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Procedia Engineering 44 (2012) 804 – 806

Procedia Engineering

www.elsevier.com/locate/procedia

**Euromembrane Conference 2012**

**[P1.056]**
# Development of polymer inclusion membranes for the extraction of antibiotics from environmental waters

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## Introduction

Tetracyclines (TCs) and sulfonamides (SAs) are among the most successful antibiotic drugs used for human and veterinary therapy. Due to their extensive use, these antibiotics are found in different environmental matrices, such as soils and natural waters, where they can affect the biological cycles and persist in the environment.

Bearing this in mind, it is of interest to develop reliable analytical methods for routine monitoring of these compounds. These methodologies normally include sample cleanup and preconcentration steps, but since these compounds can be present as ionic species with different charges in aqueous samples, depending on the pH, their extraction and separation is a difficult task.

Among the several technologies that can be used for the sample pretreatment, supported liquid membranes (SLMs) have reached a significant importance due to their selectivity and simplicity. Moreover, polymer inclusion membranes (PIMs) represent an attractive alternative to SLMs in separation processes. PIMs consist of a polymer, a plasticizer and carrier molecules, where the polymer provides mechanical strength and the plasticizer provides elasticity and constitutes the liquid phase in which the carrier molecules can diffuse.

The goal of this study is the development of a separation system based on PIMs for the transport of three TCs (i.e., tetracycline (TC), oxytetracycline (OTC) and doxycycline (DC)), and four SAs (i.e., sulfathiazole (STZ), sulfamethazine (SMN), sulfamethoxazole (SMX) and sulfapyridine (SPY)) contained in different environmental samples.

## Methods

PIMs were prepared by dissolving cellulose triacetate (CTA) (200 mg) in chloroform or polyvinyl chloride (PVC) (400 mg) in THF. The anion-exchanger Aliquat 336 (a quaternary ammonium salt) was used as carrier. Moreover, in some cases, a plasticizer (0.3 g) was also added. The solution was poured into a 9.0 cm diameter flat bottom glass Petri dish which was set horizontally and covered loosely. The solvent was allowed to evaporate over 24 h at room temperature, and the resulting film was then carefully peeled off the bottom of the Petri dish and placed in the membrane permeation cell for further studies. The exposed membrane area was 11.5 $cm^2$.

The permeation experiments were carried out using 150 mL of aqueous solution containing 5 mg $L^{-1}$ of antibiotics at pH 9 as feed solution and the same volume of 1M NaCl as stripping.

To determine the antibiotics concentration, samples were analyzed by an Agilent TM 1290 Infinity ultra performance liquid chromatograph (UPLC) system coupled to a 6430 triple quadrupole mass spectrometer.

Results


doi:10.1016/j.proeng.2012.08.578

Parameters affecting the membrane composition such as the polymer and the nature of the plasticizer were investigated. Table 1 shows the transport efficiency of the different antibiotics through PIMs made with CTA or PVC, both containing also the carrier Aliquat 336 and the plasticizer 2-Nitrophenyl octyl ether (NPOE). As it can be observed, better results were obtained when using CTA-based membranes, probably due to the lower polarity of this polymer.

**Table 1**. Effect of the membrane composition on the transport of antibiotics.

| | Transport efficiency (%) 24h | |
|---|---|---|
| **Antibiotic** | **CTA+Aliquat 336+NPOE** | **PVC+Aliquat 336+NPOE** |
| SPY | 55 | 0 |
| SMX | 91 | 66 |
| STZ | 74 | 66 |
| SMN | 79 | 11 |
| TC | 100 | 5 |
| DC | 84 | 40 |
| OTC | 100 | 12 |

The effect of the plasticizer was also investigated using CTA membranes, and results are shown in Fig. 1. As it can be observed, both NPOE and dibutyl sebacate gave the best results in terms of antibiotics transport.

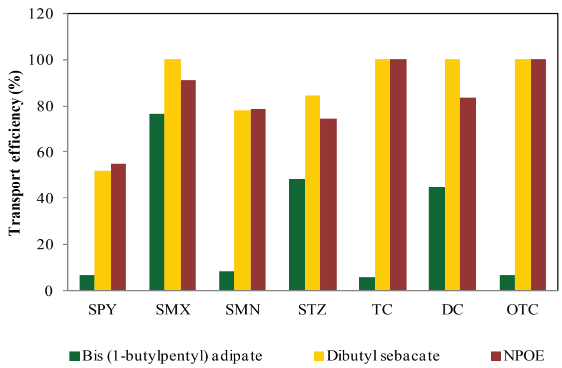


**Fig.1**. Effect of the plasticizer added to CTA/Aliquat 336 membranes on antibiotics transport after 24h.

## Discussion

PIMs based on CTA polymer containing Aliquat 336 as a carrier and NPOE as a plasticizer have shown to effectively transport antibiotics from a basic solution to a 1 M NaCl stripping phase. Moreover, this PIM system has shown its suitability for the complete removal of TCs and SAs from different aqueous samples such as river water or sewage water containing different levels of antibiotics.

## Acknowledgements

The financial support by Ministerio de Ciencia e Inovación through Project CTM2011-28765-C02-02 is gratefully acknowledged. Aida Garcia wants to acknowledge a BR2011/27 research fellowship from the University of Girona.

Keywords: polymer inclusion membranes, tetracyclines, sulfonamides, sample treatment