

# Membranes Removal of Toxic Metal Ions through Polymer Inclusion Containing Macrocyclic Ligands as Carriers

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## Abstract

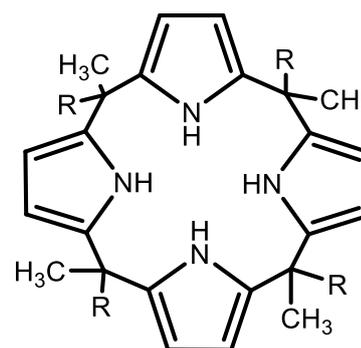
More strict environmental regulations on the discharge of toxic metals require developing various technologies for their removal from polluted streams. The separation of toxic metal ions using immobilized membranes with doped ligands, due to their high selectivity and removal efficiency, increased stability, and low energy requirements, is promising for improving the environmental quality. Cellulose triacetate-based polymer inclusion membranes (PIMs), with macrocyclic ligands as ion carriers, were studied for their ability to transport of toxic metal ions from aqueous solutions. The effect of concentration of ion carrier, pH of source aqueous phase, stripping agents on the effective transport of toxic metal ions have been assessed. All studied parameters were found to be important factors for the transport of toxic metal ions. The initial flux was determined for different conditions of transport through polymer inclusion membranes. The newly developed PIM containing macrocyclic ligands were found to be stable and highly permeable. Moreover, the prepared membranes could be potentially suitable for multiple use process for efficient removal of toxic metal ions from aqueous solutions.

**Keywords:** macrocyclic ligands, polymer inclusion membranes, toxic metal ions

## 1. Introduction

Industrial development has led to the generation of effluents, polluted streams, which if untreated may result in water, sediment, groundwater and soil pollution. Industrial wastes and emissions contain toxic compounds, most of which are detrimental to human beings. Among the various toxic pollutants, heavy metals represent an interesting group of elements due to their strong impact of the stability of aquatic ecosystems, bioaccumulation in living organisms and toxicity persistence (Zawierucha et.al, 2016). Toxic metals, commonly found in high concentrations in wastewater include arsenic, mercury, chromium and cadmium (Vera et.al., 2018). Due to the high toxicity of arsenic even at low concentrations, it is of paramount importance to perform routine analyses to monitor this pollutant in waters. Of the different separation techniques, functionalized membranes have attracted considerable attention as a valuable technology for

many analytical purposes in recent years. This is the case of polymer inclusion membranes (PIMs), which are non-porous functionalized membranes that consist of a polymer, a plasticizer, and an extractant. With the proper selection of the carrier, these membranes can effectively transport different species, such as inorganic pollutants (Almeida et. al., 2016), organic compounds (Garcia-Rodriguez et. al, 2015) and metallic species (Pont et.al, 2008). The present work deals with the transport of As(V) from sodium aqueous solutions through PIMs that contain cellulose triacetate as a support, *o*-nitrophenyl pentyl ether as a plasticizer and calixpyrrole (**1**) derivatives as an ion carriers. In the present study, in order to extend the applicability of this separation system, we have evaluated and optimized the chemical and physical parameters that can affect the PIM-based device, such as membrane composition, source phase characteristics, and membrane thickness, in order to accomplish the preconcentration of arsenic species in a more convenient timescale and to broaden the applicability of the method to more complex groundwater samples.



**Figure 1.** Structures of calixpyrrole (**1**)

## 2. Materials and Methods

### 2.1. Chemicals

Inorganic chemicals, i.e. arsenate(V) sodium, sodium chloride (NaCl) were of analytical grade and were purchased from POCh (Gliwice, Poland). Organic reagents, i.e. cellulose triacetate (CTA), *o*-nitrophenyl pentyl ether (*o*-NPPE) and dichloromethane were also of analytical grade and were purchased from Fluka and used without further purification. Aqueous solutions were prepared with double distilled water, with a

conductivity of  $0.1 \mu\text{S cm}^{-1}$ . The carrier (**1**) was purchased from Aldrich (97,0%, CAS Number 4475-42-7, C<sub>28</sub>H<sub>36</sub>N<sub>4</sub>, MW: 428,61).

## 2.2. Preparation of polymer inclusion membranes

Cellulose triacetate (CTA) (as the support), *o*-nitrophenyl pentyl ether (*o*-NPPE) (as the plasticizer), and calix[4]pyrroles (**1**) (Figure 1) (as the ionic carrier) were dissolved in dichloromethane. A specified portion of this organic solution was poured into a glass Petri dish consisting of a 5.0 cm glass ring attached to a glass plate with cellulose triacetate – dichloromethane as a glue. Dichloromethane was evaporated overnight and the resulting membrane was separated from the glass plate by immersion in cold water.

## 2.3. Transport studies

Transport experiments were carried out in a permeation cell in which the membrane film (4.9 cm<sup>2</sup> effective surface) was tightly clamped between two compartments. The aqueous source phase was a solution of sodium arsenate, the aqueous receiving phase was sodium chloride (50 cm<sup>3</sup>). Transport was conducted at a room temperature (23±25 °C) and both source and receiving aqueous phases were stirred at 600 rpm with synchronous motors. Samples (0.10 cm<sup>3</sup>) of an aqueous receiving phase were removed periodically via a sampling port with a syringe and analyzed to determine As(V) concentration. The source phase acidity was controlled by pHmeter (multifunctional pHmeter, CX-731 Elmetron, with combine pH electrode, ERH-136, Hydromet, Poland).

The metal ion concentrations were measured by flame atomic absorption spectrometry (Solar 939, Unicam).

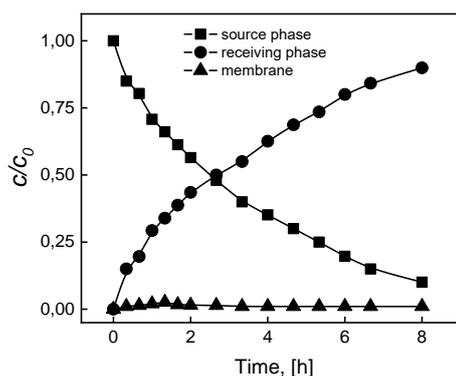
## 3. Results and Discussion

### 3.1. Kinetics and repeatability of As(V) ions transport through polymer inclusion membranes

In order to determine the kinetics and repeatability of the process of As(V) ions membrane separation through PIM containing calixpyrroles, the changes in these ions concentrations were measured in the source and receiving phases as a function of transport time.

The rate of change of concentration of As(V) ions in source, receiving phase and the membrane was analyzed for the transport of As(V) ions through PIM containing (**1**) providing concentration profile of the metal as a function of time.

As seen in Figure 2, the kinetic curves of  $c/c_0$  relationship in the function of time are of an exponential nature, that confirms the kinetic model of metal ions primary transport proposed by Danesi et al. in relation to the supported liquid membranes (SLM) (Danesi et al., 1984-85).



**Figure 2.** The profile of As(V) concentrations in source, membrane and receiving phases during the transport process across PIM.

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