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Retentions of bisphenol A and norfloxacin by three different ultrafiltration membranes in regard to drinking water treatment

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HIGHLIGHTS

- Bisphenol A and norfloxacin were treated through membrane filtration.
- Influencing factors were investigated in filtration.
- The initial concentration and ionic strength on retention were minor.
- Charge effect and adsorption have an important influence on retention.
- The adsorption forces here were relatively weak.

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ABSTRACT

The retention efficiencies of bisphenol A (BPA) and norfloxacin (NOR) by three different ultrafiltration (UF) membranes prepared in laboratory were investigated, together with the influencing factors such as initial concentration, ionic strength, pH, membrane fouling and trans-membrane pressure (TMP). The results show that the effects of initial concentration and ionic strength on retentions is minor for both BPA and NOR. BPA retentions substantially decreased as pH value approached to its p*K*a value, and for NOR they first increased and decreased afterwards with pH change. The retentions are all improved after HA fouling because of the HA block in the membrane pores and the developed cake layer, and it can be concluded that between pollutants and HA there exists not only adsorption with each other but also competitive adsorption for sites on membranes. The retentions of both BPA and NOR decrease with increasing pressure. Generally, the effects of these factors on BPA and NOR retention are different and the retentions of the three UF membranes for NOR always remain at a low level, which needs further investigation.

1. Introduction

Endocrine disrupting compounds (EDCs) and antibiotics in aquatic environment are of increasing concern in the scientific and public health field. Currently, many of EDCs/antibiotics are frequently detected in water and wastewater, indicating that conventional drinking and wastewater treatment processes cannot efficiently remove them [1,2]. Biodegradation is the most important unit in conventional treatment processes and also the most important way for degradation of EDCs and antibiotics, but their degradation mainly depend on resistant strains. Biological toxicity of EDCs and antibiotics leads to rare appearance of domesticated resistant strains and then results in inefficient removal of EDCs and antibiotics [3,4]. As for removal of trace-level organic compounds, individual coagulation is generally not effective [5] while oxidation process just transforms these compounds to another, probably increasing toxicity [2].

As an intermediate in the manufacture of epoxy, polycarbonate and other materials in industry, bisphenol A (BPA), one of the well-known EDCs, has been widely used and heavily released into the aquatic environment [6]. BPA can pattern or block the activity of natural hormones in humans and can attack the human body with its estrogen-like effect [7]. Norfloxacin (NOR), a fluoroquinolone antibacterial agent, is commonly used as drugs to treat enteritis dysentery and urinary tract infections in human. It is documented that NOR is frequently brought into aquatic environments via domestic wastewater effluents, disposal of expired pharmaceuticals and excretion in its original or metabolized form [8]. Although at a very low concentration in the environment, NOR can lead to

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the development of antibiotic resistant bacteria in the long-term low-level exposure [8,9].

Membrane filtration is an effective way for small molecules and trace-level compounds [5]. According to membrane pore size and separating force, membrane filtration can be categorized as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Bing-zhi et al. [10] studied the effect of various factors such as BPA initial concentration, pH, ionic strength and organic matter on removal efficiency from drinking water using hollow fiber microfiltration (MF) membrane, indicating that adsorption played a significant role in BPA removal. Koyuncu et al. [5] investigated the removal of several hormones and antibiotics by NF in mixed solutions and found that addition of antibiotics to hormone solution increased the hormone retentions by membrane. In the three main mechanisms of membrane filtration including size/steric exclusion, adsorption and charge repulsion, micropollutants adsorption on membrane plays a crucial role in affecting retention efficiency [10]. As we know, in these types of UF, NF and RO membrane filtration mode, UF has the relatively higher porosities and then has the most adsorption potential for EDCs and antibiotics. Moreover, UF has the relatively lower operating pressure in filtration, compared with NF and RO which needs higher equipment requirements and more energy consumption [5,11–13].

Polyvinyl chloride (PVC) has been considered as an outstanding membrane materials because of its excellent physical and chemical properties, however the PVC membrane tends to spontaneous wrinkling and its hydrophobic nature causes severe membrane fouling and permeability decline in filtration [14]. In order to improve membrane performance, some inorganic materials have been blended in during the membrane fabrication. Carbon nanotubes (CNTs) [15,16] and iron oxide (Fe_3O_4) [17,18] are the commonly used blended materials, but their mixture, that is magnetic carbon nanotubes, as the blended material is rarely reported.

In this study, three UF membranes blended with different materials (see in Table 1) were prepared in laboratory. To compare the properties of the three UF membranes and acquire a better understanding of the mechanisms concerning the removal of BPA and NOR, the effect of initial concentration, ionic strength, pH, membrane fouling and trans-membrane pressure (TMP) on retention efficiency were investigated.

2. Methods and materials

2.1. Membrane preparation and characterization

Three different blended UF membranes, made from polyvinyl chloride, were prepared in laboratory via a phase inversion method. Detailed composition and characteristics of the lab-prepared membranes are shown in Table 1. The acid-treated MWCNTs were got from ultrasonically treating with a mixture of concentrated acid (V_{H2SO4}:V_{HNO3} = 3:1) for 4 h at 65 °C. MWCNTs/Fe_3O_4 were prepared through a hydrothermal method [24]. For the preparation of PVC-II and PVC-III, acid-treated MWCNTs or MWCNTs/Fe_3O_4 were ultrasonically mixed with solvent N,N-dimethylacetamide (DMAC), followed by addition of PVC and porogen Polyvinylpyrrolidone (PVP) under stirring. The casting solution was stirred at room temperature for 12 h and was kept in the dark for 12 h to remove air bubbles. Then the casting solution was spread into membranes on a glass plate with a membrane applicator, then the membranes evaporated in air for 1 min before immersing into deionized water coagulation bath. The membranes were kept in water at room temperature for 24 h before further use. The preparation of PVC-I was performed with the procedure similar to that of PVC-II and PVC-III, by adding PVC and PVP directly into DMAC to get the casting solution [19]. The mean pore size was calculated via filtration velocity method [20]. Contact angles were characterized by a contact angle goniometer (OCA15, Dataphysics). Zeta potentials of membrane surfaces were determined by solid surface Zeta potential tester (SurPASS, Anton Paar, Austria).

2.2. Solution chemistry and chemicals

BPA and NOR were purchased from Aladdin Industrial Corporation (China). Stock solutions of BPA (100 mg L^{-1}) and NOR (50 mg L^{-1}) were prepared by dissolving 100 mg BPA and 50 mg NOR into 1 L deionized water, respectively. Table 2 describes the characteristics of BPA and NOR. $CaCl_2$ was used to adjust the ionic strength of solution. PH of solution was adjusted using 1 M HCl and NaOH. Humic acid (HA) was chosen to represent NOM and was purchased from Sigma–Aldrich (Saint Louis, Missouri, USA.). All chemicals used in this study were of analytical grade.

2.3. Filtration experiment

Filtration experiment was conducted with a dead-end UF test system at room temperature, with a constant stirring during the experiment [21]. The trans-membrane pressure was set by N_2 pressurization of the cell and could be adjusted in the range of 50–200 kPa. The cell had a volume of 300 mL and an effective filtration membrane area of 35 cm^2. Each batch experiment was conducted in the following steps. First, the fresh membrane was pre-pressured at 100 kPa with pure water in the cell to compact membrane into a stable state, where namely the flux stabilized. Then the emptied cell was filled with 250 mL feed solutions followed by continuing filtering at 100 kPa for 10 min. Concentrations of the BPA and NOR in the permeation and feed solutions were determined by an UV/vis spectrophotometer (8453, Agilent) at 278 nm and 274 nm, respectively.

The retentions were calculated using Eq. (1).

$$R = \left(1 - \frac{C_P}{C_F}\right) \times 100 \quad (1)$$

where C_P and C_F were the concentrations in the permeation and feed solutions, respectively.

Table 1
Detail composition and characteristics of the three membranes.

Membrane No.	Material	Blend material	Mean pore size (nm)	Contact angle (°)	Pure water flux (L/m^2 h)
PVC-I	Polyvinyl chloride	–	33.1 ± 1.1	72.5	90.4 ± 6.2
PVC-II	Polyvinyl chloride	Acid-treated MWCNTs	35.6 ± 0.8	69.6	111.7 ± 4.9
PVC-III	Polyvinyl chloride	MWCNTs/Fe_3O_4[a]	36.3 ± 1.1	63.5	118.3 ± 7.0

[a] Including the same weight acid-treated MWCNTs with PVC-II, prepared through a hydrothermal method described by Hou et al. [24].