



# Highly hydrophobic ceramic membranes applied to the removal of volatile organic compounds in pervaporation



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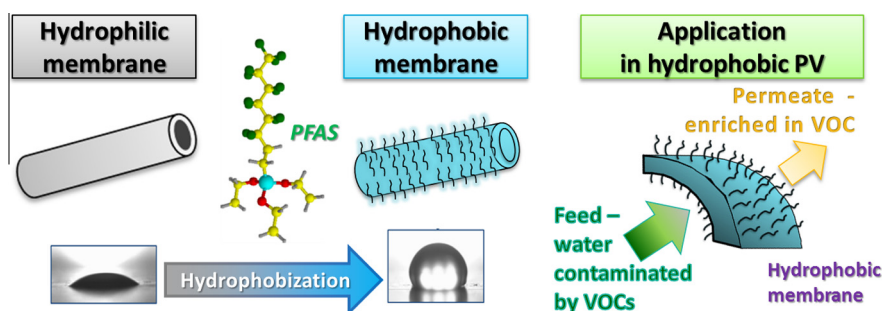
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## HIGHLIGHTS

- TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> ceramic membranes were hydrophobized by using fluorosilanes.
- Efficient removal of VOCs was obtained using hydrophobic pervaporation (PV).
- Hydrophobic ceramic membranes were successfully applied for removal of MTBE and EtAc.
- Hydrophobized TiO<sub>2</sub> membrane removed VOCs with the highest efficiency.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Highly hydrophobic titania, alumina and zirconia porous ceramic membranes were prepared by grafting of C<sub>6</sub>F<sub>13</sub>C<sub>2</sub>H<sub>4</sub>Si(OEt)<sub>3</sub> (C6) and C<sub>12</sub>F<sub>25</sub>C<sub>2</sub>H<sub>4</sub>Si(OEt)<sub>3</sub> (C12) molecules and subsequently applied in pervaporation (PV) process for removal of volatile organic compounds (methyl tert-butyl-ether/MTBE and ethyl acetate/EtAc) from binary aqueous solutions. Transport of pure water through pristine and hydrophobized membranes were compared. The transport and separation properties in PV process of investigated hydrophobic membranes were discussed. The influence of the membrane materials, pore size of the membranes as well as conditions of the grafting procedure (time and type of molecules) on the pervaporative properties was presented. All investigated membranes were selective toward organic compounds. The highest efficiency was found for the TiO<sub>2</sub> membranes, independently of the utilized system and applied grafting molecules. Better transport and selective properties were observed for membrane modified by C6 molecules than by C12 ones. TiO<sub>2</sub> and ZrO<sub>2</sub> membranes modified by C6 were characterized by high β separation factors 84 (TiO<sub>2</sub>) and 56 (ZrO<sub>2</sub>). The least effective membrane was alumina one. Additionally, the influence of contact of different solvents (water, EtAc and MTBE) with the hydrophobic layer was discussed. It was found that in the presence of organic compounds in the aqueous solution, the conformation of hydrophobic chains is changing from tangled to straight one.

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## 1. Introduction

Volatile organic compounds (VOCs) are widely used in the manufacture of various products including refrigerants, plastics,

adhesives, paints and petroleum products [1–8]. To eliminate or recover these compounds from wastewaters, the classical separation processes like distillation are usually applied, regardless high energy demand or formation of azeotropes [2,6,8–13].

New regulations regarding chemical emission limits in particular volatile organic compound (VOC) demand more efficient and less costly technologies. Recently, various techniques for

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### List of symbol and abbreviations

$\beta$	separation factor in pervaporation [dimensionless]	NF	nanofiltration
$\Delta P$	pressure difference at the liquid–gas interface [bar]	OH	hydroxyl group
$\Delta p$	pressure difference between two sides of the membrane [bar]	PDMS	polydimethylsiloxane
$\gamma_L$	surface tension of liquid [ $\text{N m}^{-1}$ ]	$P_i$	permeance coefficient of component [ $\text{kg h}^{-1} \text{m}^{-2} \text{bar}^{-1}$ ]
$\theta_{ef}$	effective contact angle [ $^\circ$ ]	PFAS	perfluoroalkylsilane
$A$	effective area of the membrane [ $\text{m}^2$ ]	$p^p$	permeate pressure [bar]
$\text{Al}_2\text{O}_3$	alumina	$p_i^{\text{sat}}$	saturated vapor pressure of the pure component $i$ at given temperature [bar]
C6	1H,1H,2H,2H-perfluorooctyltriethoxysilane	$P_i/l$	permeance [ $\text{kg h}^{-1} \text{m}^{-1} \text{bar}^{-1}$ ]
C12	1H,1H,2H,2H-perfluorotetradecyltriethoxysilane	PSI	pervaporation separation index
$C_{\text{PFAS}}$	concentration of the grafting molecules [M]	PV	pervaporation
EtAc	ethyl acetate	PVDF-HFP	poly(vinylidene fluoride-co-hexafluoropropene)
GS	gas separation	$r$	radius of the sphere [m]
$J_t$	total permeate flux [ $\text{kg h}^{-1} \text{m}^{-2}$ ]	RO	reverse osmosis
$J_i$	partial permeate flux of $i$ component [ $\text{kg h}^{-1} \text{m}^{-2}$ ]	$t$	time of permeation [h]
$J_v$	water flux across the membrane [ $\text{kg h}^{-1} \text{m}^{-2}$ ]	TCD	thermal conductivity detector
$l$	membrane thickness [m]	$\text{TiO}_2$	titania
$L_p$	hydrodynamic permeability coefficients [ $\text{kg h}^{-1} \text{m}^{-2} \text{bar}^{-1}$ ]	$t_{\text{mod}}$	grafting time of the ceramic membrane [h]
$\text{LEP}_w$	liquid entry pressure for water [bar]	$T_{\text{mod}}$	grafting temperature [ $^\circ\text{C}$ ]
MD	membrane distillation	UF	ultrafiltration
$m_t$	total weight of the compound in the permeate [kg]	VOC	volatile organic compound
MTBE	methyl-tert-butyl-ether	$Y_1$ and $x_1$	mass fractions of the compound 1 in the permeate and feed
MWCO	molecular weight cut off	$\text{ZrO}_2$	zirconia

recovering VOCs from air and water, such as adsorption, condensation, absorption, oxidation, distillation, anaerobic/aerobic biological treatment, bioreactors and membrane technology [10,12,14–19] have been implemented. Additionally, in the case of the VOCs usage, the pollution problem exists if these products are released to the environment in an uncontrolled manner.

Membrane-based separation becomes an alternative technology for many industrial applications [20–24]. The emerging membrane technology like pervaporation (PV) [9–11] can offer an appropriate replacement, especially in the removal of VOCs from industrial wastewaters or contaminated groundwaters [6,8,12]. For the water purification, the other membrane-based techniques can be utilized e.g. membrane distillation process (MD) [25–27]. The separation of water and glycerol [25] as well as removal of ethanol from water [26] can be achieved by applying sweeping gas MD. Shirazi et al. [28] used the electrospun microporous polystyrene membranes for the treatment of biodiesel wash water effluents. The purification process by depth filtration process was very efficient leading to the reduction of chemical oxygen demand by 75%, biological oxygen demand by 55%, total solids by 92% and total dissolved solids by 96% [28].

Pervaporation is a membrane separation technique which has become an industrial process in recent years [3,5–7,9,11–13,29]. This process is mostly used for the dehydration of organic solvents but it can be also applied for the separation of binary organic–organic mixtures, extraction of organics from aqueous solutions, and/or recovery of aroma compounds in the food and cosmetic industry [3,5–7,9,11–13,29–31]. Removal of organics from aqueous solutions is of particular interest for recycling process waters and for the treatment of wastewaters.

Methyl tert-butyl ether (MTBE) and ethyl acetate (EtAc) are examples of volatile organic solvents applied at industrial scale. These solvents are used in large quantities but simultaneously they are hazardous and create health problems to humans [1].

The possibility of MTBE removal by pervaporation using hydrophobic polymeric hollow fiber membranes (30 nm pore size) was investigated by Keller and Bierwagen [32]. Removal efficiencies were found to be in the range from about 20% to over 95% (with

decreasing feed flow rate) over temperature range of 23–40  $^\circ\text{C}$  for a 100 ppm aqueous MTBE feed solution. Vane et al. [16] found MTBE separation factors of up to 930 for pervaporation of 9–900 ppm aqueous MTBE solutions and temperature range of 40–80  $^\circ\text{C}$ , using silicon rubber sheet membranes. The maximum MTBE flux reported in the above study was about  $0.03 \text{ kg m}^{-2} \text{ h}^{-1}$  [16]. Kujawski [33] compared pervaporation of up to 4 wt.% aqueous MTBE solutions through polydimethylsiloxane (PDMS), zeolite-filled PDMS, and poly(ether-block-amide) membranes. For feed concentrations of 1 wt.% MTBE, the PDMS membranes provided separation factors of up to 255 with respect to MTBE over a total permeation rate in the range of  $0.025\text{--}0.2 \text{ kg m}^{-2} \text{ h}^{-1}$ . Remarkably, the zeolite presence in PDMS membrane did not significantly impact the separation factor [33]. Lower separation factors but higher fluxes were found for poly(ether-block-amide) membranes. This type of membrane demonstrated a separation factor of 38 with respect to MTBE at a total permeation rate of about  $0.7 \text{ kg m}^{-2} \text{ h}^{-1}$  [33].

Removal of EtAc from aqueous solutions is of interest for recovery of solvents and for treatment of wastewaters. Tian et al. [34] and Zhu et al. [35] used the poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) membrane to separate EtAc from its aqueous solutions. Nguyen et al. [36] prepared PDMS dense membranes cross-linked in different conditions for pervaporative separation of EtAc-water mixtures, investigating the influence of cross-linking conditions on the membrane swelling and the selectivity of solvent sorption.

Recently, a great increase of interest in the different applications of ceramic membranes can be observed [6,11,12,37,38]. This kind of membranes opens wide perspectives for commercial applications in many various separation processes such as ultrafiltration (UF) [39,40], nanofiltration (NF) [41–43], reverse osmosis (RO), gas separation (GS) or pervaporation (PV). Ceramic membranes offer several advantages over polymeric membranes such as mechanical resistance, chemical inactivity, non-swelling behavior, thermal stability and uncomplicated cleaning [27,44]. Commercial ceramic membranes are usually made from metal oxides like alumina, zirconia and/or titania. These materials originally possess a

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