

Pervaporation of volatile organohalogen compounds through polydimethylsiloxane membrane

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ARTICLE INFO

Article history:

Received 16 March 2010

Received in revised form 2 July 2010

Accepted 7 July 2010

Available online 29 July 2010

Keywords:

Tetrachloroethylene

Pervaporation

Polydimethylsiloxane membrane

ABSTRACT

The objective of this work was to apply dense polymeric membranes for pervaporation of tetrachloroethene from aqueous solution. Three membranes were evaluated: polydimethylsiloxane (PDMS-PV1 and PDMS-PV2) membranes, and a PDMS with ZSM-5 zeolite filled (PERVAP-1070) membrane. The effect of feed composition on flux and selectivity was also investigated.

Tested membranes showed good properties in the separation of tetrachloroethylene, although better selectivity and enrichment of the permeate was achieved for both PDMS-PV1 and PDMS-PV2 membranes. Compared to PERVAP-1070, much higher fluxes were accomplished for both PDMS membranes.

The results of experiments confirm that pervaporation applied to the separation of tetrachloroethylene from water is a very promising method. As a result of the process it is possible to achieve high concentrated permeate and almost complete removal of contamination.

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1. Introduction

People are exposed to volatile organic compounds (VOCs) in their homes, during the various activities of everyday life and especially at workplaces [1]. Most VOCs, particularly the chlorinated hydrocarbon solvents are known to be hazardous. These solvents are suspected of carcinogenic, mutagenic and teratogenic properties and thus represent a direct health risk to workers. VOCs can enter the human body by inhalation, dermal contact or inadvertent ingestion *via* hand-mouth contact. The chemicals then may enter the bloodstream, and may either be accumulated or be excreted, usually in a non-metabolized form with urine [2]. Results of analysis of biological fluid samples such as blood, saliva and for urine are the essential source of information about the level of human exposure to different types of VOCs.

Tetrachloroethene (PCE, also known as perchloroethylene or tetrachloroethylene) is the most commonly used solvent in dry-cleaning processes. In the case of humans, PCE is known to be toxic to the central nervous system, liver and kidneys. PCE may also irritate the upper respiratory tracts, eyes and skin. PCE belongs to a group 2A of carcinogens (probably carcinogenic to humans) accounting to the

classification of the International Agency for Research on Cancer (IARC), although it is considered that dry cleaning, as a process, entails exposure that is group 2B (possibly carcinogenic to humans) [3].

The determination of chlorinated hydrocarbon solvents in human urine samples constitutes a challenge for analytical chemists because of the complex and variable matrix composition of the samples. Typical biological samples usually require special pre-treatment prior to analysis with chromatography or related techniques. Special attention has recently been paid to the use of so-called solvent-free analyte isolation and/or enrichment techniques, which can be attributed to the development of a green analytical chemistry [4].

The most popular methods for organic analyte isolation/preconcentration from biological fluids are the following [5–11]:

- gas extraction (SHS, TLHS, PT, CLSA),
- liquid-liquid extraction (LLE),
- solid-phase extraction (SPE, SPME),
- membrane separation techniques (e.g. MIMS, PV, SBSE), and
- supercritical fluid extraction (SFE).

The list of symbols and abbreviations used is given as an appendix at the beginning of this paper.

One of the useful techniques in separating trace substances from samples characterized by the complex and/or often variable matrix composition is pervaporation (PV). This technique appears to be especially promising when the preferentially permeable component is present in the sample at low concentration. Pervaporation is a membrane-based process used for the separation of liquid mixtures [12]. In this technique, the liquid sample is in contact with one side of

Abbreviations: CLSA, Closed Loop Stripping Analysis; LLE, Liquid-Liquid Extraction; MIMS, Membrane Inlet Mass Spectrometry; PCE, Tetrachloroethene; PDMS, Polydimethylsiloxane; PT, Purge and Trap; PV, Pervaporation; SBSE, Stir Bar Sorptive Extraction; SFE, Supercritical Fluid Extraction; SHS, Static Headspace; SPE, Solid Phase Extraction; SPME, Solid Phase Microextraction; TLHS, Thin Layer Headspace; TCE, Trichloroethylene; VOCs, Volatile Organic Compounds.

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membrane, whereas the permeate, in a vapour state, is continuously removed from the other side into the vacuum (Fig. 1). The pervaporation system consists of a non-porous membrane clamped in a particular module, a feed pretreatment and delivery system, and a permeate condensation/recovery system [13]. Pervaporation can be useful comparing to the conventional methods because of the flexibility in design [14].

Membranes used for VOCs separation from water are non-porous and hydrophobic ones in a composite dense form. The basic requirement for a good pervaporation membrane is that it must provide both high flux and high selectivity for a given VOC. The desired membrane should be available at low cost for industrial applications. However both high flux and high selectivity for a one particular membrane is not always available [15].

Many different polymers, such as poly(dimethylsiloxane) (PDMS), nitrile-butadiene rubber, polybutadiene, polyurethane, ethylene-propylene terpolymer, polyamide, mixed matrix membranes have been examined for removal of VOCs from water by pervaporation [1,16,17]. Of these membranes, PDMS based membranes showed the highest selectivity and high permeability for removal of VOCs from water. However, the mechanical strength of PDMS is notably weak. In order to improve its mechanical strength, selectivity, and permeability, various PDMS derivative membranes were prepared [18].

The selective isolation and pre-concentration of low content volatile organohalogen compounds from aqueous mixture through polydimethylsiloxane (PDMS) membranes followed by a chromatographic analysis, presents a large opportunity for the analytical application of pervaporation.

However, there is not a lot of data on the determination of pervaporation PCE levels (<15 ppb) of analysis in the literature. Kim et al present pervaporation with a PDMS membrane conducted to simultaneously separate trichloroethylene (TCE) and PCE from waste solution of the non-ionic surfactant Tween 80 [19]. The experiment conditions were as follows: TCE and PCE concentration of 1000 ppm, 0.5 wt.% Tween 80, membrane thickness of 200 μm , feed flow rate of 100 ml/min and temperature of 40 $^{\circ}\text{C}$. TCE (>95%) and PCE (>90%) were simultaneously removed by a long-term operation for 100 h. Dutta and Sikdar used composite membranes of a block copolymer of styrene and butadiene (S-B-S) for the separation and recovery of PCE from the surfactant-and oil-laden aqueous emulsions of the organics [17]. The results showed that the S-B-S membrane effectively separated these compounds from the surfactant-and oil-laden aqueous emulsions of the organics. However, the fluxes were slightly lower than those for emulsion-free aqueous solutions although separation factors were higher. Mishima and Nakagawa improved PDMS membranes by plasma grafting of fluoroalkyl methacrylates (FALMA) to enhance the affinity of PDMS to PCE. The permselectivity of PCE determined by the sorption and the diffusion characteristics permeating in the membrane was high. Because the molecular volume of the PCE is greater than that of water and the permeates

quickly penetrate in rubbery membranes like PDMS, permselectivity was not affected by the diffusivity [20].

This study presents the elaboration of a new analytical procedure for determination of PCE in water and next in human urine samples taken from humans exposed to this compounds. Investigations were conducted using very diluted aqueous solutions of PCE – at around 12 $\mu\text{g/l}$ (12 ppb).

The feed and permeate mixtures obtained during PV experiments were then analyzed by a direct aqueous injection (DAI) into a thick-film, non-polar gas chromatographic (GC) column with electron capture detector (ECD). The investigation studies involved the test on different composite membranes made of polydimethylsiloxane (PDMS). Their ability to remove tetrachloroethene from water was investigated.

2. Experimental

2.1. Chemicals

The standard used for this study (C_2Cl_4 ; 200 $\mu\text{g/ml}$) was purchased from Supelco (Bellefonte, PA, USA). The CH_3OH used in the chromatography was from Merck (Darmstadt, Germany). Feed solutions were prepared using “zero water” (level of total organic carbon 1–4 $\mu\text{g/l}$ C), Milli-Q® Millipore system (Molsheim, France).

3. Membrane

Three types of PDMS based hydrophobic membranes were used in this study:

- ~ PDMS-PV1
- ~ PDMS-PV2
- ~ PERVAP-1070.

Membranes used were different in the selective layer thickness, cross-linking method of PDMS, moreover PERVAP-1070 was composed of a thin PDMS layer filled with an organophilic zeolite (ZSM-5). In Fig. 2 the morphology of the pervaporation composite hydrophobic PDMS membrane was presented. The characteristics of the investigated membranes are given in Table 1.

3.1. Apparatus

The pervaporation system consisted of a temperature-controlled feed vessel, a circulation pump, a membrane test cell, cold traps, and a vacuum pump, as indicated in Fig. 3. The system was made at the workshop of Faculty of Chemistry (Nicolaus Copernicus University, Toruń, Poland).

3.2. Procedure

~10 $\mu\text{g/l}$ PCE solution ($\text{pH} \approx 7$) was prepared by addition of methanolic PCE solution to deionized water. The 250 ml feed samples containing aqueous solution of PCE (~250 ml) were pumped into a pervaporation cell equipped with a polydimethylsiloxane (PDMS) membrane. The membrane area was equal to $1.69 \cdot 10^{-3} \text{ m}^2$. The feed

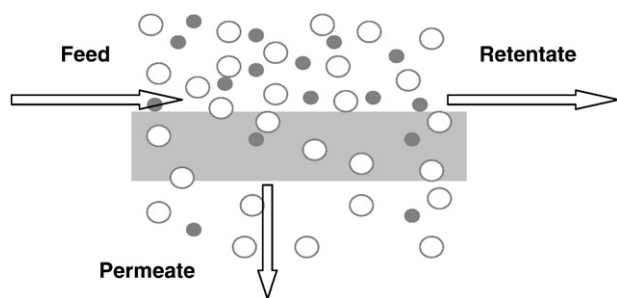


Fig. 1. Principle of the separation of compounds from liquid mixture during pervaporation. White circles represent the preferentially transported component (VOCs molecules) the filled symbols represent the less permeable component (water molecules).

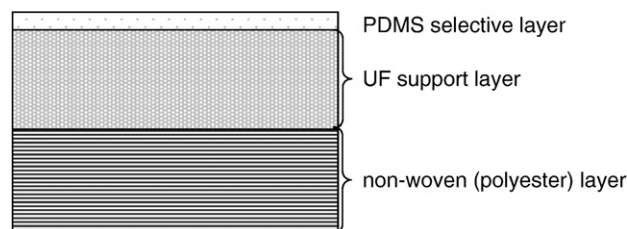


Fig. 2. Morphology of the pervaporation composite hydrophobic PDMS membrane.

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