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Ultrafiltration of Polymer-Metal Complexes for Metal Ion Removal from Wastewaters

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Summary: A case-study using macromolecular metal complexes is described. The results of a process named Polymer Assisted Ultrafiltration (PAUF) for ion removal from various types of waters is reported. The water soluble polymers such as polyetilenimine (PEI), polyacrylic acid (PAA), polyacrylic acid sodium salt (PAASS) and poly(dimethylamine–co–epichlorohydrin–co–ethylenediamine) (PDEHED) as chelating agents, the Cu^{2+} as model ion and five ultrafiltration membranes have been used. The complexing agents were previously tested to establish the binding capacity and the best operating conditions for the process. Among the tested polymers the PEI appeared the most interesting one because its binding mechanism does not involve a counter ion release. It was tested in the simulation of wastewaters treatment containing the Cu^{2+} ion chelated with citric acid; this is a problem of interest in the recycling of water from soil washing operations. The polyethylenimine quantitatively bound the copper-citrate chelate at pH 5.5 and the three component complex was separated by UF membranes producing a permeate with very low metal concentration. The polymer regeneration was carried out with good results by operating with the diafiltration method. The copper ion present in the diafiltration permeate in a form chelated with citric acid was recovered by oxidising the citrate in a membrane photoreactor. The positive results of the described case-study show that Macromolecule-Metal Complexes play a key role for running effectively and selectively the PAUF process for removing metal ions from various type of waters.

Keywords: membranes; metal-polymer complexes; ultrafiltration; wastewater treatment; water-soluble polymers

Introduction

Today wastewater treatment represents one of the most important fields of study in the wide field of solving pollution problems. Because of increased worldwide demand for water, particularly in recent years, the main challenge is to find new resources and to fully-reuse the existing ones. Water frequently contains numerous ionic solutes, many of which are not desirable for either residential or industrial purposes. The separation of these solutes can be done by using the reverse osmosis operation, but this will result in high operating costs, low permeate flow rate and low ion selectivity. In order to overcome these problems, the hybrid ultrafiltration–complexation process was introduced. It was named polymer-assisted ultrafiltration (PAUF) or polymer enhanced ultrafiltration (PEUF).[1–3] In particular, by means of this technique, UF membranes with pores smaller than the size of the used polymeric agents are employed; thus, polymer-metal complexes can be retained while the non-complexed ions pass through the membrane.[4–6]

The advantages of this method are the low energy requirements involved in UF,

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the conceptual simplicity, the modularity typical of membrane processes, the high permeate flow rate, the high removal efficiency because of effective binding while reducing the initial waste volume significantly, the selectivity achieved when an appropriate complexing agent is considered, and the optimal quality of treated water.[7,8] The PAUF process appears to be economically feasible if the polymer could be regenerated by the release of the metal or its chelate and reused.[3]

The complexation-ultrafiltration process can be applied for various purposes such as the treatment of waste effluents, groundwater and seawater;[9,10] it is mainly applied in the separation of metal ions from aqueous solutions, covering processes ranging from production of potable water, to leaching and recovery of metals from washing water of contaminated soil or from ores, to detoxification of process water and wastewater, also for water recycling and reuse.[6,11,12] Indeed, metal contamination is a dangerous cause of water pollution and it constitutes a big health hazard.[13] Some metal ions play an essential role in many biological processes, and their deficiency, unusual accumulation or imbalance may lead to biological troubles. E.g., Cu^{2+} ion is an essential nutrient, but when people is exposed to copper levels of above 1.3 mg/l for short period of time, stomach and intestinal problems occur. Long-term exposure to Cu^{2+} leads to kidney and liver damage,[14,15] producing DNA mutation, evidence of its cancerogeneous character.

In this work some polymeric agents and five membranes have been tested in order to examine the operating conditions of the PAUF process (bonding capacity, pH, pressure) and membrane performance and these results are discussed.

Fundamentals of Polymer Assisted Ultrafiltration

The key point of the PAUF process is the use of ultrafiltration for removal of ions from aqueous streams provided that they are previously bound to water-soluble polymers. The unbound ions pass through the membrane, whereas the polymers and their complexes are retained.[16,17]

Low molecular weight species such as metal ions can be bound to macromolecules by intermolecular forces, mainly ionic interaction and complex binding, or the combination of both. Formation of complexes is significantly more selective than ionic interactions. An example of this binding mechanism is the complexation reaction among the polymeric agent (PEI), the proton (H^+) and the metal cation (Cu^{2+}) that is represented by the equilibrium equations:

$$\mathrm{PEI} + \mathrm{n\,H_2O} \leftrightharpoons \mathrm{PEIH_n^{n+}} + \mathrm{n\,OH^-} \qquad (1)$$

$$\mathrm{PEI} + \mathrm{a\,Cu^{2+}} \leftrightharpoons \mathrm{PEICu_a^{2a+}} \qquad (2)$$

where $0 \leq n \leq \bar{n}$ and $0 \leq a \leq \bar{a}$ with $\bar{n}$ equal to the number of monomers contained in a single polymeric chain and $\bar{a}$ representing the maximum complexation ratio of the polymer with copper ions ($\bar{a} = \frac{\bar{n}}{4}$ for PEI-Cu complex because of Cu^{2+} tetra-coordination with four nitrogen of PEI). In particular, considering that commercial PEI, widely used in literature, has polymeric chains of MW 60 kDa and considering that a monomeric unit -CH_2-CH_2-NH- has MW 43.062 Da, $\bar{n} = 1393$.

The water-soluble polymers polyacrylic acid (PAA) and polyacrylic acid sodium salt (PAASS) bind copper cation by ion-exchange reactions described by the following equations:

$$\mathrm{PAA} + \mathrm{n\,Cu^{2+}} \leftrightharpoons \mathrm{PAACu_n} + \mathrm{2n\,H^+} \qquad (3)$$

$$\mathrm{PAASS} + \mathrm{m\,Cu^{2+}} \leftrightharpoons \mathrm{PAACu_m} + \mathrm{2m\,Na^+} \qquad (4)$$

Ionic exchange interaction mechanism has low selectivity and the disadvantage to release another ion (H^+ or Na^+ in this case) in the feed solution, so that to remove an ion from an aqueous solution another one must be released. In contrast, reactions such as Equation (2) does not present this disadvantage.

It should be taken into account that in general solid resins and water-soluble polymers have similar functional groups, which would result in similar chemical properties, e.g. ability to bind certain ions. These analogies in their properties can be used in order to predict the behaviour of an unknown hydrophilic polymer if the properties of the functional group of a resin are known.

Comparison of Copper(II) Removal from Waters by Using Various Polymers[5]

Some water soluble polymers such as polyetilenimine (PEI), polyacrylic acid (PAA), polyacrilic acid sodium salt (PAASS), and poly(dimethylamine–co–epichlorohydrin–co–ethylenediamine) (PDEHED) as chelating agents (Table 1) were tested by using the Cu^{2+} as model ion.

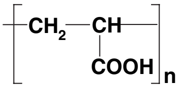
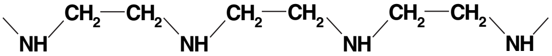
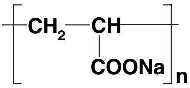
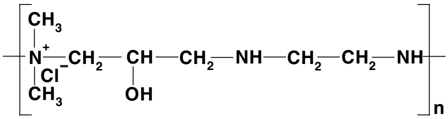
For PAA and PAASS an ionic interactions mechanism such as the equilibrium reactions (3) and (4) occurs. It is influenced by the pH: at low pH the protonation of carboxylic group of the polymer is favoured, whilst at higher pH complexation reaction is shifted at right, meaning macromolecular complex formation with the metal ion. The interaction between the copolymer PDEHED and copper ion is more complicated: the lone-pair of the nitrogen in ethylenediamine monomers and the oxygen of epichlorohydrin could bind copper with both complex bond and ionic interactions.

From Figure 1 it can be observed that copper ion is complexed by PEI, PAA or PAASS, and PDEHED at pHs higher than 6, 4.6, and 8, respectively. The decomplexation reactions took place at $pH < 3$.

To determine the binding capacity (saturation condition) of the three different polymers (maximum copper amount (g) that can be complexed by a fixed amount (1 g) of polymer), some complexation tests were carried out with a fixed polymer concentration ($volume = 20$ ml) and changing copper concentration at complexation pH.

Binding capacity was 0.333 mg Cu^{2+}/mg polymer for PEI and PAA. By taking into account that 0.333 mg Cu^{2+} correspond to $5.24 \cdot 10^{-3}$ mmol and that 1 mg of polymer contains 0.023 mmol of N and 0.014 mmol of –COOH for PEI and PAA, respectively, the weight ratios can be converted in molar ratios. Thus, complexation ratios (mmol of chelating group/mmol Cu^{2+}) of 4.4 and 2.67 were obtained for PEI and PAA, respectively. The value obtained for PEI was in agreement with the hypothesis of tetra-

Table 1.
Some polymeric binding agents

Polymer	General formula	Average molecular weight (kDa)
Polyacrylic acid(PAA)	 $\left[-CH_2-\underset{\displaystyle COOH}{CH}-\right]_n$	100
Polyethylenimine(PEI)		60
Polyacrylic acid, sodium salt(PAASS)	 $\left[-CH_2-\underset{\displaystyle COONa}{CH}-\right]_n$	30
Poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine)(PDEHED)	 $\left[-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{+}{N}}}\,Cl^-\,-CH_2-\underset{\displaystyle OH}{CH}-CH_2-NH-CH_2-CH_2-NH-\right]_n$	75

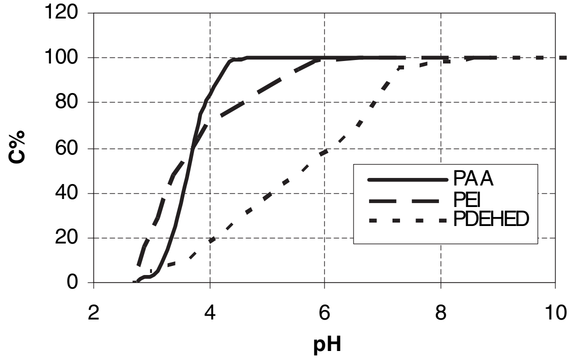


Figure 1.
Comparison of Cu-polymer complex formation C% (=(ABS/ABS$_{max}$)×100) vs pH in complexation tests of PEI (150 mg/L), PAA (150 mg/L) and PDEHED (150 mg/L) with copper (50 mg/L).

coordination put forth Equation (2). For PAA, the value of 2.67 was higher than 2, foreseen by Equation (3), meaning sub-saturation conditions. Indeed, working at lower molar ratios a PAA-Cu^{2+} complex precipitation was observed.

Concerning the copolymer, working with a polymer concentration of 50 mg/L and changing copper concentration, an optimal amount of 2 mg Cu^{2+}/ mg PDEHED was obtained at pH 8.5. At higher ratios, a cloud solution was observed due to limited complex solubility.

Ultrafiltration tests were performed at two transmembrane pressures (2 and 4 bar), by using five different membranes, and determining flux and rejection. Copper concentration was chosen at 50 mg/L to simulate the treatment of water with the same pollution load.

The results, summarized in Table 2, show that the fluxes (J_P) obtained with the PDEHED are lower than that registered using PEI and PAA. Regarding the separation efficiency, measured by the membrane rejection percentage (R%), this is in the order PDEHED > PAA > PEI. This behaviour could be caused by the higher membrane fouling and/or polarization concentration caused by the co-polymer.

Inspection of membranes at the end of the experimental runs showed a thin layer on the filtering surface: the cake was cerulean, with the colour of polymer-copper complexes, and it appeared like an incrustation in the case of PDEHED,

Table 2.
Results of ultrafiltration tests using: PEI (150 mg/L) and Cu^{++} (50 mg/L) at pH = 6.2; PAA (150 mg/L) and Cu^{++} (50 mg/L) at pH 4.6; PDEHED (50 mg/L) and Cu^{++} (50 mg/L) at pH = 8.5.

Membrane	Pressure [bar]	Polymer					
		PDEHED		PEI		PAA	
		2	4	2	4	2	4
Iris 10 kDA	J_p[L/hm^2]	93.08	55.0	120.58	173.47	105.78	143.85
	R%	100.0	99.9	99.0	98.9	99.1	99.5
Iris 30 kDa	J_p[L/hm^2]	110.0	67.7	156.5	232.7	156.5	190.4
	R%	99.9	99.9	98.7	98.5	98.3	99.3
PANGKSS HV3/T	J_p[L/hm^2]	122.7	71.9	241.2	262.3	258.1	220.0
	R%	99.9	99.8	99.1	98.7	99.5	99.5
PANGKSS HV2/T	J_p[L/hm^2]	131.2	71.9	253.9	262.3	275.0	215.8
	R%	99.9	99.8	99.1	98.6	99.6	99.5
UTC 60 ROPUR	J_p[L/hm^2]	50.8	50.8	29.6	63.5	25.4	50.8
	R%	100.0	100.0	99.9	99.9	100.0	99.9

while for PAA and PEI it was a simple deposit easily removable.

The possibility of membrane reuse in the complexation-ultrafiltration process was evaluated by carrying out three UF runs in series by using the polymer PDEHED, which gave the highest fouling. Each run was composed by four steps in sequence: i) membranes characterization with water; ii) UF test carried out till reaching steady state conditions; iii) washing of membranes and system with tap water for 2 hours without recycle (open loop); iv) washing of membranes and system with 20 L of demineralised water without recycle; return to i).

The steps iii) and iv) were carried out at maximum cross flow and minimum transmembrane pressure to avoid further cake compaction during membrane washing.

The results showed that after a flux decrease observed in the second run, membrane performance remained the same in the third run. This is important for long term use of the same membrane.

Simulation of Wastewaters Treatment Containing the Cu^{2+} ion Chelated with Citric Acid

Of the five membranes the Iris 10 and Iris 30 kDa ones were selected because of the lower fouling tendency during operation.

UF experiments were carried out in the batch system reported in Figure 2. It consisted of two stirred cells (V = 72 mL, membrane diameter = 43 mm) connected by means of a tubing system to a steel container where ultrapure water or the solution was loaded. The applied pressure was controlled by pressurized nitrogen.

The membranes were characterized with ultrapure water before and after their use, in order to evaluate membrane permeability and membrane fouling after the ultrafiltration runs. The operative trans-membrane pressure was fixed first at 4 bar to stabilize their compaction, and after reaching a steady state condition (constant flux) it was decreased to 3 bar and subsequently to 2 bar.

Previously the chemical conditions for the formation of the PEI–citrate–copper complex were determined. Because of analytical problems the Iris 10 kDa membrane at pH ~ 5.5 was tested for separating the ternary complex from the binary complex.

The ultrafiltration of a copper–citric acid solution showed that copper–citrate chelates passed through the membrane.

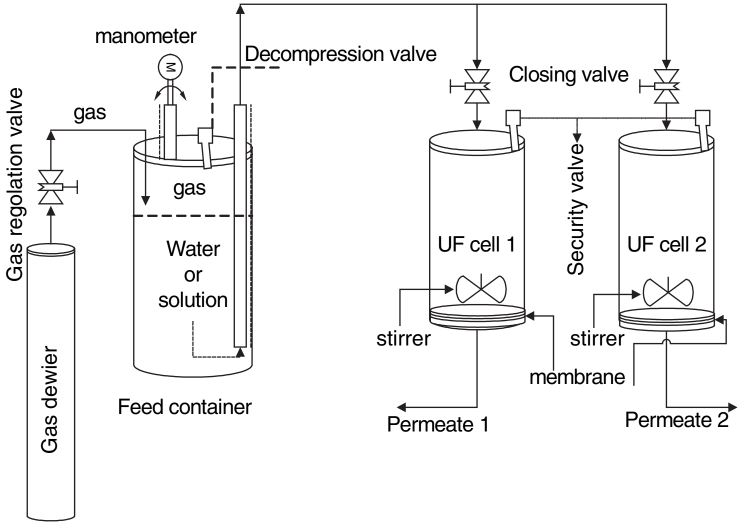


Figure 2.
Flowsheet of the ultrafiltration laboratory plant.

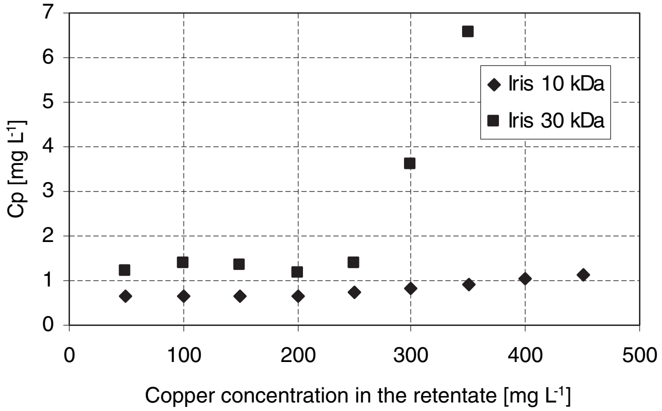


Figure 3.
Copper concentration in the permeate (Cp) vs. copper concentration in the retentate for the UF tests at increasing feed concentration: constant TMP mode (4 bar).

Spectrophotometric readings of the permeate of a PEI–citrate–copper solution at concentration respectively equal to $600\ \mathrm{mg \cdot L^{-1}}$, $800\ \mathrm{mg \cdot L^{-1}}$ and $200\ \mathrm{mg \cdot L^{-1}}$, evidenced the absence of copper complex, meaning that copper–citrate chelates did not permeate through the membrane in presence of PEI polymer. Total organic carbon (TOC) analysis of the permeate showed that only a little amount of polymer and then its complexes pass through the membrane (not detectable by spectrophotometric analysis), due to poly-disperse nature of the commercial polymer. That hypothesis was verified by performing appropriate UF tests with PEI prefiltered through the Iris 10 kDa membrane.

UF tests at increasing feed concentration were carried out to simulate the increase of retentate concentration in an hypothetical industrial plant where the permeate, free of metals, is continuously withdrawn using the PAUF technique. The aim of these tests was to determine the maximum retentate concentration for still obtaining an acceptable permeate ($[\mathrm{Cu^{2+}}] < 1.3\ \mathrm{mg \cdot L^{-1}}$), and the limiting concentration, that is the limiting feed concentration factor ($[\mathrm{Cu^{2+}}]_{\mathrm{limit}}/[\mathrm{Cu^{2+}}]_{\mathrm{feed}}$).

The concentration increase was obtained by feeding in the cells a solution with $50\ \mathrm{mg \cdot L^{-1}}$ copper concentration, 1.6 and 3 weight ratios "citric acid / copper" and "PEI/copper" at pH 5, and withdrawing the permeates. Thus, every 72 mL of collected permeate, the aqueous phase concentration increased of a factor equal to the feed concentration assuming 100% rejection of the ternary complex.

The tests were realised with two different operating approaches:

a) Constant TMP (transmembrane pressure) mode

   Obtained results, reported in Figure 3, show an increasing copper concentration in the permeate with increasing the retentate concentration. For Iris 10 kDa membrane an acceptable permeate concentration ($0.925\ \mathrm{mg \cdot L^{-1}}$) at $350\ \mathrm{mg \cdot L^{-1}}$ retentate concentration was found, while for Iris 30 kDa membrane a limit concentration equal to $250\ \mathrm{mg \cdot L^{-1}}$ was found (copper concentration in the permeate $= 1.401\ \mathrm{mg \cdot L^{-1}}$).

b) Constant permeate flow rate mode

The practical requirement for running industrial UF plants is operating at constant permeate flow rate by progressively increasing the TMP thus controlling flux decrease due to progressive membrane fouling.

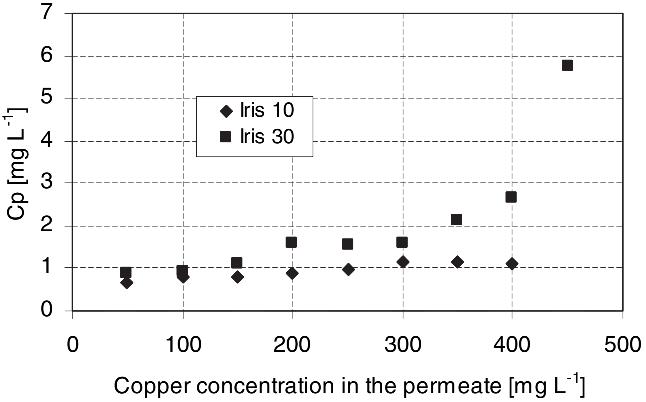


Figure 4.
Copper concentration in the permeate (Cp) vs. copper concentration in the retentate for the UF tests at increasing feed concentration: constant permeate flow rate mode (1 mL · min^{-1}).

The permeate flow rate was fixed at 1 mL · min^{-1} that means a flux of 55.8 L · h^{-1} · m^{-2}. The results obtained are reported in Figure 4 and show a limiting concentration of 400 mg · L^{-1} (TMP 4.4 bar) and 250 mg · L^{-1} (TMP 1.4 bar) for Iris 10 kDa and Iris 30 kDa membranes, respectively.

By increasing the permeate flow-rate to 1.4 mL · min^{-1} (flux 78.12 L · h^{-1} · m^{-2}) and using the Iris 30 kDa membrane the 250 mg · L^{-1} limiting concentration was confirmed (TMP 3.40 bar).

The above results were used to study Iris 30 and Iris 10 kDa membranes performance at the limiting concentrations of 250 mg · L^{-1} and 400 mg · L^{-1} copper concentrations in the feed, respectively. Experimental data showed an higher flux and a lower copper concentration in the permeate for the Iris 30 kDa membrane with respect to Iris 10 kDa, due to a lower limiting concentration. Besides, permeate concentrations were satisfactory at 2 and 3 bar for both membranes, while at 4 bar Iris 10 kDa membrane permeate was unacceptable.

The retentates, at the two limiting concentrations, obtained from the two membranes, were treated with the Diafiltration operation for determining time and water volumes needed to regenerate the polymeric complexing agent PEI. Operating the UF-diafiltration at TMP = 4 bar and pH ~ 2 the PEI was recovered in the retentate, while copper chelates in the diafiltrate.

Figure 5 show the water volumes needed to regenerate 72 mL of complexed PEI.

For Iris 30 kDa membrane 5 hours and 538 mL of water were enough to remove all copper, while 6.5 hours and 618.5 mL were required for Iris 10 kDa membrane.

Because citrate was bound to copper recovered in the diafiltrate, photocatalytic degradation of citrate was tested, among other possible methods, for recovering free copper ions.

Photodegradation tests were performed on 500 mL of diafiltrate with 0.51 g of catalyst (TiO_2) at pH 5. TOC analysis and spectrophotometric readings (λ_{peak} 245 nm) showed that 10 minutes were enough to degrade the citrate. Besides, copper concentration measurement showed complete copper recovery.

Thus, complexation-UF, followed by Diafiltration and Photocatalytic processes can be the fundamental units to assemble an integrated membrane process for soil washing.

Feasibility of the integrated membrane process was estimated by means of a rough calculation on net recovered water volume. Starting from 5760 mL and 3600 mL of simulating soil washing solution volumes to treat, and operating with Iris 10 kDa and Iris 30 kDa membranes, 5069.5 mL and

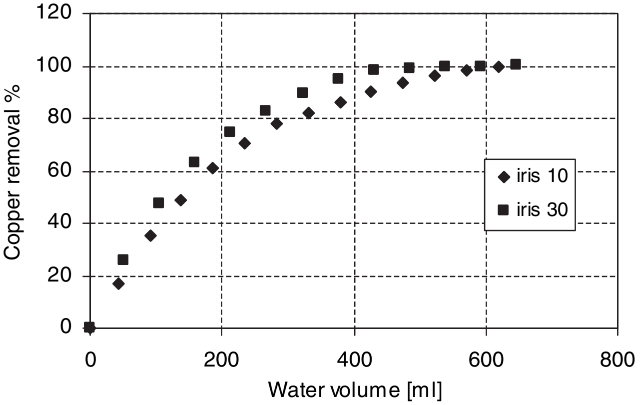


Figure 5.
Copper removal % versus water volume in the diafiltration tests at limiting concentrations for the two different membranes (pH ~ 2).

2936 mL of water, representing the 88% and 83%, respectively, of the initial volume, can be purified by the membrane process.

Conclusion

All the tested water soluble polymers polyethylenimine (PEI), polyacrylic acid (PAA), polyacrylic acid sodium salt (PAASS) and poly (dimethylamine–co–epichlorohydrin–co–ethylenediamine) (PDEHED) were able to complex copper(II) thus they can be used for running the Polymer Assisted Ultrafiltration (PAUF) process.

The PEI polymer for separating the chelate Cu^{2+}-citrate was tested in a case study of the PAUF process of interest in recycling of water from soil washing.

Obtained results showed that copper removal from wastewaters can be achieved successfully by using the PAUF process.

UF tests at increasing feed concentrations showed limiting concentrations of 250 $mg \cdot L^{-1}$ and 400 $mg \cdot L^{-1}$ of the recovered copper for Iris 30 kDa and Iris 10 kDa membranes, respectively.

UF tests at limiting concentrations evidenced an acceptable permeate concentration for Iris 30 kDa at 2, 3 and 4 bar, while for Iris 10 kDa and 4 bar an unacceptable copper concentration ($1.4\ mg \cdot L^{-1}$) was achieved.

A mass balance evidenced a slightly better performance of the IRIS 10 kDa membrane.

Diafiltration tests confirmed the possibility of regenerating, recovering and recycling the PEI polymer.

Photocatalytic degradation tests, evidenced the possibility of oxidizing the citrate in few minutes (10 min), thus recovering free copper ions.

The positive results of the described case-study show that Macromolecule-Metal Complexes play a key role for running effectively and selectively the PAUF process for removing metal ions from various type of waters.

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