Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22980

128 (2018) 358–363
October

Polymers enhancing ultrafiltration separation of Cd(II) ions

Irena Korus

Institute 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 6 April 2018; Accepted 13.August 2018

ABSTRACT

Polymer-enhanced ultrafiltration (PEUF) was applied to separate Cd(II) ions from an aqueous solution. The PEUF method involves metal ions binding with polymeric ligands and the separation of macromolecular compounds in the ultrafiltration process. Three different polymers, that is, polyethyleneimine (PEI), poly(sodium acrylate) (PSA), and poly(sodium 4-styrenesulfonate) (PSS), were used as metal-binding agents and a direct comparison of their efficiency for Cd(II) ions separation was conducted. Apart from the type of the polymer used, some other process parameters, that is, Cd(II) ions concentration, polymer-to-metal concentration ratio, pH, and the presence of additional salts, were investigated and their impact on Cd(II) rejection coefficient was determined. At selected process conditions, an ultrafiltration concentration of model Cd(II) solutions was conducted for each examined polymer, followed by a decomplexation process and a recovery of the concentrated metal from the solution. All three polymers enhanced the effectiveness of the ultrafiltration separation of Cd(II) ions. High Cd rejection coefficients $R_{Cd} > 0.9$ were observed at process conditions: polymer/Cd molar ratio of 5 (for PSA and PSS) or 7.5 (PEI) and pH ≥ 4 (for PSS), pH ≥ 5 (for PSA), and pH ≥ 6 (for PEI). After the concentration process, the decomposition of polymer-Cd bonds and the recovery of concentrated Cd(II) ions were effective at pH = 2 in the PEUF assisted with PEI or PSA.

Keywords: Polymer-enhanced ultrafiltration (PEUF); Polyethyleneimine (PEI); Poly(sodium acrylate) (PSA); Poly(sodium 4-styrenesulfonate) (PSS); Cd(II) ions

---

1. Introduction

Polymer-enhanced ultrafiltration (PEUF), also known as polymer-assisted ultrafiltration, liquid-phase polymer-based retention, or complexation-ultrafiltration, is a technique which enables the separation of small molecules from a solution by bonding them with selected polymers and rejecting the resulting macromolecular compounds on an ultrafiltration membrane. As a result, a purified permeate and a retentate containing the concentrated compound of the polymer and the separated molecules can be obtained. Due to the reversible nature of the reaction between the polymer and the bonded compound, it is generally possible to recover the concentrated separated compound after the decomposition of the bonds with the polymer.

The technique is used mainly for the separation of heavy metal ions, but other contaminants, such as boron [1] or dyes [2], can also be removed from aqueous solutions using PEUF.

The polymer used to bind the metal ions should exhibit selectivity toward the ions to be separated, good solubility in water and a sufficiently high molecular weight in order to be retained on the ultrafiltration membrane. Generally, two groups of polymers used in PEUF processes can be distinguished: chelating polymers, which form coordination bonds with metal ions, and ionic polymers, which contain ionic or ionizable functional groups. Among chelating polymers, the attention is focused on macromolecular amines, carboxylic acids, amides, alcohols, and amino acids. Among ionic polymers, the most important is polyelectrolytes, that is, macromolecular compounds, each mer of which (or a predominant amount of them) contains an ionized or ionizable group. Therefore, polyelectrolyte can

---

* Corresponding author.

Presented at the XII Scientific Conference "Membranes and Membrane Processes in Environmental Protection" – MEMPEP 2018
13–16 June 2018, Zakopane, Poland

be considered a macromolecule, that is, a polyion with associated low-molecular-weight counter-ions to ensure its electroneutrality.

The enhanced ultrafiltration separation of heavy metal ions most often uses polymers such as polyethyleneimine (PEI), ethoxylated polyethyleneimine (EPEI) [3–9], poly(acrylic acid) (PAA), and copolymers of acrylic and maleic acid (poly(acrylic-*co*-maleic acid) PAcMA), as well as PAA salts (poly(sodium acrylate) PSA, poly(ammonium acrylate) PAmA) [9–17], poly(styrene sulfonic acid) (PSSA), its salts and copolymers of styrene sulfonic acid and maleic acid [17–19], cellulose derivatives [20,21], or macromolecular quaternary ammonium salts (poly (diallyldimethylammonium chloride) PDADMAC) [22,23]. Beside synthetic polymers, chitosan, which is a macromolecular compound of natural origin, has been proved effective in the enhancement of ultrafiltration separation of heavy metals [6,7].

PEUF was successfully applied for the separation of many heavy metals, such as Cu(II), Ni(II), Co(II), Pb(II), Zn(II), Cr(III), Cr(VI), Hg(II), Mn(II), As(V), and Ag(I) [3–23], including Cd [4,10,11,14,17,19].

Although many studies have been done on the separation of Cd(II) ions using PEUF, it is difficult to compare their results with respect to the various polymers used in the process due to different testing conditions. This work is focused on the direct comparison of three polymers, that is, PEI, PSA, and PSS, with different functional groups (amino, carboxyl, and sulfonic, respectively) in relation to the effectiveness of the separation of Cd(II) ions from aqueous solutions within the PEUF process. An impact of process parameters, that is, polymer/metal molar ratio, pH, Cd(II) concentration, and the presence of additional salts, was also investigated. The process of cadmium(II) concentration with the use of the three polymers and the possibility of recovering the metal from the concentrated retentate was discussed.

2. Materials and methods

A stock solution of Cd(II) with a cadmium concentration of 1 g/L was prepared using $Cd(NO_3)_2{\cdot}4H_2O$ (POCH SA, Poland). Polymers: PEI, M_w~750 kDa, 50% aqueous solution, PSA, M_w~35 kDa, 40% aqueous solution, and PSS, M_w~70 kDa, 30% aqueous solution were purchased in Sigma-Aldrich Sp. z o.o., Poland. Next, a stock solution containing 50 mmol/L (with respect to the repeat unit of the polymer) was prepared for each polymer.

Salts used in the investigations, that is, NaCl, $NaNO_3$, Na_2SO_4, Na_3PO_4, CH_3COONa, EDTA ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$), $Ca(NO_3)_2$, and $Zn(NO_3)_2 \cdot 6H_2O$, as well as NaOH and HNO_3, applied as pH adjustment agents, were provided by POCH S.A., Poland. Such a choice of salts enabled the analysis of the effect of common monovalent and multivalent anions (Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, and CH_3COO^-), a strong complexing agent (EDTA) and cations: a light metal cation Ca^{2+} and a heavy metal cation Zn^{2+} on the process effectiveness. For each target ion, a stock solution with a concentration of 1 g/L was prepared. During the experiments, the concentration for the investigated ions was maintained at a level that was 10 times greater than the concentration of Cd(II) ions in order to evaluate the impact of the type of the ion on the cadmium separation.

Ultrafiltration equipment comprised of an AMICON 8400 stirred membrane cell (Merck Millipore, Merck Sp. z o.o., Poland), a commercial polysulfone ultrafiltration membrane EW type (GE Osmonics) provided by Sterlitech Co. and a compressed nitrogen as a pressure source. A new membrane was soaked with deionized water for 24 h and water was then filtered at the transmembrane pressure range of 0.05–0.3 MPa for 6 h. Subsequently, water permeability for the membrane was assayed experimentally and equaled 162.5 ± 2.6 L/(m^2 h MPa).

In the preliminary test, the impact of the four parameters, that is, polymer/metal molar ratio, pH, the concentration of Cd(II), and the presence of other investigated ions, on the effectiveness of cadmium removal was evaluated. Table 1 presents feed solution compositions according to the parameter being evaluated.

Feed solutions for ultrafiltration experiments were prepared by mixing appropriate amounts of Cd(II)-containing stock solution, polymer stock solution, and deionized water. In some experiments, also solutions containing investigated salts were added to a feed solution. Prior the ultrafiltration experiment, pH was adjusted using a NaOH or HNO_3 solution and the feed solution was stirred for approximately 1 h. It has been tested experimentally that it is a sufficient time for the formation of polymer-metal bonds. During the UF test, a transmembrane pressure of 0.2 MPa was applied and a permeate was collected in the amount of 10% of the feed volume. The concentrations of Cd in the feed solution and the permeate were analyzed using an atomic absorption spectrometer SpectrAA 880 (Varian) and the cadmium(II) rejection coefficient R_{Cd} was calculated as $R_{Cd} = 1–C_P/C_F$, where C_F and C_P denote cadmium(II) concentrations in the feed and permeate, respectively.

After the preliminary test, the ultrafiltration concentration of Cd(II)-containing solution was performed for

Table 1
The compositions of the feed solutions in the preliminary test

Investigated parameter	C_{Cd} (mg/L)	Polymer/Cd* molar ratio	pH	C_{ion}^{**} (mg/L)
Polymer/Cd molar ratio	50	0, 0.1, 0.5, 1, 3, 5, 7.5, 10	6	0
pH	50	5	1, 2, 3, 4, 5, 6, 7, 8, 9	0
C_{Cd}	5, 50, 100, 150, 200, 250	5	6	0
Ion type	50	5	6	500***

*Polymers tested: PEI, PSA, and PSS.

**Ions considered: Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, CH_3COO^-, EDTA, Ca^{2+}, and Zn^{2+}.

***In case of PSA, lower concentrations of Ca^{2+} and Zn^{2+} (25 mg/L) were used because of solids precipitation.

each examined polymer, applying the following process parameters: the concentration of Cd(II) in the feed solution C_F = 50 mg/L, pH = 6, and polymer/metal molar ratio depending on polymer type: C_{PSA}/C_{Cd} = 5, C_{PSS}/C_{Cd} = 5, and C_{PEI}/C_{Cd} = 7.5. The process was carried out in the batch mode at transmembrane pressure 0.2 MPa until the volume reduction factor VRF = 10 was achieved (VRF is defined as a ratio of the initial feed volume to the volume of the retentate, V_F/V_R). During the process, permeate and retentate samples were collected periodically and analyzed in relation to the cadmium(II) concentration. The cadmium(II) rejection coefficient was then calculated. Additionally, the normalized permeate flux J_v/J_w was evaluated, where J_v – permeate flux, J_w – water flux, which was determined experimentally prior each PEUF process at the same conditions (transmembrane pressure 0.2 MPa). The measured values of J_w were in the range of 31.66–33.37 L/(m^{2}h). After the concentration process, a final retentate for each polymer was subjected to the decomposition of polymer-metal bonds by acidification to pH = 2, followed by another UF process (transmembrane pressure – 0.2 MPa, collected permeate – 10% of the feed volume). The analysis of cadmium(II) concentration in the feed and the permeate collected at this process stage enabled the evaluation of the recovery degree of the concentrated metal.

3. Results and discussion

In the work, three different types of polymers were used to enhance the ultrafiltration separation of Cd(II) from an aqueous solution. All the polymers were water-soluble, but they differed in acid-base character and metal ions complexation ability due to various functional groups in the macromolecular structure.

Apart from the polymer type, one of the most important factors affecting the PEUF efficiency is the amount of the polymer used in the process. In this work, the amount of macromolecular ligands available for binding Cd(II) ions was expressed as a polymer/metal molar ratio, taking into account the mer unit of the polymer. Fig. 1 presents Cd(II) rejection coefficient in the ultrafiltration enhanced by the three different polymers (PEI, PSA, and PSS) applied in various polymer/metal molar ratios at a constant cadmium(II) concentration C_{Cd} = 50 mg/L.

Since an ultrafiltration membrane is generally incapable of rejecting heavy metal ions, practically no Cd(II) rejection was observed during the ultrafiltration without a polymer additive. In the ultrafiltration aided with PSA or PSS, a sharp increase in the Cd(II) rejection coefficient was observed with the increase in polymer amount in the feed solution. At polymer/Cd molar ratio of 5 or higher, high effectiveness of the separation of Cd(II) ions was achieved for both polymers PSA and PSS, and R_{Cd} values exceeded 0.98. PEI, the metal chelating polymer, also improved the efficiency of Cd(II) removal in the ultrafiltration process, but an increase in R_{Cd} with PEI/Cd molar ratio was not as sharp as it was observed with PSA and PSS. At the PEI/Cd molar ratio of 5, approximately 80% of cadmium(II) was separated in the PEUF process, and the separation increased with the increase in the PEI amount, reaching 96% and over 97% at PEI/Cd molar ratio of 7.5 and 10, respectively.

Fig. 2 presents the impact of pH on the effectiveness of cadmium(II) separation for the three tested polymers with an equal polymer/Cd molar ratio of 5 and a Cd(II) concentration in the feed solution being equal to 50 mg/L.

The dependence of R_{Cd} on pH for all the investigated polymers was characterized by a sigmoid-like shape and an increase in the cadmium(II) rejection was observed with the increase in basicity of the solution. PSS, the most acidic polymer among the three applied in this test, showed a sharp increase in the Cd rejection coefficient within the range of 0.003–0.987 at a pH increase from 1 to 4. The higher pH involved a greater dissociation of sulfonic functional groups and enabled the effective binding of Cd(II) ions. PSA, a polymer containing carboxyl groups with weaker acidic properties, required a higher pH to reach a sufficient dissociation degree to effectively bind cadmium(II) ions present in the feed solution. In the pH range of 1–2, ultrafiltration with the addition of PSA was completely ineffective and enabled the removal of less than 1% of Cd(II) from the solution. A decrease in acidity increased the degree of dissociation of carboxyl groups and significantly improved the effectiveness of cadmium(II) separation. At pH ≥ 5, more than 97% of the metal was rejected in the ultrafiltration process. The effectiveness of PEUF with PEI as a metal-binding agent was also dependent on pH, but the observed increase in R_{Cd} with the increase in pH was not as strong as in the case of more acidic polymers. At low pH values, a protonation of amine groups occurred and the polymer was unable to complex Cd(II) ions. With the increase in pH, a gradual increase in R_{Cd} was observed, with R_{Cd} values above 0.8 at pH ≥ 6.

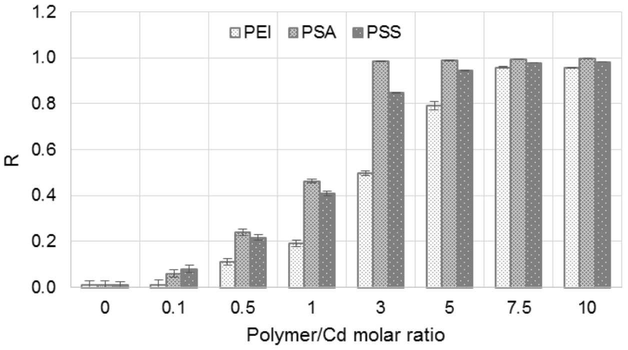

Fig. 1. R_{Cd} versus polymer/Cd molar ratio in PEUF aided with PEI, PSA, and PSS.

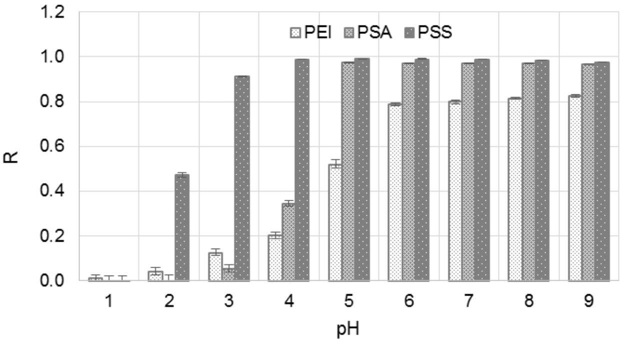

Fig. 2. R_{Cd} versus pH in PEUF aided with PEI, PSA, and PSS.

The PEI/Cd(II) molar ratio of 5, used in this stage of the investigations, was too low to achieve higher values of R_{Cd}, even at neutral and basic conditions (compare the impact of polymer/Cd ratio on R_{Cd}, Fig. 1).

The next tests were carried out to investigate the impact of cadmium(II) concentration on the process results and metal rejection coefficient. In these tests, various concentrations of Cd(II) were applied in the feed, but a constant polymer/metal molar ratio of 5 was maintained. The results are presented in Fig. 3.

The PEUF process with the use of PSA proved to be insensitive to the concentration of cadmium(II) in the solution in the analyzed range of concentrations. In the case of two other polymers used in the tests, an increase in the Cd(II) concentration induced a slight decrease in the Cd(II) retention coefficient. With a higher Cd(II) content in the solution and a constant polymer/Cd molar ratio, a higher polymer concentration occurred and a repulsive interaction between polymer functional groups hindered the formation of polymer-metal bonds. Lower R_{Cd} values observed in the tests with PEI, as compared with two other polymers, were connected with PEI/Cd(II) molar ratio, which was not sufficient to achieve higher Cd(II) rejection coefficients.

Fig. 4 presents the impact of the investigated ions on the effectiveness of Cd(II) removal for the three polymers enhancing ultrafiltration.

In the PEUF process with the use of PEI, chloride, nitrate, and acetate ions did not change the Cd(II) rejection coefficient to a significant degree. When used in a large amount (10-times greater than Cd(II) ions here), multivalent anions (SO_4^{2-}, PO_4^{3-}) noticeably diminished the effectiveness of the process. The values of R_{Cd} observed in the solutions with the addition of SO_4^{2-} and PO_4^{3-} were lower by 35% and 15%, respectively, compared to R_{Cd} without any additional salt. This can be explained by the cationic nature of the PEI polymer and its weak anion-exchange ability. The affinity of amino groups toward SO_4^{2-} and PO_4^{3-} was visibly higher than toward other, monovalent anions. A similar, negative effect of sulfate ions on the process effectiveness was also observed in the adsorption separation of Cr(VI) using PEI-functionalized adsorbents [24]. Likewise, in the competitive separation of heavy metals from Cu(II)/Cr(VI) and Zn(II)/Cr(VI) binary mixtures, an addition of SO_4^{2-} ions diminished the metal rejection coefficients, especially Cr(VI) ones [25,26]. In addition to anions, some cations can compete with Cd ions in the PEUF process aided with PEI. A significant reduction of Cd(II) rejection coefficient (by 79%) was found in a solution with a coexisting Zn(II) cation and a smaller, but still visible, reduction of R_{Cd} (by 13%) was observed in the presence of Ca(II). PEI was found to be an effective complexing agent for many heavy metals, including Zn(II) [5,6]. Tavares et al. showed that addition of PEI could increase UF separation of Ca ions from pulp and paper wastewater [27]. Therefore, the presence of these competing cations, especially Zn(II), can lower the effectiveness of Cd(II) separation. A strong complexing agent (EDTA) significantly diminished the R_{Cd} value (by 89%) as EDTA molecules competed with the PEI amino groups in the metal-ion binding.

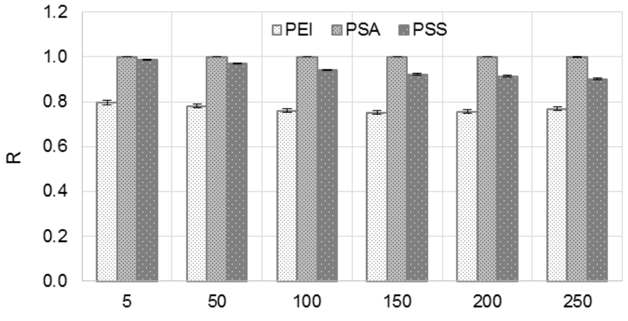

Fig. 3. R_{Cd} versus C_{Cd} in PEUF aided with PEI, PSA, and PSS.

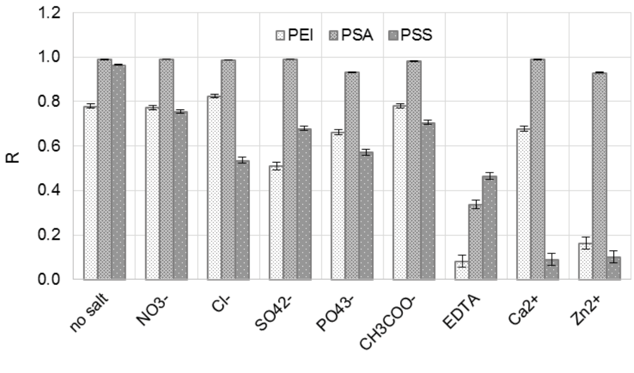

Fig. 4. An effect of selected ions on R_{Cd} in PEUF aided with PEI, PSA, and PSS.

At the process conditions applied during the experiment (pH = 6, polymer/metal molar ratio of 5), PSA – as a polymer supporting the ultrafiltration separation of Cd(II) ions – was proved to be insensitive to the presence of Cl^-, NO_3^-, SO_4^{2-}, and CH_3COO^- ions in the solution. In the case of EDTA, a clear decrease of 66% in R_{Cd} was observed with respect to the value obtained in the solution without any salt additions, which was related to the complexing ability of EDTA for Cd(II) ions. No deterioration of the Cd(II) rejection coefficient was observed in the presence of Ca ions in the solution, and in the solution containing Zn(II) ions, the reduction of R_{Cd} was insignificant (by 6%). However, it should be noted that lower concentrations of these ions were used due to precipitation in more concentrated solutions.

PSS-assisted ultrafiltration gave varying effects of Cd(II) ion separation, depending on the type of added salt. PSS is an anionic polymer, which exhibits strong cation-exchange properties. In case of this polymer, concentrations and types of cations seemed more important than anions. The largest decrease in R_{Cd} was found in the solutions containing additional divalent cations of Ca or Zn(II) (reductions by 91% and 90%, respectively). This is consistent with other works, where the possibility of binding heavy metals (including Zn(II)) [19] and alkaline earth metals (Ca, Mg) [28] by PSS was characterized. When comparing solutions with Na-containing salts, one can conclude that a larger decrease in R_{Cd} was observed for NaCl and Na_3PO_4 (decreases by 44% and 41%, respectively) than for the solutions with $NaNO_3$, Na_2SO_4, and CH_3COONa (a decrease by 23%–30%). This was probably attributable to the sodium concentration, which was higher in the solutions containing NaCl and Na_3PO_4 than in the solutions with other sodium salts at a constant anion concentration. Due to the strong interaction with Cd(II) ions, EDTA diminished the R_{Cd} value by 52% compared to the process without any additional salt.

In the next step, the procedure of the ultrafiltration concentration of Cd(II)-containing solution was carried out for each of the three polymers. In each case, the feed contained 50 mg Cd(II)/L and the pH of the solution was adjusted to 6. A polymer/Cd(II) molar ratio of 5 was applied for PSA and PSS, but a higher value of 7.5 was required for PEI to achieve more effective separation (see Fig. 1). Fig. 5 presents the Cd(II) concentrations in the retentate (C_R) and the permeate (C_P) observed during the concentration process in relation to the volume reduction factor VRF. Table 2 shows other data, that is, concentrations of feed solution C_F, final retentate $C_{R\,f}$, average permeate $C_{P\,aver.}$, the ranges of R_{Cd}, and relative flux J_v/J_w.

PEUF enabled the effective concentration of Cd(II) ions in the solution and the process took place with a similar efficiency for all the three investigated polymers supporting ultrafiltration. The concentrations of Cd(II) ions in averaged permeates did not exceed 2 mg/L and a particularly low Cd content was found in the permeate from the PSA-assisted process. Very high Cd rejection coefficients were found in the ultrafiltration, especially when PSA was used as a Cd(II)-binding agent. Despite a significant change in Cd concentration during the process, no significant reduction in the permeate flux was observed, regardless of the polymer used.

In the last stage of the study, concentrated Cd(II) solutions were acidified up to pH = 2 to destroy the polymer-Cd bonds and the next ultrafiltration was carried out to separate the concentrated Cd(II) from the polymer. The results are given in Fig. 6, where concentrations of feed solutions were compared against the concentrations of the obtained permeates.

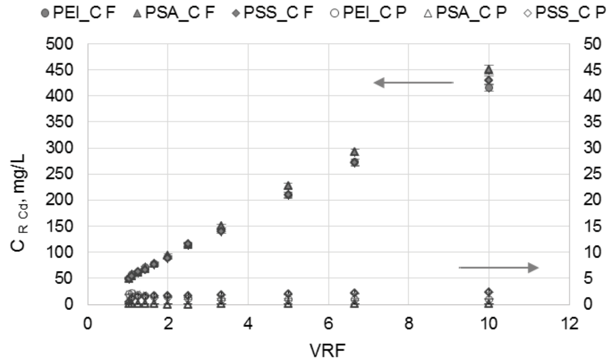

Fig. 5. Cd(II) concentration in retentate (C_R) and permeate (C_P) versus VRF.

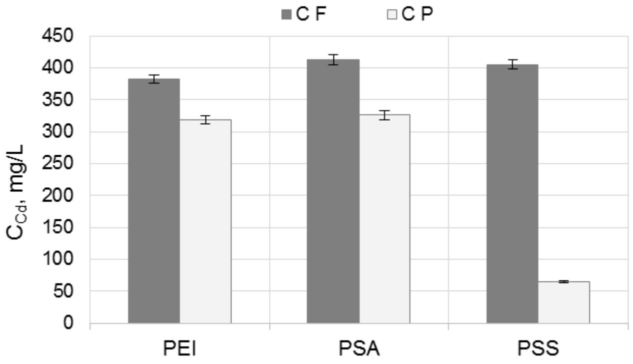

Fig. 6. Cd(II) concentration in the feed and the permeate in ultrafiltration after decomposition of polymer-Cd bonds (pH = 2).

The decomposition of polymer-Cd bonds was quite effective when PEI or PSA was used to enhance the ultrafiltration process. In pH = 2, the concentration of Cd(II) in permeate was ca. 80%–83% of concentration in post PEUF concentrate, which indicated on efficient decomplexation, if these two complexing or weak cation-exchanging polymers were applied. The same process was rather ineffective in the solution with a strong anionic polymer (PSS). In pH = 2, the ratio of concentrations of Cd(II) in permeate to feed (post PEUF retentate) was only 16%. When analyzing the R_{Cd} versus pH dependence for this polymer (Fig. 1), it may be concluded that more acidic conditions are needed to increase the efficiency of the decomposition of PSS-Cd bonds.

4. Conclusions

All the three tested macromolecular compounds, that is, PEI, PSA, and PSS, enabled effective separation of Cd(II) ions in the PEUF process despite the differences in their chemical nature and the method of binding metal ions.

The effectiveness of the process was strongly affected by the polymer/Cd molar ratio and the solution pH. In the process conditions, high R_{Cd} (over 0.9) was observed at the PSA/Cd and PSS/Cd molar ratios of 5, but a higher value of polymer/Cd molar ratio of 7.5 was needed for PEI to achieve such a level of Cd separation. The pH values, which ensured the highest effectiveness of the process was diverse depending on polymer type and was as follows: pH ≥ 4 for strong anionic polymer (PSS), pH ≥ 5 for PSA, and pH ≥ 6 for PEI. In the range of Cd(II) concentrations in the tested feed solution (5–250 mg/L) and at a constant polymer/metal molar ratio of 5, no impact of C_{Cd} on R_{Cd} was found for PSA and a small decrease of Cd rejection coefficient was observed with the increase of C_{Cd} for PEI and PSS.

Table 2
Concentrations of feed solution C_F, final retentate $C_{R\,f}$, average permeate $C_{P\,aver.}$, and the ranges of R_{Cd} and J_v/J_w observed during the concentration process

Polymer	C_F, mg/L	$C_{R\,f}$, mg/L	$C_{P\,aver.}$, mg/L	R_{Cd}	J_v/J_w
PEI	51.30 ± 0.68	416.1 ± 7.6	1.29 ± 0.03	0.96 – 1.00	0.86 – 0.92
PSA	49.42 ± 0.62	450.4 ± 8.5	0.03 ± 0.00	0.99 – 1.00	0.91 – 0.97
PSS	48.69 ± 0.71	431.3 ± 8.4	1.50 ± 0.04	0.98 – 0.99	0.96 – 1.07

When comparing directly the three types of tested polymers, it can be mentioned that PSA was less sensitive to the presence of additional ions in the solution. For all the polymer types, a strong complexing agent (EDTA) added to the feed solution decreased the Cd(II) rejection coefficient. The presence of competing ions, that is, SO_4^{2-}, PO_4^{3-} (for PEI), and Ca^{2+}, Zn^{2+} (for all polymers) as well as Na^+ (for PSS), significantly diminished the effectiveness of Cd(II) separation.

Each of the polymers proved to be effective at the process of concentration of Cd(II) ions. The process resulted in the concentrated retentate and permeate with a low Cd content, with the lowest concentration of Cd in the permeate obtained in the PSA-assisted ultrafiltration. A subsequent ultrafiltration carried out at pH = 2 enabled the decomposition of polymer-Cd bonds and the recovery of the concentrated metal for PEI and PSA. As a strongly acidic polymer, PSS requires a lower pH to increase the efficiency of the separation of the concentrated metal.

Acknowledgments

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

References

[1] C. Dilek, H.O. Ozbelge, N. Bicak, L. Yilmaz, Removal of boron from aqueous solutions by continuous polymer-enhanced ultrafiltration with polyvinyl alcohol, Sep. Sci. Technol., 37 (2002) 1257–1271.

[2] A. Ben Fradj, S. Ben Hamouda, H. Ouni, R. Lafi, L. Gzara, A. Hafiane, Removal of methylene blue from aqueous solutions by poly(acrylic acid) and poly(ammonium acrylate) assisted ultrafiltration, Sep. Purif. Technol., 133 (2014) 76–81.

[3] R. Molinari, S. Gallo, P. Argurio, Metal ions removal from wastewater or washing water from contaminated soil by ultrafiltration-complexation, Water Res., 38 (2004) 593–600.

[4] P. Cañizares, Á. Pérez, R. Camarillo, Recovery of heavy metals by means of ultrafiltration with water-soluble polymers: calculation of design parameters, Desalination, 144 (2002) 279–285.

[5] M. Schulte-Bockholt, M. Schuster, Removal enrichment and recovery of Ni(II), Zn(II) and phosphate from phosphation rinsing waters with liquid-phase polymer-based retention technique, Sep. Purif. Technol., 63 (2008) 172–178.

[6] R.S. Juang, C.H. Chiou, Ultrafiltration rejection of dissolved ions using various weakly basic water-soluble polymers, J. Membr. Sci., 177 (2000) 207–214.

[7] M.K. Aroua, F.M. Zuki, N.M. Sulaiman, Removal of chromium ions from aqueous solutions by polymer-enhanced ultrafiltration, J. Hazard. Mater., 147 (2007) 752–75.

[8] J. Llanos, Á. Pérez, P. Cañizares, Copper recovery by polymer enhanced ultrafiltration (PEUF) and electrochemical regeneration, J. Membr. Sci., 323 (2008) 28–36.

[9] J. Labanda, M.S. Khaidar, J. Llorens, Feasibility study on the recovery of chromium (III) by polymer enhanced ultrafiltration, Desalination, 249 (2009) 577–581.

[10] M. Palencia, B.L. Rivas, E. Pereira, A. Hernández, P. Prádanos, Study of polymer-metal ion-membrane interactions in liquid-phase polymer-based retention (LPR) by continuous diafiltration, J. Membr. Sci., 336 (2009) 128–139.

[11] P. Cañizares, Á. Pérez, R. Camarillo, R. Mazarro, Simultaneous recovery of cadmium and lead from aqueous effluents by a semi-continuous laboratory-scale polymer enhanced ultrafiltration process, J. Membr. Sci., 320 (2008) 520–527.

[12] I. Korus, M. Rumińska, The UV spectrophotometric studies of Cu(II) ions separation by ultrafiltration enhanced with poly(sodium acrylate), Desal. Wat. Treat., 57 (2016) 1436–1442.

[13] I. Korus, K. Loska, Removal of Cr(III) and Cr(VI) ions from aqueous solutions by means of polyelectrolyte-enhanced ultrafiltration, Desalination, 247 (2009) 390–395.

[14] J.X. Zeng, H.Q. Ye, N.D. Huang, J.F. Liu, L.F. Zheng, Selective separation of Hg(II) and Cd(II) from aqueous solutions by complexation-ultrafiltration process, Chemosphere, 76 (2009) 706–710.

[15] D.J. Ennigrou, M. Ben Sik Ali, M. Dhahbi, Copper and zinc removal from aqueous solutions by polyacrylic acid assisted-ultrafiltration, Desalination, 343 (2014) 82–87.

[16] 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.

[17] B.L. Rivas, E. Pereira, R. Cid, K.E. Geckeler, Polyelectrolyte-assisted removal of metal ions with ultrafiltration, J. Appl. Polym. Sci., 95 (2005) 1091–1099.

[18] I. Moreno-Villoslada, B.L. Rivas, Retention of metal ions in ultrafiltration of mixtures of divalent metal ions and water-soluble polymers at constant ionic strength based on Freundlich and Langmuir isotherms, J. Membr. Sci., 215 (2003) 195–202.

[19] I. Korus, Galvanic wastewater treatment by means of anionic polymer enhanced ultrafiltration, Ecol. Chem. Eng. S, 19 (2012) 19–27.

[20] M.A. Barakat, E. Schmidt, Polymer-enhanced ultrafiltration process for heavy metals removal from industrial wastewater, Desalination, 256 (2010) 90–93.

[21] K. Trivunac, S. Stevanovic, Effects of operating parameters on efficiency of cadmium and zinc removal by the complexation-filtration process, Desalination, 198 (2006) 282–287.

[22] P. Cañizares, Á. Pérez, J. Llanos, G. Rubio, Preliminary design and optimisation of a PEUF process for Cr(VI) removal, Desalination, 223 (2008) 229–237.

[23] B.L. Rivas, M. del C. Aguirre, E. Pereira, Retention properties of arsenate anions of water-soluble polymers by a liquid-phase polymer-based retention technique, J. Appl. Polym. Sci., 102 (2006) 2677–2684.

[24] X.T. Sun, L.R. Yang, H.F. Xing, J.M. Zhao, X.P. Li, Y.B. Huang, H.Z. Liu, Synthesis of polyethylenimine-functionalized poly(glycidyl methacrylate) magnetic microspheres and their excellent Cr(VI) ion removal properties, Chem. Eng. J., 234 (2013) 338–345.

[25] 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. Wat. Treat., 64 (2017) 437–446.

[26] I. Korus, P. Dawczak, E. Kępska, Competitive separation of heavy metals from binary solutions by polymer enhanced ultrafiltration, Desal. Wat. Treat., 117 (2018) 108–117.

[27] C.R. Tavares, M. Vieira, J.C.C. Petrus, E.C. Bortoletto, F. Ceravollo, Ultrafiltration/complexation process for metal removal from pulp and paper industry wastewater, Desalination, 144 (2002) 261–265.

[28] A. Tabatabai, J.F. Scamehorn, S.D. Christian, Economic feasibility study of polyelectrolyte-enhanced ultrafiltration (PEUF) for water softening, J. Membr. Sci., 100 (1995) 193–207.