Irena KORUS[1]

GALVANIC WASTEWATER TREATMENT BY MEANS OF ANIONIC POLYMER ENHANCED ULTRAFILTRATION

OBRÓBKA ŚCIEKÓW GALWANICZNYCH Z WYKORZYSTANIEM ULTRAFILTRACJI WSPOMAGANEJ ANIONOWYM POLIELEKTROLITEM

Abstract: This work is focused on polyelectrolyte enhanced ultrafiltration as an effective heavy metal separation technique. Three types of effluents, containing Zn(II), Cu(II) and Ni(II) ions, were subjected to the separation process. Poly(sodium 4-styrenesulfonate) - PSSS, a water soluble anionic polyelectrolyte was used as a metal binding agent. Two Sepa® CF (Osmonics) membranes: EW, made of polysulfone and a modified polyacrylonitrile membrane MW, were used in the ultrafiltration process. The preliminary UF tests were carried out on model solutions with target metal ion concentrations of 10, 100 and 250 mg dm^{-3}. The main parameters affecting the metal retention (the polyelectrolyte quantity and solution pH) were examined. The values of pH 6 and polymer : metal concentration ratio $C_{PSSS} : C_M = 7.5 : 1$ (mol of mer unit per mol of metal) were selected to perform the galvanic wastewater ultrafiltration-concentration tests. Three types of wastewater containing Zn(II), Ni(II) and Cu(II) ions within the concentration range of $30 \div 70$ mg dm^{-3} were used in the investigations. Very high metal retention coefficients, up to > 99%, were achieved. The retentates obtained were subjected to the decomplexation-ultrafiltration (pH = 1) and subsequent diafiltration step, which enabled partial recovery of concentrated metal ions and the polyelectrolyte. The recovered polyelectrolyte was reused toward Ni(II) ions and the high effectiveness of metal separation has been achieved.

Keywords: polymer enhanced ultrafiltration, heavy metals, galvanic wastewater, polyelectrolyte

The membrane separation processes create new possibilities for the effective purification of galvanic wastewater. One of the most interesting propositions is a polymer enhanced ultrafiltration which combines two processes: metal ions binding with soluble polymeric ligands and retention of resulting macromolecular compounds on an ultrafiltration membrane. Polymer enhanced ultrafiltration has been successfully applied to the separation of metal ions from aqueous solutions, most often Cu, Ni, Zn, Co, Cd, Hg, Cr(III) and radionuclides [1-7].

Basically, two types of polymer used in the process can be distinguished. The first one encompasses chelating polymers, able to form coordination bonds with metal ions, the other includes polyelectrolytes, which have ion-exchange properties. Typical polymers that bind

---
[1] Institute of Water and Wastewater Engineering, Silesian University of Technology, ul. Konarskiego 18, 44-100 Gliwice, Poland, phone +48 32 237 19 78, fax +48 32 237 10 47, email: irena.korus@polsl.pl

metal ions include high-molecular amines, amides, carboxylic acids, amino acids, alcohols and imines. In most studies, chelating or weak cation-exchange polymers (chitosan [8, 9], polyethyleneimine [8-11], poly(acrylic acid) or its sodium salt [11], poly(vinyl alcohol) [12]) were used as metal binding agents. This research aimed to present the possibilities for applying water soluble polyelectrolyte with strong ion-exchange groups to enhance the ultrafiltration removal of metals from galvanic wastewater.

Materials and methods

Model solutions of Cu(II), Ni(II) and Zn(II) ions with metal concentrations of 10, 100 and 250 mg dm^{-3} were prepared on the basis of appropriate metal nitrates (POCH S.A.). Three types of galvanic wastewater used in the research contained the same type of metal ions in the range of concentrations $30 \div 70$ mg dm^{-3}. Chemical characteristics of the wastewater are given in Table 1.

Table 1

Metal and anion contents in the wastewater

Ion concentration [mg dm^{-3}]	Wastewater containing		
	Zn(II)	Cu(II)	Ni(II)
M^{2+}	38.6	72.4	29.3
Cl$^-$	90.0	3.9	11.9
SO$_4^{2-}$	16.3	226.3	73.2
NO$_3^-$	6.2	-	5.8

Poly(sodium 4-styrenesulfonate) - PSSS, a water soluble anionic polyelectrolyte (30% solution, MW 70000, Aldrich) was used as a metal binding agent. pH adjustment was made by 1 mol dm^{-3} NaOH or HNO$_3$ solutions (POCH S.A.).

The ultrafiltration process was carried out, using AMICON 8400 membrane cell (membrane area of 38.5 cm^2) equipped with a magnetic stirrer and an additional tank increasing the whole system capacity up to 1200 cm^3. Two ultrafiltration Sepa® CF (Osmonics) membranes: EW (polysulfone) and MW (modified polyacrylonitrile), were used in the separation process. The water permeability coefficients determined experimentally amounted to $3.0 \cdot 10^{-10}$ m^3 m^{-2} s^{-1} Pa^{-1} (EW membrane) and $6.7 \cdot 10^{-10}$ m^3 m^{-2} s^{-1} Pa^{-1} (MW membrane).

The preliminary UF tests were carried out on model solutions with target metal ion concentrations of 10, 100 and 250 mg dm^{-3}. The influence of polyelectrolyte amount and solution pH on metal retention was determined by changing polymer : metal concentration ratios within the range C$_{PSSS}$: C$_M$ = $1 \div 10$ (mol of mer unit per mol of metal) and pH between 1 and 10. By analyzing the feed and permeate metal concentrations (atomic absorption spectrometer SpectrAA 880 (Varian)), the retention coefficient was determined according to the formula: R = 1 – C$_P$/C$_F$ (were: R - retention coefficient, C$_P$ - concentration in permeate. C$_F$ - concentration in feed solution).

The ultrafiltration of wastewater effluents was carried out in the batch mode, applying the transmembrane pressure of 0.1 MPa and the operating parameters set in the preliminary tests - polymer : metal concentration ratio C$_{PSSS}$: C$_M$ = 7.5 and pH = 6 ± 0.1. The process

was carried out until the volume reduction factor VRF = 20 was achieved, the VRF being defined as the ratio of the initial feed volume to the volume of the retentate. The effectiveness of metal ion separation was evaluated by periodic measurements of metal concentrations in the retentate and permeate, which enabled the calculation of the metal retention coefficient.
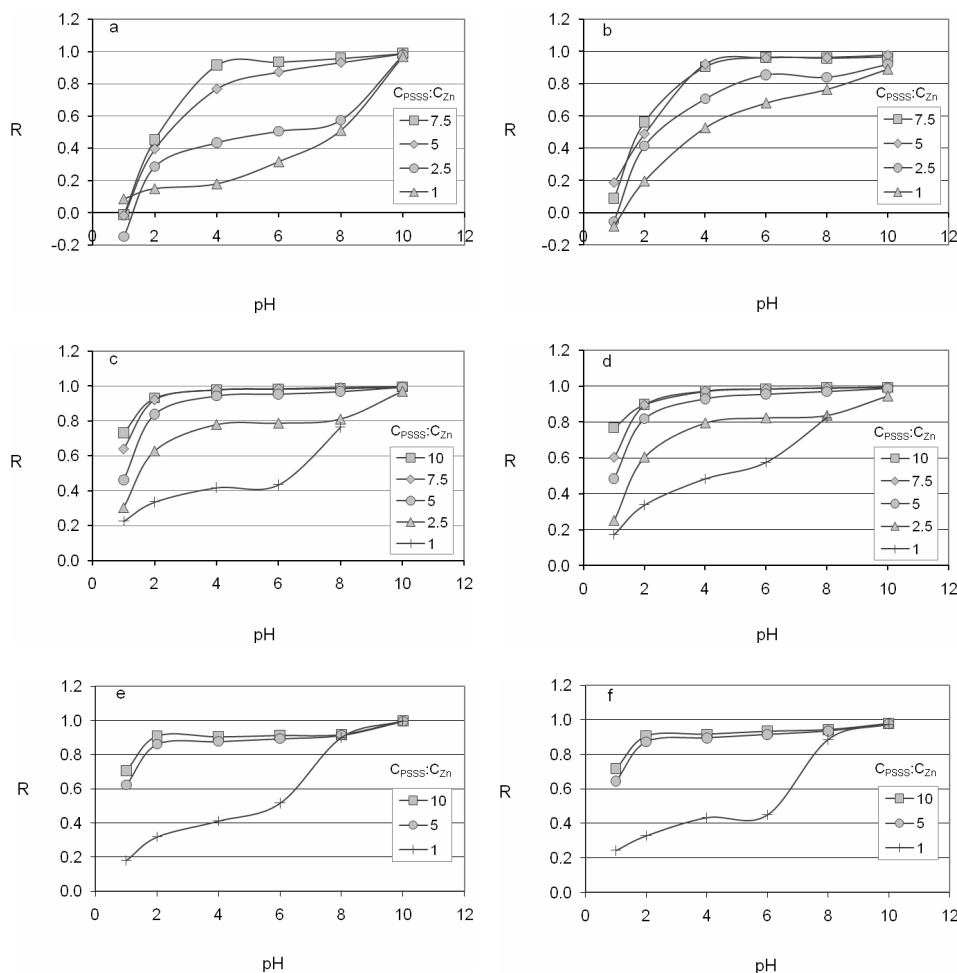

Fig. 1. Zn(II) retention coefficient (R) vs pH at different polymer : metal concentration ratios
(C_{PSSS} : C_{Zn}). C_{Zn} = 10 mg dm^{-3}, membranes: MW (a), EW (b); C_{Zn} = 100 mg dm^{-3}, membranes: MW (c), EW (d); C_{Zn} = 250 mg dm^{-3}, membranes: MW (e), EW (f)

The resulting retentate was acidified to pH = 1 (breaking of polyelectrolyte-metal bonds occurs) and then, the polyelectrolyte and the concentrated metal were separated during ultrafiltration that followed. The subsequent diafiltration step was carried out by continuously passing a five-fold amount of deionized water acidified to pH = 1.

The effectiveness of residual metal leaching was determined by analyzing the metal concentration in the retentate. The recovered polyelectrolyte was regenerated by pH correction and reused toward Ni(II) ions. The process was carried out on EW membrane. The effectiveness of metal separation has been determined.

Results and discussion

Preliminary tests. Selection of pH and polymer : metal ratio

Poly(sodium 4-styrenesulfonate) - PSSS - is a water-soluble polyelectrolyte, containing sulfonic groups. Its metal ion binding ability largely depends on solution pH, due to the cation-exchange properties of polyelectrolyte.
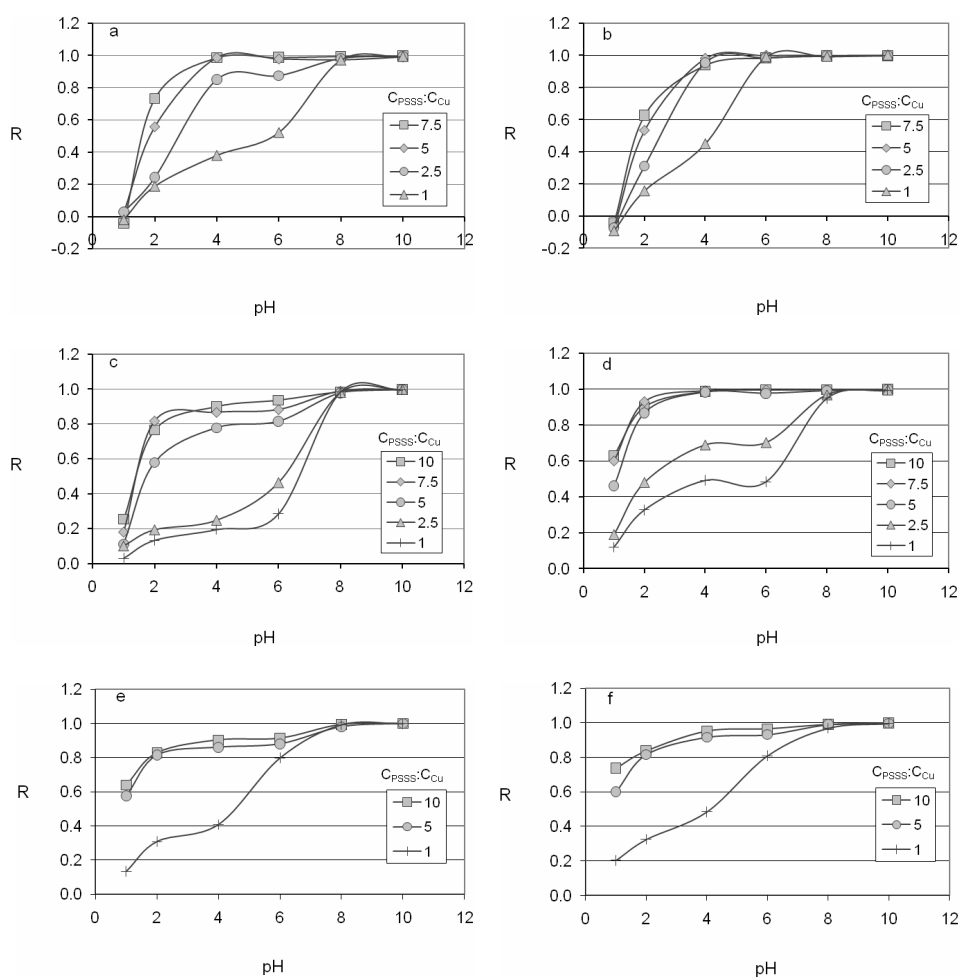

Fig. 2. Cu(II) retention coefficient (R) vs pH at different polymer : metal concentration ratios (C_{PSSS} : C_{Cu}). $C_{Cu} = 10$ mg dm^{-3}, membranes: MW (a), EW (b); $C_{Cu} = 100$ mg dm^{-3}, membranes: MW (c), EW (d); $C_{Cu} = 250$ mg dm^{-3}, membranes: MW (e), EW (f)
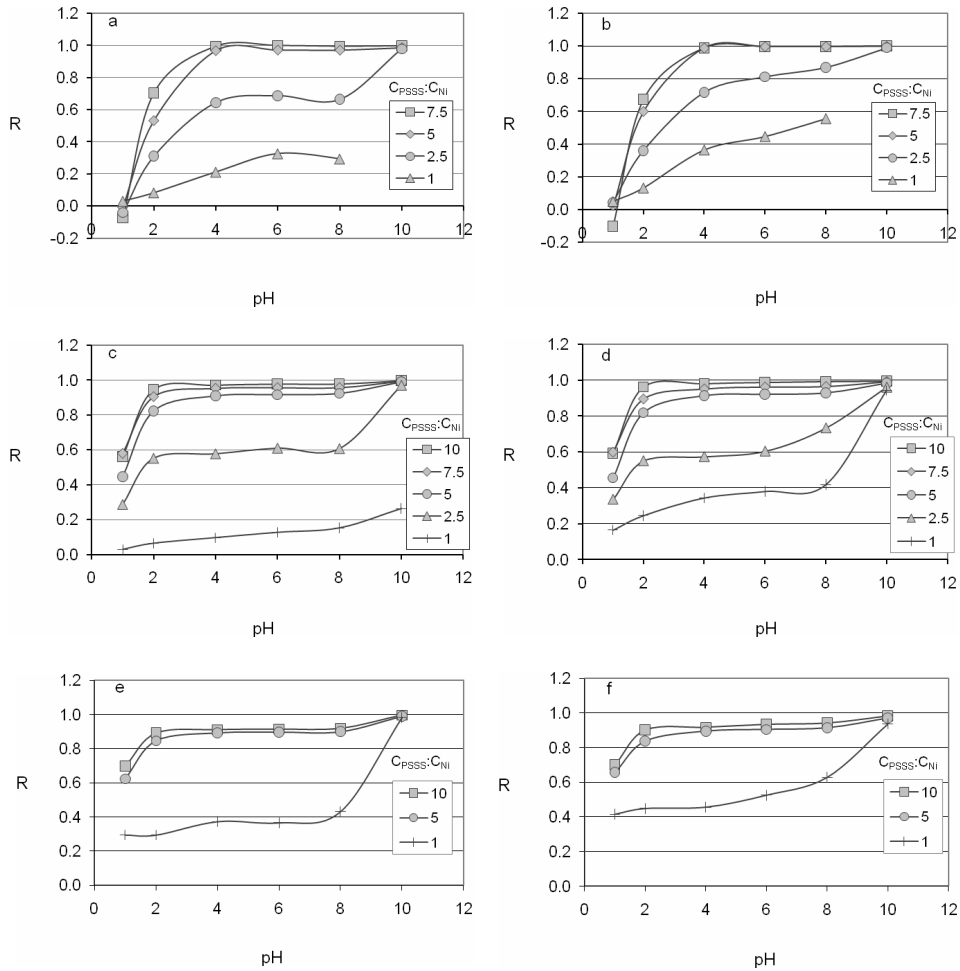
Fig. 3. Ni(II) retention coefficient (R) vs pH at different polymer : metal concentration ratios $(C_{PSSS} : C_{Ni})$. $C_{Ni} = 10$ mg dm^{-3}, membranes: MW (a), EW (b); $C_{Ni} = 100$ mg dm^{-3}, membranes: MW (c), EW (d); $C_{Ni} = 250$ mg dm^{-3}, membranes: MW (e), EW (f)

Figures 1-3 illustrate the effect of pH and the polymer : metal concentration ratio $(C_{PSSS} : C_M)$ on the metal retention coefficient in 10, 100 and 250 mg dm^{-3} model solutions.

Solution pH was a significant parameter affecting the metal separation effectiveness. Low retention coefficients were found over a pH range of 1÷2. This resulted from the protonation of sulfonic groups under acidic conditions, according to the equilibrium:

$$m[RSO_3H]_n + nM^{m+} \underset{\longleftarrow}{\longrightarrow} [RSO_3^-]_{mn} M_n + mnH^+$$
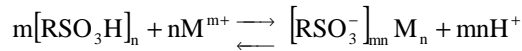
An increase in pH up to ≥ 4 produced high effectiveness of the separation process.

The considerable impact of the amount of polyelectrolyte used in the test on the metal retention coefficient was observed. Applying polymer : metal concentration ratios $C_{PSSS} : C_M < 5$, a relatively low metal separation was achieved. Higher polymer : metal concentration ratios and the solution pH ≥ 4 resulted in the metal retention coefficients $R > 0.9$. Figure 4 presents the ranges of permeate flux (J_v) recorded during the preliminary test.
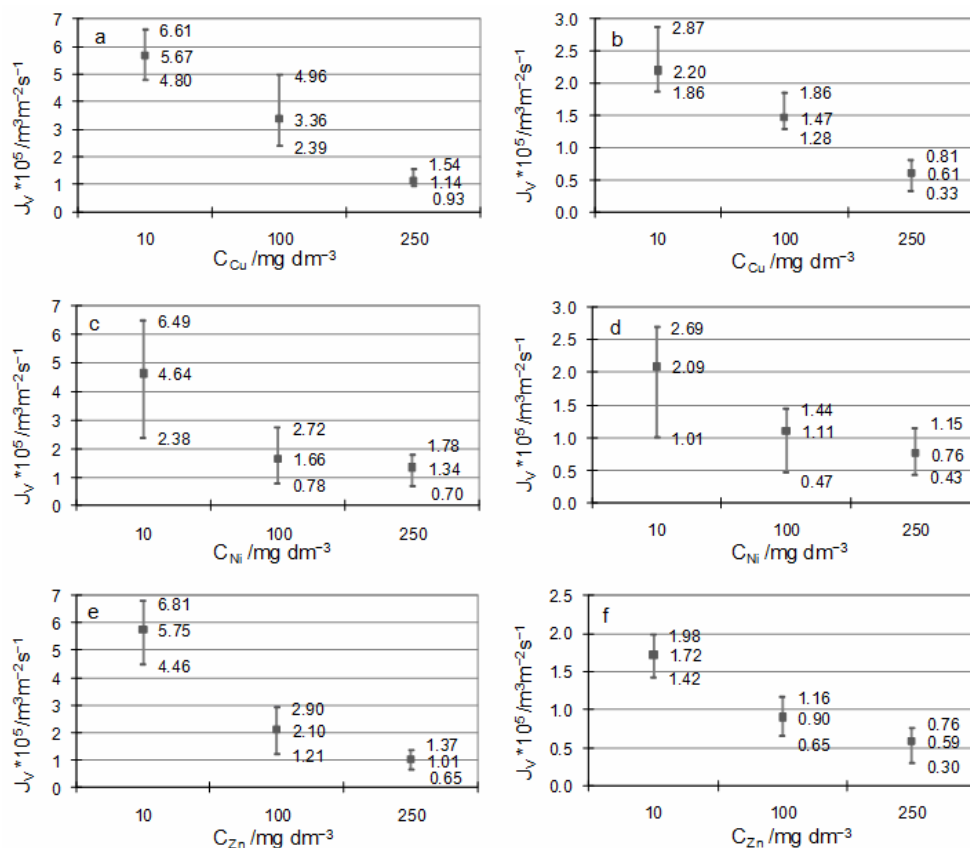

Fig. 4. Ranges of permeate flux observed in preliminary tests using model solutions containing 10; 100 and 250 mg dm^{-3} of Cu(II) (membranes: MW (a), EW (b)); Ni(II) (membranes: MW (c), EW (d)) and Zn(II) (membranes: MW (e), EW (f))

The higher J_v values, obtained for the solutions of the same metal contents, corresponds with the lower polymer : metal concentration ratios. As can be seen, the permeate flux is largely dependent on polyelectrolyte concentration, which is directly connected with the amount of metal ions.

Comparing the two types of membranes used no significant difference in process effectiveness was found out but higher permeability of MW membrane resulted in 2-3 times higher permeate flux values.

Ultrafiltration of galvanic wastewater

The ultrafiltrations of galvanic wastewater were carried out applying polymer : metal concentration ratio C_{PSSS} : C_M = 7.5 and pH = 6 ± 0.1. Figure 5 presents the changes in metal ion concentrations in the ultrafiltration streams (retentates and permeates) and the permeate fluxes observed during the gradual wastewater concentration. The course of the process was expressed by a volume reduction factor.
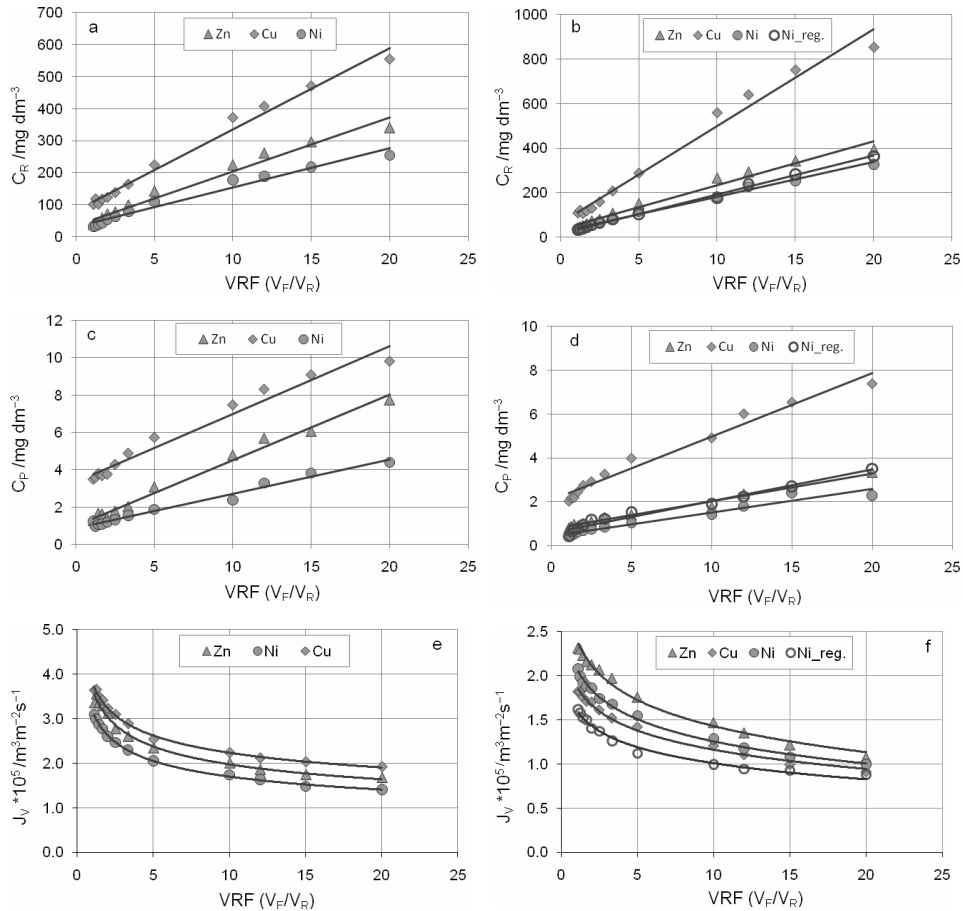

Fig. 5. Metal ion concentrations in the retentates (membranes: MW (a), EW (b)), permeates (membranes: MW (c), EW (d)) and the permeate fluxes (membranes: MW (e), EW (f)) during wastewater concentration

The results indicated a good effectiveness of proposed wastewater treatment, which was confirmed by the low metal concentrations found in the permeates. High metal retention coefficients, within the range of 0.97÷>0.99, were observed during the process for all types of wastewater treated. The metal remaining in the permeate amounted to 2.5÷4.5% of the initial metal content in the feed solutions.

The recorded permeate fluxes should be considered as satisfactory, in spite of the significant decline, down to 55% of the initial value, observed during the process.

The possibility of concentrated metal separation from polyelectrolyte was tested in the subsequent decomplexation-ultrafiltration step. The results are listed in Table 2.

Table 2

The results of decomplexation-ultrafiltration process. Metal contents in the feed solutions (concentrated retentates) and permeates

Wastewater containing	MW membrane		EW membrane	
	retentate from concentration	permeate after decomplexation	retentate from concentration	permeate after decomplexation
Zn	340 mg dm^{-3}	282 mg dm^{-3}	393 mg dm^{-3}	277 mg dm^{-3}
Cu	554 mg dm^{-3}	444 mg dm^{-3}	852 mg dm^{-3}	553 mg dm^{-3}
Ni	254 mg dm^{-3}	237 mg dm^{-3}	327 mg dm^{-3}	222 mg dm^{-3}

The ultrafiltration of the concentrated polymer-metal complex carried out in acidic conditions (pH = 1) enabled the decomposition of polyelectrolyte-metal bonds and a 65÷72% (membrane EW) and 80÷93% (membrane MW) metal ions recovery.

In order to leach the remaining metal from the retentate that contained polyelectrolyte, a 5-fold amount of acidified water (pH = 1) was used in the diafiltration process. The effectiveness of metal leaching is presented in Figure 6 (V_{H_2O}/V_F - volume of washing water per volume of feed solution treated).
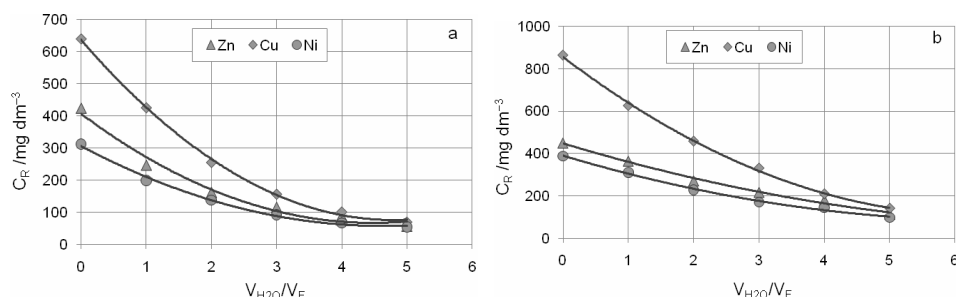

Fig. 6. Concentrations of metal remaining in retentate as a function of water volume used in diafiltration (membranes: MW (a), EW (b))

Continuously passing water gradually decreased the metal content and resulted in a 4÷6-fold (membrane EW) and 6÷9-fold (membrane MW) reduction in metal concentrations. The regenerated polyelectrolyte reused to Ni(II) ions separation (Fig. 5, EW membrane) shows similar effectiveness to fresh polymer.

Conclusions

The results confirm the high effectiveness of polyelectrolyte enhanced ultrafiltration in the removal of metal ions from galvanic wastewater. The metal retention was strongly controlled by the polyelectrolyte amount and solution pH.

The applied polyelectrolyte, poly(sodium 4-styrenesulfonate) with cation-exchange properties, proved to be a very efficient metal-binding agent, enabling a 97÷>99% retention of the target metals.

The application of the complexation/decomplexation-ultrafiltration processes to wastewater treatment leads to the recovery of both the metal-free permeate and most of the metal present in the wastewater. Furthermore, an additional diafiltration step considerably decreases the metal content in the remaining polyelectrolyte and enables the reuse of polymer.

References

[1] Molinari R, Gallo S, Argurio P. Water Res. 2004;38(3):593-600. DOI: 10.1016/j.watres.2003.10.024.
[2] Müslehiddinoglu J, Uludag Y, Özbelge HÖ, Yilmaz L. J Membrane Sci. 1998;140(2):251-266. DOI: 10.1016/S0376-7388(97)00280-9.
[3] Thompson JA, Jarvinen G. Filtrat Separat. 1999;36(5):28-32. DOI: 10.1016/S0015-1882(99)80097-4.
[4] Aliane A, Bounatiro N, Cherif AT, Akretche DE. Water Res. 2001;35(9):2320-2326. DOI: 10.1016/S0043-1354(00)00501-7.
[5] Sabaté J, Pujolà M, Llorens J. J Membrane Sci. 2004;204:139-152. DOI: 10.1016/j.memsci.2004.02.034.
[6] Cañizares P, Pérez A, Camarillo R, Mazarro R. J Membrane Sci. 2008;320:520-527. DOI: 10.1016/j.memsci.2008.04.043.
[7] Zakrzewska-Trznadel G, Harasimowicz M. Desalination. 2002;144:207-212. DOI: 10.1016/S0011-9164(02)00313-2.
[8] Juang RS, Chiou ChH. J Membrane Sci. 2000;17:207-214. DOI: 10.1016/S0376-7388(00)00464-6.
[9] Aroua MK, Zuki FM, Sulaiman NM. J Hazardous Mater. 2007;147:752-758. DOI: 10.1016/j.jhazmat.2007.01.120.
[10] Bodzek M, Korus I, Loska K. Desalination. 1999;121(2):117-121. DOI: 10.1016/S0011-9164(99)00012-0.
[11] Cañizares P, Pérez A, Camarillo R. Desalination. 2002;144:279-285. DOI: 10.1016/S0011-9164(02)00328-4.
[12] Tavares CR, Vieira M, Petrub JCC, Bortoletto EC, Ceravollo F. Desalination. 2002;144:261-265. DOI: 10.1016/S0011-9164(02)00325-9.

OBRÓBKA ŚCIEKÓW GALWANICZNYCH Z WYKORZYSTANIEM ULTRAFILTRACJI WSPOMAGANEJ ANIONOWYM POLIELEKTROLITEM

[1]Instytut Inżynierii Wody i Ścieków, Politechnika Śląska

Abstrakt: Zaprezentowano możliwość zastosowania ultrafiltracji wspomaganej działaniem polielektrolitu do separacji jonów metali z roztworów wodnych. Do badań wykorzystano roztwory modelowe o zawartości Zn(II), Cu(II) i Ni(II) w zakresie 10÷250 mg dm^{-3} oraz 3 rodzaje ścieków galwanicznych, z których każdy zawierał jeden z wymienionych jonów metali o stężeniu 30÷70 mg dm^{-3}. Metale wiązano za pomocą poli(4-styrenosulfonianu sodu) - PSSS, co umożliwiało ich retencję na membranie ultrafiltracyjnej. Badania wstępne, wykonane na roztworach modelowych, miały na celu dobór głównych parametrów decydujących o efektywności procesu: stosunku stężeń polimer : metal oraz pH roztworu. Badania właściwe obejmowały ultrafiltracyjne zatężanie ścieków z zastosowaniem wybranych wartości stosunku stężeń polimer : metal (7,5 : 1) oraz pH (pH = 6). Uzyskano wysokie wartości współczynników retencji metali, powyżej 99%. Zatężone retentaty zakwaszono do pH = 1 w celu rozerwania połączeń polimer-metal oraz poddano kolejnemu procesowi ultrafiltracji z następującą po nim diafiltracją, co umożliwiło częściowy odzysk zatężonych metali oraz polielektrolitu. Zregenerowany polimer, po korekcie pH, został ponownie wykorzystany w procesie separacji jonów Ni(II), a obserwowane rezultaty nie odbiegały od wyników uzyskanych przy użyciu polimeru świeżego.

Słowa kluczowe: ultrafiltracja wspomagana polimerem, metale ciężkie, ścieki galwaniczne, polielektrolit