



Electrochemical regeneration of partially ethoxylated polyethylenimine used in the polymer-supported ultrafiltration of copper

Javier Llanos*, Ángel Pérez, Manuel A. Rodrigo, Pablo Cañizares

Chemical Engineering Department, University of Castilla-La Mancha, Edificio Enrique Costa Novella, Campus Universitario s/n, 13071 Ciudad Real, Spain

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ABSTRACT

This work is focussed on the application of an electrochemical technology to regenerate the bonding agent of a polymer-supported ultrafiltration process, technique commonly used to remove metal ions from wastewaters. To do this, a batch rotating-electrode electrochemical cell has been set up to recover the copper bind to partially ethoxylated polyethyleneimine by electrodeposition. The influence of the main parameters (current efficiency, stirring rate, pH, electrode material and nature of the counterion) on the performance of the process has been studied. Current efficiency is clearly enhanced with the stirring rate, reaching values as high as 0.93 for the optimum working conditions. Regarding pH, this variable has been observed to play an important role in process efficiency. Thus, it has been found that the reactor can operate at pH 4 without affecting process performance. This is a clear advantage with respect to other regeneration techniques and also to previous works of electrochemical regeneration. The electrode material seems to have a clear influence on process behaviour and especially on the appearance of a first transitory stage with lower current efficiency. Finally, the electrolyte salt also influences significantly on the results and the presence of sulphate as counterion leads to the best system performance.

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1. Introduction

The development of new treatment technologies for wastewaters containing heavy-metal ions represents an important target to face the new environmental and economical challenges. It is not only important to recover these metal ions avoiding their discharge to the environment, but it is also important to minimize and/or recycle reagents in order to reduce the cost of the treatment processes.

Polymer-supported ultrafiltration (PSU) is a reactive process of separation with membranes, successfully applied in the treatment of wastewater effluents with heavy-metal ions such as copper [1,2], cadmium [3,4], chromium [5,6], lead [3,7] or mercury [8,9]. In this technique, the target metal ion reacts with a water-soluble polymer in order to acquire macromolecular dimension. Afterwards, this macromolecular complex can be retained by an ultrafiltration membrane. In this process, regeneration of the polymer and metal recovery are essential to assure its economical viability [10,11]. To carry out this step in reactive processes of separation with membranes, several alternatives have been studied. Amongst them, different chemical and electrochemical procedures have been proposed, such as electrodialysis with bipolar membranes [12], chemical regeneration consisting of a pH decrease-ultrafiltration

stage [11,13] and a combination of pH decrease with ultrafiltration and photocatalysis [14]. These techniques have several drawbacks, such as high water consumption, low fluxes in ultrafiltration stage (high area requirements) and/or generation of a final mud that must be treated (as electrodialysis is the case). Metal electrodeposition is an interesting alternative to face this aim [10,15,16] because it allows to recover the metal in its most valuable form, it offers the possibility of a zero discharge process and the main reagent (the electron) is a clean one [17].

Copper is one of the most important metal ions for the global economy because it is a key component in building and electrical industries. Within the last three years, its price has increased by almost a factor of 3 and its recovery has become in a subject matter of the major importance. Although copper electrodeposition is a well-known process (extensively studied during many years in both technical [18–20] and scientific publications [21,22]), very few articles have dealt with the regeneration of bonding agents in PSU processes by electrochemical techniques. This represents a special case of study because it usually requires working with much diluted streams. In these cases, a careful cell design and the selection of optimum operation conditions are important to assure that mass transfer does not reduce significantly the efficiency of the process.

Feasibility of the electrochemical regeneration step of the PSU process, in terms of polymer stability and operation parameters, was checked in a previous work of this group [16]. In that work, the efficiencies obtained were very low (around 35%) because of a non-optimized design of the electrochemical cell. In the present

* Corresponding author. Tel.: +34 926 29 53 00x3511; fax: +34 926 29 52 56.
E-mail address: javier.llanos@uclm.es (J. Llanos).

work, a rotatory-electrode cell is proposed to improve the efficiencies of the electrochemical regeneration process (as a consequence of the enhancement of the mass transfer phenomena). The effects of operation parameters (current density and stirring rate), electrode materials and solution characteristics (pH, supporting electrolyte) on the efficiency of the regeneration have been studied in this experimental setup.

2. Material and methods

2.1. Analytical techniques

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, SpectrAA 220). All solutions were prepared with ultrapure water.

2.2. Experimental setup

Fig. 1a shows a schematic PSU-electrodeposition process for the continuous recovery of heavy metals. Fig. 1b gathers details of the rotating-electrode electrochemical cell used in this work. Basically, it consists of a single-compartment glass reactor (Inner Diam-

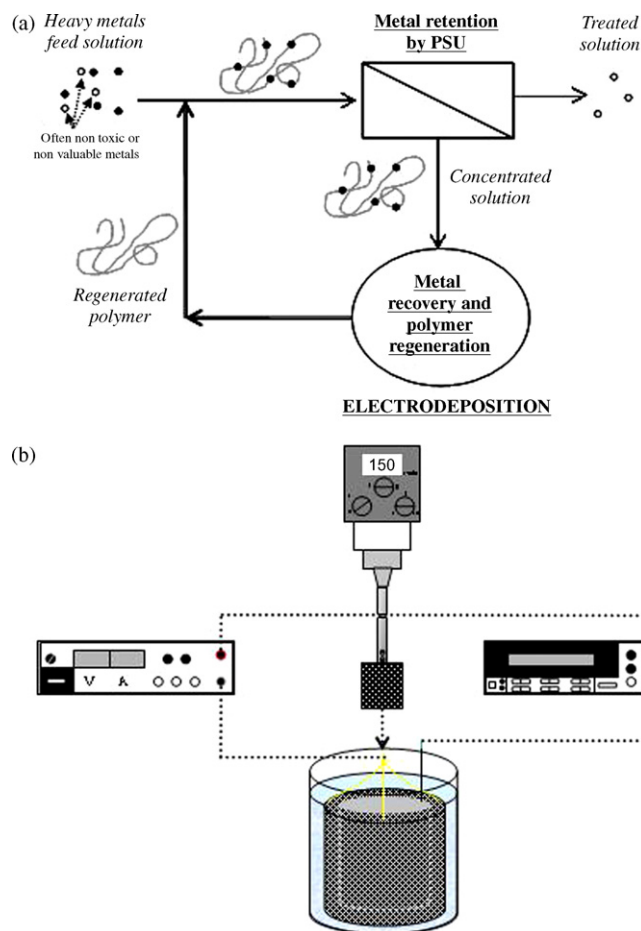


Fig. 1. PSU and regeneration processes. (a) Whole PSU-electrodeposition process for the recovery of heavy metals. (b) Schematic layout of the batch rotating-electrode setup.

Table 1

Main characteristics of the porous graphite electrode.

Average pore diameter (μm)	350
Open porosity (%)	96
Total porosity (%)	75
Density (g cm^{-3})	0.55
Oxidation resistance ($^{\circ}\text{C}$)	>400
Heat capacity ($\text{J g}^{-1} \text{K}^{-1}$)	0.7

ter = 105 mm; height = 150 mm) which operates in batch mode. The working electrode (cathode) is a rotating porous graphite one with a square-parallelepiped shape (side = 60 mm; thickness = 10 mm) from PocoFoam. It acts as working electrode and as mixer simultaneously. Its main characteristics are gathered in Table 1. The working electrode stirring rate is set and measured by a Heidolph R7R 2021 stirrer. The counter-electrode (anode) is a cylindrical porous graphite electrode, from Sofatel (Inner Diameter = 80 mm, thickness = 10 mm, Outer Diameter = 100 mm, height = 120 mm). Its cylindrical shape was selected in order to assure a good distribution of current lines. The electrical current was applied using a Delta ES030-05 Power Supply and the working electrode potential was measured vs. Ag/AgCl reference electrode using a Keithley 2000 Digital Multimeter.

3. Results and discussion

All the experiments of the present work have been carried out in discontinuous mode with an initial copper concentration of 200 ppm. This value was selected in order to simulate the retentate stream obtained in an ultrafiltration stage (feed and bleed or discontinuous) of a solution of 125 ppm of Cu^{2+} (this was the concentration of the target effluent treated in a previous work of our research group [16]). In order to work with the optimal polymer/metal ratio previously obtained [16], the polymer concentration was fixed to 0.096% (w/w). The initial pH was adjusted by adding the necessary amount of 10% H_2SO_4 .

3.1. Electrodeposition of copper from metal-polymer complexes

Fig. 2 shows the copper concentration changes and the evolution of the electrodeposition process efficiency during a typical discontinuous experiment (temperature, 25°C ; stirring rate, 200 min^{-1} ; initial pH, 2; current density, 4.2 mA dm^{-2} ; supporting media, $0.15 \text{ M Na}_2\text{SO}_4$). Three different zones can be clearly distinguished:

- A first zone in which the efficiency increases up to its maximum value. During this stage, the rate of copper removal (slope of the m_t/m_0 vs. time plot) increases continuously with the electrical charge passed.
- A second zone in which the maximum efficiency is maintained. It corresponds to linear copper concentration decay (constant removal rate).
- A third zone in which mass transfer clearly limits the efficiency of the process. This stage corresponds to an exponential shape in the copper concentration decay (characteristic of the first-order kinetics of an electrochemical process limited by mass transfer). Furthermore, it is worth to mention the drastic decrease in the efficiency with the current charge passed.

Fig. 3 shows the cell potential and pH changes during the electrolysis. The evolution of the cell potential might correspond to the three stages previously described and they may be related to the changes on the cathode surface. Initially, the cathode surface is graphite but this material is progressively covered by copper and after the initial stage, copper coats completely all the graphite. As graphite is a porous media, there is an important surface reduction.

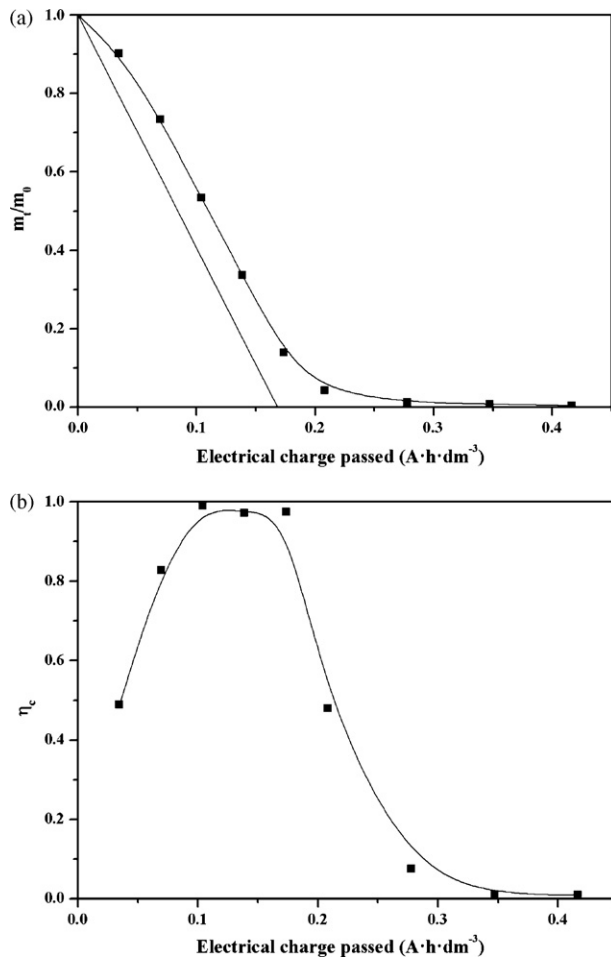


Fig. 2. Dynamic responses of normalised copper concentration (a) and current efficiency (b) in a typical electrodeposition experiment. Temperature, 25 °C; initial copper concentration, 200 ppm; polymer concentration, 0.096% (w/w); current density, 4.2 mA dm⁻³; stirring rate, 200 min⁻¹; supporting media, 0.15 M Na₂SO₄ + H₂SO₄; initial pH, 2.

In addition, due to the electrodeposition, the ions concentration decreases during the process (reduction of the conductivity) and this also makes the cell potential to increase.

The pH change seems not to be very important. At this moment, the high initial proton concentration has to be taken in mind. With such a high value, a small pH variation corresponds to a significant protons concentration increase. The proton concentration changes can be caused by water oxidation process (oxygen evolution) as it is shown in Eq. (1).



Another factor to be considered is the polymer presence into the synthetic wastewater. This kind of polymers presents a high capacity to bind the ions contained in the solution [23,24] and, consequently, they can act as pH buffers.

3.2. Effect of the stirring rate and current density

Fig. 4 shows the effect of the stirring rate (ranging from 0 to 200 min⁻¹) for different current densities (ranging from 1.4 to 4.2 mA cm⁻³) on the copper removal from synthetic wastewaters of a typical composition (polymer concentration: 0.096%, w/w, pH 2, supporting media: 0.15 M Na₂SO₄).

As expected, a stirring rate increase results in a more efficient process with higher slopes in the copper-removal curves and, as

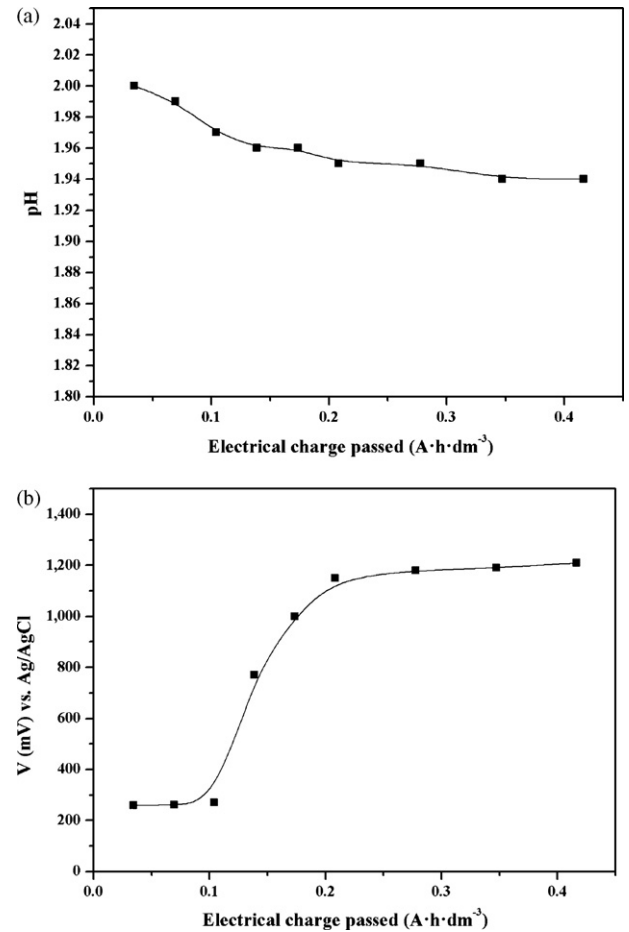


Fig. 3. Dynamic responses of pH (a) and cathode potential (b) in a typical electrodeposition experiment. Temperature, 25 °C; initial copper concentration, 200 ppm; polymer concentration, 0.096% (w/w); current density, 4.2 mA dm⁻³; stirring rate, 200 min⁻¹; supporting media, 0.15 M Na₂SO₄ + H₂SO₄; initial pH, 2.

a consequence, with higher copper deposition rates. This is clearly due to the improvements in the mass transfer of the system. Here, it is important to note that for each current density, there is a stirring rate threshold which marks two different behaviours. Above these mixing conditions, the process efficiencies cannot be improved with a further stirring rate increase and the regeneration works at the maximum rate, very close to the best theoretical results, shown continuous line (current efficiency of 1 during the complete process). In these conditions mass transfer only limits the process for very low concentrations of copper in solution.

The threshold value of the stirring rate seems to increase with current density. Thus, mass transfer control for high copper concentrations is only observed for the experiment at 0 min⁻¹ for the 1.4 mA cm⁻³ current density, but at 0 and 35 min⁻¹, for experiments carried out at 4.2 and 6.9 mA cm⁻³. In this point, it is important to take in mind the limiting current density concept. This is an important parameter that indicates the current density for which the amount of copper ions reaching the cathode surface equals the amount of copper that can be electrodeposited. The relationship between the limiting current density and the mass transfer coefficient is given by Eq. (2) [25].

$$j_{lim} = n \cdot F \cdot K \cdot [Cu] \quad (2)$$

where j_{lim} is the limiting current density (A m⁻²), n the number of electrons that reacts with each Cu²⁺ ion ($n=2$), F is the Faraday constant (96,500 C mol⁻¹), K is the mass transfer coefficient (m³ m⁻² s⁻¹) and $[Cu]$ is the copper concentration (mol m⁻³).

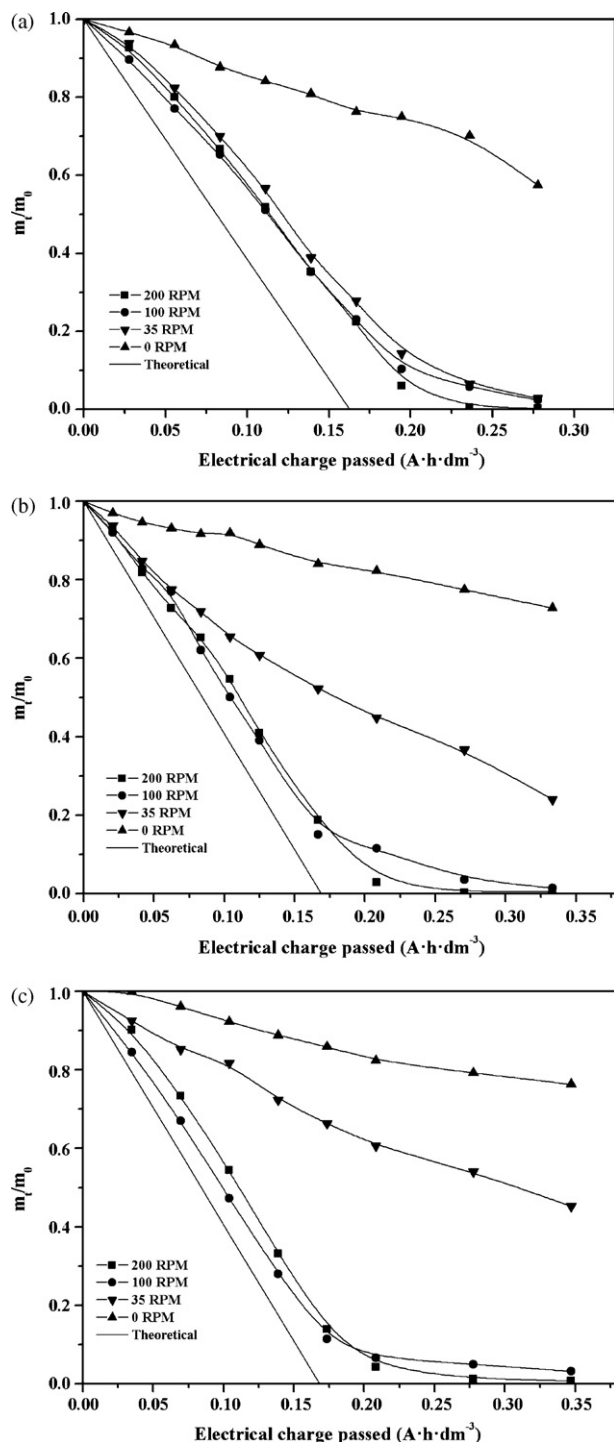


Fig. 4. Stirring rate influence on the normalised copper concentration changes as a function of electrical charge passed for current densities of 1.4 mA dm^{-3} (a), 4.2 mA dm^{-3} (b) and 6.9 mA dm^{-3} (c). Temperature, 25°C ; initial copper concentration, 200 ppm; polymer concentration, 0.096% (w/w); supporting media, 0.15 M $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$; initial pH, 2.

As it can be deduced from this equation, the higher the working current density the higher the mass transfer coefficient required (higher stirring rate) to have a process not limited by mass transfer. In addition, for a given mass transfer coefficient, the higher the copper concentration, the greater the current density that can be applied without mass transfer control.

In order to compare the different stirring rates and current densities behaviour, the current efficiencies have to be compared. Fig. 5

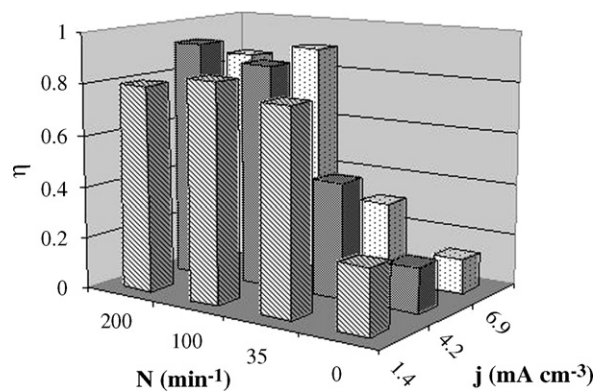


Fig. 5. Current density and stirring rate influence and regeneration process efficiency. Temperature, 25°C ; initial copper concentration, 200 ppm; polymer concentration, 0.096% (w/w); supporting media, 0.15 M $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$; initial pH, 2.

shows this comparison using efficiencies arbitrarily obtained for a total current charge passed of $0.162 \text{ A h dm}^{-3}$. This particular value of current was selected because this is the theoretical value at which all copper in solution would be deposited for a current efficiency of 100%.

As it can be observed, current efficiency dramatically increases with stirring rate. A marked variation of the current efficiency can be observed for the different experiments at 35 min^{-1} , decreasing when current density increases, due to the appearance of mass transfer control, as it has been previously explained. For experiments carried out at 100 and 200 min^{-1} , efficiency is always over 0.8, reaching a maximum of 0.93 for a stirring rate of 200 min^{-1} and a current density of 4.2 mA cm^{-3} . These maximum efficiency conditions were selected to carry out the study of three more inputs influence: pH, electrode material and electrolyte counterion.

3.3. Effect of pH and electrolyte salts

Initially, pH is expected to be a key parameter in this type of electroregeneration processes because it influences on the equilibria between cations and the polymer used to capture them. To check this effect, different tests were carried out working at the conditions of maximum efficiency previously obtained (200 min^{-1} , 4.2 mA cm^{-3}) and varying the pH from 2 to 6. Fig. 6 shows the copper concentration changes during these tests.

As expected, copper electrodeposition process is hindered when pH is increased to 6, due to the formation of the macromolecular complex with the polymer. Eqs. (3) and (4) represent the schematic equilibria in which the polymer (its functional groups are represented by L) may be taking part.



As it can be guessed, for lower pH values, a larger concentration of functional groups can react with protons, according to Eq. (4). Therefore, the macromolecular complex PEPEI-Cu strength can be weakened and, as a consequence, the copper ions ability to migrate to the electrode surface should be enhanced [15]. However, in spite of this, there seems to be no difference between working at pH 2 and 4. This means that experiments could be carried out at pH 4 without diminishing the copper electrodeposition efficiency. This result is a clear advantage with respect to other regeneration methods in polymer-supported ultrafiltration processes, like chemical regeneration, where large acidic pH values are needed to carry out the polymer regeneration [7,16]. Moreover, with regard to previous works of our group [16], the electrode change to a one with higher

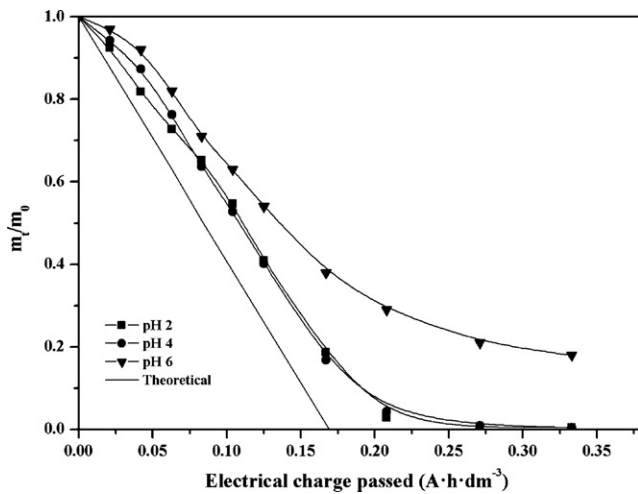


Fig. 6. pH influence and regeneration process efficiency. Temperature, 25 °C; initial copper concentration, 200 ppm; polymer concentration, 0.096% (w/w); current density, 4.2 mA dm⁻³; stirring rate, 200 min⁻¹; supporting media, 0.15 M Na₂SO₄ + H₂SO₄; initial pH, 2.

efficiency in terms of mass transfer, allows to work at higher pH values without affecting the process performance. This is clearly an advantage from operational, economical and environmental points of view. In this point, it is important to mark that no perceptible changes in the polymer properties were observed during different test, although further work should be made in order to confirm this observation.

The solution counterion influence was tested using three different anions as electrolytes: sulphate, phosphate and perchlorate. The selected supporting media concentration for phosphate and perchlorate was fixed to maintain the same total ionic strength than in sulphate experiments. Fig. 7 gathers the results obtained in terms of copper concentration and efficiency vs. total charge passed.

As it can be observed, sulphate and perchlorate show a similar behaviour. The main difference between both tests is observed during the first stage: the lower efficiency of this stage seems to be more marked when perchlorate is in the reaction media. With respect to phosphate, current efficiency seems to be lower throughout all the experiment, being the first stage as marked as for perchlorate. The influence of these anions on the results is difficult to explain and it should be caused by their effect on the chemical equilibria.

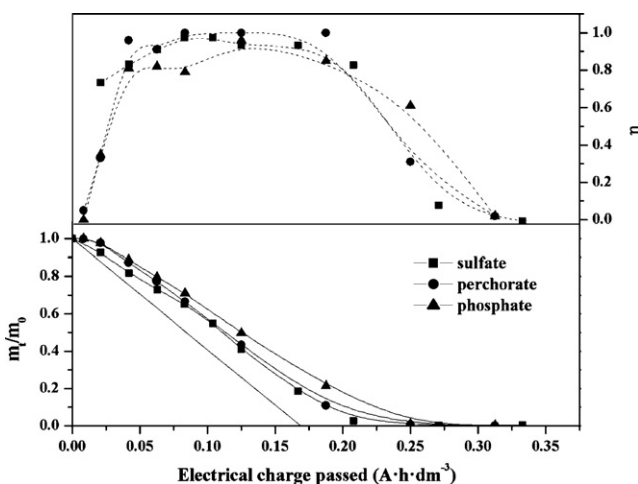


Fig. 7. Counterion nature influence and regeneration process efficiency. Temperature, 25 °C; initial copper concentration, 200 ppm; polymer concentration, 0.096% (w/w); current density, 4.2 mA dm⁻³; stirring rate, 200 min⁻¹; initial pH, 2.

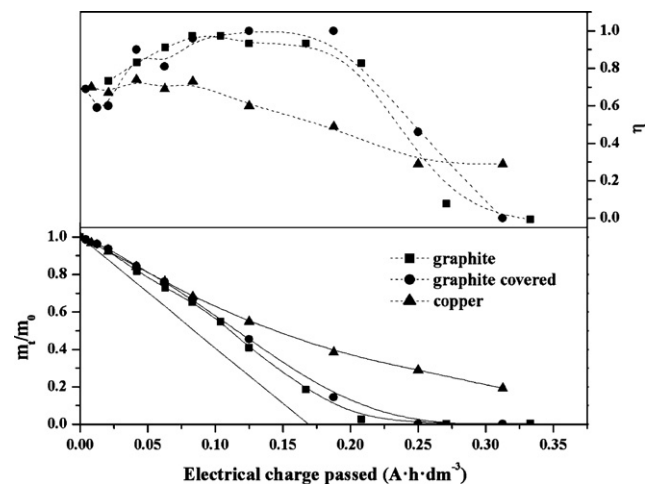


Fig. 8. Working electrode material influence and regeneration process efficiency. Temperature, 25 °C; initial copper concentration, 200 ppm; polymer concentration, 0.096% (w/w); current density, 4.2 mA dm⁻³; stirring rate, 200 min⁻¹; supporting media, 0.15 M Na₂SO₄ + H₂SO₄; initial pH, 2.

3.4. Effect of the electrode material

The most unexpected point in this work is the efficiency increase during the first stage of the discontinuous process (Fig. 2). An initial hypothesis to explain this observation can be the important cathode surface change. It initially consists of porous graphite, that it is covered with copper during the treatment. After some current charge almost all the cathodic surface can be considered covered by cooper.

In this part of the study, the electrode material influence was tested. To do this, results obtained when using raw graphite as cathode have been compared to those reached when a copper sheet or a fully covered graphite (after total electrodeposition of a 1000 ppm Cu²⁺ solution) was used directly as cathode.

Fig. 8 shows the copper concentration changes and the efficiency evolution during these tests. The copper electrode is observed to present the worst behaviour, with an electrical efficiency always under 0.7. Nevertheless, the experiment carried out with the covered electrode behaves similarly to the untouched graphite. This suggests that the graphite electrode surface was not totally covered and the electrode porous structure was not noticeable modified. These results also agree with the fact that the experiment efficiency only decreases when copper concentration in the reactor descends till very low concentrations and it is not affected by the continuous copper deposition upon the electrode surface. This is a necessary requirement for future applicability of the process to a continuous configuration and, furthermore, it justifies the porous graphite electrode use to treat such low copper concentrations.

With respect to the first step of increasing efficiency, it is necessary to emphasize that this stage does not appear in the experiment with the copper sheet. This means that the electrode nature can play an important role in this initial loss of efficiency. Although the process efficiency throughout the first steps of the experiments is not a practical drawback for future real applications, it deserves a special attention that we will take into account in future works.

4. Conclusions

From this work, the following conclusions can be drawn:

- (1) Electrochemical technology can be successfully used to recover copper and to regenerate the partially ethoxylated polyethylen-

imine used in a polymer-supported ultrafiltration process. Very high current efficiencies and removals of copper are obtained.

- (2) The use of a discontinuous regeneration process shows three clear stages: an initial stage in which current efficiency improves progressively, a kinetic-controlled stage in which the process works at the maximum efficiency and a mass transfer-controlled efficiency stage in which the current efficiency falls significantly.
- (3) Stirring rate and current density have a clear effect upon the electrodeposition process performance because of their influence on the mass transport processes. Likewise, pH plays an important role in the process as it controls the strength of the complex that copper forms with the polymer. Working at the conditions of maximum efficiency, the optimal working pH was found to be less extreme than that necessary in other regeneration techniques in PSU processes and in previous electrochemical regeneration works.
- (4) The formation of a copper deposited layer seems not to hinder metal electrodeposition. Sulphate was the counterion that shows the best behaviour for copper deposition when compared with phosphate and perchlorate.

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