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Removal of hazardous volatile organic compounds from water by vacuum pervaporation with hydrophobic ceramic membranes

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ABSTRACT

Hydrophobic alumina and titania micro and mesoporous ceramic membranes were prepared by grafting of $C_6F_{13}C_2H_4Si(OEt)_3$ (C6) molecules and subsequently applied in a pervaporation (PV) process to the removal of hazardous organic solvents (MTBE, EtAc and BuOH) from binary aqueous solutions. The transport and separation properties of investigated membranes were discussed. Additionally it was found that membrane material and grafting time have an important impact of the pervaporative properties. All tested membranes were selective toward organics. Titania membrane was the most efficient and was characterized by the highest value of PSI and the highest value of permeate flux of organic compounds in water–EtAc ($J_{EtAc}=1.1$ kg h^{-1} m^{-2}; $PSI_{EtAc}=140$ kg h^{-1} m^{-2}) and water–MTBE ($J_{MTBE}=1.0$ kg h^{-1} m^{-2}; $PSI_{MTBE}=194$ kg h^{-1} m^{-2}) systems. This behavior of titania membrane was also discussed based on the Hansen solubility parameters. In presented work the evaluation of MTBE removal degree with titania modified membrane from water binary mixture in the pervaporation process was discussed.

1. Introduction

Currently, many industries apply organic solvents in technological processes. The production of huge amounts of wastewaters is a negative side-effect of industrial activity, as wastewaters cause serious environmental problems and can generate health problems to humans [1–5]. Volatile organic compounds (VOCs) are widely used in the manufacture of various products including refrigerants, plastics, adhesives, paints and petroleum products [2,4,6–11]. To eliminate or recover these compounds from wastewaters, the classical processes as distillation are usually applied, regardless high energy demand or formation of azeotropes [5,6,9,11–15].

The treatment methods for removing VOCs include air stripping, adsorption, advance oxidation, distillation, anaerobic/aerobic biological treatment, bioreactor and membrane technology [13,15–21]. The methods have some shortcomings and limitations. Air stripping is conventionally used for this purpose due to its simplicity and low cost of operation [13,16]. However, it is effective for high volatile compounds (high Henry's constants). Besides, it shifts the water pollution to air pollution. Adsorption is economic only at low VOC levels due to the high cost of the adsorbents and the need for its frequent regeneration [22]. Biological treatment is a clean method, but it is time consuming and effective only at low VOC level. Advanced oxidation is efficient for specific compound but it maybe forms new products that are more harmful than the original ones.

Wijmans et al. proposed a hybrid process combining air-stripping with a membrane separation to recover VOCs from the stripper off-gas [23]. This can avoid a water pollution problem becoming an air pollution problem. Vapor permeation through membranes offers significant opportunities of energy saving and reuse of VOCs compared to the conventional VOC control process, particularly if the VOC concentration is high.

The emerging membrane technologies like pervaporation (PV) [12–14] and membrane distillation (MD) [6,14] could become appropriate alternatives, especially in the removal of volatile

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Abbreviations: BuOH, butanol; C6, 1H,1H,2H,2H-perfluorooctyltriethoxysilane; EtAc, ethyl acetate; J_t, total permeate flux [kg h^{-1} m^{-2}]; J_i, partial permeate flux of i component [kg h^{-1} m^{-2}]; LEP_w, liquid entry pressure for water [MPa]; MD, membrane distillation; MTBE, methyl tert-butyl-ether; MWCO, molecular weight cut off; PDMS, polydimethylsiloxane; PFAS, perfluoroalkylsilane; PFSA, poly fluoro sulfonic acid; PSI, pervaporation separation index; PV, pervaporation; PVDF-HFP, poly(vinylidene fluoride-co-hexafluoropropene); TEOS, tetraethyl orthosilicate; T_f, feed solution temperature [°C]; T_p, permeate solution temperature [°C]; T_{mod}, temperature of modification [°C]; t_{mod}, modification time [h]; VOC, volatile organic compound; Δ, distance parameter [MPa$^{1/2}$]; δ_d, Hansen's dispersion solubility parameter [MPa$^{1/2}$]; δ_p, Hansen's polar solubility parameter [MPa$^{1/2}$]; δ_h, Hansen's hydrogen bonding solubility parameter [MPa$^{1/2}$]

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organic compounds (VOCs) from industrial wastewaters or contaminated groundwater [9,11,15].

Methyl tert-butyl ether (MTBE), ethyl acetate (EtAc) and butanol (BuOH) are examples of volatile organic solvents utilized at industrial level. These solvents are used in large quantities but simultaneously they are hazardous and create health problems to humans [1,2]. Table 1 gathers properties of selected VOCs like BuOH, EtAc and MTBE. Additionally in Table 1 hazardous classification of these solvents according the REACH regulation is presented [24].

MTBE is produced on a large scale from isobutene and methanol and is used as a fuel enhancer to improve the octane rating [10,11]. In USA, MTBE had been used as a gasoline additive at low levels since 1979 due to its antiknocking properties. Between 1992 and 2004, MTBE had been used at concentrations of up to 5% in gasolines to fulfill the oxygenate requirements set by Clean Air Act [10,11]. For that reason, the production of MTBE in USA increased from 0.2 to 9.5 million tons per year between 1995 and 2004 (Fig. 1A). However, the presence of MTBE in groundwater and drinking water has become a significant environmental issue especially in California [10]. The global demand of MTBE in 2000 was over 19 million tons, decreasing to 12 million in 2011. Nowadays, the leader in the MTBE production is the Asia-Pacific region [2,26].

Ethyl acetate is a very important solvent (Table 1) in the chemical industry, and it is widely used in production of perfumes, plasticizers, varnishes, synthetic resins and adhesive agents because of its low toxicity, good volatility (heat of vaporization is 31.9 kJ mol^{-1}) and favorable solubility (miscible with almost all common organic liquids) [28,29].

The production of EtAc is commonly based on an esterification process of acetic acid with ethanol [15,28–31]. Removal of EtAc from aqueous solutions is of interest for recovery of solvents and for treatment of wastewater. Tian and Jiang [32] and Zhu et al. [33] used the poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) membrane to separate EtAc from its aqueous solutions.

Table 1
Chosen physicochemical properties of investigated solvets and their hazardous classification [14,17,18].

Properties of solvents	Water	Butanol	MTBE	Ethyl acetate
Molecular weight (g mol $^{-1}$)	18.01	74.12	88.15	88.11
Molar volume (ml mol^{-1})	18.1	91.5	119.0	97.8
Boiling point (°C)	100.0	117.5	55.2	77.1
Solubility of solvent in water (g/100 g H_2O)	–	9	4.8	8.3
Solubility of water in solvent (g/100 g solvent)	–	19.7	1.4	3.3
Dielectric constant at 20 °C	80.1	17.9	4.5	6.02
Dipole moment (D)	1.82	1.66	1.32	1.78
Kinetic diameter (Å)	2.65	5.0	6.2	7.0
p_{sat} at 35 °C (kPa)	5.61	1.83	50.00	20.14
Hazardous classification according to REACH [16]	–	H226, H302, H315, H318, H335, H336	H225, H315	H225, H319, H336

H225 highly flammable liquid and vapor.
H226 flammable liquid and vapor.
H302 harmful if swallowed.
H315 causes skin irritation.
H318 causes serious eye damage.
H319 causes serious eye irritation.
H335 may cause respiratory irritation.
H336 may cause drowsiness or dizziness.

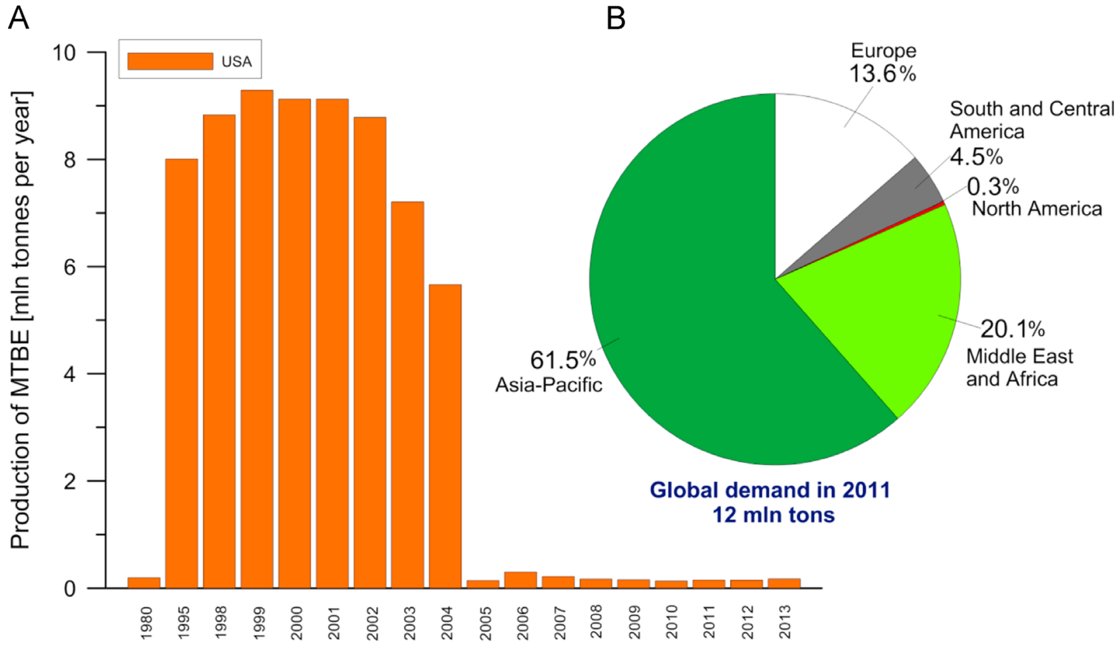

Fig. 1. A – Production of MTBE in Europe and USA; B – MTBE global demand by region in percentage in 2011 [10,11,27].