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Water-soluble polymer ultrafiltration process at pilot scale: Study of hydrodynamics and factors limiting flux

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ABSTRACT

In the present work, the hydrodynamic behaviour of a water-soluble polymer (ethoxylated polyethylenimine) ultrafiltration process has been studied at pilot scale using multichannel ceramic membranes. In a first step, the effects of tangential velocity, transmembrane pressure and temperature on both polymer rejection coefficients and permeate fluxes, have been studied for a given polymer concentration. Secondly, two discontinuous closed-loop experiments have been set up to study the influence of polymer concentration and operation time on design parameters. Next, the presence of concentration–polarization and fouling has been firstly studied and subsequently quantified by means of a resistance in series model. Moreover, a design equation that relates permeate flux to polymer feed concentration has been obtained. Finally, the concentration evolution in both feed tank and recirculation loop has been successfully modelled.

1. Introduction

Amongst membrane processes, Polymer Supported Ultrafiltration (PSU) emerged as a technique to recover metal ions at the early eighties [1], although it has been developed within the last 15 years [2–9]. The first step of this process consists of a reaction between a target metal ion and a water-soluble polymer, giving the former macromolecular dimension. Afterwards, the metal ion can be retained in an ultrafiltration stage and, therefore, be separated from other non-target ions. A permeate stream (the stream that passes through the membrane) with a low concentration of the target ion is finally produced. This technique offers some advantages with respect to lower pore size membrane techniques such as higher permeate fluxes (lower area requirements) and higher selectivity.

In previous works of our research group, some studies have been carried out in the PSU treatment of water effluents containing heavy metal ions [10–12]. In these studies, tubular ceramic membranes, Carbosep from Novasep, were used at both laboratory and pilot scales. Specifically, in a recent study [13] the removal of copper from water effluents was studied and optimised at laboratory scale, using partially ethoxylated polyethylenimine (PEPEI) as water-soluble polymer. With respect to these former studies, tubular membranes have been substituted by multichannel ones, Kerasep from Novasep, with a slightly higher molecular weight cut-off (15,000 Da vs. 10,000 Da).

In a PSU process, polymer significantly modifies solution properties. For this reason, every PSU research work to treat water effluents with metal ions must comprise a deep study of the system hydrodynamics with polymer solutions.

The main aim of this work is to demonstrate the technical viability of the water-soluble polymer (PEPEI) ultrafiltration step for its subsequent use in a PSU process to recover copper. The four main contributions of the present work to reach this global aim are put forward:

- This work has been carried out in a pilot scale ultrafiltration plant and with multichannel ceramic membranes. On the one hand, this scale approximates results to a real application. On the other hand, multichannel membranes present higher permeate flux (higher MWCO than Carbosep tubular membranes) and more membrane area for a given volume (higher packing density). This leads to higher permeate flux per unit volume of the membrane element [14]. Furthermore, these membranes have lower hydraulic diameter than Carbosep ones (3.5 mm vs. 6 mm) what allows a better hydrodynamic behaviour.
- The polymer used in this work (partially ethoxylated polyethylenimine) overcomes some of the disadvantages of polyethylenimine as the very acidic conditions required in the polymer regeneration stage [13].

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- In the present investigation, working conditions (tangential velocity, transmembrane pressure, temperature) that minimise concentration–polarization and fouling and maximise rejection coefficient have been selected. These working conditions permit that membrane resistance was the governing one in a broad concentration range.
- Finally, the last goal of the present work is to obtain a design equation that relates permeate flux with polymer bulk concentration. This equation can be used in a subsequent plant design.

To reach these aims, the experimental program has been scheduled in two clearly differenced stages that correspond to two different modes of operation:

(1) The first step has been carried out in total recirculation mode working with an open-loop system. This stage of the work consisted of checking the influence of three key variables in the system hydrodynamics for a given polymer concentration (0.06%, w/w) [13]: temperature, tangential velocity and transmembrane pressure. The evolution of both polymer rejection coefficient (R) and permeate flux (J_p), vs. these three variables was studied and the working conditions that optimise these design parameters were selected.
(2) Next, two batch tests were carried out in order to analyse the polymer concentration influence on design parameters (permeate flux and rejection coefficients). These two tests will let us check if a concentration increase can lead to concentration polarization and fouling and will give very important raw data to obtain design equations that can be used for a further plant design. The presence of concentration–polarization and fouling has been tested in two stages: (1) assuming that one of them is the flux controlling mechanism; (2) applying a resistance in series model. In this part of the work, an empirical model has been proposed to be used as a design equation.

Finally, concentration evolution with time in the feed tank and the recirculation loop was successfully modelled.

2. Experimental

2.1. Material and apparatus

The installation set-up used in this work is a cross-flow ultrafiltration device with a recirculation loop, which can operate with different pilot plant modules. A schematic plot of this plant is represented in Fig. 1, where the main parts it consists of are gathered.

With respect to the module and membrane, a stainless steel ultrafiltration Mini-Kerasep module was selected. It has an inner ceramic multichannel membrane, with 19 channels (Length = 380 mm, Channels diameter = 3.5 mm, Area = 0.0816 m^2, MWCO = 15,000 Da, TiO_2 active phase).

The polymer used in the present study was 80% ethoxylated polyethyleneimine (Mw = 50,000 g mol^{-1}; 37% (w/w) aqueous solution) from Aldrich. The initial polymer experimental concentration was always 0.06% (w/w). All rejection coefficient values presented here are observed rejection coefficients. To calculate them, both permeate and bulk polymer concentration, were measured with a total organic carbon (TOC) analyser (Shimadzu 5050A). pH was adjusted with NaOH and H_2SO_4 from Panreac. Water used to prepare all solutions was produced by a reverse osmosis pilot plant with a maximum allowed conductivity of 10 μS/cm.

2.2. Procedure

2.2.1. Experiments at total recirculation mode

Total recirculation mode was used in the first step of this work, this is to say, both permeate and recycled stream were returned to the feed tank. In this case, the recycled stream flow rate that comes from the recirculation loop was high enough to assure that

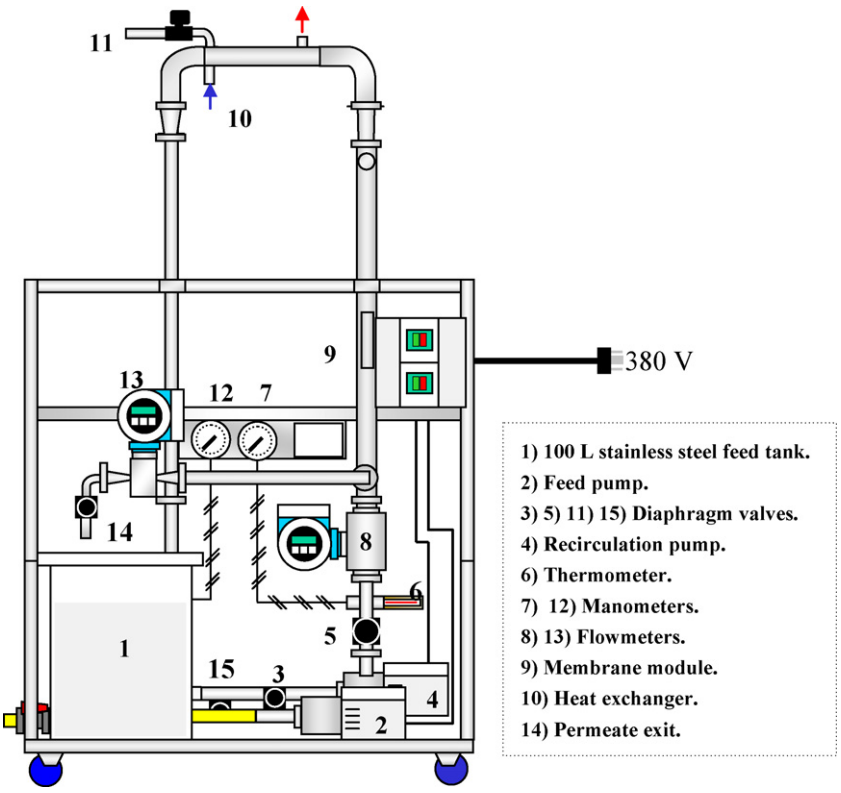

Fig. 1. Schematic pilot plant diagram.