



## Copper recovery by polymer enhanced ultrafiltration (PEUF) and electrochemical regeneration

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### ABSTRACT

In this work, the removal of  $\text{Cu}^{2+}$  from a synthetic effluent has been tested by means of polymer enhanced ultrafiltration (PEUF), using partially ethoxylated polyethylenimine (PEPEI) as water-soluble polymer. Overall, the two necessary steps of a hypothetical continuous process, metal retention (in total recirculation and discontinuous mode) and polymer regeneration (in discontinuous mode), have been confronted individually. On the one hand, the values of temperature ( $T$ ), transmembrane pressure ( $\Delta P$ ), metal-polymer ratio and pH that maximize both, permeate fluxes and rejection coefficients, have been obtained by ultrafiltration tests, reaching  $\text{Cu}^{2+}$  retention coefficients higher than 97%. On the other hand, the polymer regeneration step has been carried out by the electrochemical technique, which consists in the metal electrodeposition on the cathode of an electrochemical cell. In a first step, cyclic voltammeteries have been carried out to assure the polymer does not suffer any oxidation or reduction process. From these tests, a cathodic working potential has been selected to minimize hydrogen evolution reaction ( $-0.7\text{ V}$  vs.  $\text{Ag}/\text{AgCl}$ ). Working at this voltage in deposition tests, a pH of 3.3 has been selected from experiments at different pH values. This pH is less extreme than the pH necessary if this step was carried out chemically (pH 2).

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### 1. Introduction

Metal ions recovery is a key challenge from both, environmental and economical points of view. Copper is one of the most important metal ions for the global economy as it is a key component in building and electrical industries, with a market share of 48 and 17%, respectively of its world consumption. Moreover, its price has increased by almost a factor of three within the last 3 years, according to London metal exchange data.

Several methods have been applied to face the treatment of diluted aqueous effluents with heavy metals. Amongst them, polymer enhanced ultrafiltration (PEUF) technique has been extensively studied and used in the separation and concentration of metal loaded water effluents with different aims, either analytical or technological. On the one hand, this technique has been applied as a method for the concentration of heavy metals as a previous step for the application of analytical techniques [1,2]. On the other hand, this separation method can be used in the treatment of water effluents with heavy metals [3], either sewage water, under-

ground water or with radionuclides [4]. Recently, several works have studied the optimization of design parameters for both, the metal retention and the polymer regeneration steps [5,6]. Moreover, the heavy metal retention by means of polymer enhanced ultrafiltration has been successfully modelled using equilibrium models [7], as well as carried out and modelled in semi-continuous mode [8] and simulated in continuous mode [9].

A wide variety of water-soluble polymers have been utilized in PEUF processes for the recovery of heavy metals. Amongst them, polyethylenimine has been one of the most extensively used [10–13]. This polymer has been applied in such a separation process mainly because of its high water solubility, its high capacity to bind metal ions and its physical and chemical stability. One of the main disadvantages of working with this polymer in PEUF processes is that it is necessary to reach very low pH values to get the complex breakage, due to the high stability of the macromolecular complex formed. This fact can entail complexity and high cost of the regeneration stage. In order to minimize this drawback and improve polymer selectivity, in the present study partially ethoxylated polyethylenimine (PEPEI) has been used as water-soluble polymer. In this polymer, 80% of primary amines (the most active functional groups) have been substituted by hydroxyl groups. This polymer has not been deeply studied as water-soluble polymer in PEUF processes.

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In respect of economy and technical viability of the process, polymer regeneration stage is a key step, as it represents one of its main costs [13,14]. In PEUF processes, this stage has been carried out by two main different techniques. On the one hand, a chemical process involving a decrease on pH and a subsequent ultrafiltration stage can be used to face this aim. In this stage, permeate stream contains the free target metal ion meanwhile retentate stream retains the water-soluble polymer that can be recycled [5,8,9,13,15]. Polymer regeneration by means of a chemical procedure has some advantages such as operative simplicity or low energetic cost. On the contrary, the metallic content of the final permeate stream, low recovery percentage of the treated solution and high water consumption are the main disadvantages of this kind of regeneration technique [8,15].

On the other hand, electrochemical regeneration seems to be a clear alternative to traditional chemical regeneration [16–18]. In this method, a pH decrease is produced initially to weaken the macromolecular complex. Next, the target metal ion electrodeposition is carried out in an electrochemical cell. This alternative offers three clear advantages: (1) the metal ion is recovered in its most valuable form, that is, as metal; (2) does not exist any final effluent with metal ions content, achieving high water recovery percentages; (3) the main reagent, the electron, is a “clean reagent”, making this technique fully compatible with environmental regulations [19]. Although this method offers clear advantages from the environmental and operational points of view, very few works have been focused on coupling electrochemistry and reactive membrane separation techniques. Amongst them, some attempts have been done with micellar enhanced ultrafiltration [20,21] or polymer enhanced ultrafiltration [22,23]. One additional electrochemical regeneration technique consists in using electrodialysis with bipolar membranes [24]. The main disadvantage of this last method is the presence of a final mud with the target metal ion hydroxide.

The main aim of the present work is the study of the copper recovery from a synthetic effluent by means of a PEUF process, using PEPEI as water-soluble polymer. In the present work, a rising water effluent from an electrolytic copper plating process has been simulated, consisting of acidic baths with  $\text{CuSO}_4$  and  $\text{Na}_2\text{SO}_4$ . In this context, the two key steps of the whole process, metal retention and polymer regeneration, have been studied individually. First, the effect of the most important operational variables (temperature, ionic strength, transmembrane pressure, pH and loading ratio) on design parameters (permeate flux and rejection coefficients) has been studied and optimized. Furthermore, the main phenomena that affect permeate flux (fouling and concentration polarization)

have been studied in discontinuous mode. Secondly, in respect of polymer regeneration step, the viability of an electrochemical technique has been researched. This study comprises two stages. First of all, several cyclic voltammeteries have been carried out with different solutions. With these tests it can be checked if PEPEI suffers either oxidation or reduction processes and the optimal operation voltage can be selected. This first stage is a clear advance in comparison with previous studies dealing with electrochemical regeneration of macromolecular ligands in PEUF processes. Finally, the influence of pH on both, deposition rate and current efficiency, has been studied with constant voltage experiments.

## 2. Experimental

### 2.1. Materials and apparatus

Ultrafiltration experiments, both in total recirculation and in discontinuous mode, were carried out in a laboratory scale ultrafiltration installation which details are gathered in previous articles [13,25]. A MicroCarbosep 20 UF module with an inner ceramic membrane (MWCO = 10 kDa,  $A = 0.004 \text{ m}^2$ , i.d. = 6 mm,  $\text{ZrO}_2\text{-TiO}_2$  active layer) was used. A stainless steel rod (outer diameter = 5 mm) was placed inside the membrane with the aim of improving the system hydrodynamic behaviour.

The electrochemical cell is schematised in Fig. 1. It consists of a discontinuous stirred reactor, with a thermostatic jacket, in which the working electrode (cathode) was a ceramic ultrafiltration membrane, discarded after its use in ultrafiltration experiments due to its low permeate flux. The electrodeposition is carried out upon the outer surface of its graphite support, which acts as cathode. The area in contact with the solution is  $31.42 \text{ cm}^2$ . An inert platinum electrode was used as counter electrode. The potential was measured and controlled in respect of the working electrode using a Ag/AgCl reference electrode. In order to control and visualize both, operating voltage and intensity, a potentiostat/galvanostat VOLTALAB PGP-201 was used.

The polymer used was 80% ethoxylated polyethylenimine ( $M_w$  50,000) in aqueous solution (37%, w/w) supplied by Aldrich. Its concentration was measured by a total organic carbon (TOC) analyzer Shimadzu 5050A. The metallic salt used was copper sulphate 5-hydrate of analytical grade from Panreac. Ionic strength was fixed by adding sodium sulphate 10-hydrate of analytical grade from Panreac. Copper concentration was measured by atomic absorption spectrophotometry (Varian, SpectraAA 220). All solutions were prepared using ultrapure water.

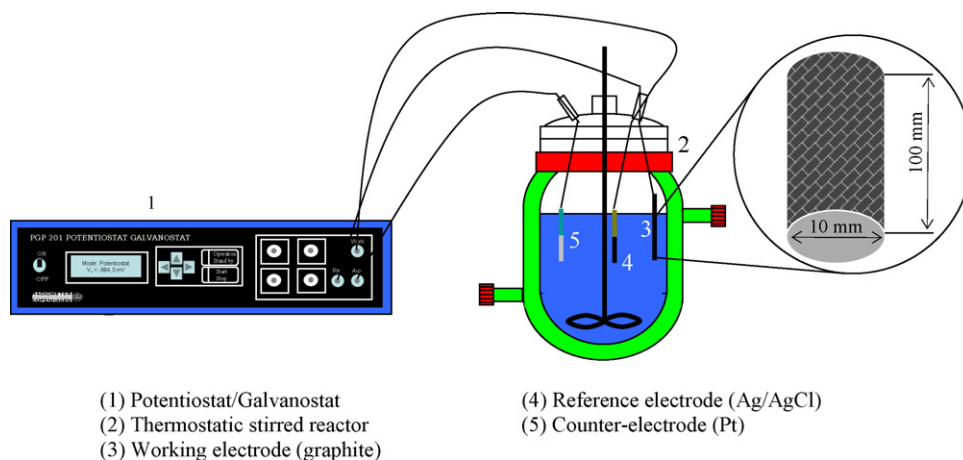


Fig. 1. Electrochemical regeneration schematic installation.

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