IRENA KORUS

Silesian University of Technology
Institute of Water and Wastewater Engineering
ul. Konarskiego 18, 44-100 Gliwice, Poland
e-mail: irena.korus@polsl.pl

Removal of Pb(II) ions by means of polyelectrolyte enhanced ultrafiltration

Summary — This work proposes polyelectrolyte enhanced ultrafiltration to remove Pb(II) from aqueous solutions. Model solutions containing 1—100 mg Pb/dm^3 were used in the research. Poly(sodium 4-styrenesulfonate) (PSSS), which is a water-soluble polymer containing strong cation-exchange groups, was used as a metal binding agent. The process was conducted on a polysulfone membrane with molecular weight cut-off 60 000. The main parameters determining the effectiveness of lead retention (the polyelectrolyte quantity and solution pH) were examined. High retention coefficients (>0.98) were achieved for pH > 4 and 2.5—5-fold excess of polyelectrolyte to metal. Ultrafiltration concentration of Pb(II) solution (50 mg/dm^3) was carried out according to the previously determined polymer/metal concentration ratio, and at optimum pH. The lead retention coefficient (*R*), observed during the process, was within the range of 0.98—0.99. The retentate obtained was used in the next decomplexation-ultrafiltration step (ultrafiltration at pH = 1), which made possible the separation of polyelectrolyte (retentate) and the recovery of 85 % of concentrated Pb ions (permeate). The residual lead, still remaining in the polymer solution, was diafiltred by a 5-fold amount of water acidified to pH = 1.
Key words: lead(II), polyelectrolyte, ultrafiltration, polysulfone membrane.

USUWANIE JONÓW Pb(II) W PROCESIE ULTRAFILTRACJI WSPOMAGANEJ DZIAŁANIEM POLIELEKTROLITU
Streszczenie — W pracy zaproponowano ultrafiltrację wspomaganą działaniem polielektrolitu jako metodę usuwania jonów Pb(II) z roztworów wodnych. Badania prowadzono na modelowych roztworach zawierających 1—100 mg Pb/dm^3. Polielektrolitem użytym do wiązania jonów ołowiu był poli(4--styrenosulfonian sodu) (PSSS), rozpuszczalny w wodzie polimer anionowy, zawierający grupy o silnych właściwościach kationowymiennych. W ultrafiltracji wykorzystano membranę polisulfonową Sepa® CF EW (Osmonics) o rozdzielczości granicznej 60 000. Badania wstępne prowadzono stosując roztwory zawierające 1, 10 lub 100 mg Pb/dm^3, zmieniając stosunek molowy polimer/metal w zakresie 0,5—10 oraz pH w zakresie 1—10. Na podstawie wyznaczonych wartości współczynnika retencji metalu (*R*) (rys. 1) stwierdzono wysoką efektywność procesu rozdziału (R > 0,98) w warunkach pH > 4 i przy stosunku molowym polimer/metal wynoszącym 2,5 (1 i 10 mg Pb/dm^3) lub 5 (100 mg Pb/dm^3). Kolejny etap badań obejmował ultrafiltracyjne zatężanie roztworu o stężeniu 50 mg Pb/dm^3. Proces prowadzono z zachowaniem 5-krotnego nadmiaru polimeru w stosunku do metalu, przy pH = 6, stosując ciśnienie 0,1 MPa. W trakcie procesu, którego postęp wyrażono za pomocą współczynnika redukcji objętości (*VRF*), analizowano wartości stężeń metalu w retentacie (rys. 2a) i permeacie (rys. 2b) oraz określano strumień permeatu (rys. 2b), mierząc objętość permeatu uzyskaną w jednostce czasu z jednostkowej powierzchni membrany. Uzyskano wysoką efektywność procesu. Wyodrębniony retentat, o stężeniu Pb ok. 20-krotnie wyższym od stężenia roztworu wyjściowego, poddany został procesowi dekompleksowania i diafiltracji. Proces dekompleksowania-ultrafiltracji, polegający na rozbiciu połączeń polimer-metal i separacji zatężonego metalu, pozwolił na odzyskanie ok. 85 % metalu (punkt V_{H2O}/V_F = 0 na rys. 3), natomiast diafiltracja prowadzona 5-krotną objętością wody umożliwiła 15-krotne obniżenie stężenia metalu pozostałego w retentacie, dzięki czemu możliwe staje się odzyskanie i ponowne wykorzystanie zawartego w nim polielektrolitu.
Słowa kluczowe: ołów(II), polielektrolit, ultrafiltracja, membrana polisulfonowa.

Over the last few years, there have been literature reports revealing that ultrafiltration enhanced with water soluble polymers had been successfully applied to the separation of metal ions from aqueous solutions

[1—6]. The group of complexing polymers which form coordinate covalent bonds, and polyelectrolytes that have ion-exchange properties can be distinguished. Typical polymers that bind metal ions include high-molecular amines, amides, carboxylic acids, amino acids, alcohols and imines. Majority of the papers deal with the application of poly(acrylic acid) [1], poly(vinyl alcohol) [2], chitozane [3, 4] and polyethyleneimine [2—5].

The previous studies of the author, dealing with these problems, were based on two binding polymers: poly(acrylic acid) or its sodium salt showing weak cation-exchange properties and polyethyleneimine, displaying chelating properties towards metals. The proved suitability of those polymers for the ultrafiltration removal of metals such as Ni, Zn, Cu, Cd, and Pb [6, 7] acted as an encouragement to extend the research on polyelectrolytes with strong cation-exchange groups in the macromolecular structures. Herein, poly(sodium 4-styrene sulfonate) was used as the agent which binds Pb(II) ions thus making possible their removal during the ultrafiltration.

<div align="center">EXPERIMENTAL</div>

Materials

Lead(II) nitrate(V) [Pb(NO$_3$)$_2$] was purchased from POCh S.A. (Gliwice). As a polyelectrolyte poly(sodium 4-styrene sulfonate) (PSSS), from Aldrich, characterized by molecular weight $\overline{M}_w$ = 70 000 was used.

Method of investigation

The solutions used had a concentration of 1—100 mg Pb/dm^3. Metal ions were bound with PSSS and pH was adjusted using 1 mol/dm^3 NaOH or HNO$_3$ solutions.

Ultrafiltration was carried out in an AMICON 8400 membrane cell, membrane area of 37.5 cm^2, equipped with an additional tank which increased the volume of the system up to 1200 cm^3. A Sepa® CF EW (Osmonics) polysulfone membrane with molecular weight cut-off (MWCO) 60 000 and distilled water permeability of 1.98 · 10^{-10} m^3/(m^2 · s · Pa) was used in the separation process. Ultrafiltration of the model solutions containing 1, 10 or 100 mg Pb/dm^3 with PSSS as a lead binding agent was carried out. The results were analyzed assessing the effect of pH and the amount of polyelectrolyte added on lead retention coefficient (*R*). pH was adjusted in a range of 1—10, while the polymer/metal concentration ratio (mol of mer unit/mol of Pb) in a range of 0.5—10. The analysis of lead concentration, making possible the determination of *R* coefficients, was made using a SpektrAA 880 (Varian) atomic absorption spectrometer. The coefficient *R* was calculated as follows:

$$R = 1 - C_P/C_F \qquad (1)$$

where: *C*$_P$ — *concentration of Pb(II) ions in the permeate*, *C*$_F$ — *concentration of Pb(II) ions in the feed solution*.

pH values and polymer/metal molar ratios selected after the initial tests were used to concentrate a solution containing 50 mg Pb/dm^3. The process was carried out until volume reduction factor (*VRF* defined as the ratio of the initial feed volume and the volume remaining in the retentate) of 25 was achieved. Ultrafiltration was conducted at 0.1 MPa, recording permeate flux values and analyzing periodically the concentrations of Pb(II) in the retentate and permeate (SpectrAA 880 Varian).

The retentate produced during the concentration process was subjected to decomplexation-ultrafiltration process, carried out under conditions which secured the breaking of the bonds between lead and polyelectrolyte (pH = 1) and separation of the metal and polymer. The concentrations of lead in the retentate and permeate were analyzed during that process. Then, the retentate that contained concentrated polyelectrolyte along with remaining lead was subjected to diafiltration by continuously passing a five-fold amount of deionized water acidified to pH = 1. The efficiency of lead leaching was evaluated by analysis of Pb(II) concentration in the retentate during diafiltration.

<div align="center">RESULTS AND DISCUSSION</div>

Effect of polymer amount and pH of the solution on the effectiveness of lead separation

PSSS is a water-soluble polyelectrolyte containing sulfonic groups and hence its cation-exchange properties. Its ability to bind metal ions is largely dependent upon pH of the solution, due to protonation of sulfonic groups under acidic conditions. The effect of pH and the polymer/metal molar ratio on the effectiveness of lead separation from 1, 10 and 100 mg/dm^3 solutions are given in Figure 1. pH is a significant parameter which affects the effectiveness of lead separation. This is proved by the wide distribution of retention coefficients found. Low retention coefficients, indicating the lack of lead binding with the polyelectrolyte, were found at pH range of 1—2. An increase in pH up to ≥ 4 produced high effectiveness of the separation process.

In the solutions of low concentration (1 mg Pb/dm^3), an effective lead retention took place at even equimolar polymer/metal ratio. Higher concentrations of lead (100 mg Pb/dm^3) needed larger amounts of polyelectrolyte, exceeding 5-fold the molar amount of lead in the solution.

Ultrafiltration of Pb(II) solution

The concentration process was carried out at 5-fold excess of polyelectrolyte to lead ions and pH = 5.9—6.1.

Figure 2 depicts the changes in lead concentration in the retentate, permeate and permeate flux observed during the ultrafiltration concentration of 50 mg Pb/dm^3 solution. The course of the process was expressed by
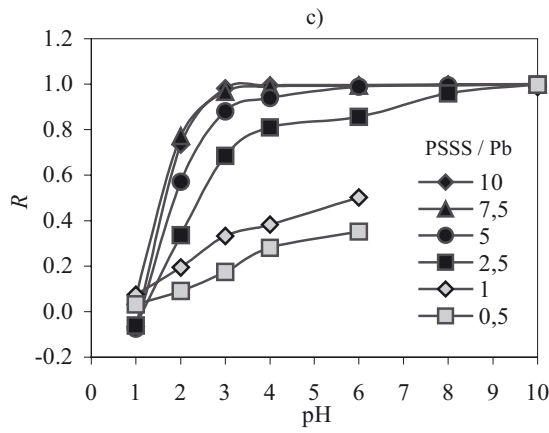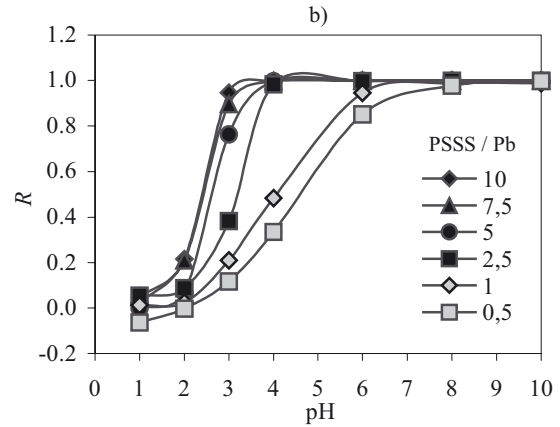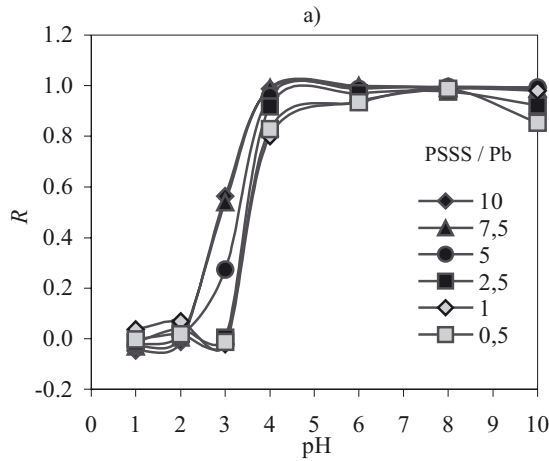
Fig. 1. *Lead retention coefficient (R) as a function of solution pH for different polymer/metal molar ratios (PSSS/Pb = 0.5—10) and for concentration of Pb(II) ions equal to: a) 1 mg/dm³, b) 10 mg/dm³, c) 100 mg/dm³*

VRF factor. The data indicate high effectiveness of the suggested method of lead removal from aqueous solutions, proved by lead *R* coefficient values, within the range 0.98 — > 0.99.

The separation process resulted in the retentate with about 20 times higher lead concentration in relation to feed solution and the permeate (96 % of the initial solution volume) in which averaged Pb(II) concentration was a mere 0.41 mg/dm³. A 30 % decrease in the permeate flux was observed during the process, which can be explained by the gradual increase in lead and polyelec-trolyte concentrations in the retentate. The biggest changes were found at the initial stage of the process, until *VRF* of 5 was reached.

Figure 3 shows an attempt to recover the concentrated metal from the final retentate, employing decomplexation-ultrafiltration at pH = 1 (point $V_{H2O}/V_F = 0$ in the graph) and the following diafiltration with a 5-fold amount of water acidified to pH = 1.

Having broken the polymer-metal bonds in acidic conditions it was possible to recover 85 % of lead present in the retentate (point $V_{H2O}/V_F = 0$). The subsequent
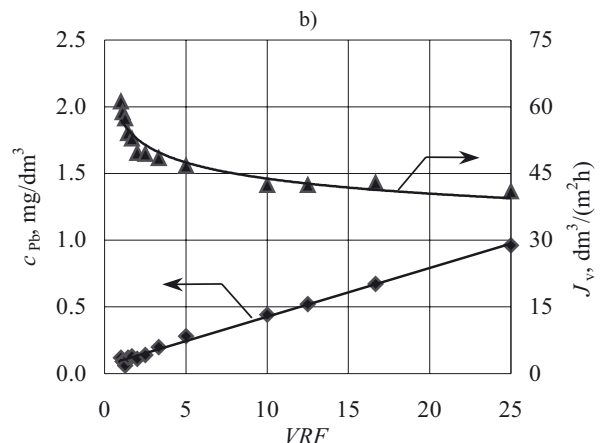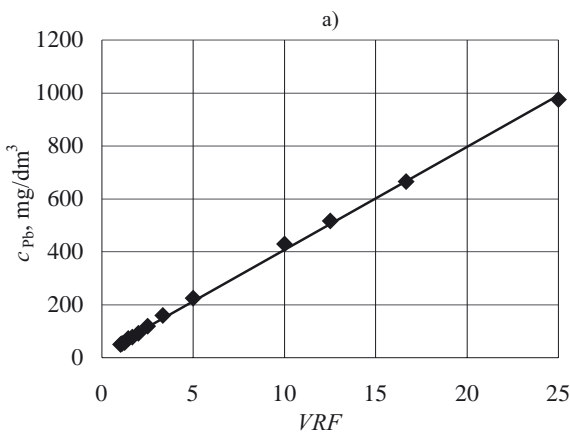

Fig. 2. *Effect of volume reduction factor (VRF) on lead concentration (C_{Pb}) in: a) retentate, b) permeate and permeate flux (J_v) for feed solution of 50 mg Pb/dm³*
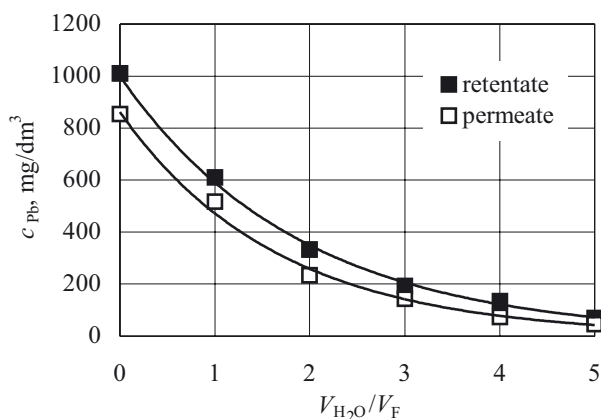
Fig. 3. Concentrations of lead C_{Pb} in retentate and permeate observed during decomplexation-ultrafiltration (point $V_{H2O}/V_F = 0$) and diafiltration, at different volume ratios of diafiltered water and feed solution (V_{H2O}/V_F)

diafiltration step made possible a 15-fold decrease in lead concentration in the retentate. The data indicate an efficient leaching of lead that remained in the concentrated polyelectrolyte.

CONCLUSIONS

The results herein confirmed the possibility of using a polyelectrolyte with strong cation-exchange properties to aid ultrafiltration removal of Pb(II) ions from aqueous solutions. Both pH and the polymer/metal molar ratio had a decisive influence on the effectiveness of such separation process.

The combination of two ultrafiltration processes carried out under suitable pH conditions led to a considerable decrease in Pb(II) concentration in the filtered solution and a separation of the concentrated stream containing Pb(II) ions. Furthermore, the application of diafiltration made it possible to use the polymer again by leaching lead that remained in it.

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