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Removal of trace phthalate esters from water by thin-film composite nanofiltration hollow fiber membranes

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HIGHLIGHTS

- NF hollow fiber membrane could remove PAEs from water effectively.
- The steric hindrance played an important role in PAE removal.
- The effects of operation parameters on the removal of PEAs were investigated.

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ABSTRACT

Rejection behavior of five kinds of phthalate acid ester (PAEs) including dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), di-n-octyl phthalate (DnOP) and diethylhexyl phthalate (DEHP) from water sources using lab-fabricated hollow fiber nanofiltration (NF) membranes were investigated. Adsorption kinetic behaviors of PAEs were studied as well as the different operation parameters on the rejection of PAEs. The results showed that the times in which PAEs reach saturation adsorption on membrane surface are different. The equilibrium time increased with the molecular weight of the PAE increase. After the PAE reached adsorption equilibrium, the rejection rates of DMP, DEP, DBP, DnOP and DEHP by NF membranes were 82.3%, 86.7%, 91.5%, 95.1% and 95.4%, respectively. The influence of operation parameters including the operation pressure, pH, ionic strength, and temperature on PAE rejection behaviors were also studied.

1. Introduction

Since the 1990 s, endocrine disrupting chemicals (EDCs) in water resources have received significant attention worldwide due to their adverse effects on human health and other organisms, including disruption to endocrine systems and the development of the nervous and immune systems, and other organs [1–4]. EDCs consist of different kinds of compounds, such as polychlorinated biphenyl, phthalate ester, polyaromatic hydrocarbons, bisphenol A, natural hormone, pesticides, etc. [5,6]. Among them, phthalate esters (PAEs), one of the most widely used synthetic substances, has been considered the most common EDCs detected in water resources [7].

PAEs are used as nonreactive plasticizers in the industrial processes of many plastic products, including toys, cosmetics, building materials, insect repellents, automobile parts and food packaging [8,9]. As a result of extensive manufacturing and applications, approximately five million tons are produced globally every year [10]. Thus, PAEs have been detected in all types of environmental samples around the world—not only in air, water, soils and sediments—but also in tissues and fluids of wildlife [11–15]. Potential health risks of PAEs have become a great public concern because everyone is inevitably exposed to PAEs from the consumption of contaminated surface water and aquatic organisms [16]. Recent studies on PAEs and their metabolites indicate that they have a negative influence on reproductive processes, and they will disturb endocrine system activities [11,17]. The crux of this problem lies in the inability of conventional water treatment processes to control these emerging micro-pollutants effectively. More effective

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technologies have to be introduced to remove PAEs from water before they are discharged into the environment.

Membrane separation technologies can be an alternative to conventional water treatment systems due to their high removal efficiency of micro-pollutants, non-toxic byproduct reactions, and ease of operation [18]. Among them, nanofiltration (NF) is a relatively new pressure-driven membrane process, which can separate and remove EDCs and PAEs by reverse osmosis (RO) and ultrafiltration (UF) [19]. Compared with RO, NF has some outstanding advantages, such as: a high permeability for monovalent ions and a low permeability for multivalent ions, lower operation pressure, higher permeate flux and lower energy consumption. Compared to UF, NF membranes have a lower molecular weight cut-off (MWCO) ranging from 200 to 1000 Da [20,21]. As a result, NF has been widely investigated as a feasible and promising option for the removal of EDCs from water, such as bisphenol A [18,22], natural hormones [23,24], polyaromatic hydrocarbons [25,26], and pesticides [27,28]. However, research concerning the use of NF membranes for the removal of PAEs has rarely been reported [29,30]. Moreover, it should be noted that the membranes used in the aforementioned studies concerning the removal of EDCs, including PAEs, were all thin-film composite NF flat-sheet membranes.

Hollow fiber membranes provide a considerably larger surface area per unit module volume, are mechanically self-supporting, and are easier to handle during module fabrication and system operation compared to flat-sheet membranes [31]. Therefore, in recent years there has been a growing interest in developing thin-film composite NF hollow fiber membranes for the treatment of wastewater containing micro-pollutants. To the best of our knowledge, however, there is no literature available on the study of thin-film composite NF hollow fiber membrane performance for the removal of PAEs from water.

Accordingly, the purpose of the present study is to explore the possibility of trace PAE removal from water by the thin-film composite NF hollow fiber membranes. Experimental research will be mainly focused on five kinds of PAEs, such as dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), di-n-octyl phthalate (DnOP) and diethylhexyl phthalate (DEHP). Adsorption kinetic behaviors of PAEs on the NF hollow fiber membranes were studied. The performance of NF hollow fiber membranes for the removal of PAEs were also investigated by varying the following experimental parameters: operation pressure, feed pH, ionic strength and temperature.

2. Methodology

2.1. Materials

The thin-film composite NF hollow fiber membranes, prepared in our lab and characterized previously, will be employed to remove PAEs from water [32]. The hollow fiber membranes were made by interfacial polymerization of piperazine and trimesoyl chloride on PS/PES supporting membranes. The detailed characteristics of NF hollow fiber membranes are presented in Table 1. The pure water flux and $MgSO_4$ rejection rate was tested at pH 7 and 0.4 MPa with temperature of 25 °C. The $MgSO_4$ solution concentration was 1 g/L.

All tested PAEs listed in Table 2 (purity > 99.0%) were purchased from Aladdin Chemistry Company, China. The chemical structures of five kinds of PAEs are shown in Fig. 1. HPLC-grade n-hexane, methanol and ethanol were purchased from Tianjin Shield Chemical Reagent Company, China. All other chemicals are analytic grade and used without further purification. Deionized water (DI) (pH ≈ 6.8), treated with reverse osmosis membranes, and was used in all experiments.

Table 2
Characteristic of the tested solutes.

Solutes	Molecular formula	Molecular weight	Molecular width (nm)	Molecular length (nm)	Log k_{ow}
DMP	$C_{10}H_{10}O_4$	194.18	0.366	1.048	1.60
DEP	$C_{12}H_{14}O_4$	222.24	0.405	1.190	2.47
DBP	$C_{16}H_{22}O_4$	278.34	0.409	1.451	4.90
DnOP	$C_{24}H_{38}O_4$	390.56	0.394	1.968	8.10
DEHP	$C_{24}H_{38}O_4$	390.56	0.525	1.658	7.60

2.2. Experimental setup

The NF membrane performance experiments in this study were conducted using a lab-scale cross-flow filtration apparatus at a constant flow in a batch circular mode. Both the permeation and retentate were recycled back to the feed tank in order to keep a constant concentration during the nanofiltration run. The schematic diagram of the NF experimental apparatus is shown in Fig. 2. In the experiments, each NF membrane module contains 8 hollow fibers with a 0.8 mm inner diameter and an approximately 17.0 cm length, resulting in an effective area of approximately 34 cm^2. The feed solution is pumped into the lumen side of hollow fibers, while the permeate solution exits from the shell side.

2.3. Membrane performance

Each PAE solute was dissolved in methanol at ca. 1000 mg/L first. A stock solution of each PAE is prepared by dissolving appropriate amount methanol solution in DI water prior to conduct the experiments. Concentrations of PAEs in both the feed and permeate are measured to study the adsorption kinetics behavior of the NF hollow fiber membranes. The performance of NF hollow fiber membranes in terms of PAEs rejection rates and permeate flux under different operation conditions, such as operation pressure, feed pH, ionic strength and temperature, were studied. The filtration characteristics, including permeate flux (F) and solute rejection rate (R), were determined.

The permeate flux is calculated according to the following formula:

$$F = \frac{V}{A \cdot \Delta t} \tag{1}$$

where V is the volume of the water or solution permeated during the experiment (L), A represents the membrane area (m^2), and Δt denotes the operation time (h).

The solute rejection rate (R) is defined as:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{2}$$

where R is the observed rejection rate, C_p and C_f (μg/L) are the concentrations of the solute in the permeate and feed, respectively.

Table 1
Characteristics of NF hollow fiber membranes used in this study.

Characteristics	Material	MWCO	Isoelectric Point (IEP)	pH tolerance	$MgSO_4$ rejection	Pure water flux	Tensile strength
NF hollow fiber membranes	Polyamide	520 Da	6.6	2–11	96.2%	47.5 (L/m^2h)	7.7 MPa