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Polymer assisted ultrafiltration for copper–citric acid chelate removal from wash solutions of contaminated soil

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Abstract

The removal of heavy metals from aqueous systems such as wash-solutions of contaminated soil by using Polymer-Assisted Ultrafiltration (PAUF) has been studied. For the extraction of metal ions from contaminated soil citric acid is used as a chelating agent. Cu^{2+} as metal ion and the polymer polyethylenimine (PEI) as ligand were used in the various experiments. Optimal chemical conditions for copper complexation by citric acid were determined by means of complexation tests. The results showed that citric acid is able to chelate copper ions at pH 5.5, while decomplexation occurs at $pH \leq 2$. Maximum bonding capacity (saturation condition) was 0.625 mg Cu^{2+} per mg citric acid, meaning 2 mol Cu^{2+} per mol citric acid. Complexation tests in the system polyethylenimine–citric acid–copper showed that the polymer is able to complex the copper–citric acid chelate at $pH = 6$ while release occurs at $pH < 3$. The saturation condition was 0.333 mg Cu^{2+} per mg PEI. The ultrafiltration tests, carried out at three trans-membrane pressures (2, 3 and 4 bar), showed the possibility of using the PAUF technique for copper ion removal from aqueous solutions.

1. Introduction

Soil may be contaminated by heavy metals (HMs), such as zinc, cadmium, lead and copper present in sludge or urban composts, pesticides, fertilizers and emissions from municipal waste incinerators, car exhausts, residues from metal-ferrous mining and the metal smelting industry [1]. Heavy metals are highly persistent in soil with residence times in the order of thousands of years [2].

Excessive accumulation of HMs can have deleterious effects on soil fertility, affect ecosystem functions and constitute a health risk to both animals and human beings. Indeed, metal ions play an essential role in many biological processes and their deficiency, unusual accumulation or imbalance may lead to biological problems. Nevertheless, because of their competition with essential metals in binding with proteins, heavy metal ions are potent enzyme inhibitors exerting toxic effects on living systems. For example, Cu^{2+} ions are essential nutrients, but when people are exposed to copper levels of above 1.3 mg l^{-1} for short periods of time, stomach and intestinal problems occur. Long-term exposure to Cu^{2+} leads to kidney and liver damage [3], producing DNA mutation, evidence of its oncogenicity.

The clean-up of soils contaminated with HMs is one of the most difficult tasks for environmental engineering. A number of techniques have been developed [4–7], including landfill after waste excavation, chemical–physical immobilisation and soil extraction (flushing/washing). These methods are based on two principles: (1) immobilization (solidification/stabilisation and vitrification), by increasing the retention of heavy metal on soil or by decreasing the mass transfer rate of the metal; (2) mobilization, by the removal of metal from the soil matrix [8]. The most significant drawbacks of immobilization are that: (i) the metal still remains in the soils, so they do not return to their original state and they are not suitable for further use; (ii) the long-term stability and effects on the bio-systems (plant/animal) are unknown [9]. Immobilization is thus not a permanent solution. Soil washing, a water based process that employs chemical and physical extraction processes to remove contaminants from the soil, has recently become a common *ex-situ* technique for remediating sites contaminated with organic and inorganic pollutants [10]. These techniques, to be economically and technically feasible, should lead to a volume reduction of hazardous materials and/or chemical transformation of contaminants to non-hazardous substances [9, 11].

Several studies have attempted to optimise the extraction of HMs from contaminated soils using various washing solution agents including strong mineral acids, reducing agents, surfactants, and a number of chelating agents, such as ethylenediamine-tetra-acetic acid (EDTA), pyridine-2,6-dicarboxylic acid (PDA), etc. [12, 13].

Pressure driven membrane processes (e.g. ultrafiltration) have become a routine technique for the removal of environmentally relevant and hazardous substances from aqueous systems [14, 15]. In particular, in the past 20 years ultrafiltration has been shown to be promising for the removal of trace metals from wash-solutions of contaminated soil, provided that the metallic chelates were primarily bounded to water–soluble polymers. Unbound chelates pass through the membrane, while polymers and their complexes are retained [16–18].

Advantages of this method, known as polymer assisted ultrafiltration (PAUF), are: the low energy requirements involved in UF, the conceptual simplicity, modularity, the high removal efficiency due to effective binding, and the optimal quality of treated water.

This technology has applicability in many areas involving the removal/recovery of metal ions from a variety of aqueous streams [19] as well as heavy metal-ion-contaminated soils.

The PAUF process appears to be economically feasible if the polymer can be regenerated by the release of the metal, or its chelate, and reused.

In the present work, the removal of heavy metals from aqueous systems such as wash-solutions of contaminated soil using the Polymer-Assisted Ultrafiltration (PAUF) process was studied. In particular, the extraction of the model ion Cu^{2+} from contaminated soil was simulated by using citric acid as the extracting chelating agent, and the water soluble polymer polyethylenimine (PEI) was used as macromolecular complexing agent. This polymer has the advantage of no release of other ions in treated water because it does not work by means of ion exchange but by complexing counter-ions to form neutral complexes [14, 20].

The determination of chemical conditions for complexation, de-complexation and maximum bonding capacity are discussed and the results of ultrafiltration tests on five different membranes are reported.

2. Materials and methods

2.1. *Reagents*

Copper sulphate penta-hydrate ($CuSO_4 \cdot 5H_2O$) from Fluka Chemika (MW = 249.68 g mol^{-1}, purity > 99%) was used for preparing Cu^{2+} solutions. Citric acid monohydrate from Sigma–Aldrich (MW 210.1) was the chelating agent utilised. Poly-(ethylenimine) 50% wt. solution in water from Sigma–Aldrich (MW 60 000) was the polymer used. Other chemicals used were: H_2SO_4 (purity 95–97%) purchased from Riedel de Haen and NaOH (purity > 99%) from Merck.

2.2. *Membranes*

Five different flat sheet UF membranes were tested measuring retention and water permeate flux. Some of their characteristics are reported in Table 1, where fluxes measured during membrane characterisation with distilled water at transmembrane pressure (TMP) of 2, 3 and 4 bar are also reported.

The retention R_{TC}, for the target component (TC), was measured using the definition:

$$R_{TC} = 1 - [C_{TC,P}/C_{TC,R}] \quad (1)$$

where $C_{TC,P}$ and $C_{TC,R}$ are the concentrations of the target component (in this study Cu^{2+}) in the permeate and in the retentate solution, respectively. Multiplying by 100 the rejection percentage R% was obtained.

The other important parameter, the volume permeate flux (J), generally expressed as the volume (V) obtained per unit time (t) and per unit of membrane surface area (S), was measured by the following equation:

$$J = V/(t\ S) \quad (2)$$

It should be taken into account that an optimal PAUF process should generate high permeate flux (J_P) with low copper concentration ($C_{TC,P}$), meaning high rejection (R). So, in order to compare membrane performances, the parameter $J_p \times R$ was introduced. This parameter satisfies the previous requirements to optimise PAUF processes, and has a flux dimension, representing the flux corrected by separation efficiency of the membrane.

2.3. *Analytical and instrumentation*

Copper concentration was measured using an analytical test (Carlo Erba Reagenti), based on measurement of colour intensity (absorbance reading at a 600 nm wavelength) of the blue-coloured complex formed by the reaction of copper with bis-cyclohexylidenidrazide of oxalic acid in an ammonium tartrate environment. Concentration measurement reproducibility was within 5%. Absorbance reading was performed using a

Table 1. Type of membranes and measured water fluxes

Membrane	Membrane material	Cut-off/kDa*	Manufacturer	Water flux/l h^{-1} m^{-2} (2–3–4 bar)
Iris 10	Poly ether sulphone (PES)	10	Tech-Sep	67.7–93.1–126.9
Iris 30	Poly ether sulphone (PES)	30	Tech-Sep	122.7–173.5–232.7
PAN GKSS HV3/T	Polyacrylonitrile (PAN)	30	GKSS	215.8–300.4–359.6
PAN GKSS HV2/T	Polyacrylonitrile (PAN)	50	GKSS	220.0–296.2–359.6
PAN 40 kDa	Polyacrylonitrile (PAN)	40	GKSS	101.5–126.9–169.2

*Da, Dalton, is a measure unit of atomic mass = 1.66×10^{-24} g.

Recording Spectrophotometer UV-Visible 160 A (Shimadzu Corporation-Analytical Instruments Division).

Formation of citric acid–Cu chelate, PEI–Cu complex, and PEI–citric acid-Cu complex was verified by visible spectroscopy at wavelengths of 745, 620 and 620 nm, respectively. A pH meter (Orion Research Incorporated - Expandable ion Analyzer EA 920) with a combined glass electrode was used for pH measurements.

The LT 100–1 thermostat, the LASA 100 photometer and two analytical tests LCK 380 and LCK 381 (depending on concentration of total carbon estimated in the sample to analyse) were used for carrying out Total Organic Carbon (TOC) measurements.

2.4. *Procedure of complexation tests*

Optimal chemical conditions for copper complexation (bonding), decomplexation (release) and maximum bonding capacity were determined by means of complexation tests. These experiments were carried out in test tubes by preparing 20 ml of aqueous solutions containing chelating agent, polymer and copper at appropriate concentrations, and changing the pH. Isothermal conditions at a temperature of 25 °C ± 1 °C, were maintained. For each complexation step, the liquid phase was stirred three times every 10 min. After a resting period of not less than 2 h, to reach equilibrium, complex formation was evaluated and another complexation step was initiated after pH correction.

2.5. *Description of the experimental system*

The ultrafiltration plant (Figure 1) permitted the simultaneous testing of five UF membranes. It comprised three sections: (i) an electric panel, to control plant operation; (ii) a feed section, comprised of a feed reservoir of 25 l, in which a cooling coil was immersed with a thermostat and a level control sensor; (iii) an ultrafiltration section, with a centrifugal pump LOWARA CKM 70/34 that generated the flow (max flow rate = 1.5 m^3 h^{-1}; max pressure = 4.5 bar), five steel plane cells (useful membrane surface area 14.18 cm^2) equipped with manometers and flow meters to control transmembrane pressures and tangential flow rates of the concentrate (retentate).

The thermostatic system controlled the operating temperature using tap water as coolant, so that the process took place under isothermal conditions (T = 25 °C ± 1 °C).

The membranes were characterised with demineralised water before and after use in order to evaluate membrane permeability and membrane fouling after the ultrafiltration runs. The transmembrane pressure was initially fixed at 4 bar to stabilise membrane compaction and after reaching steady state conditions (constant flux) was decreased to 3 bar, and then to 2 bar.

The Cu^{2+} ultrafiltration tests were carried out by initially setting the pressure at 2 bar and then at 3 and 4 bar after reaching steady state conditions for each parameter. The plant was operated in batch mode, recycling the five permeates to the feed reservoir. Every 30 min, starting at time t = 0 min, the permeates were collected for 2 min and their volumes were measured in order to calculate instantaneous flux (collected volume (l) per unit time (h) and area (m^2)); they were also analysed for copper concentration. Each ultrafiltration run was stopped (or pressure was changed) when the steady state was reached, i.e. the permeate flux and copper concentration were practically constant. The average time to reach the steady state was between 2.5 and 3 h.

Permeates collected in the steady state condition were also submitted to Total Organic Carbon (TOC) measurements to verify if the polymer had leaked through the membranes.

3. Results and discussion

3.1. *Determination of operating conditions*

Optimal chemical conditions for copper complexation by citric acid were determined by means of tests carried out at citric acid and copper concentrations of 800 and 200 mg l^{-1}, respectively. The results, reported in Figure 2 as bonding percentage ((absorbance/absorbance max) × 100) vs pH showed that the chelating process of

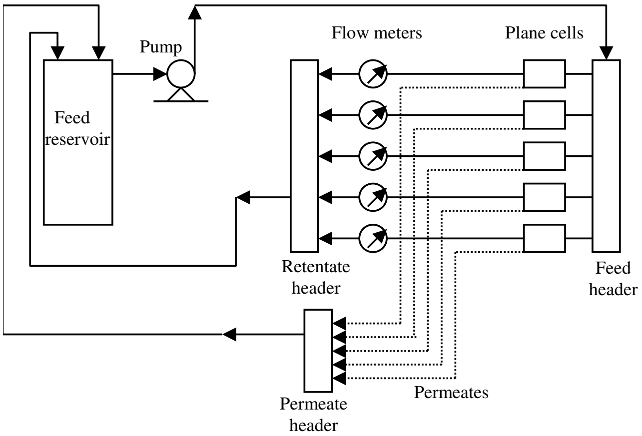

Fig. 1. Flowsheet of the ultrafiltration laboratory plant.

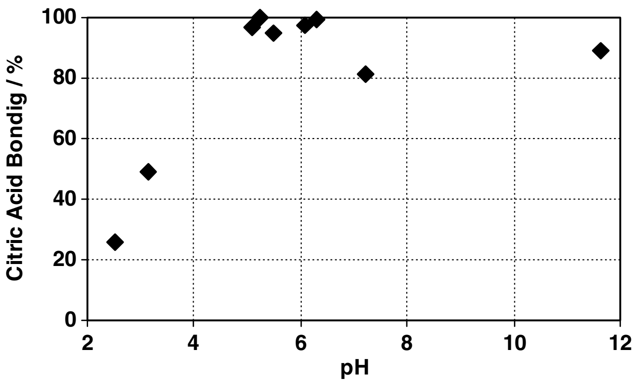

Fig. 2. Bonding percentage vs pH of citric acid (800 mg l^{-1}) with copper (200 mg l^{-1}), (ABS_{max} = 0.146, λ = 745 nm).

copper ions by citric acid is maximal at pH 5 and 6, while decomplexation occurs at pH $\leq$ 2. Similar results were obtained by working at different chelating agent and copper concentrations, showing that the pH of maximum bonding does not also depend on citric acid concentrations. pH between 5 and 6 is practically the operative condition of soil washing with aqueous solution containing citric acid as chelating agent, and it agrees with that obtained in other published work (5.5) [10].

To determine the bonding capacity (saturation condition) of citric acid (maximum copper amount (g) that can be complexed by a fixed amount (1 g) of chelating agent), other complexation tests were carried out with citric acid concentration of 800 mg l^{-1} and changing copper concentration at a fixed pH of 5.5. Results showed that the maximum amount of copper that can be chelated by 800 mg l^{-1} of citric acid is equal to 500 mg l^{-1}, giving a saturation condition of 0.625 mg Cu^{2+} per mg citric acid (2 mol Cu^{2+} per mol citric acid). Increasing the copper concentration above 500 mg l^{-1}, gave cloudy solutions, due to copper hydroxide formation and precipitation. Taking into account that the solubility product constant = $[Cu^{2+}][OH^{-}]^2 = 1.26 \times 10^{-20}$, at 25 °C, the maximum feed pH to avoid copper hydroxide formation and precipitation is approximately 5.6 for an aqueous concentration of copper of 50 mg l^{-1}, while in these complexation tests the operative pH was approximately 5.5. Thus, the excess copper (not chelated metal) remains in solution as hydroxide.

Copper hydroxide formation and precipitation is a serious disadvantage of membrane filtration, as it is closely related to membrane fouling. In order to avoid its formation, a citric acid excess was used with respect to copper ion (citric acid and copper concentrations of 800 and 200 mg l^{-1}).

Optimal chemical conditions for copper complexation by polyethylenimine were determined by complexation tests carried out at polymer and copper concentrations of 150 and 50 mg l^{-1}, respectively. The results, reported in Figure 3, showed that PEI is able to chelate copper ions at a pH of ca. 6, while decomplexation occurs at pH $\leq$ 3. The identification of the release condition is fundamental for recovering and recycling the binding polymeric agent.

To determine the bonding capacity of PEI, some complexation tests were carried out with a polymer concentration of 150 mg l^{-1} (volume = 20 ml) and changing copper concentration at a fixed pH of 6. It should be taken into account that one important cost of the PAUF process is represented by polymer consumption and its bonding efficiency: this justifies the convenience of using the polymer at its maximum complexation capacity. Results, reported in Figure 4, show that the maximum copper amount that can be complexed by 150 mg l^{-1} PEI is equal to 50 mg l^{-1}, that is 0.333 mg Cu^{2+} per mg PEI. This value is also confirmed in Figure 5 for various concentrations of Cu^{2+} and polymer. Also in this case the excess copper remains in solution as hydroxide.

Complexation tests performed in the more complex polyethylenimine–citric acid–copper system showed that:

- the PEI–citric acid–Cu^{2+} complex read at the same wavelength of PEI–copper one (620 nm);
- the polymer had almost equal bonding conditions and capacity with the copper–citric acid chelate to those observed with copper ion alone.

Concerning the polymer–copper and polymer–chelate bonds, it is well known that the electron lone pair on the

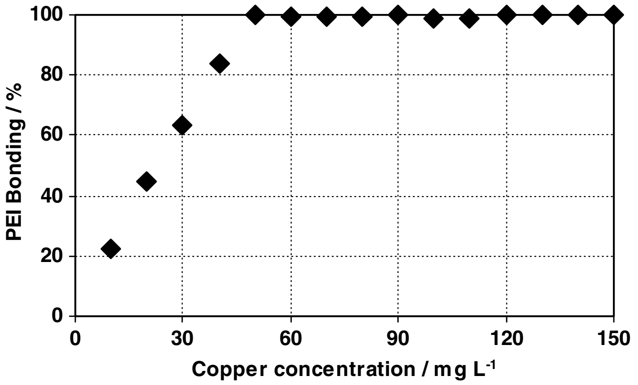

Fig. 4. Cu-PEI complex formation vs copper concentration (initial PEI concentration = 150 mg l^{-1}, pH = 6).

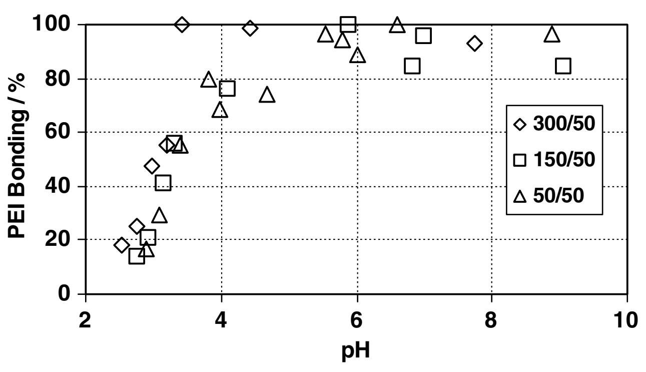

Fig. 3. Cu-PEI complex formation ($(ABS/ABS_{max}) \times 100$, $\lambda = 620$ nm) vs pH in complexation tests of PEI (300, 150 and 50 mg l^{-1}) with copper (50 mg l^{-1}).

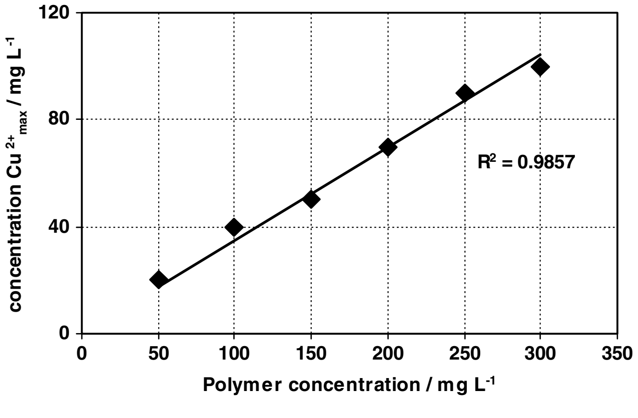

Fig. 5. Determination of the binding capacity of PEI 60000 (pH = 6).

nitrogen atom of non protonated PEI is able to form a coordination donor bond with unsatured metal ions. In the presence of chelating agents such as citric acid, the binding of PEI with metal chelates is believed to be caused by the Lewis acid–base interaction and/or electrostatic interaction rather than coordination, as indicated for PEI interaction with phosphate anions [21]. In particular, it can be assumed that the following reactions take place [22], where ionic charges are omitted for simplicity:

$$(\text{Cu-citric acid}) + \text{mPEI} \leftrightarrows (\text{Cu-citric acid})(\text{PEI})_m \quad (1)$$

$$\text{PEI} + \text{nH} \leftrightarrows \text{PEIH}_n \quad (2)$$

$$(\text{Cu-citric acid}) + \text{pPEIH}_n \leftrightarrows (\text{Cu-citric acid})(\text{PEIH}_n)_p \quad (3)$$

Reactions (1) and (2–3) are referred to as acid-base and electrostatic interaction mechanisms, respectively.

UF tests carried out using a batch system, showed that free metal ions and citric acid-metal chelates could largely pass through the Iris 10 kDa membrane at pH ~ 5.5. In contrast they were completely retained by the membrane when PEI polymer was introduced into the aqueous phase. Therefore, the formation of PEI–citric acid–copper complex at pH ~ 5.5 can be assumed.

This result is interesting because soil washing is usually done at pH 5.5 and this means that the wash-water can be submitted at the complexation step, practically without treatment, meaning process simplicity.

3.2. *Ultrafiltration tests*

From the above results ultrafiltration tests were carried out at polymer, citric acid and copper concentrations of 600, 800 and 200 mg l^{-1}, respectively, pH approximately 6 and three trans-membrane pressures (2, 3 and 4 bar).

Initially, the membranes were characterised using demineralised water. Data, reported in Table 1 and in Figure 6, show perfect linearity of flux compared to applied transmembrane pressure, thus meaning that the TMP between 2 and 4 bar were lower than the critical value. PAN GKSS membranes also gave the same performance.

Results of the PAUF tests, reported in Figures 7 and 8 in terms of obtained permeate fluxes J_p and $J_p \times R$ at steady state conditions, respectively, show that the best performance was obtained operating with the Iris 30 kDa membrane at a transmembrane pressure of 3 bar, while the worst results were obtained with the 'dry' PAN 40 kDa membrane. PAN GKSS membranes also performed well.

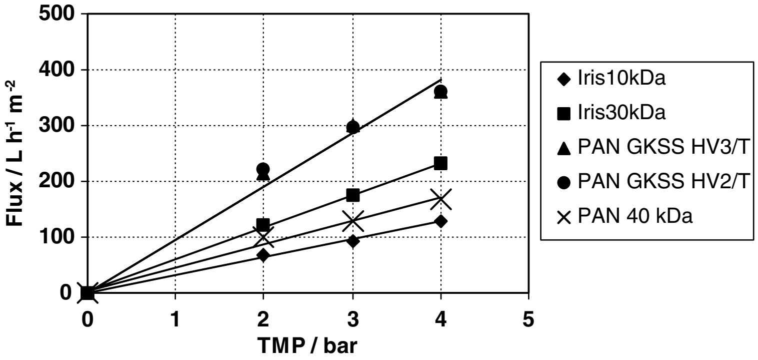

Fig. 6. Permeate water flux obtained in membranes characterisation with demineralised water.

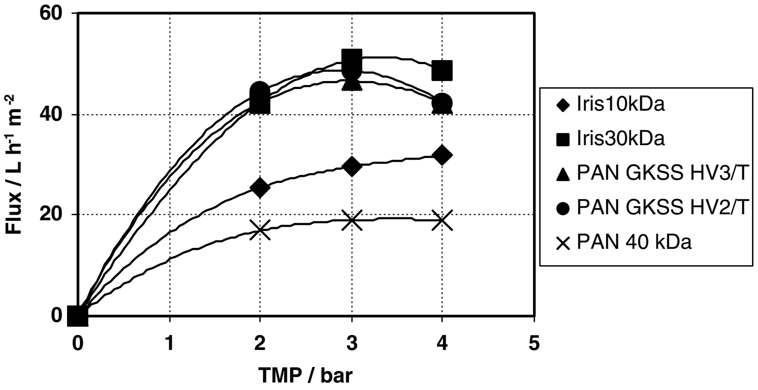

Fig. 7. Flux (L h^{-1} m^{-2}) vs transmembrane pressure (bar) in the PAUF tests (polymer concentration = 600 mg l^{-1}, citric acid concentration = 800 mg l^{-1}, copper concentration = 200 mg l^{-1}, pH = 6).

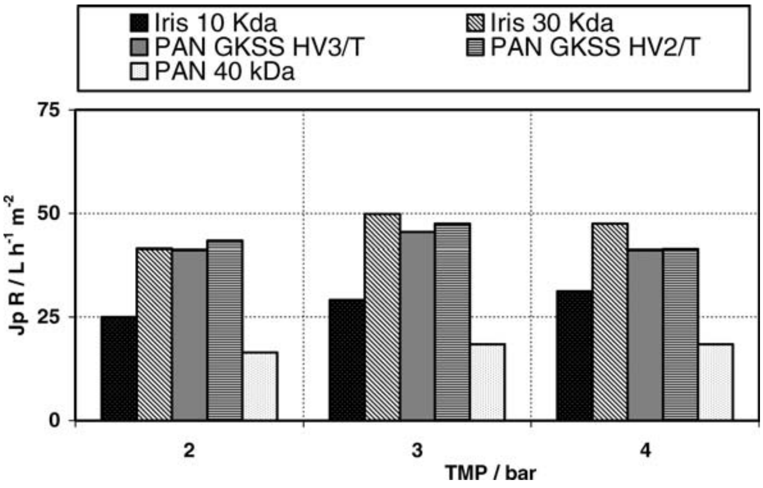

Fig. 8. J_p R for the five membranes at the three operative transmembrane pressures (polymer concentration = 600 mg l^{-1}, citric acid concentration = 800 mg l^{-1}, copper concentration = 200 mg l^{-1}, pH = 6).

The Iris 10 kDa membrane showed (Figure 7) a flux increase with TMP, meaning that, in this case, fouling was negligible, whilst for the Iris 30 kDa and PAN GKSS membrane fouling was evident. In fact, increasing operating transmembrane pressure to 4 bar, a membrane flux decline was observed, due to fouling and/or cake compaction.

5. Conclusion

This study of polymer assisted ultrafiltration shows: (i) the possibility of using the PAUF technique to remove copper ions from wash-solutions of contaminated soils; (ii) the importance of using optimal chemical conditions to obtain a maximum chelating capacity of citric acid; (iii) the importance of using optimal chemical conditions to obtain a maximum bonding capacity of polyethylenimine; (iv) the role of different types of UF membranes in order to use this process in the removal of metal ions from aqueous systems.

In the case of Cu^{2+}-citric acid chelate removal by complexation with PEI the best results were obtained with the Iris 30 kDa membrane at a TMP of 3 bar, reaching a copper concentration in the permeate of 3.75 mg l^{-1} and a flux of 50.8 l h^{-1} m^{-2}. Increasing operating transmembrane pressure to 4 bar, a membrane flux decline was observed, due to fouling and/or cake compaction.

Considering that both soil washing and PAUF techniques are relatively new: (i) an accurate approach to the chemistry of the process, considering other chelating and macromolecular bonding agents; (ii) a specific study on chelating agent and polymer regeneration, recovery and reuse and (iii) a thorough study of fluid dynamics may improve soil washing and PAUF performance. Therefore, a combination of these two techniques could be used in the future on a large scale for metal removal and/or recovery from contaminated soil wash-solutions thus becoming technically and economically feasible.

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References

1. B. Sun, F.J. Zhao, E. Lombi and S.P. McGrath, *Environ. Pollut.* **113** (2001) 111.
2. A.H.M. Veeken and H.V.M. Hamelers, *Wat. Sci. Tech.* **40** (1999) 129.
3. G.C. Steenkamp, K. Keizer, H.W.J.P. Neomagus and K.M. Krieg, *J. Membr. Sci.* **197** (2002) 147.
4. D.M. Hamby, *Sci. Tot. Environ.* **191** (1996) 203.
5. K.J. Hong, S. Tokunaga and T. Kajiuchi, *Chemosphere* **49** (2002) 379.
6. A. Majid and S. Argue, *Miner. Eng.* **14** (2001) 1513.
7. C.N. Mulligan, R.N. Yong and B.F. Gibbs, *J. Haz. Mater.* **85** (2001) 111.
8. I.M.C. Lo and X.Y. Yang, *Water Air Soil Pollut.* **109** (1999) 219.
9. R.W. Peters, *J. Hazard. Mater.* **66** (1999) 151.
10. R. Bassi, S.O. Praxher and B.K. Simpson, *Environ. Prog.* **19** (2000) 275.
11. R. Semer and K. Reddy, *J. Haz. Mater.* **45** (1996) 45.
12. R. Doong, Y.W. Wu and W. Lei, *Water Sci. Technol.* **37** (1998) 65.
13. F.G. Kari and W. Giger, *Wat. Res.* **30** (1996) 122.
14. K.E. Geckler and K. Volchek, *Environ. Sci. Technol.* **30** (1996) 725.
15. C. Blocher, J. Dorda, V. Mayrov, H. Chmiel, N.K. Lazaridis and K.A. Matis, *Water Res.* **37** (2003) 4018.
16. R.S. Juang and R.C. Shiau, *J. Membr. Sci.* **177** (2000) 207.
17. R.S. Juang and C.H. Chiou, *J. Membr. Sci.* **187** (2001) 119.
18. I.M. Villoslada and B.L. Rivas, *J. Membr. Sci.* **215** (2003) 195.
19. C.R. Tavares, M. Vieira, J.C.C. Petrus, E.C. Bortoletto and F. Ceravollo, *Desalination* **144** (2002) 261.
20. R. Molinari, S. Gallo and P. Argurio, *Wat. Res.* **38** (2004) 593.
21. R.S. Juang and M.N. Chen, *J. Membr. Sci.* **119** (1996) 25.
22. R.S. Juang and M.N. Chen, *Ind. Eng. Chem. Res.* **35** (1996) 1935.