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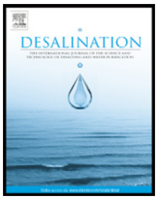

Study of Cr(III) desorption process from a water-soluble polymer by ultrafiltration

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ABSTRACT

Polymer Enhanced Ultrafiltration (PEUF) has been reported as a suitable process to separate heavy metals from pollutant wastewaters. Desorption of metal ion is a required step in order to recycle the polymer. At acidic pH values, nearly quantitative desorption has been achieved for divalent ions but a limited efficiency has been reached for trivalent ions. This paper studies the Cr(III) desorption yield from ethoxylated polyethylenimine (EPEI) by means of an ultrafiltration ceramic membrane. Experimental results show that about only 20% of the chromium (III) remains adsorbed at pH 1. The feasibility of several sorption isotherms (Langmuir, Freundlich, Redlich–Peterson and Temkin) was tested to describe the binding of chromium (III) and EPEI and the Freundlich one showed the best fits with experimental data at all pH values. Further, it was observed that normalized permeate fluxes decreased as initial Cr(III) concentration and pH were higher. Membrane fouling was analyzed by long–term experiments at different pHs which indicate that the intermediate pore blocking was the main mechanism of fouling.

1. Introduction

Ultrafiltration combined with water-soluble polymers is a useful process for removing metal ions from pollutant wastewaters [1,2]. The use of this technology in the leather industry for recovery of Cr(III) from the residual waters could work better than the conventional process [3–6].

Metal ion removal with ultrafiltration membranes is based on the formation of metal ion–polymer complexes. Metal ions bound to the polymer are retained by the membranes, whereas unbound metal ions pass through the membranes. Metal ion–polymer bonds are generated by electrostatic attraction or electron coordination, depending on the nature of the polymer and metal ion considered. The determination of the quantity of metal ion bond to the polymer can be conducted by potentiometric titration with selective electrodes, UV absorbance and/or membrane filtration [7–9].

The interactions between metal ion and water-soluble polymer were studied by the definition of chemical reactions of complexation that enable the determination of the quantity of metal ions bound to the polymer [10,11]. The chemical reactions postulated to understand the complexation mechanism normally are established depending on the experimental data obtained.

Recently, a modification in the classic complexation reactions for the determining of the binding constants was reported [12]. The study proposed that the whole solution should be conceived as divided into two regions: (1) the polymer region, which is occupied by polymer chains with and without bounded metal ions and some water, and (2) the remaining solution with the unbound metallic ions.

The similarity of the complexation reactions to the ion-exchange process, in which the polymer is a water-insoluble solid, was used to analyze the binding capacity of the water-soluble polymers as an equilibrium sorption. In this case, the metal ion–polymer interactions are quantified by the affinity constants of the classic ion-exchange models, such as the Langmuir or Freundlich isotherms [13,14]. Isotherms as a model for the binding of small molecules by polymers have been used in several biological systems as well [15–17]. The main advantage versus isotherms from complexation reactions is that isotherms describe the binding process with a few parameters, even in complex systems where the molecular mechanisms of binding are unknown.

Cr(III) is a metal cation with a high tendency to form complexes with a variety of polymers. The literature shows that the quantity of Cr(III) bound to the polymer decreases as pH goes down [18,19]. The Cr(III) desorption process from a polymer, which it is also named polymer regeneration, has not been widely studied. Unlike mono and divalent metal ions, Cr(III) still binds polymers that contain carboxylic, phosphonic and sulfonic ligand groups at low pH values [20–22]. Thus, partial desorption of Cr(III) was achieved decreasing the solution pH from different polymers: poly(acrylic acid) [23], humic acids [24], biosorbents [25] and cation exchange resins [26]. Alternatively, the use of EDTA as regenerant solution and H_2O_2 for the oxidation of Cr(III) to chromate improved effectively the Cr(III) desorption process from ion exchange resins [27,28].

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The aim of the present paper is to study the Cr(III) desorption process from a polyelectrolyte with amines as a functional groups and the influence of operational variables on the permeate flux in order to characterize the membrane fouling phenomena. The water-soluble polymer used is ethoxylated polyethylenimine (EPEI). Bound and unbound Cr(III) ions have been separated by cross-flow ultrafiltration ceramic membrane. In a first stage, the Cr(III) was adsorbed onto polymer chains and then the desorption process was carried out decreasing the solution pH. The correlation between the concentration of Cr(III) bound to the polymer chains and free Cr(III) concentration has been analyzed by four different isotherms.

2. Theories

2.1. Sorption isotherms

Four sorption isotherms have been used for chemical adsorption: Langmuir, Freundlich, Redlich–Peterson and Temkin isotherm equations. The Langmuir isotherm [29] assumes energetic homogeneity of the adsorption sites without steric effects and it is defined by a second order kinetic reversible process between adsorption and desorption. The Freundlich isotherm [30] is an empirical equation and it can be used for nonideal sorption that involves heterogeneous sorption. The Redlich–Peterson isotherm [31] incorporates the features of the Langmuir and the Freundlich isotherms and, then, contains more parameters. The Temkin isotherm model [32] assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. As they are well known, we do not show the equations.

2.2. Membrane fouling

The general expression that describes the decrement of permeate flux as a function of operation time is the following [33]:

$$\frac{\partial J_v}{\partial t} = -K\cdot(J_v - J_e)\cdot J_v^{2-n} \tag{1}$$

where J_e is the permeate flux in steady state, K is a phenomenological coefficient and n is the general index that depended on the fouling mechanism ($n=1.5$ for standard pore blocking, $n=1$ for intermediate pore blocking and $n=0$ for cake layer formation).

Eq. (5) can be solved with the initial condition of permeate flux at $t=0$ and the obtained equations for the three mechanisms are the following mathematical expressions [33]:

- Standard pore blocking

$$J_v^{-1/2} = J_o^{-1/2} + K_{spb}\cdot t \tag{2}$$

- Intermediate pore blocking

$$J_v(t) = \frac{J_o\cdot J_e\cdot \exp(K_b\cdot J_e\cdot t)}{J_e + J_o\cdot(\exp(K_b\cdot J_e\cdot t) - 1)} \tag{3}$$

- Cake layer formation

$$t(J_v) = \frac{1}{K_{cp}\cdot J_e^2}\cdot \ln\left[\left(\frac{J_v\cdot(J_o - J_e)}{J_o\cdot(J_v - J_e)}\right) - J_e\cdot\left(\frac{1}{J_v} - \frac{1}{J_o}\right)\right] \tag{4}$$

where J_o and J_e are the initial and the steady state permeate fluxes, and K_{spb}, K_b and K_{cp} are phenomenological fouling coefficients of standard pore blocking, intermediate pore blocking and cake layer formation , respectively.

3. Materials and methods

3.1. Materials

The water-soluble polymer used in this study to determine the binding equilibrium for the removal of Cr(III) was ethoxylated polyethylenimine (EPEI) with an average molecular weight of 70,000 g mol^{-1}, which was purchased from Sigma-Aldrich (Spain). This polymer binds and releases the chromium ions as a function of pH, as demonstrated elsewhere [19]. The rest of the reagents were pure grade and used as received from Sigma-Aldrich (Spain). The water used was distilled water purified by a Millipore Milli-Q system and filtered through a 0.45 μm pore diameter membrane.

3.2. Experimental procedure

First, a fixed weight of the polymer was diluted to the required concentration in water. The polymer solution was diafiltred by a ceramic membrane with molecular weight cut-off of 15,000 g mol^{-1} in order to eliminate low-molecular-weight molecules. Polymer concentration was determined as TOC (total organic carbon) and the diafiltration process was stopped when the TOC rejection was higher than 98%.

The adsorption of chromium ions was conducted at pH 5 to avoid the precipitation of chromium hydroxide [34,35]. Precipitates appeared when we tried to conduct adsorption experiments at pH 7. In this circumstances, the permeate flux in the ultrafiltration process decreased dramatically, making ultrafiltration experiments meaningless.

Polymer aqueous solutions (50 ml of 0.5 wt.%) and Cr(III) solutions (from 4 to 30 mM, 50 ml), prepared by dissolving $Cr_2(SO_4)_3$, and fixed to the required pH and ionic strength (50 mM in NaCl), were mixed and stirred constantly at 60 °C for 24 h, which permitted to attain the steady state Cr(III) concentration in all cases. The final pH of the solutions were adjusted to the fixed value by adding small amounts of aqueous solution of sodium hydroxide or hydrochloric acid at intervals of about 2 h until no further change in pH was found. In order to carry out desorption the pH of the initial solution was adjusted to pH 3 or 1. Then, those solutions were stirred constantly at 60 °C overnight to reach the new equilibrium of the reaction.

The used membrane module was configured by a tubular ceramic membrane of 15 kDa molecular weight cut-off (MWCO), supplied by Tami (France), with its length at 24.6 cm and the cross-section area of each channel measuring 0.167 cm^2. The total filtration area was 120.9 cm^2. The retentate stream circulated tangentially to the membrane surface with a linear velocity of 11.2 cm·s^{-1} at 25 °C. Both permeate and retentate were returned to the stirred feed tank in order to achieve steady state operation. Experiments were performed under constant transmembrane pressure difference ($\Delta P = 400$ kPa) and the permeate flux rate was $2.34\cdot10^{-6}\pm2.2\cdot10^{-7}$ m·s^{-1}. Samples of permeate and retentate were collected for the analysis of chromium concentration, which was measured with an inductively coupled plasma spectrometer (ICPS-5000, Shimadzu Seisakusho), and pH and conductivity were also measured. Between runs, membrane was cleaned circulating pure water, 1% HNO_3 aqueous solution, and 1% NaOH—150 ppm NaClO aqueous solution and pure water again.