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Poly(sodium-4-styrenesulfonate) assisted ultrafiltration for nickel and copper removal from aqueous solutions: optimization several parameters

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ABSTRACT

Nickel and copper removal from aqueous solution by polyelectrolyte enhanced ultrafiltration (PEUF) process was investigated using poly (sodium 4-styrenesulfonate) (PSS) with average molecular weight 70 kDa. In fact the application of PEUF, permitted to reach retention rate higher than 88% and 94%, respectively, for nickel and copper. Several parameters have been optimized such as transmembrane pressure, poly(sodium 4-styrenesulfonate) concentration, pH and ionic strength to improve the retention of the metal ions. The fouling resistance represented more than 40% of the total resistance for high polyelectrolyte. The experimental results showed a considerable influence of the pH solution on the metal ions retention, a maximum retention was obtained at pH 5. The study of ionic strength effect demonstrates that it decreases the retention of metal ions and increases the permeate flux. The adsorption capacity of this membrane was tested out using nickel and copper ions. The results showed that, in all cases, adsorption can be illustrated by Freundlich or Langmuir isotherms. The complexing ability of PSS toward copper ions is higher than toward nickel. When both metals are present in the same solution, retention rate decreases compared with single metal solutions, which is more significant in the case of nickel ions. Polyelectrolyte enhanced ultrafiltration method was proved to be effective and efficient for processing waste solutions containing nickel and copper ions.

Keywords: Nickel; Copper; Recovery; Polyelectrolyte enhanced ultrafiltration; Mixture solution; Isotherm modeling

1. Introduction

One of the most startling groups of water contaminants are those of heavy metals due to their accumulation in biological systems and their toxicity even at relatively low concentrations [1–3]. Sources of heavy metal water contamination are varied and can be seen in every step of production from mining, purification and processing, metal finishing and electroplating, and even end use [4].

Many industrial wastewater streams such as industries of pulp, paper, mines and quarries contain toxic metal cations, for example, Ni^{2+}, Cu^{2+}, etc. or their oxyanions in up to few hundred mg dm^{-3}, which must be removed before water recycling or discharging directly into surface waters. Impact of nickel can be manifested in allergic reactions, chronic toxicity (dermatitis nausea, chronic asthma, coughing, abdominal cramps, diarrhea, vertigo and lassitude), but acute toxicity is not typical. It is known that nickel is a human carcinogen [5]. Similarly, copper ions are essential nutrients, but when people are exposed to copper levels above 1.3 mg L^{-1} for even short periods of time, stomach and intestinal problems occur. Longer exposure leads to kidney and liver damage [6]. The conventional processes to treat this kind of wastewater are, for example, chemical precipitation, ion exchange, membrane separations such as electrodialysis, nanofiltration, reverse osmosis and ultrafiltration (UF), adsorption or biosorption.

In environmental sciences, water-soluble functional polymers can be used to remove pollutants. The water-soluble

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polymers that contain one or more amine, amide, carboxylic acid, hydroxyl, phosphonic acid, quaternary ammonium salts, and sulfonic acid groups at the backbone or side chain and their ability to remove ion pollutants from aqueous solutions. There are different experimental procedures, including the liquid-phase polymer based retention (LPR) technique that combines the use of water-soluble polymers and UF membranes, as well as arsenic removal by combining LPR and electrocatalytical oxidation (EO) techniques. EO and LPR can also be coupled off-line to remove arsenic inorganic species from aqueous solutions. A variety of studies show that the functional groups on the polymer and the solution pH have a marked effect on ion removal.

Complexation and UF is a hybrid pressure-driven membrane technology based on the complexation of metal ions with water soluble polymers in combination with UF. This technology has demonstrated its effectiveness in removing heavy metal ions from aqueous solutions, such as nickel and copper [6–15].

In polyelectrolyte enhanced ultrafiltration (PEUF), the macromolecular ligands seem more advantageous since they have a relatively high binding capacity. The ligands and their metal complexes can be retained by an ultrafilter, whereas the free metal ions pass though the membrane [16]. With this method, using different water-soluble polymers or introducing new functional groups to the polymer [17,18], it is possible to achieve selective separation and removal of heavy metals with low energy requirements. Metal complexation with polymers takes place in the homogeneous phase, consequently, there is no difficulty related to heterogeneous reactions [19].

Water-soluble polymers with sulfonate functionality have commercial utility in a number of applications [20–22]. Other uses and chemical properties have been widely described in the literature [23–26]. The sulfonate groups have been extensively employed in ion-exchange resins, but their use in water-soluble polymers with the ability to bind metal ions has been less studied.

In the literature, some of these equations are, for example, Langmuir, Elovich, Flory–Huggins, Harkins–Jura, Dubinin–Radushkevich, Redlich–Peterson and other isothermal models. In this work, the equilibrium data of nickel and copper adsorption by the UF membrane were modeled by Langmuir and Freundlich models. The objective of this study was to investigate the removal of nickel and copper from aqueous solution by complexation–ultrafiltration with poly(sodium 4-styrenesulfonate) (PSS). Experiments were performed as a function of transmembrane pressure, aqueous pH, polymer/M^{2+} ratio, and electrolyte concentration with CR membrane. Selectivity was studied using a solution containing the two metal ions.

2. Materials and methods

2.1. Materials and analysis

The chemical reagents used in the experiments were poly(sodium 4-styrenesulfonate) (PSS) with an average molecular weight of 70 kDa (Sigma-Aldrich, Germany), nickel chloride ($NiCl_2.6H_2O$) and copper chloride ($CuCl_2.2H_2O$), were provided by Sigma-Aldrich (Germany). All the chemicals were of analytical grade. Solutions were prepared with ultrapure water produced by Milli-Q gradient unit (Millipore). For the pH arrangement of feed solutions, hydrochloric acid and sodium hydroxide solutions were used. Sodium chloride of analytical grade supplied by Sigma-Aldrich (Germany) was used to control ionic strength in solution.

Nickel and copper concentrations in feed and permeate streams were measured by means of AA spectrophotometer using the Analytik Jena AAS Nov AA 400 P atomic absorption spectrophotometer (Germany). A pH meter (Metrohm 654) was used for pH measurements of feed and permeate solutions throughout the study.

To evaluate the filtration efficiency in removing nickel and copper ions from the feed solution, we used the observed retention defined as follows:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{1}$$

where C_p and C_f are, respectively, the concentrations (mg L^{-1}) of the metal ions in the permeate and the feed solution.

2.2. Experimental set up and procedure

Laboratory scale experiments were performed using a tangential cell system (Minitan-S Millipore). The inlet flux was held constant (up to 0.5 m s^{-1}) and a transmembrane pressure was varied from 1 to 3 bar by restricting the outlet tube. Regenerated cellulose membrane with molecular weight cut-off (MWCO) of 5 kDa and an effective filtration area of 50 cm^2 were used (PTGC OMS 5, Millipore). UF experiments were carried out preparing 100 mL of $NiCl_2.6H_2O$ or $CuCl_2.2H_2O$ with a feed concentration equal to 100 ppm. These solutions are circulated in the system by totally recycling the permeate and the retentate. When a steady state is reached, 15 mL samples were collected. The temperature of the feed solution and the transmembrane pressure was held constant at 25°C, respectively.

Permeate flux (J_v) was calculated using Eq. (2):

$$J_v = \frac{V_p}{S \times t} = L_p \times \Delta P \tag{2}$$

where J_v is the permeate flux (L h^{-1} m^{-2}), V_p is the volume of the permeate (L), S is the effective membrane area (m^2), and t is the time (s); L_p (L h^{-1} m^{-2} bar^{-1}) is the permeability of aqueous solution and ΔP (bar) is the transmembrane pressure.

Loading ratio (L) is calculated as follows to indicate the concentration ratio of poly(sodium 4-styrenesulfonate) (C_{PSS}) to metal ions concentration (C_M^{2+}). The observed loading ratio defined as Eq. (3):

$$L = \frac{C_{pPSS}}{C_M^{2+}} \tag{3}$$

2.3. Resistances determination

The pure water flux through membrane at one particular transmembrane pressure is usually expressed with Darcy's law:

$$J_{wi} = L_p^0 \Delta P = \frac{\Delta P_m}{\eta \times R_m} \tag{4}$$

L_p^0 is the permeability of solvent, it depends on the solvent viscosity η and morphologic characteristics of membrane.

Hydraulic membrane resistance R_m is estimated by measuring permeate flux using ultrapure water before the *N*th experiment, using cleaned membrane.

In order to explain permeate flux decline with various filtration resistances including concentration polarization, the resistance-in-series model is usually used [27–30].

$$R_{\text{tot}} = R_m + R_f + R_p \tag{5}$$

where the total filtration resistance R_{tot} is composed of each filtration resistance caused by the hydraulic membrane resistance R_m, R_f is the fouling resistance caused by internal pore clogging and R_p is the fouling resistance caused by the accumulation and deposition of polymers at the membrane surface. The effect of R_p on overall resistance R_{tot} can be removed by replacing the feed solution with clean water [31].

The most important factor for flux decline is fouling resistance, R_f, which can be reduced by proper methods such as cross flow filtration. The fouling can be divided into reversible and irreversible fouling.

$$R_m + R_f = \frac{\Delta P}{\eta \times J_{\text{wf}}} \tag{6}$$

$$R_f + R_p = R_{\text{tot}} - R_m = \frac{\Delta P}{\eta \times J_{\text{wf}}} \tag{7}$$

where J_{wi}, J_{wf}, and J_v are the fluxes (L h^{-1} m^{-2}) using pure deionized water in the initial and final stages and solutions, respectively.

The calculation of R_m, R_f and R_p (m^{-1}) values can be made using the above three equations and flux data.

3. Results and discussion

3.1. Ultrafiltration of metal ions solution

Fig. 1 represents the variation of nickel and copper retention as a function of the transmembrane pressure for a feed metal ions concentration equal to 100 mg L^{-1} at 25°C. It shows that the metal ions rejection is low and do not exceed 10% and 12% for nickel and copper, respectively.

Permeate fluxes for metal ions solution (J_v) as a function of transmembrane pressure ΔP are shown in Fig. 2.

Pure solvent flux is proportional to transmembrane pressure, as it could be predicted by Eq. (2). The slopes of the straight lines are the aqueous nickel and copper solutions permeability, respectively, $L_p(\text{Ni}) = 8.431$ L h^{-1} m^{-2} bar^{-1}, $L_p(\text{Cu}) = 8.374$ L h^{-1} m^{-2} bar^{-1}.

The hydraulic membrane resistance and a total filtration resistance have as values $6.26 \pm 3 \times 10^{13}$ m^{-1} and $1.25 \pm 6 \times 10^{14}$ m^{-1}, respectively. It implies that the presence of metal ions does not generate some significant additive resistance, generally manifested when solutes were filtered through the membrane.

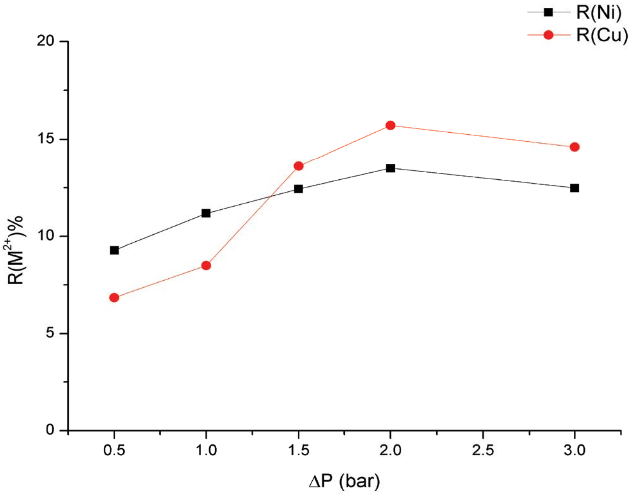

Fig. 1. Nickel and copper retention as a function of transmembrane pressure, $[M^{2+}] = 100$ mg L^{-1}, $\theta = 25$°C.

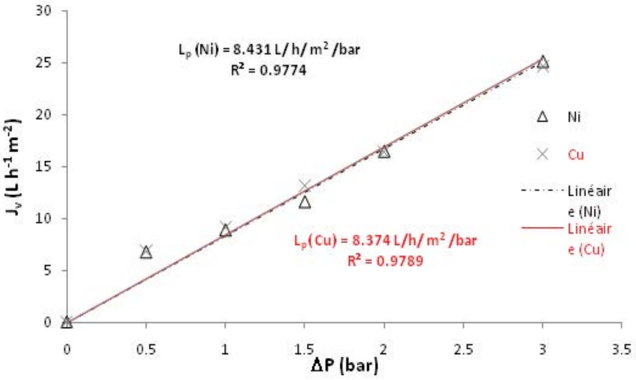

Fig. 2. Permeate fluxes as a function of transmembrane pressure, $[M^{2+}] = 100$ mg L^{-1}, $\theta = 25$°C.

3.2. Ultrafiltration of PSS solution

Fig. 3 displays the variation in permeate flux as a function of the transmembrane pressure for different PSS concentrations. It shows that the permeate fluxes increase with transmembrane pressure and decrease with the increase of PSS concentrations. The curves shown in Fig. 3 are line segments passing through the origin reflecting the negligible effect of the osmotic pressure and negligible concentration polarization. A deviation from the straight line representing J_v vs. ΔP for different PSS concentrations studied compared with pure water line.

The experiment procedure to determine experimental measurements of permeability and resistances consisted of several cycles of membrane filtration and is based on the resistance-in-series model. The first step consisted on determining the pure water permeability of membrane to determine the hydraulic resistance membrane R_m and the total filtration resistance of each solution. In order to eliminate membrane blocking effects after UF of solution, a step of washing was performed at low pressure. Pure water washing allowed determining the fouling and concentration

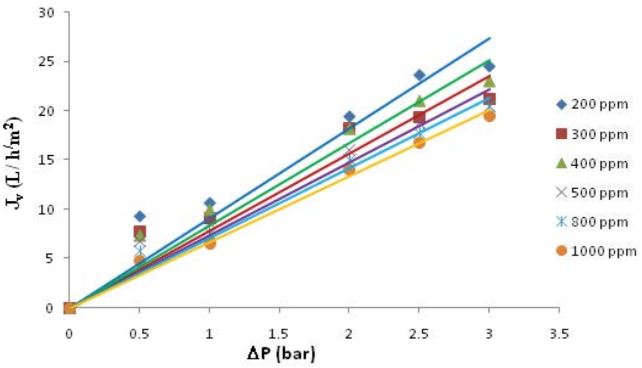

Fig. 3. Permeate flux as a function of transmembrane pressure for different PSS feed concentrations.

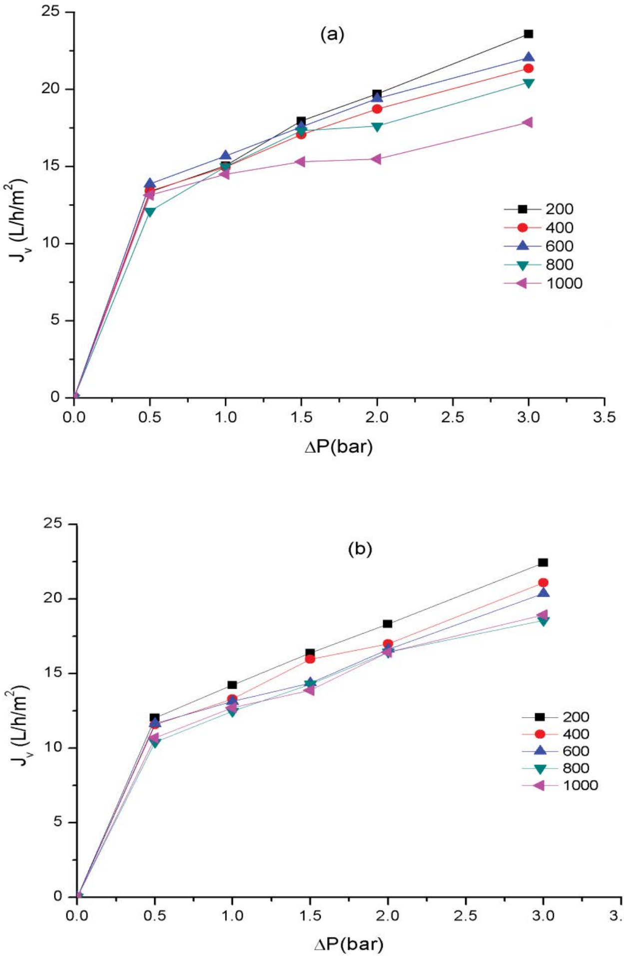

Fig. 4. (a) Permeate flux as a function of transmembrane pressure at different PSS concentrations, [Ni^{2+}] = 100 ppm; (b) permeate flux as a function of transmembrane pressure at different PSS concentrations, [Cu^{2+}] = 100 ppm.

polarization resistances R_f and R_p. The end of the wash step is to measure again the new ultrapure water permeability of the membrane to determine the fouling resistance (R_f).

In Table 1 the experimental measurements of permeability and resistances to the solvent transfer of PSS solutions in the absence of metal ions was reported. It reveals a reduction in the permeability followed by an increase in total filtration resistance, when PSS concentrations increase from 200 to 1,000 ppm. It is also noticed that total filtration resistance is the same in the concentration range studied. However, the total hydraulic resistance increased to a value substantially equal to twice the hydraulic membrane resistance, this is attributed to the formation of a reversible blocking applied in the high transmembrane pressures.

3.3. Effect of transmembrane pressure

The variation of the permeate flux according to the transmembrane pressure at different PSS concentrations, with the presence of Ni(II) and Cu(II), respectively, are represented in Figs. 4a and b. The permeate flux increases with transmembrane pressure and decreases when PSS concentrations increases from 200 to 1,000 ppm. This reduction in permeate flux may be due to the membrane fouling and concentration polarization [10].

In fact, experimental measurements of permeability and resistances to the transfer of the solvent in metal ions–PSS solution are shown in Table 2. It can be observed that L_p decreases with increasing PSS concentrations. The total filtration resistances values for mixture solution (PSS–metal ions) are two times higher than when PSS is alone (Table 1). This can be explained by the difference of molecular weight between PSS–metal ions mixture in solution and PSS alone in solution. In fact, the increase in the molecular weight of PSS, after complexing metal ions, produces a decrease in the polyelectrolyte mobility, leading to a reduction in the diffusion from the membrane to the feed solution.

Table 1
Experimental measurements of permeability and resistances to the solvent transfer as a function of PSS concentrations

[PSS] (ppm)	L_p (L h^{-1} m^{-2} bar^{-1})	r^2	R_{tot} (m^{-1})	$R_f + R_p$ (m^{-1})
200	9.099	0.923	6.26×10^{13}	2.06×10^{13}
300	7.850	0.918	6.26×10^{13}	2.06×10^{13}
400	8.355	0.952	6.26×10^{13}	2.06×10^{13}
500	7.407	0.950	6.26×10^{13}	2.06×10^{13}
800	7.115	0.959	6.26×10^{13}	2.06×10^{13}
1,000	6.676	0.989	6.26×10^{13}	2.06×10^{13}

On the other hand, it was thought that the overlapping of PSS chains at the membrane surface would cause an exponential extension in filtration resistance. Indeed, the resistance due to clogging represented more than 40% of the total filtration resistance in the case where the concentration of PSS is above 800 ppm and only 30% when the PSS concentration is between 200 and 600 ppm.

However, we note that the polarization phenomenon is negligible compared with the reversible blocking. This result shows that the importance for step washing and cleaning membranes allow us to eliminate the majority of clogging particles [32,33].

This result shows that CR-5 membrane is more sensitive to clogging, especially for high PSS concentrations.

Table 2
Experimental measurements of permeability and resistances to the transfer of the solvent in metal ions–PSS solution

[PSS] (ppm)	L_p (L h^{-1} m^{-2} bar^{-1})	R_{tot} (m^{-1})	R_f (m^{-1})	R_p (m^{-1})	R_m/R_{tot} (%)	R_f/R_{tot} (%)
200	8.961	6.26×10^{13}	2.09×10^{13}	0	66.60	33.38
400	8.532	6.59×10^{13}	2.25×10^{13}	0.17	63.27	34.14
600	8..511	6.86×10^{13}	2.59×10^{13}	0.10	60.78	37.75
800	8.173	7.06×10^{13}	2.75×10^{13}	0.14	59.06	38.95
1,000	7.788	10.26×10^{13}	5×10^{13}	1.09	40.64	48.73

In addition to that, the variation of nickel and copper retention as a function of transmembrane pressure for different PSS concentrations is represented, respectively, in Figs. 5a and b that the increase of the transmembrane pressure has a slight effect on the removal of metal ions. A maximum retention was observed at 1,000 ppm PSS concentration which values are nearly 90% for both metal ions.

3.4. Effect of pH on rejection

It is well known that the pH is the most important parameter to take into account in the formation of the macromolecular complexes. pH sensitivities of metal–polymer complex formation vary significantly from metal to metal, this can be exploited for their selective separation. The effect of pH on the nickel and copper retention was investigated in the range 2.0–9.0 at loading ratio $\left(\frac{[\mathrm{PSS}]}{[M^{2+}]}\right)=10$ ($L = 10$) and transmembrane pressure of 3 bar.

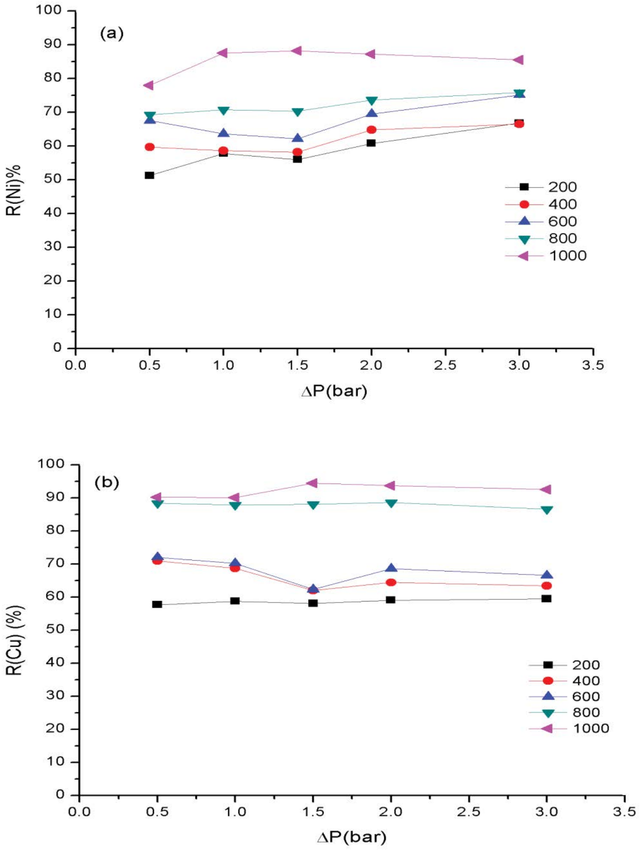

Fig. 5. (a) Nickel retention as a function of transmembrane pressure at different PSS concentrations, [Ni^{2+}] = 100 ppm; (b) copper retention as a function of transmembrane pressure at different PSS concentrations, [Cu^{2+}] = 100 ppm.

Fig. 6 shows the pH effect on the retention of nickel and copper. At low pH, where the majority of the acid groups are protonated, affinity toward metal ions is poor and the stability of the complex is low. As the pH increases, the affinity and stability of PSS–M^{2+} complexes increase [16]. Above pH 5 the nickel retention increases and attain a maximum value 89% at pH 8. An increase in pH leads to an increase in deprotonated sulfonate groups of PSS, which favors the formation of macromolecular polymer–metal complexes, and subsequently an increase in metal retention [34].

3.5. Effect of pH on flux

Fig. 7 shows the average flux vs. pH for solutions mixture PSS-Ni, PSS-Cu and water. The water solution flux was used as a reference solution for these experiments. It can be seen that the pH has a little effect on the permeate flux with values fluctuating between 15 and 25 L h^{-1} m^{-2}, which

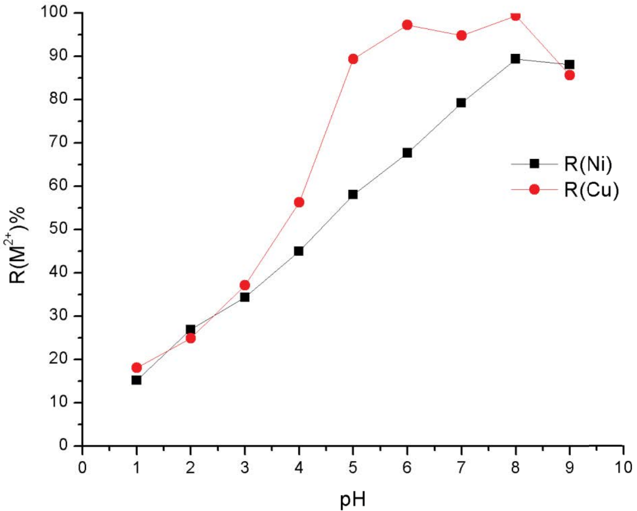

Fig. 6. Metal ion retention as a function of pH, $\left(\frac{[\mathrm{PSS}]}{[M^{2+}]}\right)=10$, $\Delta P = 3$ bar.

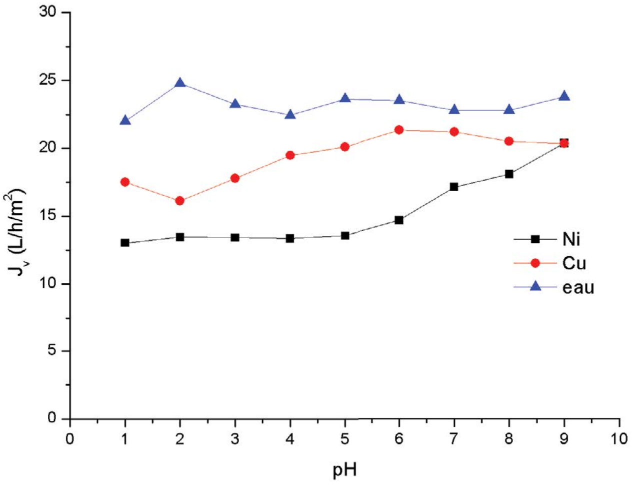

Fig. 7. Permeate fluxes of water, Ni(II) and Cu(II) as a function of the feed pH, $\left(\frac{[\mathrm{PSS}]}{[M^{2+}]}\right) = 10$, $\Delta P = 3$ bar.

represents 10%–20% of the water flux. In fact, increase of pH provokes molecule expansion, which increases slightly viscosity of polymer solutions. This behavior can be explained on the basis of conformational changes of polymer structure and interactions between polymer molecules themselves and membrane. This polymer configuration can produce a fouling phenomenon by pore blocking and may explain the observed moderate in permeate flux [35].

3.6. Effect of the ionic strength on rejection

Figs. 8a and b show the effect of adding salt (NaCl) on nickel and copper removal. UF experiments at all the different ionic strengths (10^{-4}, 10^{-3}, 5.10^{-2}, 10^{-1} M), were conducted with the varied transmembrane pressure, loading ratio equal to 10. The nickel and copper removal rate decreases sharply to 25% and 30%, respectively, after the ionic strength greater than 10^{-3} M, while the removal rate is at more than 90% with any NaCl added (10^{-4} M). These results can be explained by a conformational change on the polymer chains, a competitive adsorption between Na^+ and M^{2+} on negatively charged polymer and the attenuation of the electrostatic repulsion [36]. It is well known that negatively charged polyelectrolytes interact with positively charged divalent metal ions stronger than with monovalent ions [37,38]. When increasing the salt concentration, the metal ions retention decreases, and this behavior can be related to the compression of a double electrical layer relatively with the increase of the added salt concentration, and therefore the electrostatic attraction is greatly reduced between the positively charged metal ions and the negatively charged PSS. As a result, the unbound Ni(II) and Cu(II) ions pass through the membrane leading to a lower retention of these ions [39].

3.7. Effect of ionic strength

The permeate flux of nickel and copper solutions in the absence and presence of NaCl solution is represented in Fig. 9. This figure shows that the permeate flux is more important when not adding salt to the solution. In the presence of NaCl, the permeate flux values of Ni and Cu are almost the same. Indeed, previous studies have shown that the UF in the presence of salt solutions revealed a reduction of the permeate flux and the increase of ionic strength causes an increase in the thickness of the layer of solute adsorbed, which increases the flow resistance [40].

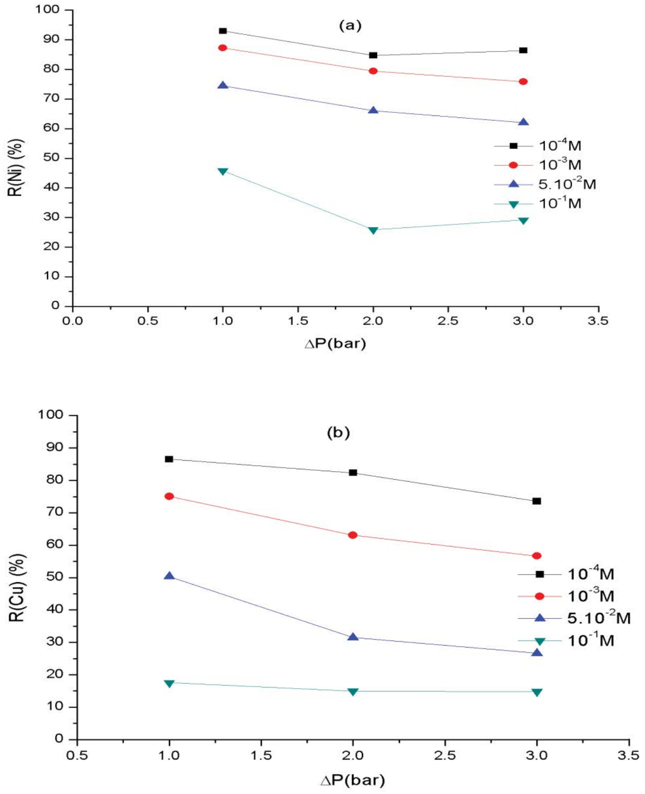

Fig. 8. (a) Nickel retention as a function of transmembrane pressure at different NaCl concentration and (b) copper retention as a function of transmembrane pressure at different NaCl concentrations, $\left(\frac{[\mathrm{PSS}]}{[M^{2+}]}\right) = 10$.

3.8. Isotherm modeling

In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention of a substance from the aqueous porous media or aquatic environments to a solid phase at a constant temperature and pH [41,42]. An adsorption isotherm describes the relationship between the amount of solute retained by the solid and the solute concentration dissolved in the equilibrium liquid.

The amount of the adsorbed solute can be calculated by the following equation:

$$Q_e = \left(C_0 - C_e\right) \times \frac{V}{m} \tag{8}$$

where V: the volume of the solution (L); m: mass of adsorbent (g); C_0: initial concentration in the liquid phase (mol L^{-1}); C_e: equilibrium concentration (mol L^{-1}).

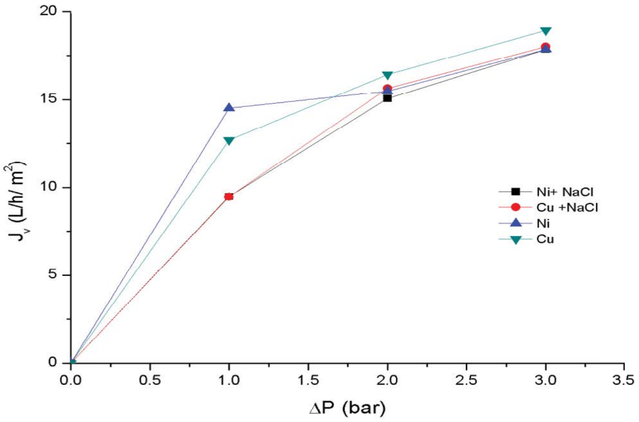

Fig. 9. Permeate flux of metal solution vs. transmembrane pressure with and without salt, [NaCl] = 5.10^{-2} M, $\left(\frac{[\text{PSS}]}{[M^{2+}]}\right) = 10$.

In this part, the equilibrium data of nickel and copper adsorption by the UF membrane in the presence of PSS were modeled by Langmuir and Freundlich equations.

3.8.1. Langmuir model

Langmuir isotherm assumes monolayer sorption onto a surface containing a finite number of sorption sites of uniform strategies of sorption; this model assumes uniform adsorption energies on the surface and no ion transmigration in the membrane [43].

This model is very useful for the monomolecular adsorption of a solute on the monolayer surface of membrane [44].

Following Langmuir's procedure for the adsorption of gases onto surfaces, the equilibrium situation is described by the following formula:

$$Q_e = \frac{Q_m \times K_L \times C_e}{1 + K_L \times C_e} \qquad (9)$$

where Q_e is the amount of metal ions bound to the polymer per monomeric unit; C_e is the equilibrium concentration of the solute in the crude solution (mol L^{-1}); Q_m is the maximum amount of metal ions that may condense on the polymer surface and K_L is the apparent thermodynamic constant for a given ionic strength.

The linear form of the Langmuir isotherm is given by the next equation:

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{Q_m K_L} \times \frac{1}{C_e} \qquad (10)$$

Fig. 10 represents the variation of (1/Q_e) according to (1/C_e) according to the model from Langmuir.

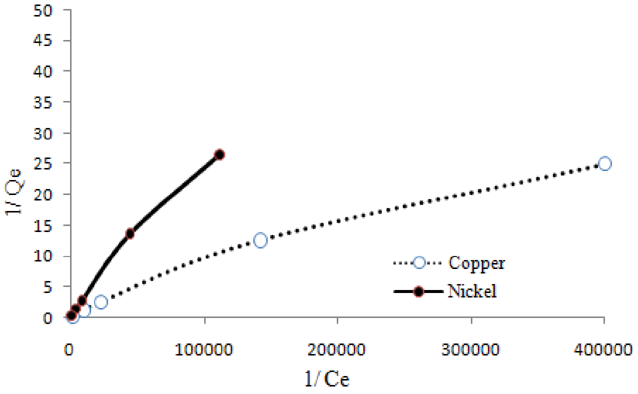

Fig. 10. Variation of (1/Q_e) according to (1/C_e) according to the model from Langmuir.

Table 3
Isotherm constants for the adsorption of M(II) in the presence of the polyelectrolyte

Model	Parameters	M^{2+}	
		Cu^{2+}	Ni^{2+}
Langmuir	Q_m	1.216	0.817
	K_L	4,111.8	20,399.8
	R^2	0.987	0.979
Freundlich	K_F	1,564.9	2,074.9
	n	1.085	1.176
	R^2	0.998	0.997

The linear plot of 1/Q_e as a function of 1/C_e shows that the adsorption obeys the Langmuir model (Fig. 10). The values of constants Q_m and K_L were calculated and reported in Table 3. The maximum monolayer adsorption capacities (Q_m) for the adsorption of M^{2+} on the membrane were 1.216 and 0.817 mol L^{-1} for copper and nickel, respectively.

The figure shows that the variation of (1/Q_e) as a function of (1/C_e) does not evolve linearly and, consequently, Eq. (10) is not verified. The Langmuir isotherm is, therefore, not satisfactory for the adsorption of copper and nickel. This can be explained by the fact that the adsorption on the membrane is not monolayer.

3.8.2. Freundlich model

The Freundlich model can be applied to non-ideal adsorption on heterogeneous surfaces as well as multilayer adsorption and expressed by the following equation:

$$Q_e = K_F C_e^{1/n} \qquad (11)$$

where 1/n is the heterogeneity factor, and it is a measure of the deviation of adsorption from linearity, n is a constant of the intensity adsorption and K_F is a constant of the relative adsorption capacity. The fit of adsorption data to Freundlich isotherm indicates the heterogeneity of the membrane surface.

The n value indicates the degree of nonlinearity between solution concentration and adsorption as follows: If the value of $n = 1$, the adsorption is linear; if $n < 1$, the adsorption process is chemical; if $n > 1$, the adsorption is a favorable physical process [45].

Eq. (11) can be linearized in the form of Eq. (12) and the constants can be determined by the following equation:

$$\log Q_e = \log K_F + \frac{1}{n}\log C_e \tag{12}$$

Fig. 11 represents the variation of $\log Q_e$ as a function of $\log C_e$ according to the Freundlich model.

The linear plot of $\log Q_e$ as a function of $\log C_e$ shows that the adsorption obeys to the Freundlich model. The correlation coefficients, $R^2 \geq 0.997$, obtained from the Freundlich model, were comparable with that obtained from Langmuir model (Table 3). This result proves that the experimental data fit to the Freundlich model and $n > 1$ indicating that adsorption for copper and nickel in the presence of the polyelectrolyte is a favorable physical process.

3.9. Ultrafiltration of mixture metal ions solution

To achieve a selective separation of the two metal ions, the variation of PSS concentration was tested. A solution of Ni(II) and Cu(II) was adjusted at 100 ppm concentration and a varying PSS concentration, a transmembrane pressure was fixed at 3 bar.

Fig. 12 shows the evolution of the rejection coefficient for both metal ions in the mixture solution according to PSS concentrations. The results show for all PSS concentrations, copper retention is higher than nickel. This result was also obtained when only a single metal ion is alone in solution. On the other hand, interactions between the sulfonate groups of PSS and metal ions are observed and are more important with copper ion. At the same time, the retention coefficient of Cu complexation is higher than that of Ni. This indicates that the Cu–PSS complex is less stable than the Ni–PSS one. It may be the consequence of the characteristics of d electrons of copper which are more tightly held and less available for π bonding and which request high excess of complexing agent to form a complex.

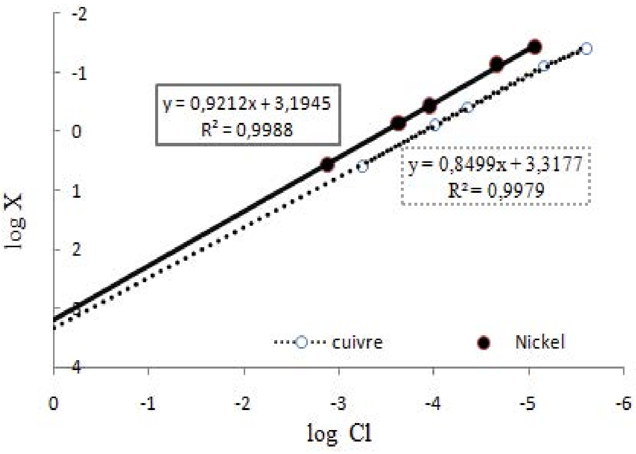

Fig. 11. Variation of $\log Q_e$ as a function of $\log C_e$ according to the Freundlich model.

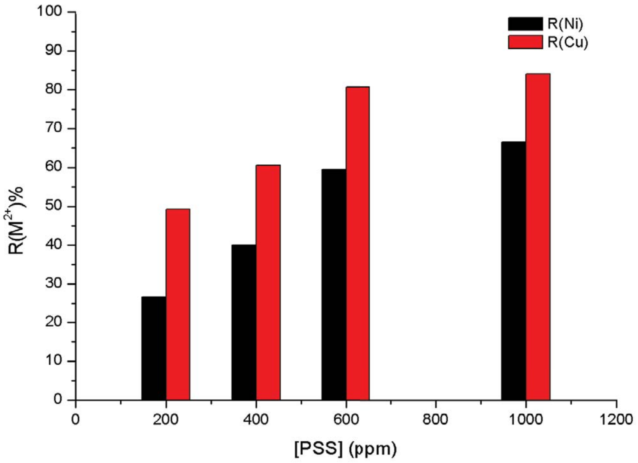

Fig. 12. Retention of nickel and copper ions in a mixture solution according PSS concentrations, $[M^{2+}] = 100$ ppm, $\Delta P = 3$ bar.

4. Conclusions

The PEUF process is suitable to remove nickel and copper ions from aqueous solution with the help of water-soluble polymeric ligand PSS. Effects of various operating parameters on Ni and Cu rejection were investigated. In the absence of PSS, rejection of free metal ions Ni(II) and Cu(II) are low and they do not exceed 10% and 12%, respectively.

The variation of permeate flux as a function of the transmembrane pressure for different feed concentrations of PSS. It shows that the permeate flux increases with transmembrane pressure and decreases with the increase of polyelectrolyte concentrations.

The effect of transmembrane pressure showed a maximum retention observed at 1,000 ppm PSS concentration which values are nearly 90% for both metal ions.

The pH effect on the nickel and copper recovery revealed a maximum retention around, respectively, 89% and 99% for pH 5. An increase in pH leads to an increase in deprotonated sulfonate groups of PSS, which favors the formation of macromolecular polymer–metal complexes, and subsequently an increase in metal retention.

The effect of adding salt concentration on nickel and copper removal showed the best retention without salt, nickel and copper removal rate decreases sharply to 25% and 30%, respectively, after the ionic strength greater than 10^{-3} M, this decrease in retention can be explained by a conformational change of the PSS polymer and a competitive adsorption between ions Na^+ and Cu^{2+} or Ni^{2+} on the negatively charged polymer, as well as the attenuation of electrostatic repulsions. It can be also observed that permeate fluxes are more important when not adding salt to the solution.

The equilibrium data were fitted to the Langmuir and Freundlich models, and they were best described by the Freundlich model. The correlation coefficients, $R^2 \geq 0.997$, obtained from the Freundlich model, were comparable with those obtained at from the Langmuir model. This result indicates that the experimental data correspond to the Freundlich model and that $n > 1$ indicates that the adsorption of copper and nickel in the presence of the polyelectrolyte is a favorable physical process.

When both metals are present in the same solution, copper retention is higher than nickel for different PSS concentrations. This result was also obtained when only a single metal ion is alone in solution. The interactions between the sulfonate groups of PSS and metal ions are observed and are more important with copper.

Symbols

PSS — Poly(sodium 4-styrenesulfonate)
PEUF — Polyelectrolyte enhanced ultrafiltration
UF — Ultrafiltration
C_p — Metal ion concentration in the permeate, mg L^{-1}
C_f — Metal ion concentration in the feed solution, mg L^{-1}
J_v — Permeate flux, L h^{-1} m^{-2}
V_p — Volume of the permeate, L
S — Effective membrane area, m^2
t — Time, s
L_p — Permeability of aqueous solution, L h^{-1} m^{-2} bar^{-1}
ΔP — Transmembrane pressure, bar
L — Loading ratio
L_p^0 — Permeability of solvent
η — Solvent viscosity, dL g^{-1}
R_m — Hydraulic membrane resistance, m^{-1}
R_{tot} — Total filtration resistance fouling resistance, m^{-1}
R_f — Fouling resistance fouling resistance, m^{-1}
R_p — Fouling resistance, m^{-1}
J_{wi} — Water flux in the initial stage of ultrafiltration, L h^{-1} m^{-2}
J_{wf} — Water flux in the final stage of ultrafiltration, L h^{-1} m^{-2}
M^{2+} — Ni^{2+} or Cu^{2+}
V — Volume of the solution; L
m — Mass of adsorbent; g
C_0 — Initial concentration in the liquid phase; mol L^{-1}
C_e — Equilibrium concentration; mol L^{-1}
Q_e — Amount of metal ions bound to the polymer per monomeric unit
Q_m — Maximum amount of metal ions that may condense on the polymer surface
K_L — Apparent thermodynamic constant for a given ionic strength
n — Constant indicative of the intensity of the adsorption
K_F — Constant indicative of the adsorption capacity

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