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POLYMER INCLUSION MEMBRANES (PIMs) AND SURFACE MODIFIED PIMs: CHARACTERIZATION AND OPTIMIZATION OF THE SEQUESTERING ABILITY TOWARDS Sn(II) BY A MULTI-ANALYTICAL APPROACH

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The employment of polymeric membranes to afford a wide range of energy- and environmental-related applications has attracted both research and industry. Among them, Polymer Inclusion Membranes (PIMs) have been investigated to produce materials with appealing properties in fields such as separation science, sensors, water treatment, while featuring cost competitiveness and ease of processability. PIMs are usually composed by a polymeric matrix, i.e. PVC or CTA (polyvinylchloride or cellulose triacetate), an extractant (a carrier) and a plasticizer and/or modifier. Such a simple chemistry may be finely tuned to gain membranes able to exert selective pollutants extractions with high efficiency, avoiding the environmental issues of organic solvents use. Bearing this in mind, this work has been focused on the synthesis of PIMs and surface modified PIMs able to exert sequestering properties towards Sn^{2+}. For this purpose, several PIMs were prepared, containing different amounts of PVC and CTA as polymeric matrix, Aliquat 336 or Alicy as plasticizers, and Thiomalic acid (SMAL) or montmorillonite modified with a thiolic group as extractants. In this last case, the use of a compatibilizing agent 3-aminopropyltriethoxysilane (APTES) was necessary to anchor the inorganic montmorillonite with the organic matrix of the polymer. The aim of this double approach is to obtain membranes where the extraction of the metal can be connected either to its diffusion within the bulk of the membrane or to a specific interaction with the functionalized surface. The sequestering ability of the PIMs was evaluated in a solution of Sn(II) 1 ppm by differential pulse – anodic stripping voltammetry. The PIMs was immersed directly into the electrochemical cell, thus allowing to collect a scan every two minutes and to profile the absorption kinetic in one hour. The composition of PIMs and the solution in which test their sequestering ability were selected with a D-Optimal experimental design. A total of 9 factors, 6 of which are 3-levels and 3 are 2-levels, while the maximum number of experiments to performed is 30. The candidate points submitted for the D-optimal design were planned on the basis of a fractional factorial design (1/12) and resulted to be 16.

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Table 1. Factors influencing the sequestering ability of a PIM towards Sn^{2+} and their levels of variation.

Factors	**level -1**	**level 0**	**level +1**
ratio w/w polymer/additive	1	---	4
polymer	PVC	---	CTA
Ionic medium	NaCl	---	$NaNO_3$
additive	Alicy	no additive	Aliquat
sequestrant	SMAL	no sequestrant	MMT-SH
ratio w/w polymer/sequestrant	2	5	10
pH	2	3	4
surface area	2x2	2 x (1x2)	tea bag
Ionic strength	0	0.12	0.25

All the tested membranes were characterized by means of Thermogravimetric Analysis (TG-DTA), Differential Scanning Calorimetry (DSC), static contact angle measurements, tensile module, thickness and Raman investigations.