

Separation of diethyl phthalate from water by pervaporation

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Abstract: - Seventeen different kind of membranes - based on Matrimid, Ultem polymers and DAM/DABA - were prepared and applied for pervaporation of diethyl phthalate from water. They were compared to the commercial materials like PDMS, PP and PS. The components of active layer played a crucial role on membrane process. Newly prepared membranes showed an exceptional sorption capacity (up to 100 %) comparing to the commercial membranes (around 20 %), all by reaching equivalent pervaporation results of all tested membranes (close to 40 %). The fastest permeation was achieved by raising the temperature to 50 °C with PDMS membrane, reaching total elimination of DEP. Diethyl phthalate was preferentially passing through the membranes due to dissimilar affinity of the separation materials.

Key-Words: - pervaporation, diethyl phthalate, water.

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1 Introduction

Emerging Contaminants (ECs) present one of the most challenging environmental problem. The problem is emphasized by a large structural variety of the compounds, affecting even at trace concentration, bioaccumulation for of low biodegradability, and persistent in Wastewater Treatment (WWT) effluents [1, 2]. Categorizing these ECs can be complex due to diverse sources, uses and effects; e.g. Pharmaceuticals (PhACs), Personal Care Products (PCPs), Endocrine Disrupting Compounds (EDs), Antibiotics (ATBs) etc.. The main sources of ECs are industrial manufactories, agricultural chemicals, hospitals, and domestic. The compounds are released by different ways to the environment - water (wastewater), air

(airborne deposition for volatile compounds) or soil (adsorption). EDs can affect different environments biota, also humans via different type of expositions. Many researchers reported the presence of these compounds (e.g. Phthalates) in food packing materials, outdoor and indoor air, ground and surface water, and in some fruits and vegetables around the globe [3-6].

Plastics invaded our daily life used materials. Phthalates Esters (PAEs) are widely applied as plasticizer for different plastic and other products like resin, constructive materials, food and drinks packing, PCP, polycarbonates, Flame retardant in furniture and households etc. [7, 8]. PAEs, only physically bounded to the materials [9, 10], may be easily leached by solvents and evaporate in the air [6]. Therefore, PAEs can be found almost

everywhere: packed food, drinks, soil, water biota, tissues and so on. Leached or evaporated from daily used materials. The most direct source to human body of this contamination coming from bottled water and packed food [11]. Globally bottled water industry production is exceeding milliard liters per year, and it is continually rising each year. Even though different studies reported the contamination of mineral water from the source, due to groundwater contamination [12-14]. And the presence of PAEs the environment present many risks for human health and biota [15]. The exposition of Zebra fishes to PAEs presented estrogenic and endocrine distrusting effects [16]. Moreover other studies reported that these PAEs including DEP are identified as endocrine distributor affecting various vital organism like thyroid receptors, male fertilities by decreasing sperms concentration, carcinogenic effects, hepatic and renal diseases, asthma and allergy, cardiovascular system, or hemostasis [17-19].

World Health Organization (WHO) and European union Environmental with Planning Law Department had published the tolerated daily intake of phthalate [20, 21]. To respect those regulations and environment sustainable protection, advanced wastewater treatments are necessary. Some researcher focus on Advanced Oxidation Processes (AOPs) performed mainly in pilot scale. The technology allows to mineralize directly ECs [22-24]; still, environmental impact assessment and experience are required for full scale applications [25, 26]. Ozonation, Activated Carbon or Membrane filtrations are already used in full-scale mainly in Europe, Australia and America [26-28]. Nevertheless, Ozonation struggle with by-products which can be harmful for the environment. Activated Carbone require high energy for preparation, and concentrated waste management is challenging after adsorption process. And membrane filtrations suffer from fulling. Furthermore, by-products and concentrated solution can be far more challenging to handle and manage [25, 29]. Advanced treatments must be further studied.

Pervaporation is a membrane separation method frequently used to dehydrate organic substances forming azeotropic mixtures with water; e.g. methanol [30], ethanol [31, 32], or isopropyl alcohol [33]. It is also used for desalination of sea water [34] and waste water treatment [35]. The mixture is divided by partial evaporation through a non-porous membrane, made of ceramic or polymeric (homogeneous and composite) materials. Polydimethylsiloxane membranes are typical example of homogenous materials, based on one polymer [36]. Composite ones contains two or more

polymers, e.g. a polyvinyl alcohol layer deposited on a polysulfone and a polyester [33]. The polymers may have an internal microporosity (PIM), too [37]. Among various membranes suitable for pervaporation [38-40], Metal Organic Framework (MOF) [41], zeolites [42] or silica based materials [43] are well known candidates.

During pervaporation, one side of tested membrane is in direct contact with the separating liquid mixture, the other side always with the separated component (pervaporate) desorbed into low pressure medium - vacuum. It offers a low energy consumption due to mild conditions and separation of mixtures that cannot be exposed to higher temperatures without the need to mix other substances. The separation of the mixture itself takes place on the basis of the different affinities of the each component for the membrane and their different transport rates within the membrane. Therefore, the final composition of the pervaporate may not correspond to liquid-vapor equilibrium. It depends on solubility and diffusion coefficient of the components, which is also the control process of the separation, and its driving force is the pressure gradient [38, 44].

The present paper focuses on water purification from DEP, applying different flat organophilic membranes in sorption and pervaporation processes. The membrane with incorporated different amount of fillers such as graphene oxide and TS-1 zeolite were compared to several commercial hydrophobic membrane, suitable for pervaporation process. During pervaporation, the influence of a temperature was also investigated.

2 Experimental part

2.1 Materials

The flat-sheet, composite membranes with organophilic surface properties were chosen for sorption and pervaporation tests. Their characteristics are given in **Error! Reference source not found.** The materials were based on Ultem, Matrimid and 6FDA-DAM:DABA 3:1 and different types of filling materials was added into the matrix. In case of Matrimid and 6FDA-DAM:DABA 3:1 the different fraction of graphene oxide was added, TS-1 zeolite (Si/Ti=100) was added into the Matrimid.

Graphene oxide membrane was prepared by graphite oxidation via the improved Hummers method, also called the Tour method, according to the procedure described by Jankovsky et al [45].

TS-1 zeolite particles were prepared by hydrothermal synthesis from mother solution obtained by rapid mixing of two individually

Table 1. Characteristics of tested membranes.

Membrane	Type/Filler	Material	Thickness (mm)	Diameter (mm)	Weight (mg)
Ultem	No filler	Ultem	0.05	4	0.04
	GO* 0.5%				
	GO* 2.5%				
	GO* 5%				
Matrimid	No filler	Matrimid	0.04	4	0.04
	TS-1 Z* 10%				
	TS-1 Z* 20%		0.05	4	0.04
	TS-1 Z* 30%				
	ETS -10 Z* 30%				
6FDA-DAM:DABA 3:1	No filler	6FDA-DAM:DABA 3:1	0.04	4	0.03
	GO* 0.5%				
	GO* 2.5%				
	GO* 5%				
PERVAP™	4060	PDMS	0.200	30	95.9
PP	-	PP	0.004	38	4.2
PS	-	PS	0.029	38	34.7

* GO = Graphene oxide

* Z = Zeolite

prepared solutions A and B. Solution A (the silica source) was prepared by mixing the desired amount of TEOS (tetraethoxysilane) and TPAOH (tetrapropylammonium hydroxide), while solution B (titanium source) was prepared by mixing TBOT (titanium (IV) n-butoxide) and 2-propanol. After the addition of water to reach the final molar ratio of the solution 0.01 TiO₂:1 SiO₂:0.18 TPAOH:75 H₂O followed the hydrolysis and hydrothermal step. The detailed procedure description can be found in the work [46].

Polymers used as continuous phases were commercial polyimide Matrimid® 5218 kindly supplied by Huntsman, commercial polyetherimide Ultem® 1000 supplied by SABIC, and 6FDA-DAM:DABA 3:1 synthesized in our laboratory. The polyimide 6FDA-DAM:DABA 3:1 was synthesized using a two-step polycondensation reaction (synthesis of polyamic acid and thermal imidization in solution) as described in work [47].

Commercial PDMS membrane PERVAP 4060 was purchased from DeltaMem AG. PERVAP 4060 is a thin film composite membrane consisting of PDMS thin layer and PET (polyethylene terephthalate) porous support. The membrane is commonly used for organophilic pervaporation. PS and PP are clear dense polymeric films purchased from GoodFellow Cambridge Ltd.

Diethyl Phthalate (DEP) purity 99.5% purchased from Sigma-Aldrich was used as model pollutant. Ultrapure water given from purification system

(Simpli Lab, Millipore S. A., Molsheim, France) set up at institute laboratory.

2.2 Methods

Membrane testes were carried out using *pervaporation* set-up at laboratory equipment of the Institute of Chemical Processes of the Academy of Sciences of the Czech Republic, schematized in Fig. 1. The set-up is composed of three glass reactor cells. Cells temperature is controlled using thermostat Julabo F25 (25-50°C). The volume of 150 mL of DEP solution (300 mg/L) has been in contact with membrane, placed at position 1 of the schema inside glass reactor, during whole experiment. The model wastewater solution has been stirred by magnetic stirrers. The circular surface of each tested membrane was equal 2.05 cm². DEP that permeated through tested membrane has been collected in cooling trap. This was maintained at -25 °C with vacuum applied at the permeate site as a driving force enhancer (80 KPa).

Each membrane has been applied in the *sorption* experiment in order to inspect the affinity of DEP towards the membrane as well as a membrane capacity. DEP solution of concentration 70 mg/L was introduced in clean dark glass bottle. A round shape piece of the tested membrane (2.2 cm diameter) was inserted into 50 ml of DEP solution. The membranes kept swaying in the solution by mechanical agitator Witeg Lbortechnik GmbH, SHO Orbital Shaker set on 115 RPM AT 25° C.

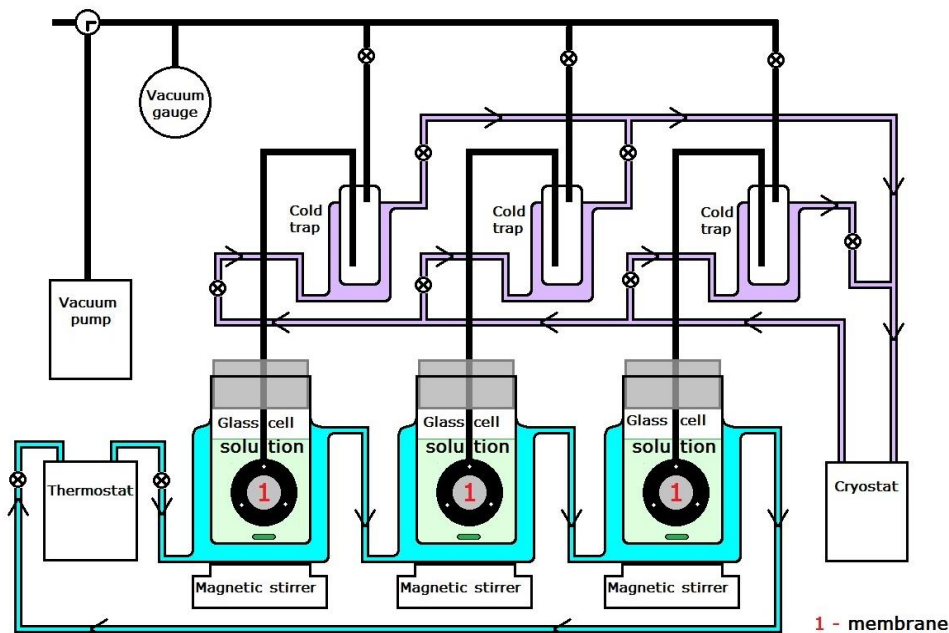


Fig 1. Pervaporation set-up

2.3 Sample analysis

HPLC measurements were carried out on a Dionex 3000 Ulti Mate HPLC from Thermo Scientifics equipped with a binary pump, degasser, diode array detector (DAD), solvent tray and an auto sampler. The used chromatographic column was Luna C18 (5 μ m, 4.6 \times 150 mm, Phenomenex). The detection wavelength was 254 nm. The method for HPLC used isocratic flow of mobile phase composed of 90 % acetonitrile and 10 % ultra-pure water with 0.1 % formic acid as buffer. Temperature was 20-22 $^{\circ}$ C and flow rate was 0.5 mL/min for total time of 10 min.

2.4 Flux

Flux is a key parameter of membrane processes. The eq. (1) was used to calculate the flux of pervaporation experiment. J parameter depends on permeate mass m_{Permeate} diffused through specific surface area A of tested membrane, during a time interval Δt . The flux is expressed on $\text{mg}/\text{h}\cdot\text{m}^2$.

$$J = \frac{m_{\text{Permeate}}}{\Delta t A} \quad (1)$$

3 Results and discussion

In frame of screening various membranes, the separation materials have been tested in *sorption tests* of DEP. Starting concentration of DEP in water was 70 mg/L. All laboratory made membranes were capable to adsorb total amount of DEP during the time of experiments; except membranes based on Matrimid, which were saturated before the end of experiment. A small peak of DEP was visible by

HPLC for this material even at 45th day of sorption. On the contrary, the membranes DAM:DABA have proven to be the fastest sorbents: 50 % of DEP in 6 days. The rest of tested membranes, based on Ultem, have showed a medium sorption capacity. An explication of influence of different fillers is being proceeded.

Newly prepared membranes showed an exceptional sorption capacity (up to 100 % of sorbed DEP) comparing to the commercial membranes (up to 20 % for PDMS, PP and PS).

Pervaporation tests were proceeded with laboratory made membranes. Four of them are presented as an example in Table 2.

Fig. 2. shows DEP elimination from water using different membranes described in Table 2.

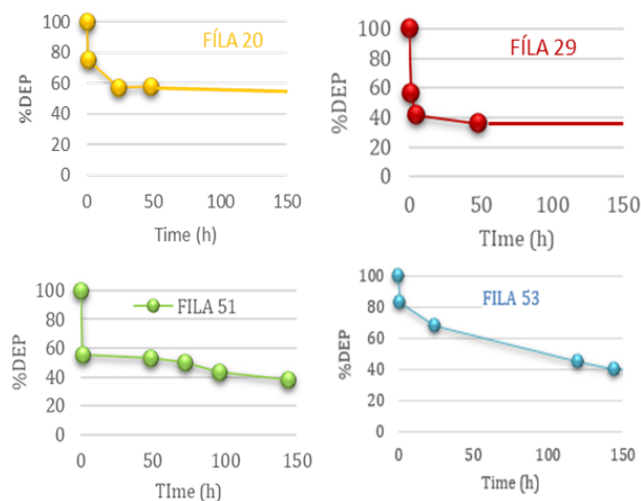


Fig 2. DEP elimination using different membranes.

Table 2. The pervaporation tests applying the membranes made in laboratory.

Membrane	Abbreviation	Temperature (°C)	c DEP (mg/L)	Thickness (mm)	Active surface (cm ²)	Weight (g)
Ultem GO* 2.5%	FILA 20	25	70	0.04	3.6	0.03
Ultem GO* 0.5%	FILA 29			0.05		0.04
Matrimid TS-1 Z* 10%	FILA 51			0.05		0.04
Matrimid TS-1 Z* 20%	FILA 53			0.05		0.04

FILA 51 and 53 (in green and blue below) are both based on Matrimid, however, a difference between their pervaporation activities is visible, depending on % of zeolite. Membrane 51 allows pervaporation of almost 50 % of DEP within the 1st hour, while the membrane 53 is slower. Still, both reach 40 % of DEP in the feed in 150h.

FILA 29 and 20 (in red and yellow below) are – again – made of similar material, Ultem, with noticeable differences in pervaporation process, in favor to the membrane 29 with higher amount of graphene oxide.

Commercial membranes reached similar pervaporation results than laboratory made separation materials, up to 40 % of eliminated DEP. The results have also confirmed expected: the free volume of polymer at higher temperature (50 °C) expands and eases the transfer of DEP through the PDMS membrane, avoiding a saturation (in red and blue for the experimental temperature 25 and 30 °C respectively).

The flow of all tested membranes was between 250 - 50 mg/L.m².h. These dissimilarities are linked to a nature of separation material.

Table 3. The pervaporation tests applying the commercial membranes.

Test	Membrane	Temperature (°C)	c DEP (mg/L)	Thickness (mm)	Active surface (cm ²)	Weight (g)
1	PERVAP™ 4060	25	70	0.18	3.6	0.05
2		30				
3		50				

Pervaporation tests detailed in Table 3 were progressed with commercial membrane. The tests should serve as references to the laboratory made separation materials. The tests were carry on at the different temperatures as well (an example of PDMS in Fig. 3.).

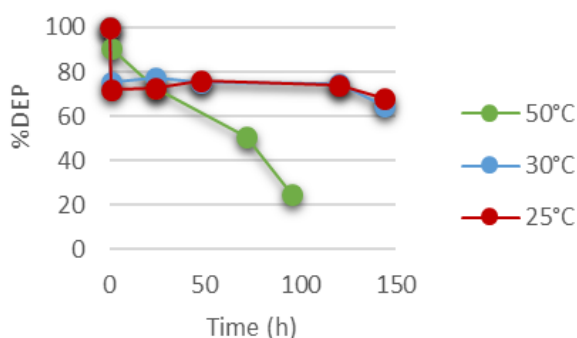


Fig. 3. Elimination of DEP from water in time by commercial membranes.

4 Conclusion

Different kind of membranes, based on Matrimid, Ultem polymers and DAM/DABA, were prepared and applied for pervaporation of diethyl phthalate from water, systematically compared to the commercial materials such as PDMS, PP and PS. Newly prepared membranes showed an exceptional sorption capacity (up to 100 %) comparing to the commercial membranes (around 20 %). The components of active layer played a main role on membrane process. The materials based on Ultem, Matrimid and 6FDA-DAM:DABA 3:1 showed that different types of filling materials added into the matrix have their optimum with respect to the final efficiency of the membrane process. In case of Matrimid and 6FDA-DAM:DABA 3:1 0.5 % of graphene oxide was the most optimal, while 10 % of TS-1 zeolite (Si/Ti=100) added into the Matrimid is slightly more advantageous than 20 %. Nevertheless, all tested membranes - laboratory and commercial - reached similar final pervaporation results, up to

40 % of eliminated DEP. The fastest permeation was achieved by raising the temperature to 50 °C with PDMS membrane, reaching successfully total elimination of DEP in 5 days.

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Contribution of individual authors to the creation of a scientific article (ghostwriting policy)

Flastimil Fila and Jana Gaálová have cooperated on the conceptualization of the research. Mahdi Bourassi, Emma Humbert Martin and Mélanie Bourre have investigated the experiments. Mahdi Bourassi has wrote the original draft of publication. Jana Gaálová has reviewed and edited the publication. All authors have read and agreed to the published version of the manuscript.

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