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Removal of heavy metal ions by polymer enhanced ultrafiltration Batch process modeling and thermodynamics of complexation reactions

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ABSTRACT

A batch process of polymer enhanced ultrafiltration (PEUF) for the removal of Cu(II) ions from aqueous effluents has been developed in an installation equipped with mineral membranes at laboratory scale. It has been proposed a model based on mass conservation equations and kinetics of complex formation reactions of macromolecular species comprising a metallic ion and a water-soluble polymer. The model predicts the temporal evolutions of metal concentration in permeate and rejected streams. Moreover, it enables to establish the operating pH values to tackle the stages of metal retention and polymer regeneration, and also to calculate conditional formation constants of the macromolecular complex as a function of pH and temperature.

1. Introduction

Membrane filtration processes have been successfully applied for the separation and/or enrichment of several species from different aqueous streams [1–3]. Micellar enhanced ultrafiltration (MEUF) is a physico chemical membrane separation technique aimed at improving the performance of ultrafiltration membranes by capturing the small size pollutants into larger structures called micelles [4]. More effective retention of certain inorganic ions can be achieved by complexing previously these ions with water-soluble polymers by means of polymer enhanced ultrafiltration (PEUF) [5]. At the end of this process, a diluted permeate stream (discharged as a less pollutant waste or employed for specific purposes) but also a retentate stream with a high concentration of metallic ions bound to the polymer are produced.

In order to make feasible both technical and economical viability of the process, these ions in concentrated stream should be released from polymer [6,7]. This regeneration of polymer can be chemically achieved in three successive steps by adding firstly an acid (with protons that compete with metal ions for binding sites of polymer), a second ultrafiltration process, and finally, the return of regenerated polymer into process after neutralization.

PEUF processes have been modeled in batch [8–9], semi-continuous [10–12], and continuous [13] modes. Models help to obtain a deeper understanding of the whole process and predict results under untested conditions [14]. These models allow predicting rejection coefficients [15] or to measure equilibrium constants for complexation of metal ions by synthetic and natural ligands [16].

In this paper, a well-known couple of metal ion (Cu^{2+}) and water-soluble polymer (PEI) has been selected. They can be considered as standard substances to develop a PEUF process. In the case of copper, because it is a heavy metal that has been recycled for hundreds of years. For poly(ethylenimine) (PEI), because it is a chemical chameleon that can be evaluated as a selective binder or even used like polymeric vector for gene delivery [17–18].

Although in bibliography there are plenty of papers related to the modeling of PEUF processes, few of them are based on the kinetic theory of reactions applied to partially open systems. On the one hand, the aim of this paper is to develop a kinetic model simpler than those previously proposed that allows: 1. To successfully predict the copper ion concentrations in permeate and rejected streams; 2. To calculate conditional formation constants of the macromolecular complex. On the other hand, operating conditions to develop both metal retention and polymer regeneration stages have been optimized. Moreover, thanks to the calculation of the formation enthalpy of PEI–Cu complex, a thermochemical regeneration of polymer is proposed, since the increase in permeate flux compensates the energy needs, working at milder pH values and reducing the consumption of strong inorganic acids.

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2. Theory

2.1. The reaction of complex formation and the influence of pH value

The reaction of complex formation between Cu(II) ions and amine groups of macromolecular ligand, considering the latter as a polyfunctional ligand, can be written in a simplified form as:

$$M + mL \leftrightarrow ML_m \tag{1}$$

where M symbolizes the free metal ions and L the repeating unit for polymer. Charges have been intentionally omitted.

The selected polymer, poly(ethylenimine) (PEI), is obtained from monomer ethylenimine. The monomer consists of a three-membered ring. Two corners of the molecule consist of $–CH_2–$ linkages. The third corner is a secondary amine group, –NH–. In the presence of a catalyst this monomer is converted into a highly branched aliphatic polyamine with about 25% primary amine groups, 50% secondary amine groups, and 25% tertiary amine groups. In Fig. 1, the structure for this polymer proposed by the supplier (Aldrich) is depicted. In order to simplify the polymer structure it will be considered as a macromolecule composed of repeating structural units denoted L (ethylenimine).

The functional groups show an acidic character, which means the amine groups can experience a competitive reaction of protonation into LH.

$$L + H \leftrightarrow LH \tag{2}$$

In absence of metallic ions, the amounts of LH and L in solution are related with the pH value by a Hasselbach type equation:

$$pH = pK_a - n \cdot \frac{\log(1-\alpha)}{\alpha} \tag{3}$$

where pK_a is the dissociation constant of LH, n is a constant depending on each polyelectrolyte which accounts for nearest neighboring interaction, and α is the protonation degree of PEI expressed as:

$$\alpha = \frac{[L]}{[L]_0} \tag{4}$$

being $[L]_0$ the initial concentration of PEI in solution.

From Eqs. (3) and (4) the concentration of [LH] and [L] as function of pH can be obtained:

$$[L] = [L]_0 \left[1 + 10^{\frac{pK_a - pH}{n}}\right]^{-1} \tag{5}$$

$$[LH] = [L]_0 \left[1 - 10^{\frac{pK_a - pH}{n}}\right] \tag{6}$$

Von Zelewsky et al. [17] found that this kind of polymer exhibits a pK_a of 7.69 and n equal to 7 for protonation degree values higher than 0.3. On the contrary, when the protonation degree is lower than 0.3, pKa and n can reach 8.39 and 2, respectively. The change with pH of the relative concentration of both PEI forms in solution, L and LH, with respect to the initial concentration in solution can be observed in [19]. As can be seen, the PEI becomes less charged as the pH value increases.

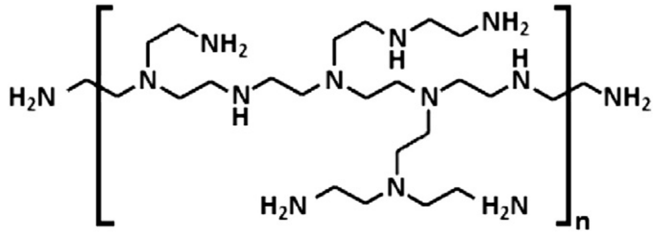

Fig. 1. Poly(ethylenimine) (PEI) structure (Aldrich).

In the presence of metallic ions, taking into account Eq. (1), the initial concentration of ligand in solution $[L]_o$ will be:

$$[L]_0 = [L] + [LH] + m[ML_m] \tag{7}$$

At a fixed pH value in solution and considering that [L] is the concentration of free ligand (neither protonated nor taking part in metallic complex ML_m), a conditional complex formation constant can be defined as:

$$K_f^* = \frac{[ML_m]}{[M][L]^m} \tag{8}$$

The value of this complex formation constant will depend on the pH value of solution.

2.2. Modeling of batch process

The batch mode is the simplest one and requiring the minimum filtration area (A) to reach a determined separation per unit of time. In concentration mode, a feed with initial volume V is filtered at a constant pressure, removing permeate stream, so the system volume diminishes with time, while retained species are concentrated in feed stream.

Equations that describe the change of volume and total mass of a determined solute in a batch operation in absence of chemical reaction [20] are:

$$-\frac{dV}{dt} = J_V \cdot A \tag{9}$$

$$V_0 \cdot C_{S0}^f = V_t \cdot C_{St}^f + A \cdot \int_0^t \mathrm{J}_{vt} \cdot C_{st}^p \cdot dt \tag{10}$$

In these equations, V is system volume, J_v is permeate flux, and C_s is molar concentration of solute at each time t. Subindexes 0 and t refer to initial conditions and conditions at an arbitrary time t, respectively. Superindexes f and p refer to feed and permeate streams, respectively. If we consider a system where a complex ML_m is formed from a transition metal ion (M) and the representative constitutional unit of a polymer (L), this case can be described in kinetic terms by the reversible chemical reaction (charges are omitted):

$$M + mL \underset{k_2}{\overset{k_1}{\leftrightarrow}} ML_m \tag{11}$$

Conditional formation constant will be the ratio between kinetic constants of complex formation (k_1) and dissociation (k_2). In systems with metal concentration small enough with regard to polymer concentration, the rate of complexation reaction will be:

$$k_1 \cdot [M] \cdot [L]^m = k_1^* \cdot [M] \tag{12}$$

while the rate of dissociation can be written as follows:

$$k_2 \cdot [ML_m] \tag{13}$$

Evolution of metal concentration in retentate and permeate streams can be described with a model based on the theory of kinetics of reactions of complexation-dissociation and the irreversible transfer of M across the membrane [21–22]. Designate the concentrations of retained metal form ML_m as C_2 and of free metal form M as C_1.