



Simultaneous recovery of cadmium and lead from aqueous effluents by a semi-continuous laboratory-scale polymer enhanced ultrafiltration process

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ABSTRACT

Performance of a semi-continuous polymer enhanced ultrafiltration (PEUF) process has been investigated for the simultaneous recovery of cadmium and lead from binary mixtures. This method uses poly(acrylic acid) as water-soluble polymer to bind these metals. Experiments have taken place in a laboratory-scale system. Loading ratio (mg total metal ions/g polymer) and pH values for separation of cadmium and lead have been studied by means of preliminary experiments, analyzing their influence on permeate flux, metal rejection coefficients and separation factor.

The proposed process includes three different stages: total retention of metal ions, selective separation and polymer regeneration. Operating pH values for total retention of metal ions and polymer regeneration processes are 5 and 2, respectively. Selective separation has been investigated working at an intermediate pH value. In this way, if a stream containing 12.5 ppm of each metal ion (1:1 in weight) is treated in the first stage, two different streams enriched in each metal ion are obtained in the second stage. Permeate stream is enriched in cadmium with a proportion near 5:1 in weight, and retentate is enriched in lead with a similar proportion.

Finally, the three stages have been modelled successfully with a mathematical model based on conservation equations and chemical reactions taking place in solution.

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1. Introduction

Many industrial wastewaters and process streams contain metals as multi-component mixtures. Recovering metal ions from them is very interesting from both environmental and economic points of view. European Economic Community has provided different Council directives which control the pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (Council Directives 76/464/EEC and 80/68/EEC) or establish limit values and quality objectives for these discharges, such as Council Directive 83/513/EEC for cadmium. Recently, it established a framework for Community action in the field of water policy (Directive 2000/60/EC). Cadmium (II) and lead (II) are heavy metal cations and constitute highly pollutant substances, especially cadmium. Waste streams containing both cadmium and lead come from metallurgical lead production, battery industries and leachates.

Regarding the economic point of view, cadmium is a minor metal whose price is increasing slightly, while lead is a base metal

whose price has suffered a 400% increase in recent years. For this reason, there is not only an urgent need for efficient separation techniques that may reduce the concentration of heavy metals in industrial effluents to low values, but also metals should be recovered with a high purity. Consequently, to enable further processing and to achieve recovery of metals, their separation should be selective [1].

Some conventional wastewater treatment processes such as sedimentation and ion exchange are often unsatisfactory [2]. The main disadvantage of sedimentation is that in this method there is elimination but not recovery of heavy metals. In ion exchange there are difficulties related to heterogeneous reactions (interface transfer and long contact time problems of multiphase separation processes) and production of large volume of regeneration waters [2,3].

Thus, the use of membrane techniques in wastewater treatment as a replacement for or as an aid of traditional methods seems to be an attractive suggestion [4]. It has been reported that ultrafiltration combined with other physical and chemical processes could be effectively used for the removal of heavy metal ions from aqueous solutions [5]. There are two widely used separation techniques: micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF). MEUF and PEUF combine ultrafiltration with

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the presence of water-soluble surfactants and polymers, respectively [6].

In PEUF the macromolecular ligands seem more advantageous since they have a relatively high binding capacity. The ligands and their metal complexes can be retained by an ultrafilter, whereas the free metal ions pass through the membrane [7]. With this method, using different water-soluble polymers or introducing new functional groups to the polymer [8,9], it is possible to achieve selective separation and recovery of heavy metals with low energy requirements. Metal complexation with polymers takes place in the homogeneous phase, consequently, there is not difficulty related to heterogeneous reactions [1].

The studies on the separation of heavy metals from binary mixtures are relatively few [1]. In literature we can find some papers about this [4,10,11] but a system comprising a mixture of cadmium and lead has never been studied.

In our previous study [12], performance of semi-continuous laboratory-scale PEUF method was investigated for recovery of cadmium or lead from single solutions using poly(acrylic acid).

In the present paper the possibility of retention and further selective separation of both metal ions from binary mixtures was studied.

The main parameters affecting on complexation of target metal ion with polymer are metal and polymer nature, loading ratio (the ratio of metal ion to polymer concentrations) [1,7], pH value and existence of other metal ions in the solution. The performance of the ultrafiltration process can be affected by feed flow rate, transmembrane pressure, temperature, membrane type and polymer concentration [1].

Loading ratio and pH value are two of the most important factors in the interaction of a metal ion with a binding polymer [1,4,13].

The majority of the processes studied in bibliography have been performed in batch mode. There are very few examples studying the continuous mode. On the one hand, Sabaté et al. published a continuous PEUF simulation in order to evaluate and optimize the process feasibility [14]. On the other hand, a pilot-scale steady-state continuous process has been developed for arsenic removal [15]. Semi-continuous mode presents an intermediate step, as it was shown in our previous paper [12]. Some important advantages of this operation mode are: greater connection with industrial-scale processes and possibility to treat larger effluent volumes.

There are some aims in this paper. (1) To carry out recovery of cadmium and lead from binary mixtures by adjustment of parameters pH value and loading ratio. (2) To perform selective separation of both metal ions by means of optimization of separation pH value. (3) To adapt a model representing semi-continuous PEUF processes with single metal ion solutions in the case of binary solutions.

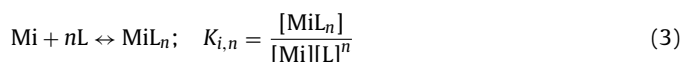
2. Theory

Models help to obtain a better understanding of the whole process and predict results of untested conditions [14,16,17]. On the one hand, “physical–chemical models” take into account molecular interactions between polyelectrolytes and ions to explain ultrafiltration results. On the other hand, “macroscopic models” consider chemical reactions, equilibrium equations, mass balance and some assumptions to reach expressions of metal rejection as a function of different parameters (equilibrium constants, feed concentrations, etc.). These parameters can be taken from bibliography or determined from ultrafiltration experiments [7,13], titration measurements [18,19], etc.

The following model belongs to the second kind, and it is based on our previous paper for a single component system [12], being

all assumptions and definitions made essentially similar to those described in that paper.

Let us consider a multi-component aqueous solution containing several divalent metal ions, under conditions where insoluble hydroxides are not formed. Generally, the reactions occurring in the solution include the dissociation of PAA (HL) and the binding of PAA with metal ions (Mi):



where n is the average coordination number of PAA ligands bound to one metal ion.

In this system, global, polymer and metal ions mass conservation equations can be expressed as:

$$Q_F(t) = Q_P(t) \quad (4)$$

$$V_R \frac{d[\text{L}]_R}{dt} = -Q_P[\text{L}]_P \quad (5)$$

$$V_R \frac{d[\text{Mi}]_R}{dt} = Q_F[\text{Mi}]_F - Q_P[\text{Mi}]_P \quad (6)$$

Combining Eqs. (5) and (6) with expressions for the rejection coefficients of polymer and metal ions [12], respectively, the following relations are obtained:

$$V_R \frac{d[\text{L}]_R}{dt} = -Q_P[\text{L}]_R(1 - R_L) \quad (7)$$

$$V_R \frac{d[\text{Mi}]_R}{dt} = Q_F[\text{Mi}]_F - Q_P[\text{Mi}]_R(1 - R_{\text{Mi}}) \quad (8)$$

The total concentration of each metal ion in the reactor solution and in the permeate stream can be expressed as:

$$[\text{Mi}]_T = [\text{Mi}] + \sum_n [\text{MiL}_n] \quad (9)$$

$$[\text{Mi}]_P = [\text{Mi}](1 - R_{\text{FMi}}) + (1 - R_L) \sum_n [\text{MiL}_n] \quad (10)$$

Thus, Eqs. (11a) and (11b) can be obtained by combining Eqs. (9) and (10):

$$R_{\text{Mi}} = 1 - \frac{[\text{Mi}]_P}{[\text{Mi}]_T} = 1 - \frac{[\text{Mi}](1 - R_{\text{FMi}}) + (1 - R_L) \sum_n [\text{MiL}_n]}{[\text{Mi}] + \sum_n [\text{MiL}_n]} \quad (11a)$$

$$R_{\text{Mi}} = \frac{[\text{Mi}]R_{\text{FMi}} + R_L \sum_n [\text{MiL}_n]}{[\text{Mi}] + \sum_n [\text{MiL}_n]} \quad (11b)$$

Considering the effective stability constants of the complexes, the rejection coefficient of metal ions can be determined as follows:

$$R_{\text{Mi}} = \frac{R_{\text{FMi}} + R_L \sum_n K_{i,n} [\text{L}]^n}{1 + \sum_n K_{i,n} [\text{L}]^n} \quad (12)$$

In expression (12) the only unknown quantity is the concentration of the free ligand [L], which can be calculated from the mass balance for the polymer:

$$[\text{L}]_T = [\text{L}] + [\text{HL}] + \sum_i \sum_n n [\text{MiL}_n] \quad (13)$$

Using acid dissociation constant, K_A , and effective stability constants of complexes, $K_{i,n}$, the overall concentration of the polymer

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