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Polyethersulfone nanofibers for the removal of endocrine disruptors

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ABSTRACT

Polyethersulfone (PES) nanofibers were prepared by using electrospinning technique, and then were used for the removal of several endocrine disrupters from aqueous solutions. The structure of the nanofibers was characterized by scanning electron microscopy (SEM). The PES nanofibers could remove bisphenol A and other hydrophobic endocrine disrupters, and showed larger adsorption capacity and fast kinetics of uptaking target species than PES microfibers and PES particles reported in our earlier publications. Furthermore, the adsorbed endocrine disrupters could be effectively removed by ethanol, which indicated that the PES nanofibers could be reused. These results showed that the PES nanofibers have the potential to be used in the environmental application.

Keywords: Polyethersulfone nanofiber; Electrospinning; Adsorption; Endocrine disrupter; Hydrophobic interaction

1. Introduction

Nowadays, the widespread use of chemical compounds around the world has led to serious environmental pollution, especially, the compounds termed endocrine disruptors such as bisphenol A (BPA), biphenyl (BP), p-hydroquinone (BPhe) and so on [1,2]. Endocrine disruptors are active at low concentrations and disturb hormone activities, thereby affecting health, reproduction, and development of humans and animals [3].

Several studies have been reported to remove endocrine disruptors using different methods. Evaporation using hydrophobic polydimethylsiloxane membrane is a good method to remove endocrine disrupters [4]. There is also the method of ultrafiltration process using PES–PVP membranes as well as degradation of endocrine disruptors using bacteria [5,6]. Adsorption of endocrine disruptors is an effective and convenient method. UV-irradiated DNA matrixes can selectively bind endocrine disruptors with a planar structure in aqueous solutions [7]. Endocrine disruptors can be selectively removed by sorption using polydimethylsiloxane membrane [8]. Carbonaceous [9] and clays [10,11] materials can also be used for the BPA removal.

Polyethersulfone (PES) is a well known polymeric material. The PES and PES-based membranes show outstanding oxidative, thermal, and hydrolytic stabilities as well as good mechanical and film-forming properties. The polymer has been widely used in the fields of biomedicine, food, hemodialysis, plasma separator, and water purification, etc. [12–15].

PES hybrid particles and molecularly imprinted particles were prepared to remove endocrine disrupters in our recent studies [16,17]. Molecularly imprinted PES microfibers were also prepared by dry-wet spinning method [18]. In this study, we wonder whether PES nanofiber

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could also be used for endocrine disruptor removal. To prepare nanofibers, electrospinning has been very attractive in the past decade because it is a simple and versatile approach for producing a matrix of fibers with diameters ranging from a few nanometers to micrometers [19].

In the present study, PES nanofibers were fabricated by using electrospinning, and then used for the adsorption of several endocrine disrupters from their aqueous solution. The adsorption capacity and kinetics of uptaking target species were investigated, and the results were compared with the PES particles and PES microfibers.

2. Experimental

2.1. Materials

Polyethersulfone (PES, Ultrason E 6020P, CAS No.25608-63-3) was purchased from BASF chemical company (Germany), and was used to prepare the PES nanofibers. Bisphenol A (BPA), phenol (Phe), p-hydroquinone (BPhe), biphenyl (BP), and ethidium bromide (EB) were purchased from Shanghai Chemical Reagent Co. Ltd. (China), and were used as the model endocrine disrupters. Dimethyl acetamide (DMAC) and ethanol were obtained from Chengdu Chemical Reagent Co. Ltd. (China). All the chemicals are of analytical grade and are used without further purification unless otherwise described. Distilled water passed through ion-exchange columns was used throughout the studies.

2.2. Preparation of the nanofibers

The PES solutions for electrospinning were prepared by dissolving PES in DMAC at room temperature, and the concentration was 21 wt%. The electrospinning was carried out in air at room temperature. The spinning solution was placed in a syringe and was extruded to the spinneret fixed with a metal needle with an inner diameter of 0.5 mm. The tip of the needle was pretreated. The spinneret was connected to a high-voltage supply, which could generate direct-current voltages ranging from 0 to 60 kV. A piston pump was used to feed the polymer solution at the flow rate of 6.0 ml/h. A high voltage was applied to the spinneret, through which the polymer solution was spun with the help of an electrode. The applied voltage used in electrospinning was 15 kV. The tip-collector distance (TCDs) was 6 cm. The fibers were collected in distilled water. Then the fibers were immersed in heated water (80°C) for over 3 days to elute the residual DMAC.

2.3. Preparation of the microfibers and particles

The general methods to prepare the microfibers [18] and particles [19] had been described in detail in our previous papers. Both the microfibers and the particles were prepared by a modified procedure of the phase inversion method. PES solution with the concentration of 21 wt% in dimethylacetamide (DMAC) was extruded into distilled water by using a syringe needle (0.6 mm) at room temperature to prepare porous microfibers with the diameter of about 85 μm. The polymer solution was dropped into distilled water by using a 0.6 mm diameter syringe needle at room temperature to prepare porous particles.

2.4. Scanning electron microscope of the nanofibers

For the SEM observation, the nanofiber samples were freeze-dried. After attaching the samples to the sample supports and coating with a gold layer, a scanning electron microscope (JSM-5900LV, JEOL, Japan) was used for the morphology observation of the nanofibers.

2.5. Specific surface area

Mercury porosimetry (Micromerities, USA, Model no. 1300) was used to determine the specific surface area in the nanofiber, microfiber and particles. The samples were dried at room temperature; about 0.1 g dried sample was used.

2.6. Adsorption experiments and desorption experiments

BPA was dissolved in ethanol, and then diluted in distilled water. The adsorption experiments were carried out as follows: about 0.05 g (wet weight) of the PES nanofibers were applied to 50ml of BPA solutions, with the initial concentrations of 100, 200, 300 μmol/L, respectively, and the temperature 25°C. The BPA concentrations at certain time intervals were determined by using an UV-vis spectrophotometer U-200A (Shanghai Spectrum Instruments Co., Ltd., Shanghai, China) at the wavelength of 276 nm.

The removal ratio and adsorbed capacity of BPA were calculated by using the following formulas:

$$R_t = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

$$Q_t = \frac{(C_0 - C_t) \cdot V}{m} \times 100\% \tag{2}$$

where R_t (%) is the removal ratio of BPA by the nanofibers at the time t; C_0 is the initial concentration of the BPA solutions (μmol/l); C_t is the concentration at the time t (μmol/l); Q_t is the adsorbed BPA amount per gram of the nanofibers at the time t (μmol/g); V is the volume of the BPA solution (l); and m is the weight of the PES nanofibers (g).

The adsorption experiments of several other endocrine disrupters, including phenol (Phe), p-hydroquinone (BPhe), biphenyl (BP), and ethidium bromide (EB), were also carried out using the same method. The concentrations of Phe, BPhe, BP, and EB solutions were measured at the wavelengths of 234 nm, 288 nm, 248 nm, and 286 nm, respectively.

The desorption experiments were carried out as follows: after the adsorption, the PES nanofibers were immersed into 50 ml ethanol, and stirred using a shaker at a speed of 50rpm at room temperature. The concentration of the BPA in the ethanol was determined by using the UV–vis spectrophotometer U-200A. The desorption ratio (Rd) was calculated using following equation:

$$R_d = \frac{m_d}{m_a} \times 100\% \tag{3}$$

where m_d is the amount of the BPA desorbed to the solution; m_a is the amount of the BPA adsorbed to the PES nanofibers, which was calculated from the adsorption experiments.

3. Results and discussion

3.1. Characterization of the nanofibers

An electrospinning method was employed to fabricate the PES nanofibers from PES–DMAC solution. Nonsolvent water was selected as the coagulation medium, which was commonly used to prepare PES membrane. Here, water showed high solubility for DMAC but not for PES and. Therefore, when the PES–DMAC solution was extruded into water, liquid–liquid phase separation that was caused by the rapid exchange of the solvent DMAC and water occurred. With the completion of the exchange between the solvent and the non-solvent, the nanofibers were prepared. Fig. 1 shows the scanning electron micrograph (SEM) photograph of the nanofibers which were magnified 1500×. As we can see, the nanofibers were crisscrossed, accompanied by some beads which were related to the concentration of PES solution [20], and the diameter of the nanofibers ranged from 150 to 500 nm.

3.2. Adsorption of BPA in various concentration solutions

To study the adsorption capacity of the PES nanofibers, adsorption experiments were carried out firstly in various BPA concentrations (100, 200, and 300 μM BPA aqueous solutions) at room temperature. Fig. 2 shows the adsorption kinetic curve of BPA to the PES nanofibers in BPA aqueous solutions. The adsorption amounts (μmol/g) increased with time and the saturated adsorption amounts were observed after about 6 h for all the solutions. The saturated adsorption amounts of BPA were about 88.7, 112.9, 144.0 μmol/g for the PES nanofibers in 100, 200 and 300 μM BPA solutions, respectively. With the increase of BPA concentration in the aqueous solutions, the adsorbed amounts increased. These can be explained by the adsorption theory reported earlier [21].

As shown in the figure, the adsorption was fast at the beginning; in this case, BPA might enter some easy accessible pore sites and bind with the PES nanofibers. After 180 min, the adsorption speed decreased, and the BPA molecules might diffuse into deeper and smaller pore.

3.3. Adsorption of BPA by nanofibers, microfibers, and particles

In this study, the adsorption capacity of PES nanofibers, PES microfibers and PES particles were investigated. The specific surface area of nanofiber, microfiber and particles were summarized in Table 1. Fig. 3 shows the adsorption kinetics of BPA to the three kinds of PES based materials. The saturated adsorption for the particles was observed after 60 h [19]; while that was observed after about 12 h for the microfibers with the diameter of about 85 μm [18], and was observed after about 6 h for the nanofibers. The saturated adsorption amounts of BPA were about 8.3, 23.9 and 88.7 μmol/g, for the particles, the microfibers and the nanofibers, respectively. The adsorption amount for the nanofibers is much larger than

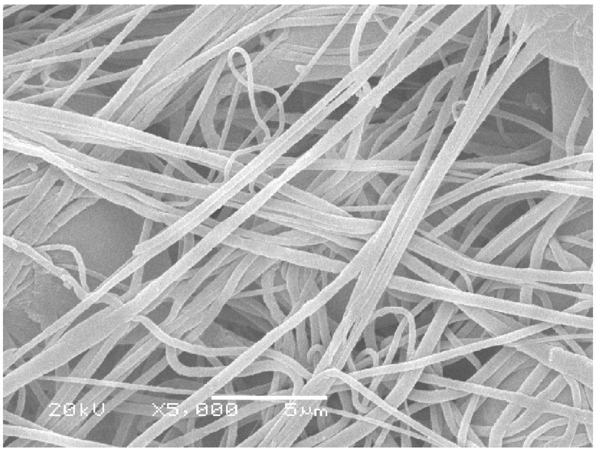

Fig. 1. The scanning electron micrograph (SEM) photographs of the nanofibers which were magnified 1500×.

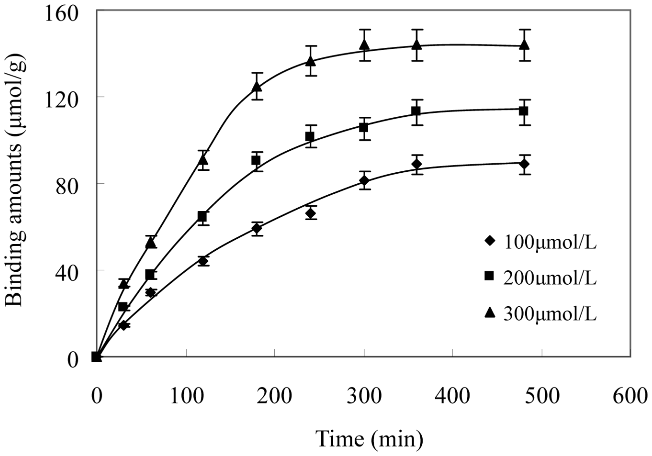

Fig.2. The binding amounts per unit mass of the PES nanofibers in BPA aqueous solutions of different concentrations.

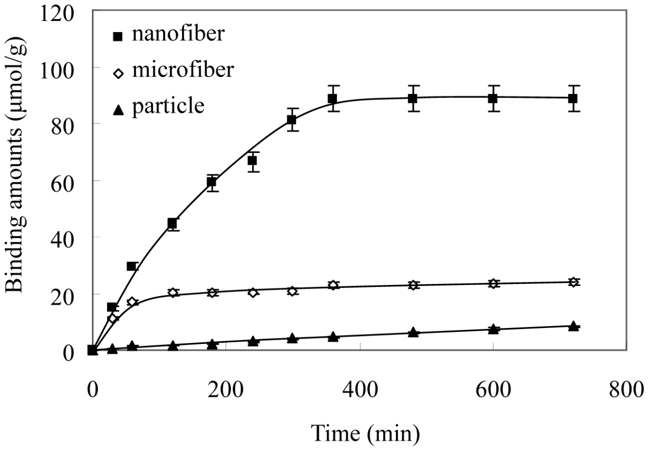

Fig. 3. Binding amounts of nanofibers, microfibers and particles in 100 μmol/L BPA aqueous solutions.

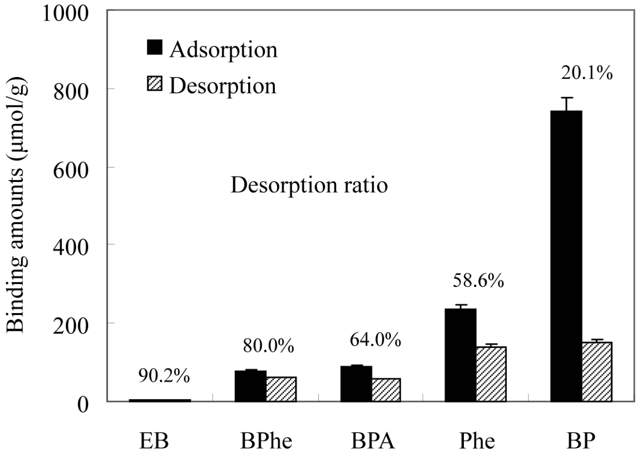

Fig. 4. Binding amounts and desorption ratio of the PES nanofibers for EB, BPhe, Phe, BPA, and BP.

Table 1
Specific surface area of nanofiber, microfiber and particles

	Specific surface area (m^2/g)
Nanofiber	89.40
Microfiber	38.61
Particles	22.13

that for the microfibers and the particles. This might be explained by the largest specific surface area caused by the nano-scale diameter of the nanofiber.

3.4. Adsorption and desorption of endocrine disruptors

To further study the application of the PES nanofibers, the removal of other kinds of endocrine disrupters, such as EB, Bphe, Phe and BP was also investigated. The nanofibers (0.05 g, wet weight) were incubated in the respective aqueous solutions (100 μM, 50 ml) of these compounds for 6 h, then their concentrations were measured, and their adsorbed amounts were calculated using Eq. (2), data are shown in Fig. 4. As shown in the figure, the adsorption amount of EB, Bphe, BPA, Phe and BP were 5.4, 75.8, 88.7, 235.7 and 739.7 μmol/g, respectively. The octanol–water distribution coefficients (LogPow) of the endocrine disruptors EB, BPhe, BPA, Phe, and BP were –1.1, 0.59, 2.02, 1.48, and 3.16, respectively [22,23]. It was found that the adsorption amount of the endocrine disruptors by the nanofiber increased with the increase of LogPow except Phe, which has a smaller molecular weight than the others. According to our previous study [22], the removal of endocrine disrupters is caused by the hydrophobic interaction between the PES and the endocrine disrupters and the microsphere porosity. In this study, we also noticed that with increase of the hydrophobicity of the endocrine disrupters, the adsorbed amounts increased. These indicated that the hydrophobic interaction played more important role than the porosity.

Desorption experiments were also carried out after the adsorption experiment. The nanofibers adsorbed the endocrine disrupters above were immersed into 50 ml ethanol for 24 h respectively. After measuring the respective absorbance, the desorbed amounts were calculated using Eq. (3), data are shown in Fig. 4. As can be seen from the figure, with the increase of the hydrophobicity of the endocrine disrupters, the desorption efficiency decreased. This can also be explained by the hydrophobic interaction between the PES and endocrine disrupters. Furthermore, the removal ratio of BPA, for example, reached nearly 100% after immersed into ethanol for three times (each time for 12 h). These results indicated that the PES nanofibers could be reused.

3.5. Adsorption kinetics study

To investigate the mechanism of adsorption, a simple kinetic model was used to test the experimental data, by applying the equation of the Lagergren [24], which is the first developed equation describing the adsorption of liquid–solid systems based on solid capacity.

$$\ln\left(q_e - q_t\right) = \ln q_e - K_1 t \qquad (4)$$

where q_t is the adsorbed BPA amount at time t (mg/g); q_e is the adsorbed BPA amount at the equilibrium (mg/g); K_1 is the rate constant of pseudo-first-order equation. The slope and the intercept of each linear in Fig. 5 are used to calculate the first-order constant (K_1) and q_e (see Table 2). The correlation coefficients (r^2) of the first order kinetic model are 0.9105, 0.8395, and 0.7862 for 100, 200, and 300 μM BPA solutions, respectively. The values of q_e are 99.6, 156.8 and 235.4 mg/g, respectively, which are

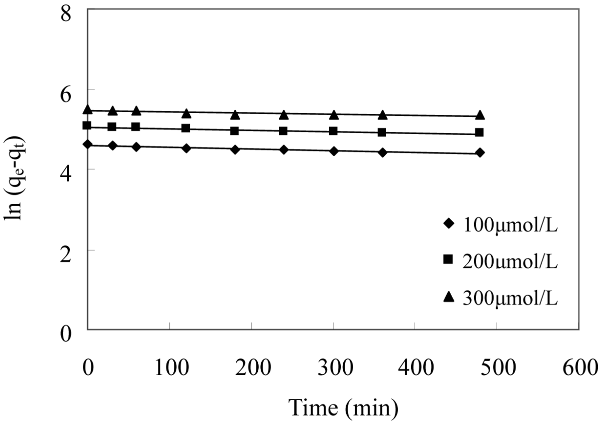

Fig. 5. Application of the pseudo-first-order adsorption model for the adsorption of BPA onto the nanofibers.

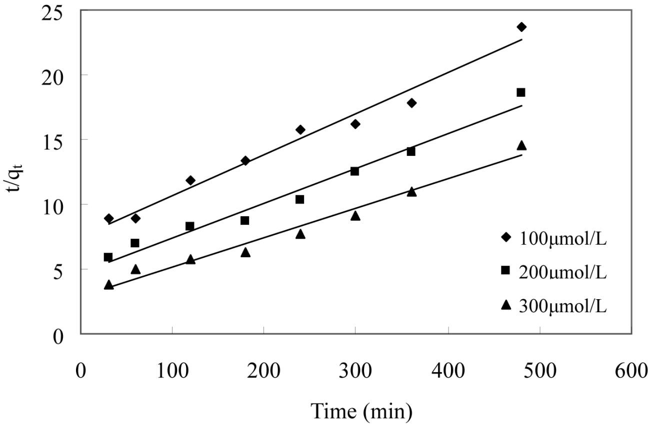

Fig. 6. Application of the pseudo-second-order adsorption model for the adsorption of BPA onto the nanofibers.

far larger than the data obtained from the experiment. These results suggested that the adsorption of BPA onto the PES nanofibers fitted the pseudo-first-order model not very well.

To further analyze the experimental data, the pseudo second-order equation was used [25,26]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{C_e}{q_e} t \tag{5}$$

where K_2 is the rate constant (gmg^{-1}min^{-1}), of pseudo-secondorder adsorption; q_e and q_t have the same meanings as those in Eq. (4). Fig. 6 shows the curves obtained from the experimental data (t/q_t) vs. t. All the correlation coefficients (r^2) reached 0.97 (Table 2), which indicated that the adsorption of BPA onto the PES nanofibers fitted the pseudo-second-order kinetic model very well. But the q_e was bigger than that obtained from the experiment.

Considering that the pseudo-first-order and the pseudo-second order model could not identify the diffusion mechanism, the intraparticle diffusion model [24] was used. The initial rate of the intraparticle diffusion may be expressed by the following equation:

$$q_t = K_p t^{1/2} \tag{6}$$

where K_p is the rate parameter for the intrafiber diffusion; q_t has the same meaning as that in Eq. (4). By plotting q_t vs. $t^{1/2}$ [24], we could justify whether the process of adsorption is controlled by pore diffusion. As can be seen in Fig. 7, there are two regions for the curves. The first one is a straight line passing through the origin, it correlated with the diffusion mechanism [27], and the slope of the linear curve is the rate constant of the intraparticle transport (K_p). The rate of the uptake might be affected by the

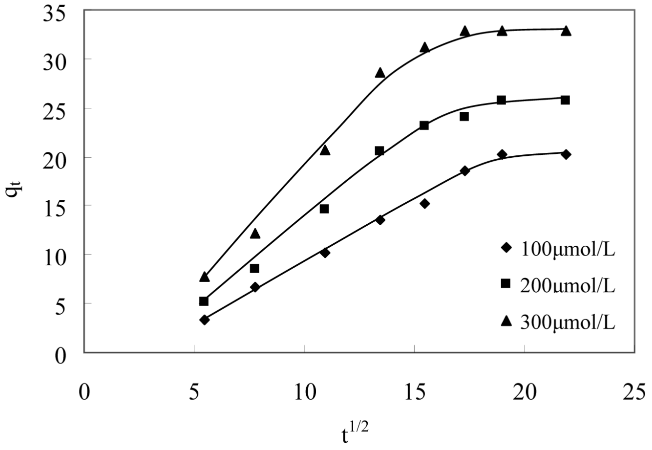

Fig. 7. Application of the intraparticle diffusion model for the adsorption of BPA onto the nanofibers.

Table 2
The first-order constants and the second-order constants for BPA adsorption

BPA concentration (μmol/L)	Pseudo-first-order			Pseudo-second-order		
	K_1 (×10^{-3} min^{-1})	q_e (mg/g)	r^2	K_2 (10^{-6} gmg^{-1}min^{-1})	q_e (mg/g)	r^2
100	0.5	99.6	0.91	188	33.2	0.98
200	0.4	156.8	0.84	58	77.4	0.97
300	0.3	235.4	0.79	97	97.6	0.97

size of the adsorbate molecule, the concentration of the adsorbate solution and the affinity to the adsorbent, the diffusion coefficient of the adsorbate in the bulk phase and the pore-size distribution [27]. The second region is attributed to the equilib-rium stage, where interfiber diffusion starts.

4. Conclusions

The goal of this study is the preparation of PES nanofibers by using electrospinning technique, and their application for the removal of endocrine disrupters. Our data shows that the PES nanofibers have a good performance on adsorption of hydrophobic endocrine disrupters due to the hydrophobic interaction between PES and endocrine disrupters. Nanofiber exhibited great capacity and fast kinetics of uptaking target species than microfiber and particle due to the large specific surface area. Our experiments also showed that the adsorbed endocrine disrupters can be effectively removed by ethanol, which indicated that the PES nanofibers could be reused. These results showed that the PES nanofibers have the potential to be used in the water treatment and environmental application.

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