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Influence of the operating conditions on the elimination of zinc ions by nanofiltration

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Abstract

In the present work, we were interested to study the influence of applied pressure, solution concentration and recirculation flow on the zinc retention by nanofiltration. The results have shown that the Zn^{2+} retention increases with the pressure and reaches a maximum of 90% which varies slightly with the concentration. These observed retention values have been found higher in comparison of other metals retention such as copper or cadmium (40%) as it was be noted in literature. We have attributed this difference in behavior to the electrostatic repulsion charge of the $ZnCl_3^-$ and $ZnCl_4^{2-}$ forming complexes present in solution which were calculated and found in dominant proportion. This explication was verified and confirmed by studying the Zn^{2+} retention when using nitrates co-ions in place of chlorides ions. Otherwise, the recirculation flow was studied and the results have shown that the Zn^{2+} retention rises when the recirculation flow increases. We have attributed this result to the polarization concentration phenomenon which can be reduced when recirculation flow increases.

Keywords: Nanofiltration; Salts of zinc; Mass transfer; Selectivity

1. Introduction

Zinc and its alloys are mostly used in mechanical engineering and building. It is estimated that 10 million tons of zinc was used in the year 2001. However, industrialization and urbanization are often accompanied by large pollution emissions. Against this increased pollution, very strict standards were imposed for heavy metal content in water because of their high toxicity. The maximum concentration acceptable for zinc in water intended for consumption must be lower than 5 mg/l (French

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regulation law—decree no. 89–3 modified 2003), to be extended to 2 mg/l in 2006. In industry, the purpose of this process is the purification of waste products and the recovery of metals in order to use them for recycling. The processes used are chemical precipitation by EDTA or NTA [10], electrolysis [12], electrodialysis [21], ion exchange resin [6], ultrafiltration [1]. These processes are particularly used for initial high metal concentrations.

The techniques of separation by membranes which are characterized by their aptitude to clarify, concentrate, continuously separate molecular compounds of differing charge and mass, are potentially interesting for liquid waste processing with the objective of recycling. Among the membrane processes, nanofiltration (NF), placed between ultrafiltration (UF) and reverse osmosis (RO) makes it possible to combine the advantages of RO and UF by the use of moderate pressure (5–30 bars) while allowing the separation from the aqueous solutions of molar masses ranging from 300 to 1000 Da and whose radius is about 1 nanometer.

Studies of heavy metals retention as zinc, copper, cadmium or nickel by nanofiltration were carried and published by several authors [1,8,9,11,15,20,23]. The rejection rate is variable according to operating conditions as well as the nature of the membrane used. The recent development of nanofiltration in water treatment has made it necessary to know the transfer and retention mechanisms of the various ions to be eliminated. These mechanisms of man transport in the membranes of nanofiltration are still not very well-known. The scientists who use this method currently base their knowledge on their own experimental observations. The particular characteristics of the membranes used explain the complexity of ionic transfer mechanisms through the membrane. From this complexity, as well as lack of information on the structure and the physicochemical properties of the commercial membranes [24], rises an absence of theory, allowing quantitatively to envisage the performance of the process before its implementation. It is within this framework that we were interested in the elimination of zinc ions by a commercial membrane of nanofiltration and this, with an aim of acquiring knowledge on the zinc mechanism of ionic transfer as well as associated anions and thus proposing a model to envisage the selectivity of the membrane.

The objective of this work is to study the retention of zinc salts according to the operating conditions such as the pressure, the concentration, the recirculation flow and the effect of the co-ions on the selectivity of the membrane.

2. Materials and methods

2.1. Description of the pilot

The pilot used is a commercial apparatus Millipore Proscale with 12 l of a capacity (Fig. 1). It is equipped with a spiral wound polymeric membrane (Nanomax 50, Millipore USA) with a filtration area of 0.37 m^2. The Nanomax 50 is a composite membrane having a negatively charged thin skin layer (0.4 μm) made of polyamide arylene on a polysulfone support layer. The data of the manufacturer announce a cut-off about 300 Da for uncharged solutes and a pore diameter of 0.5 nm.

2.2. Procedure

The experiments were carried out on 4 l of solution containing zinc salts ($ZnCl_2$; $Zn(NO_3)_2$, $6H_2O$; $ZnSO_4$, $7H_2O$) in concentration ranging from 10 to 100 mg/l for zinc. The experiments were performed in a batch circulation mode. Both permeate and retentate were returned to the feed vessel in order to keep a constant concentration. These solutions were prepared in demineralized water (conductivity $= 1$ μS/cm) at the temperature 20°C $\pm$ 0.5 over pressure