



Treatment of copper (II)-loaded aqueous nitrate solutions by polymer enhanced ultrafiltration and electrodeposition

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ABSTRACT

In this investigation the main design parameters of a process for the recovery of copper (II) ions from synthetic aqueous solutions have been obtained. The proposed process comprises the following stages: metal ion retention, polymer regeneration and metal recovery. Metal ion retention was performed by a batch polymer enhanced ultrafiltration (PEUF) process. For this, a bench-scale plant configured in closed-loop has been used. Selected water-soluble polymer was an industrial grade antiscalant called Colloid 208[®] (poly(acrylic acid) sodium salt, Mw 50,000 g mol⁻¹). This polymer is responsible to sequester metal ion and to form macromolecular metallic complexes that can be rejected by an UF ceramic membrane (Carbosep M5; 10,000 Da). Temporal decrease of permeate fluxes has been reproduced with an empirical fouling model and evolution of metal rejection coefficients was estimated with a model taking into account chemical equilibriums in solution and mass conservation equations. Polymer regeneration and metal recovery stages have been tackled by both chemical (diafiltration) and electrochemical (electrodeposition) points of view. Electrodeposition showed more advantages, namely null water consumption, recovery of copper in its most valuable form and absence of regeneration solutions to be treated or reused. Moreover, it has been checked that polymer did not suffer oxidation or reduction reactions because of the electrochemical stage.

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1. Introduction

Development of clean technologies for control and purification of wastewaters has been one of the aims of the successive Action Programmes R+D of European Community concerning Environment. Characteristics of separation processes based on PEUF (high selectivity, efficiency in separation of target compounds, use of an homogeneous liquid phase, use of modular equipments of easy scaling-up, etc.) make them particularly attractive for the reuse of valuable compounds from industrial liquid effluents and treated water recycling.

Polymer enhanced ultrafiltration (PEUF) is a membrane technology that makes possible to separate, concentrate and recover selectively some heavy metal ions existing in an aqueous liquid stream (natural waters, process streams or industrial effluents) [1–6]. Amongst heavy metals, copper application areas cover a wide variety of different disciplines: architectures, automotive, electrical, tube, pipe and fittings, fuel gas, industrial, seawater, machined products and telecommunications. As an example of its impor-

tance, its price was increased by almost a factor of three within the 3 years before the World Financial Crisis and its worldwide production reached 18 million metric tons in 2007, according to data reported by the World Bureau of Metals Statistics. These data mean that copper is the second non-ferrous metal in terms of production, after aluminium. Moreover, this metal is the world's most reusable resource, according to Copper Development Association Inc.

Since metal ions are microsolute that would go through UF membrane, selective separation process is based on the increase of macromolecular size by previous formation of complexes with either synthetic [7–8] or natural water-soluble polymers [9–10]. An additional advantage of this technique is working in homogeneous liquid phase because polymers are water-soluble and mass transfer processes are favored.

These polymers are actually polyelectrolytes containing functional groups capable of forming stable bonds with ions [11–13] or exerting an interaction with them through electrostatic attraction [14]. Water-soluble polymers are sometimes non-ionic but capable of forming complexes with anions [15].

PEUF process is essentially composed of two steps: (1) metal retention and (2) polymer regeneration and metal recovery. In the first step metal ions react with a water-soluble polymer to form a macromolecular complex. Next, solution containing macromolecular complex is pumped through an ultrafiltration membrane that

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retains the complex, and only permits low molecular weight compounds pass through. The almost metal-free permeate stream is then collected and the rejected stream returns to reactor. In the second step, metal-rich rejected stream can be treated (protonated) in order to break down complex into metal ions and regenerated polymer, capable of being used again in the separation process [16,17]. Other ways to regenerate the polymer can be chemical precipitation of target ion [18], electrodeposition [19–21] or electrodialysis with bipolar membranes [22].

Despite of maturity of PEUF technique [23,24], most works have been developed in lab-scale modules, and there are scarce studies at pilot scale [5,16,18,25] and patents [26–30].

This paper has two main purposes. Firstly, technical viability of a bench-scale PEUF process for the recovery of copper (II) ions was studied. As a result of the important quantity of polymer required to carry out this operation at bench-scale, it was necessary to use an industrial grade polymer (Colloid 208[®]), 80 times cheaper than respective analytical grade polymer (poly(acrylic acid) sodium salt), since technical viability of both polymers had been checked in a previous research [31]. Present experimental conditions were similar to those in a lab-scale installation, paying attention to maintain specific key dimensions (membrane diameter and molecular weight cut-off) and other working conditions (feed flow rate, permeate and rejected streams pressures, temperature), which ensured a correct linear scale-up of process [32]. This kind of scale-up uses several identical modules with a parallel arrangement, which allows enlarging plant capacity without altering significantly working conditions and yielding. Another key dimension that should be kept constant is membrane length, even though commercial offer of modules forces a length increase in process on a large scale [33]. This increase in membrane length may provoke a decrease in permeate fluxes for pilot plant with regard to lab plant, due to a pressure drop by friction. At any rate these pressure drops along membrane are often negligible for tubular modules [32].

Moreover, evolution of permeate flux in discontinuous experiments has been modeled with a simple empirical fouling model. Rejection coefficients have also been predicted as a function of free and complexed metal concentrations, and free metal and ligand rejection coefficients. In order to work with this model, it was necessary to calculate conditional polymer dissociation and complex formation constants at 50 °C by modified Bjerrum's potentiometric method. These results appeared in previous papers [34].

The second purpose of this paper is the confrontation between two different polymer regeneration techniques. On the one hand, a chemical regeneration method has been studied. This regeneration method has been tested at bench-scale and comprised a pH decrease and a subsequent diafiltration stage. On the other hand, the feasibility of an electrochemical regeneration method at lab-scale has been also tested. In this regeneration method, copper was deposited upon the cathode of an electrochemical cell, leaving the polymer untouched. Here, it is important to point out that it was the first time this regeneration method had been tested in a PEUF process with an industrial grade polymer.

2. Theoretical basis

2.1. Permeate flux

Solvent flux through membrane at one particular transmembrane pressure is usually expressed with Darcy's Law:

$$J_v = \frac{\Delta P}{\mu R_m} \quad (1)$$

According to this equation, the permeate flux (J_v) depends on transmembrane pressure (ΔP), dynamic viscosity of solvent (μ) and hydraulic resistance of the membrane (R_m).

Presence of macrosolutes in aqueous solution can alter to some extent the viscosity of solution. Even correcting the effect of viscosity, experimental permeate fluxes are usually lower than those predicted from Eq. (1), since concentration polarization and fouling phenomena appear [34]. One easy way to take into account these two phenomena is by means of a resistance in series model:

$$J_v = \frac{\Delta P}{\mu(R_m + R_f + R_c)} \quad (2)$$

where μ is the solution viscosity (Pa s) and R_m , R_f and R_c are, respectively, the membrane, fouling and polarization resistances (m^{-1}).

Another way to reproduce permeate fluxes is by means of empirical fouling equations. One of the most commonly used is based on the existence of a steady state flux (J_{ss}) that is reached after an exponential decrease:

$$J_v = J_{ss} + a e^{-bt} \quad (3)$$

2.2. Metal rejection coefficients

In a previous paper, a model was developed to reproduce metal rejection coefficients in batch PEUF experiments with weak acid polyelectrolytes, like PAA [31]. This model is based on mass conservation equations and chemical equilibriums taking place in solution. When pH is slightly acid (5.5–6) and loading ratio (g polymer/g metal) is high enough (≥ 25), secondary reactions between metal ions and hydroxyl ions in solution can be neglected.

Once these equations and equilibriums are explained, and taking into account general expression for metal rejection coefficient (R_M), Eq. (4) is obtained:

$$R_M = \frac{R_{FM} + R_L \sum_n [L]^n K_n}{1 + \sum_n K_n [L]^n} \quad (4)$$

Free metal rejection coefficient (R_{FM}) and polymer rejection coefficient (R_L) are calculated from ultrafiltration experiments, and complex formation constant (K_n) is measured in potentiometric titration experiments of polymer–metal solutions, according to an analytical method widely used [35].

The only unknown term in Eq. (4) is $[L]$ (dissociated polymer form concentration), which can be calculated applying a numerical method to the following equation:

$$[L]_0 = [L] + \frac{[L][H]}{K_a} + \frac{[M]_R \sum_n n K_n [L]^n}{1 + \sum_n K_n [L]^n} \quad (5)$$

Eq. (5) considers the different species of polymer in solution (as ionized ligand, non-ionized ligand and reacting with metal ions).

In Eq. (5) appears $[H]$, that it to say, pH affects complex formation equilibriums. $[M]_R$ (total metal concentration in rejected stream) can be calculated if we considered the following conditions:

$$\text{for } t = 0, \quad [M]_R = [M]_0 \quad (6)$$

$$\text{for } t = t, \quad [M]_R V_t = [M]_0 V_0 - \int_0^t A J_v [M]_P dt \quad (7)$$

where $[M]_0$ is total metal concentration at the beginning of experiment, $[M]_P$ is total metal concentration in permeate stream, V_t is solution volume at time t , V_0 initial solution volume and A is membrane area.

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