

The removal of bisphenol A by ultrafiltration

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Received 17 December 2006; accepted 3 January 2007

Abstract

The removal of bisphenol A (BPA) from drinking water by ultrafiltration membrane (UF) using dead-end model was investigated. The experiment was focused on the effect of various factors on removal efficiency with respect to BPA initial concentration, molecular weight cut offs (MWCOs) of membrane, pH, ionic strength and organic matter. The results showed that UF could remove BPA effectively. UF with 2000–10,000 MWCOs removed BPA by over 92%, with initial concentration of BPA ranging from 100 to 600 µg/L. As pH of solution approached to pK_a (9.6–11.3) of BPA, BPA removal efficiency dropped significantly. The effect of ionic strength on BPA removal was not found. The influence of humic acid on BPA removal was minor. It can be concluded that adsorption play a significant role in BPA removal in UF process.

1. Introduction

The effects of endocrine disrupting chemicals (EDCs) on both human and the environment are of increasing concern [1]. Bisphenol A, one of EDCs, is main material for the manufacture of epoxy, polycarbonate, polysulfone and certain polyester resins. It had been documented that BPA had estrogenic activity and its effects on health have been concerned [2]. In China, a investigation on concentration of EDCs in Huangpu River, which supplied 80% of drinking water for Shanghai city found that many EDCs such as

dibutyl phthalate (DBP), BPA, nonyl phenol (NP) and atrazine presented in Huangpu River, in which the concentration of BPA was as high as 4.36 µg/L [3]. Intensive attempts have been made to develop an effect treatment for EDCs removal [4,5]. It has been reported that NF/RO processes are capable of removing EDCs [6,7]. Katsuki Kimura et al. found that RO removed over 90% of EDCs [8]. Thomas Wintgens et al. conducted experiment for removal of NP and BPA using eleven types of NF having different contact angel and found that removal efficiency was in the range of 70% and 100% and that removal of NP was decreased with increased membrane contact angel [9].

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Presented at the conference on Desalination and the Environment. Sponsored by the European Desalination Society and Center for Research and Technology Hellas (CERTH), Sani Resort, Halkidiki, Greece, April 22–25, 2007.

The objective of this study was to evaluate the removal efficiency of BPA by the UF membrane and investigate the factors influencing retention, such as BPA initial concentration, molecular weight cut offs of membrane, pH of solution, ionic strength and NOM.

2. Materials and methods

Membrane Technique R & D Center Shanghai Institute of Nuclear Research Chinese Academy of Sciences provided UF membrane and cell for this test. The material of membrane was Polyethersulphone (PES) and effect filtration area was $3.32 \times 10^{-3} \text{ m}^2$. Before filtration, the new membrane was soaked in ultra-pure water (Milli-Q) for over 24 h. The main characteristics of membrane are shown in Table 1.

Dead end filtration was used in this test. Ultra-pure water was first introduced into cell (350 mL), pressured at 100 kPa for 1–2 h until stable flux was reached, and then 300 mL of BPA sample was introduced into cell for filtration. When permeate volume was reached 200 mL, filtration was stopped and retentive and permeate sample was collected for analysis.

The test solutions were prepared by dissolving a certain amount of BPA in the ultra-super water (Milli-Q). The BPA (HPLC-grade) was purchased from Sigma Aldrich, China. A Shimadzu LC-2010AHT HPLC system equipped with shim-pack VP-ODS column (150 mm \times 4.6 mm), which has a detection limit of 1 $\mu\text{g/L}$ was used for analysis of BPA in the feed and permeate

Table 1
Main UF membrane characteristics

MWCOs (Da)	Contact angle ($^\circ$)	Pressure (kPa)	Ultra-super water flux ($\text{L/m}^2 \text{ h}$)
10,000	71	100	67.8
6000	61	100	31.2
2000	66	100	15

samples. The mobile phase was acetonitrile (CAN).

Retention and adsorption are calculated by following equations:

$$R = \frac{C_f - C_p}{C_f} \times 100\% \quad (1)$$

$$A = \frac{C_f \cdot V_f - C_v \cdot V_v - C_p \cdot V_p}{C_f \cdot V_f} \times 100\% \quad (2)$$

where C_f , C_v , C_p , and V_f , V_v , V_p are concentration and volume of feed, retentive and permeate, respectively.

3. Results and discussion

3.1. Removal of BPA by UF membrane with different MWCOs

Fig. 1 shows the effect of MWCOs on removing BPA. As initial concentration was below 100 $\mu\text{g/L}$, BPA retention was greater than 95%, regardless of MWCOs. As initial concentration was 100 $\mu\text{g/L}$, BPA retention was slightly reduced from 97.7% with 2000 Da to 93% with 10,000 Da. These results show that although the pore size of membranes tested was several orders of magnitude larger than that of BPA, ultrafiltration has a good effect for removing BPA.

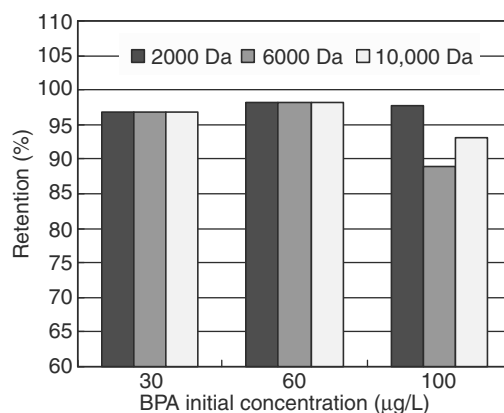


Fig. 1. Effect of MWCOs on removing BPA.

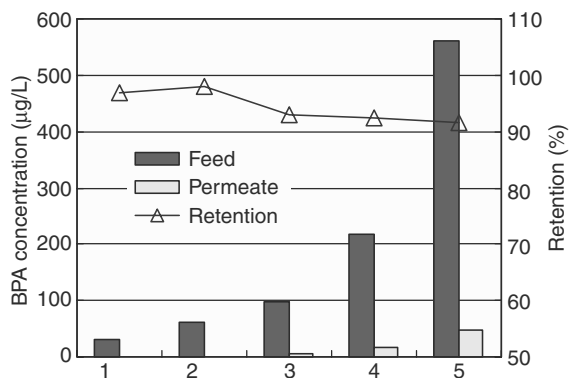


Fig. 2. Effect of initial concentration on removing BPA.

3.2. Effect of initial concentration on removal efficiency

The impact of initial concentration on removing BPA by membrane with 10 kDa of MWOCs is shown in Fig. 2. From Fig. 2, it can be seen that while feed concentration increased permeate concentration was slightly increased with retention slightly reduced from 96% to 92%. This result suggests that initial concentration has no significant effect on BPA retention, which can be contributed to a constant partition coefficient for BPA between membrane and bulk solution [10].

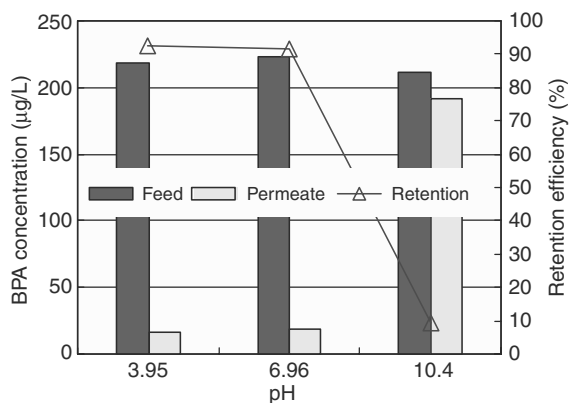


Fig. 3. Effect of pH on retention of BPA.

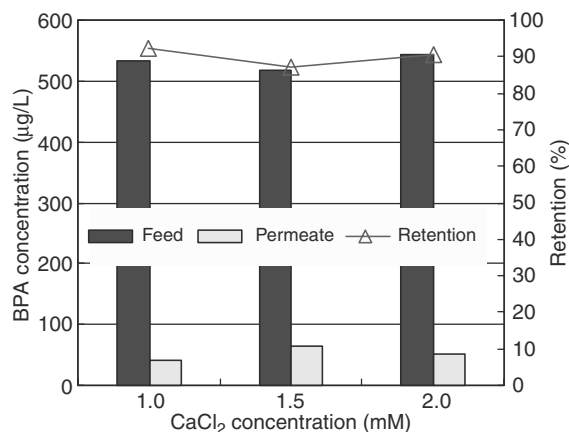


Fig. 4. Effect of CaCl₂ concentration on BPA retention.

3.3. Effect of pH on BPA removal

From Fig. 5, it can be seen that at 3.95 and 6.96 pH values, retention of BPA exhibit as high as over 90%, however, as pH value increase to 10.4, retention drop substantially to 9.3%. This result suggests that low and neutral pH favor retention of BPA by UF membrane. As pH value close the acid dissociation constant pK_a of BPA (9.6–11.3), BPA molecular loses its proton, becoming the negatively charged specie $HO-C_{15}H_{14}-O^-$ and the repulsion force between BPA and negatively charged membrane was

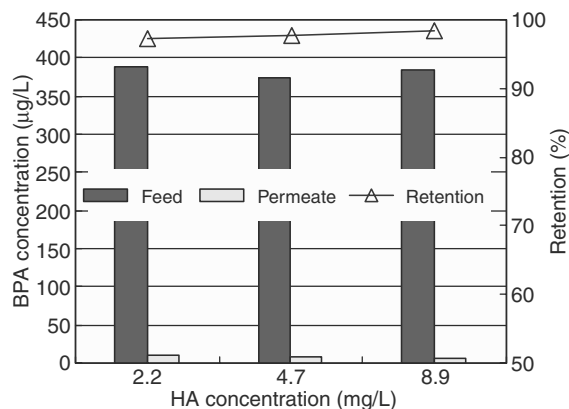


Fig. 5. Effect of HA concentration on BPA retention.

occurred. Because the size of BPA was far below the pore size of membrane, they can easily penetrate pore of membrane, resulting in a reduction in retention.

3.4. Effect of Ca on BPA removal

Effect of CaCl_2 concentration on BPA retention is shown in Fig. 4. Fig. 4 shows that although there is some variation in BPA retention as CaCl_2 concentration increased from 1 mM to 2 mM, no significant change in BPA retention is found. This result indicates that the influence of Ca^{2+} on BPA retention in drinking water is minor, which is in agreement with the result by L.D. Nghiem et al. [1].

3.5. Effect of dissolved organic matter (DOM) on BPA removal

Humic acid (HA) used as a background organics was spiked to solution containing about 380 $\mu\text{g/L}$ BPA to examine the influence of NOM on BPA retention. From Fig. 5, it can be seen that BPA retention was slightly increased from 97.2% to 98.4% with increasing HA from 2.2 mg/L to 8.9 mg/L. This result suggests that HA presented in water favour BPA retention. There are many inconsistent reports with respect to influence of NOM on EDCs retention. E.C. Devitt found that atrazine rejection was greatly enhanced in the presence of NOM and hypothesized that atrazine could associated with macromolecular NOM such as tannic acid through hydrogen bonding to form a atrazine-macromolecular associations and enhanced rejection by size exclusion [11]. Yeomin Yoon et al. experiment showed that the fluoranthene retention by NF and UF was decreased in the presence of NOM and contributed to competition for adsorption sites and pore blockage by NOM [12]. To better understand influence of NOM on BPA retention, two experiments were conducted. One experiment was performed in two steps: first the solution containing

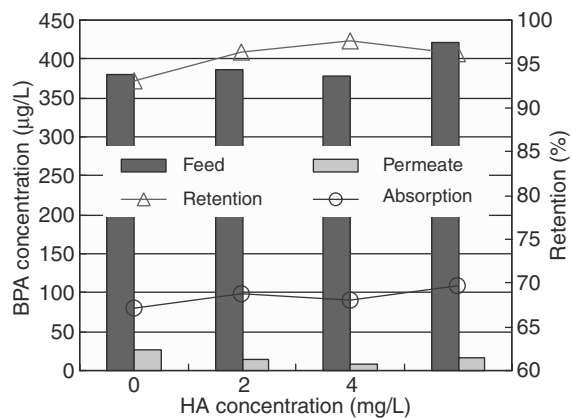


Fig. 6. Effect of HA on BPA retention with BPA after HA filtration.

HA only was filtrated, after that cell was emptied and the solution containing BPA only was filtrated. Another experiment was conducted with the solution containing both HA and BPA. The result is shown in Figs. 6 and 7. Fig. 6 shows that BPA retention and adsorption were more effective in the presence of HA than in the absence of HA. This result can be contributed to the more hydrophobicity of membrane surface by adsorption or rejection of HA.

The BPA retention in mixture of BPA + HA solution filtration is shown in Fig. 7. From Fig. 7, it can be seen that BPA retention was the same as

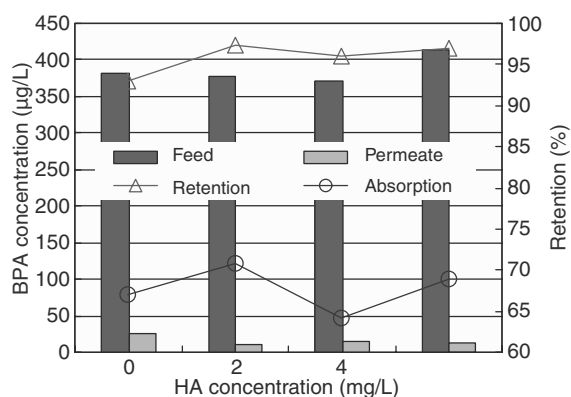


Fig. 7. Effect of HA on BPA retention with mixture of BPA + HA filtration.

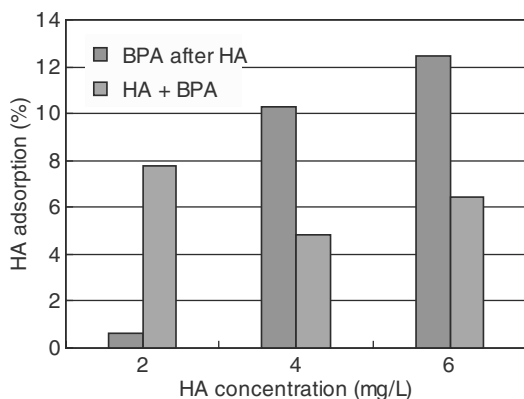


Fig. 8. Effect of BPA on HA adsorption.

Fig. 6, so did BPA adsorption except for 4 mg/L of HA. In order to more distinguish BPA retention mechanism, the HA adsorption with two tests was examined as shown in Fig. 8. In BPA after HA filtration, HA adsorption was increased with HA concentration increased. However, in mixture of HA + BPA filtration, the HA adsorption was lower than that with BPA after HA filtration, except for 2 mg/L concentration. If HA-BPA complexes exist as literatures stated [4,5], HA adsorption should be increased with HA concentration increased. However, this phenomenon is not observed. This result suggests that HA + BPA complex does not exist in this experiment. It is interesting to note that HA adsorption was decreased in the presence of BPA. This phenomenon is explained as the competition for adsorption sites between HA and BPA. The result shows that BPA has a stronger adsorption potential than HA.

4. Conclusions

In this study, BPA retention with a UF membrane using dead-end filtration was examined. The experiment was focused on the effect of various factors on BPA retention in terms of BPA initial concentration, molecular weight cut offs (MWCs) of membrane, pH, ionic strength

and organic matter. The obtained results are summarized as follows:

BPA initial concentration appears to be a minor effect on BPA retention. Although BPA retention was slightly increased with MWCs decreased, no significant effect of MWCs on BPA retention was found. In ultrafiltration of 100 µg/L BPA concentrations at 100 kPa pressure, BPA retention with MWCs of 10 kDa, 6 kDa and 2 kDa were 93.0%, 88.9% and 97.7%, respectively.

As pH values closed to pK_a value of BPA, BPA retention was substantially decreased from around 92% at 3.95 pH and 6.96 pH to 9.3% at 10.4 pH.

BPA retention in the presence of humic acid was favored. The combination of hydrophobic adsorption and competition adsorption for sites appeared to be a major mechanism for BPA retention.

Acknowledgement

This research is financially supported by the National Science Technology Supporting Project “The Key Treatment Technology for safe drinking water for small town” (2006BAJ08B02).

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