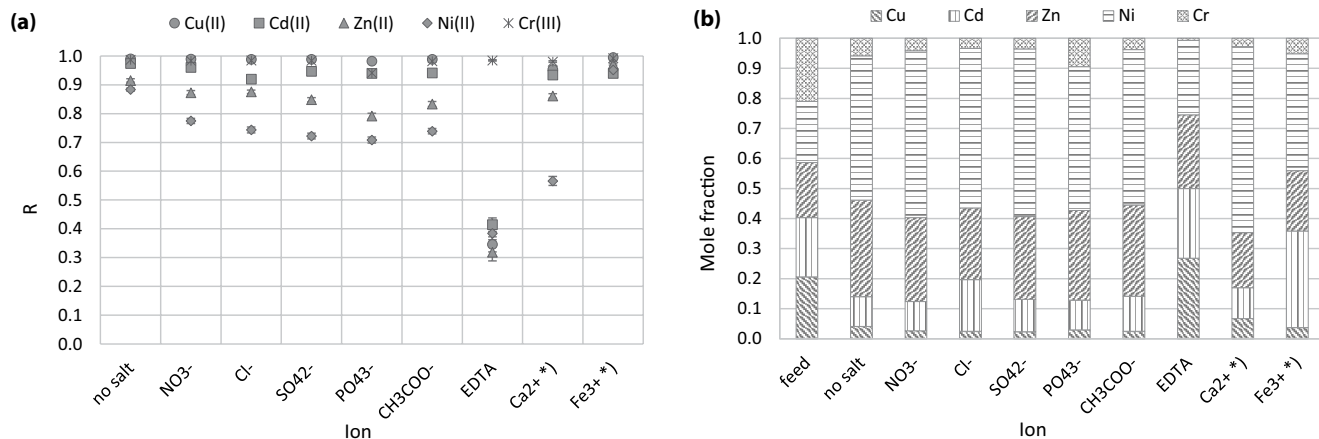


Fig. 4. Effect of coexisting ions on the individual metal rejection coefficients (a) and the composition of permeates (b). $C_{PSA}/C_M = 5$; $pH = 5$; $C_{ion}/C_M = 10$ w/w; $C_{ion}/C_M^* = 2.5$ w/w.

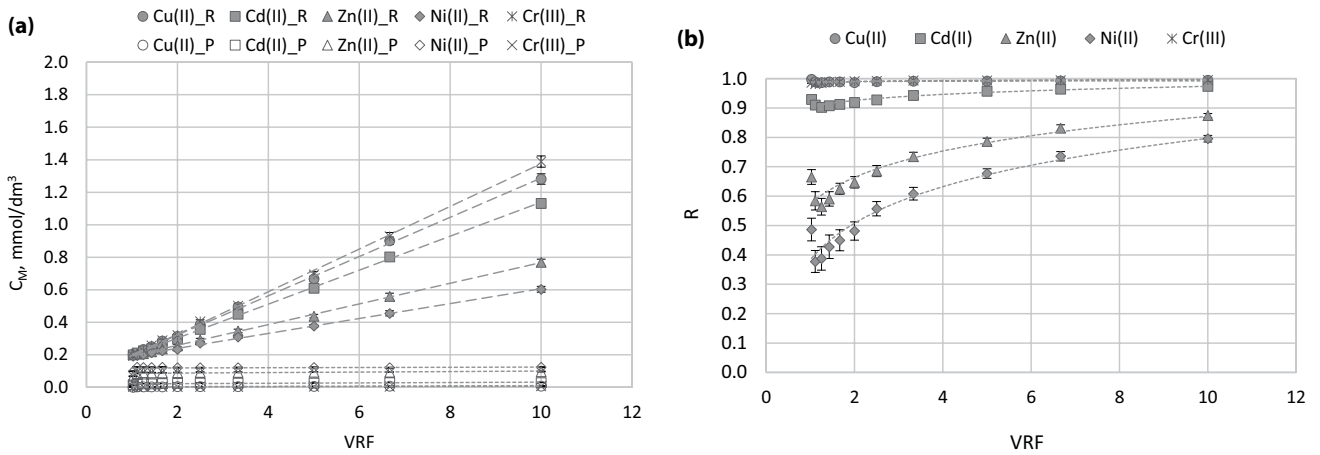


Fig. 5. Ultrafiltration concentration of heavy metal multicomponent mixture at $C_{PSA}/C_M = 2$; pH = 5 (Conc. 1). Concentration of metals in permeate and retentate (a), and rejection coefficients (b) vs. volume reduction factor.

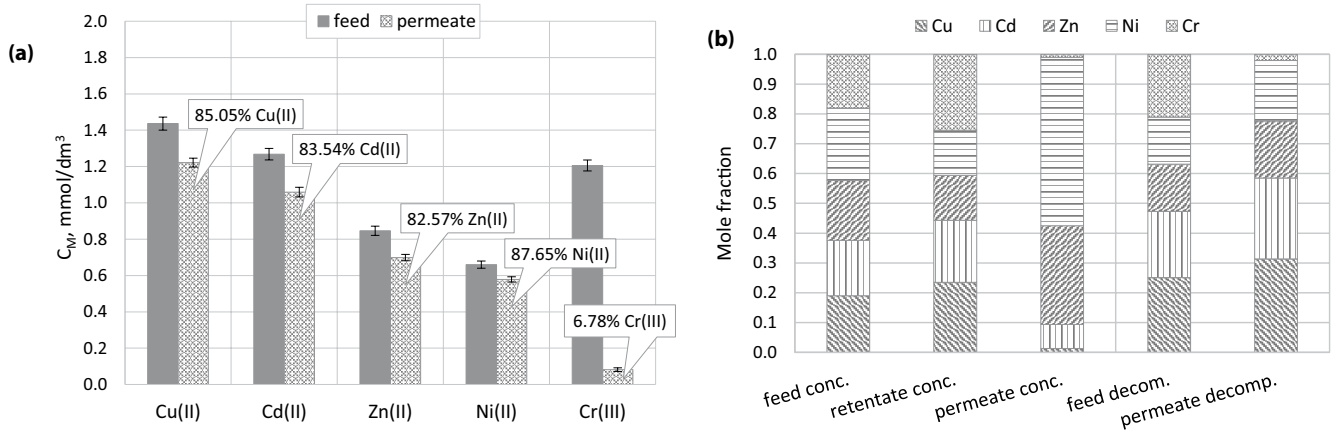


Fig. 6. Decomplexation-ultrafiltration (pH 2) of retentate achieved at the concentration step at $C_{PSA}/C_M = 2$; pH = 5 (a); metal mole fractions in various process streams (b).

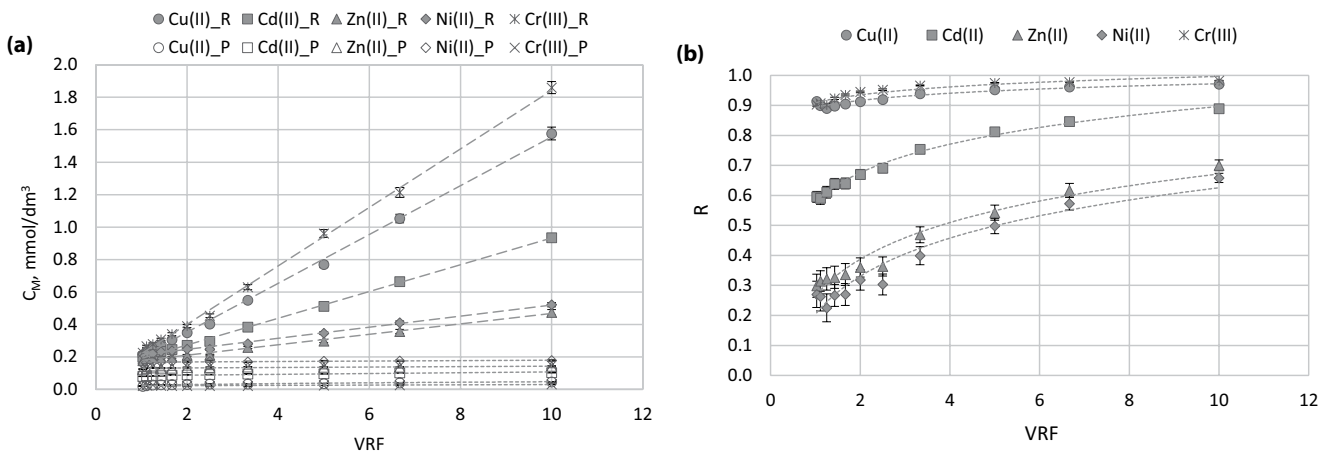


Fig. 7. Ultrafiltration concentration of heavy metal multicomponent mixture at $C_{PSA}/C_M = 5$; pH = 4 (Conc. 2). Concentration of metals in permeate and retentate (a) and rejection coefficients (b) vs. volume reduction factor.

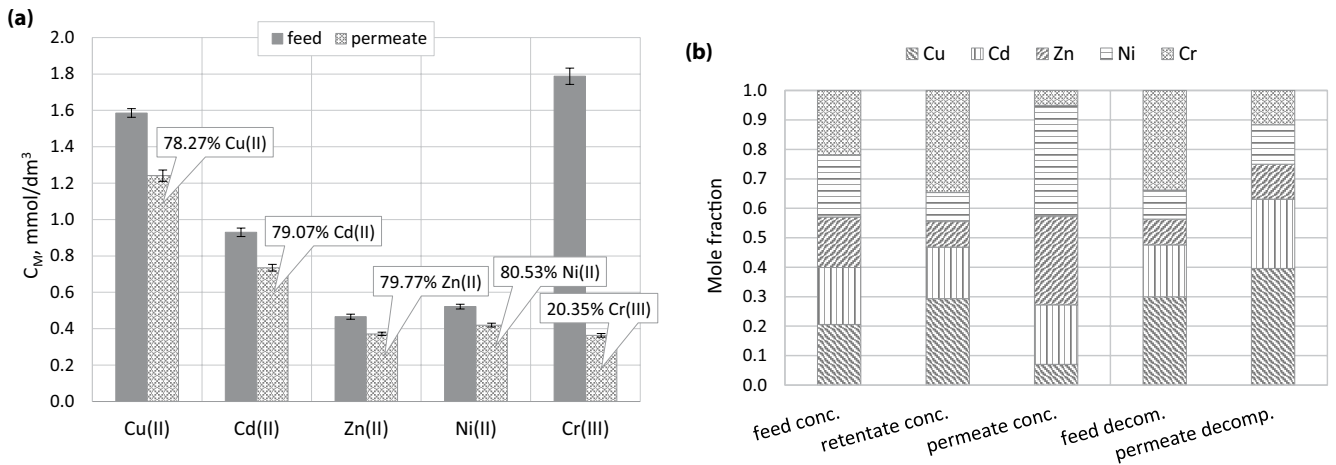


Fig. 8. Decomplexation-ultrafiltration (pH 2) of retentate achieved at the concentration step at $C_{PSA}/C_M = 5$; pH = 4 (a); metal mole fractions in various process streams (b).

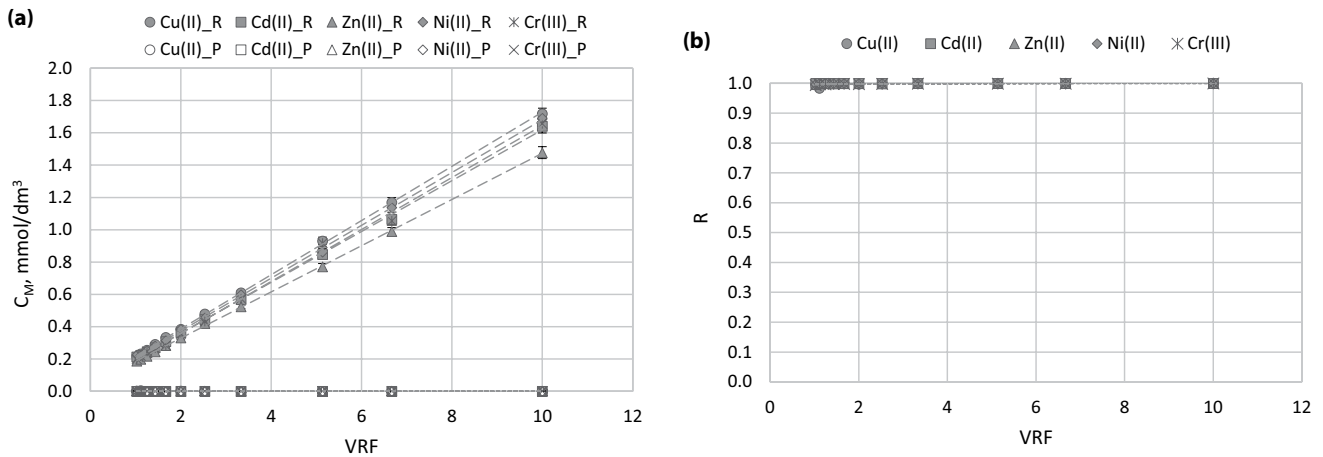


Fig. 9. Ultrafiltration concentration of heavy metal multicomponent mixture at $C_{PSA}/C_M = 7$; pH = 6 (Conc. 3). Concentration of metals in permeate and retentate (a) and rejection coefficients (b) vs. volume reduction factor.

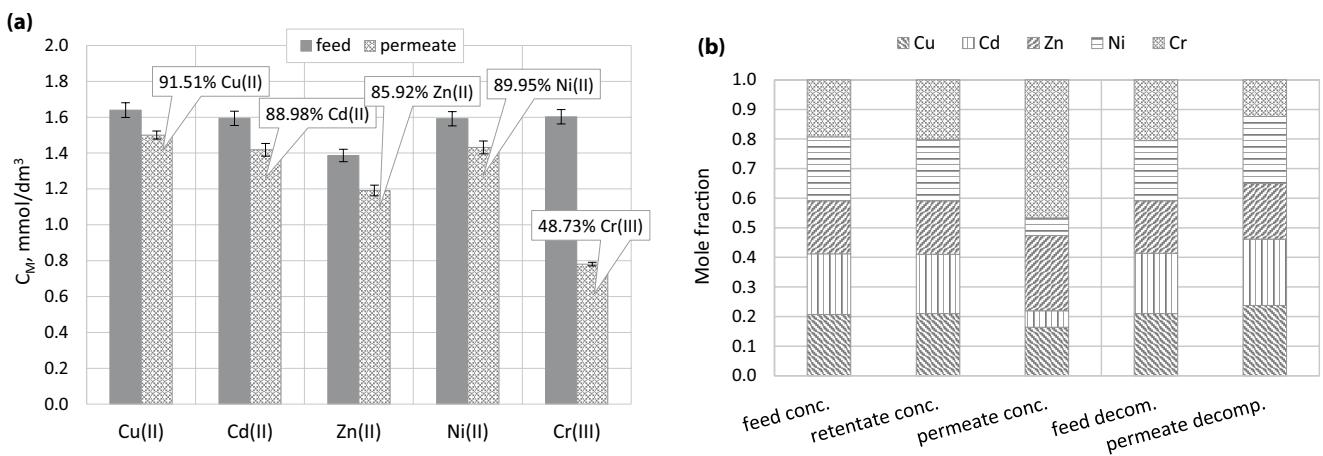


Fig. 10. Decomplexation-ultrafiltration (pH 2) of retentate achieved at the concentration step at $C_{PSA}/C_M = 7$; pH = 6 (a); metal mole fractions in various process streams (b).

partially selective separation of heavy metals (Fig. 5). During the process, high values of the retention coefficients of Cu(II), Cd(II) and Cr(III) ($R > 0.9$) were observed, while the retention coefficients of Zn(II) and Ni(II) remained at a moderate level in the range of 0.58–0.87 (Zn(II)) and 0.38–0.8 (Ni(II)). Due to the diversified metal separation effectiveness, the retentate enriched in Cu(II), Cd(II) and Cr(II) and the average permeate with an increased mole fraction of Zn(II) and Ni(II) were obtained from the equimolar feed solution of heavy metals. The decomplexation of the final retentate, followed by ultrafiltration, enabled recovery of over 80% of Cu(II), Cd(II), Zn(II) and Ni(II) but only 6.78% of Cr(III) (Fig. 6). The permeate after the decomplexation–ultrafiltration step contained 1.22, 1.06, 0.70, 0.58, and 0.08 mmol/dm³ of Cu(II), Cd(II), Zn(II), Ni(II) and Cr(II), respectively.

Similarly, partially selective separation of heavy metals was observed during the PEUF concentration at a lowered pH (Fig. 7). The main difference was the lower rejection coefficient of Cd(II), ranging from 0.60 to 0.89, and the lower rejection coefficients of Zn(II) and Ni(II), in the range of 0.30–0.70 and 0.27–0.66, respectively. As a result, the retentate enriched in Cu(II) and Cr(III) and the average permeate containing the prevailing amount of Zn(II) and Ni(II) were produced (Fig. 8). Approximately 80% of heavy metals were separated from the polymer by the decomplexation process, with the exception of Cr(III), for which the recovery rate was about 20%. The molar concentrations of Cu(II), Cd(II), Zn(II), Ni(II), and Cr(III) in the permeate from the decomplexation–ultrafiltration step were equal to 1.24, 0.74, 0.37, 0.42, and 0.36 mmol/dm³, respectively.

It can be concluded that the selective separation was not complete but was significant. The permeates and retentates clearly differed in composition (mole fraction of metals) compared to the feed solution. Other parameters that may affect the selective separation, such as the non-equimolar composition of the metal-containing solution, should be further investigated.

The PEUF process performed with the sufficient amount of metal-binding polymer (PSA) and at the appropriate pH enabled the simultaneous concentration of heavy metals in the multicomponent mixture (Fig. 9). The very high rejection coefficient (>0.99) of all heavy metals was observed, leading to concentrated retentate with approximately equal mole fractions of individual metals. In the decomplexation–ultrafiltration process, over 91% of Cu(II), and ca. 86% of Zn, 89% of Cd(II) and 90% of Ni(II) was recovered. PSA–Cr(III) bonds decomposed to the smallest extent and only about 49% of the chromium permeated through the membrane. The concentrations of individual metals in the permeate were 1.50, 1.42, 1.19, 1.43, and 0.78 mmol/dm³ for Cu(II), Cd(II), Zn(II), Ni(II) and Cr(III), respectively. The molar fractions of concentrated heavy metals in the permeate from the decomplexation–ultrafiltration step were similar to those in the feed solution from the initial concentration–ultrafiltration step, except for a slightly higher value for Cu(II) and a lower value for Cr(III). The total concentration of recovered heavy metals was over 6 times higher than the concentration in the original feed solution.

4. Conclusions

An ultrafiltration enhanced with poly(sodium acrylate) is an effective method of heavy metal separation from multicomponent mixtures. The effectiveness of the process depends, to a large extent, on the ratio of polymer/metals concentrations, pH and the type of ions coexisting in the solution. In a five-component equimolar mixture containing Cu(II), Cd(II), Zn(II), Ni(II), Cr(III) the affinity of PSA towards individual metals is as follows: Cr(III) \approx Cu(II) $>$ Cd(II) \gg Zn(II) $>$ Ni(II). Partially selective metal separation is possible at a reduced polymer/metal concentration ratio $C_{\text{PSA}}/C_{\text{M}} = 2$ (lower retention of Zn(II) and Ni(II), retentate enriched in Cu(II), Cr(III) and Cd(II)) or at a reduced pH = 4 (lower retention of Cd(II), Zn(II), Ni(II), retentate enriched in Cu(II) and Cr(III)). Simultaneous metal separation is possible with a sufficiently high polymer/metal ratio $C_{\text{PSA}}/C_{\text{M}} = 7$ and a suitably high pH of 6. The decomposition of concentrated polymer–metal complexes, taking place in the decomplexation–ultrafiltration step at a pH of 2, enabled the recovery from about 80% to over 90% of Cu(II), Cd(II), Zn(II), Ni(II) and only 6.78%–48.73% of Cr(III), depending on the conditions of the initial ultrafiltration concentration step.

Acknowledgements

This work was supported by the Republic of Poland's Ministry of Science and Higher Education within statutory funds.

References

- [1] V. Beaugeard, J. Muller, A. Graillot, X. Ding, J.-J. Robin, S. Monge, Acidic polymeric sorbents for the removal of metallic pollution in water: a review, *React. Funct. Polym.*, 152 (2020) 104599, doi: 10.1016/j.reactfunctpolym.2020.104599.
- [2] Y. Huang, X. Feng, Polymer-enhanced ultrafiltration: fundamentals, applications and recent developments, *J. Membr. Sci.*, 586 (2019) 53–83.
- [3] B. Lam, S. Déon, N. Morin-Crini, G. Crini, P. Fievet, Polymer-enhanced ultrafiltration for heavy metal removal: influence of chitosan and carboxymethyl cellulose on filtration performances, *J. Cleaner Prod.*, 171 (2018) 927–933.
- [4] N.H. Baharuddin, N.M. Nik Sulaiman, M.K. Aroua, Unmodified starch as water-soluble binding polymer for chromium ions removal via polymer enhanced ultrafiltration system, *J. Environ. Health Sci. Eng.*, 12 (2014) 61, doi: 10.1186/2052-336X-12-61.
- [5] R.-S. Juang, R.-C. Shiau, Metal removal from aqueous solutions using chitosan-enhanced membrane filtration, *J. Membr. Sci.*, 165 (2000) 159–167.
- [6] A. Yürüm, A. Taralp, N. Bıçak, H.Ö. Özbelge, L. Yılmaz, High performance ligands for the removal of aqueous boron species by continuous polymer enhanced ultrafiltration, *Desalination*, 320 (2013) 33–39.
- [7] C. Cojocaru, L. Clima, Polymer assisted ultrafiltration of AO7 anionic dye from aqueous solutions: experimental design, multivariate optimization, and molecular docking insights, *J. Membr. Sci.*, 604 (2020) 118054, doi: 10.1016/j.memsci.2020.118054.
- [8] A. Ben Fradj, A. Boubakri, A. Hafiane, S. Ben Hamouda, Removal of azoic dyes from aqueous solutions by chitosan enhanced ultrafiltration, *Results Chem.*, 2 (2020) 100017, doi: 10.1016/j.rechem.2019.100017.
- [9] D.A. Palacio, Y. Becerra, B.F. Urbano, B.L. Rivas, Antibiotics removal using a chitosan-based polyelectrolyte in conjunction with ultrafiltration membranes, *Chemosphere*, 258 (2020) 127416, doi: 10.1016/j.chemosphere.2020.127416.

- [10] D.A. Palacio, L.M. Leiton, B.F. Urbano, B.L. Rivas, Tetracycline removal by polyelectrolyte copolymers in conjunction with ultrafiltration membranes through liquid-phase polymer-based retention, *Environ. Res.*, 182 (2020) 109014, doi: 10.1016/j.envres.2019.109014.
- [11] B.L. Rivas, E.D. Pereira, M. Palencia, J. Sánchez, Water-soluble functional polymers in conjunction with membranes to remove pollutant ions from aqueous solutions, *Prog. Polym. Sci.*, 36 (2011) 294–322.
- [12] G. Crini, N. Morin-Crini, N. Fatin-Rouge, S. Déon, P. Fievet, Metal removal from aqueous media by polymer-assisted ultrafiltration with chitosan, *Arabian J. Chem.*, 10 (2017) S3826–S3839.
- [13] M. Chen, K. Shafer-Peltier, S.J. Randtke, E. Peltier, Competitive association of cations with poly(sodium 4-styrenesulfonate) (PSS) and heavy metal removal from water by PSS-assisted ultrafiltration, *Chem. Eng. J.*, 344 (2018) 155–164.
- [14] J. Llanos, R. Camarillo, Á. Pérez, P. Cañizares, Polymer supported ultrafiltration as a technique for selective heavy metal separation and complex formation constants prediction, *Sep. Purif. Technol.*, 73 (2010) 126–134.
- [15] J. Müslehiddinoğlu, Y. Uludağ, H.Ö. Özbelge, L. Yilmaz, Effect of operating parameters on selective separation of heavy metals from binary mixtures via polymer enhanced ultrafiltration, *J. Membr. Sci.*, 140 (1998) 251–266.
- [16] R. Molinari, T. Poerio, P. Argurio, Selective separation of copper(II) and nickel(II) from aqueous media using the complexation-ultrafiltration process, *Chemosphere*, 70 (2008) 341–348.
- [17] I. Korus, S. Kaboczyk-Kuc, Application of PEUF to competitive separation of Cu(II) and Cr(VI) from aqueous solutions containing chloride or sulphate ions, *Desal. Water Treat.*, 64 (2017) 437–466, doi: 10.5004/dwt.2017.11439.
- [18] I. Korus, P. Dawczak-Chmielewska, K. Ewelina, Competitive separation of heavy metals from binary solutions by polymer-enhanced ultrafiltration, *Desal. Water Treat.*, 217 (2018) 108–117.
- [19] S.I. Kadioglu, L. Yilmaz, N. Aydogan, H. Onder Ozbelge, Removal of heavy metals from multicomponent metal mixtures by polymer enhanced ultrafiltration: effects of pH, ionic strength and conformational changes in polymer structure, *Sep. Sci. Technol.*, 45 (2010) 1363–1373.
- [20] Y.-R. Qiu, L.-J. Mao, Removal of heavy metal ions from aqueous solution by ultrafiltration assisted with copolymer of maleic acid and acrylic acid, *Desalination*, 329 (2013) 78–85.
- [21] D. Jellouli Ennigrou, M. Ben Sik Ali, M. Dhahbi, Copper and zinc removal from aqueous solutions by polyacrylic acid assisted-ultrafiltration, *Desalination*, 343 (2014) 82–87.