

Electrosprayed Porous Microspheres for the Removal of Endocrine Disruptors

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ABSTRACT: Polyethersulfone (PES) porous microspheres were prepared via electrospraying technique, and then were used for the removal of endocrine disruptors from aqueous solutions. The surface and the internal structures of electrosprayed microspheres were characterized by scanning electron microscopy (SEM) and the results showed that they were porous. The electrosprayed porous PES microspheres can remove biphenyl A and biphenyl effectively. At the same time, they showed larger adsorption capacity and fast kinetics of uptaking target species than PES injected spheres reported in the

earlier publications. The hydrophilicity and porosity of electrosprayed microspheres can be controlled by changing the amount of hydrophilic polyethylene glycol (PEG), which influences the adsorption properties of the microspheres. The results showed that electrosprayed porous PES microspheres have the potential to be used in the environmental application. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2648–2653, 2011

Key words: microspheres; electrospraying; polyethersulfone; adsorption; endocrine disrupter

INTRODUCTION

Nowadays, the widespread use of endocrine disruptors such as biphenyl A (BPA), biphenyl (BP) around the world had led to serious environmental problems.^{1,2} Endocrine disruptors can be hormonal response even at low dose exposures and can promote imbalance in the endocrine system. As a result, they harmed the environment and human health seriously.^{3,4}

Some research about removing endocrine disruptors had been reported. For example, hydrophobic porous polymer membranes, hydrophobic porous polymer particles, water-insoluble DNA, UV-irradiated DNA matrices, carbonaceous, clays materials, and so on, could selectively remove endocrine disruptors.^{5–11} There is also the method of ultrafiltration process using PES-PVP membranes as well as degradation of endocrine disruptors using bacteria.^{12,13} In this study, we conjecture porous polymer

microspheres with diameters ranging from a few nanometers to micrometers could also remove endocrine disruptors effectively, because they have very large specific surface area due to the small diameters and the porous structure.

It has been known that most polymer microspheres can be produced by many methods including interfacial polymerization, *in situ* polymerization, interfacial precipitation,^{14–17} etc. With the rapid development of electrospinning technology, electrospraying has also begun to be used in preparation of polymer microspheres recently.^{18–21} Electrospraying can be seen as a special case of electrospinning. The differences between the two processes center on chain entanglement and resulting elongational viscous forces that operate in polymer solutions undergoing electrospinning. So when a dilute solution of a polymer is electrospun, it is common to obtain electrosprayed microspheres.²² Compared with other methods for preparing polymer microspheres, there are several advantages of electrospraying:¹⁷ (1) relative ease of setup, (2) open-atmosphere operation without a sophisticated chamber, (3) high production efficiency due to the direction of microspheres onto the collector under an electric field, and (4) well dispersed microspheres due to self-repulsion resulting from the electric charges on the microspheres, resulting great potential applications.

Additional Supporting Information may be found in the online version of this article.

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TABLE I
The Constituent of the Solution

	Concentration (wt %)	Polymer	Additive (wt % PEG/PES)	Solvent
P-0	9	PES	0	DMSO
P-20	9	PES	20	DMSO
P-80	9	PES	80	DMSO
P-140	9	PES	140	DMSO

At present, the preparation of microspheres with diameters ranging from micro- and nanoscales via electrospaying has been reported in the literature. The conditions of the preparation process, the surface structure and morphology as well as the formation mechanism for surface porous structure has been studied, respectively.^{18–21} However, the disquisitions on the endocrine disruptors' removal of electrospayed porous microspheres have not been reported. In this study, polyethersulfone (PES) microspheres were prepared via electrospaying technique; both the surface and the internal structures of electrospayed microspheres were porous. Then the porous microspheres were used for the adsorption of endocrine disrupters from their aqueous solution, the adsorption capacity and efficiency of electrospayed PES microspheres and injected PES spheres were also compared. To improve the adsorption capacity, the adsorption properties of the microspheres were regulated by adding PEG. The experiment results revealed that the endocrine disrupters can be removed effectively.

EXPERIMENTAL

Materials

PES (Ultrason E 6020P, CAS No. 25608-63-3) was purchased from BASF chemical company (Germany) and was used to prepare the PES microspheres. Polyethylene glycol (PEG, $M_w = 10,000$ g/mol) purchased from Japan. BPA and BP were purchased from Shanghai Chemical Reagent (China), and were used as the model endocrine disrupters. Dimethyl sulfoxide (DMSO) and ethanol were obtained from Chengdu Chemical Reagent (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.

Preparation of the microspheres

PES and PEG were dissolved in DMSO at 70°C for 4 h until it became a homogeneous solution. The

constituent of the solution which prepared microspheres was shown as Table I. For producing microspheres, direct current high-voltage generator (ZGF Chuan Gao electro-tech, China) was used to provide voltage of 10 kV. The solution was placed in a 50-mL syringe, to which a capillary tip of 0.5 mm inner diameter was attached. The positive electrode of high-voltage power supply was connected to the capillary tip. The grounded electrode was connected to a metallic collector immersed in a water bath. The distance between the tip and the collector was maintained at 6 cm and the flow rate was 1 mL/h.

Calculation of the porosity of the microspheres

The porosity of microspheres was estimated from the density of polymer and the weight change before and after drying, as the following formula:²³

$$\text{Porosity}(P) = \frac{(W_B - W_A)/\rho_W}{W_A(1 - C\%)/\rho_P + W_A \times C\%/\rho_C + (W_B - W_A)/\rho_W} \times 100\% \quad (1)$$

where W_B is the weight of microspheres before drying (g); W_A is the weight of microspheres after drying (g); ρ_W (1.0 g/cm³) is the density of water; and ρ_P (1.43 g/cm³) is the density of the PES; $C\%$ is the additive ratio in microspheres; ρ_C is the density of additive (PEG).

Scanning electron microscope of the microspheres

The morphology of microspheres was observed with scanning electron microscopy (SEM and EDS Inspector F, FEI Company, all operation at an accelerating voltage of 10 kV). The samples were coated by an E-1045 ion sputter coater with Au/Pd to reduce charging. The microspheres were dispersed in distilled water by ultrasonic vibration, and then were frozen into hard ice with liquid nitrogen, the hard ice was broken into powder rapidly; the powder was naturally unfrozen and dried, the cross sections of the microspheres with morphologies maintained well were obtained.

Thermal gravimetric analysis

Thermogravimetric analysis of microspheres was carried out by using thermal gravimetric analysis (TGA/TA Q600, TA Instruments, USA) under a nitrogen atmosphere from 50 to 800°C at heating rate of 10°C min.

The residual weight percentage of PEG in microspheres samples were estimated by using the

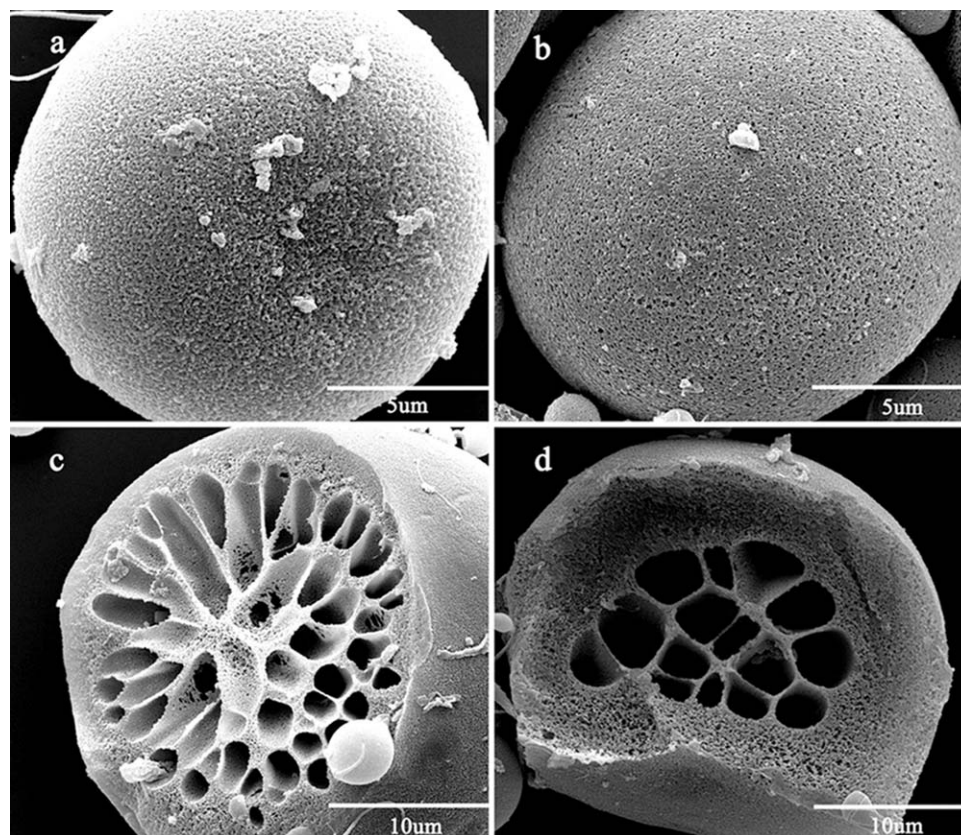


Figure 1 SEM images of electrospayed porous microspheres surfaces of P-0 (a), P-20 (b), and internal structure P-0 (c), P-20 (d).

following formulas (derivation of the formula is shown in electronic supplement material):

$$m_B = \frac{m_A \times C_C}{C_B} \quad (2)$$

$$\omega_B = \frac{m_B}{m_A} \times 100\% \quad (3)$$

where m_B is the weight of PEG in microspheres (g); m_A is the weight of PES/PEG microspheres (g); C_C is the weight loss percentage of PEG in microspheres; C_B is the weight loss percentage of pure PEG; and ω_B is the residual weight percentage of PEG in microspheres.

Adsorption experiments

BPA was dissolved in ethanol and diluted with distilled water. The adsorption experiments were carried out as following: microspheres were dispersed into 10 mL of BPA solution at 20°C with initial concentrations of 100, 200, and 300 μM , respectively. The BPA concentrations at certain time intervals were detected with UV-Vis spectrophotometer U-200A (Shanghai Spectrum Instruments, Shanghai, China) at the wavelength of 276 nm.

The removal ratio and adsorbed capacity of BPA were calculated as following:

$$R_t = \frac{C_0 - C_t}{C_0} \times 100\% \quad (4)$$

$$Q_t = \frac{(C_0 - C_t) \cdot V}{m} \quad (5)$$

where R_t (%) is the removal ratio of BPA by microspheres at time t ; C_0 is the initial concentration of BPA solutions ($\mu\text{mol/L}$); C_t is the concentration at time t ($\mu\text{mol/L}$); Q_t is the adsorbed BPA amount per gram of microspheres at time t ($\mu\text{mol/g}$); V is the volume of BPA solution (L); and m is the weight of microspheres (g).

The adsorption experiment of BP was also carried out with similar method as BPA. The concentration of BP solution was measured at the wavelength of 248 nm.

RESULTS AND DISCUSSION

Characterization of the microspheres

The porous microspheres with diameters ranging from 3 to 20 μm were prepared via electrospaying. Figure 1 shows the SEM images of PES microsphere.

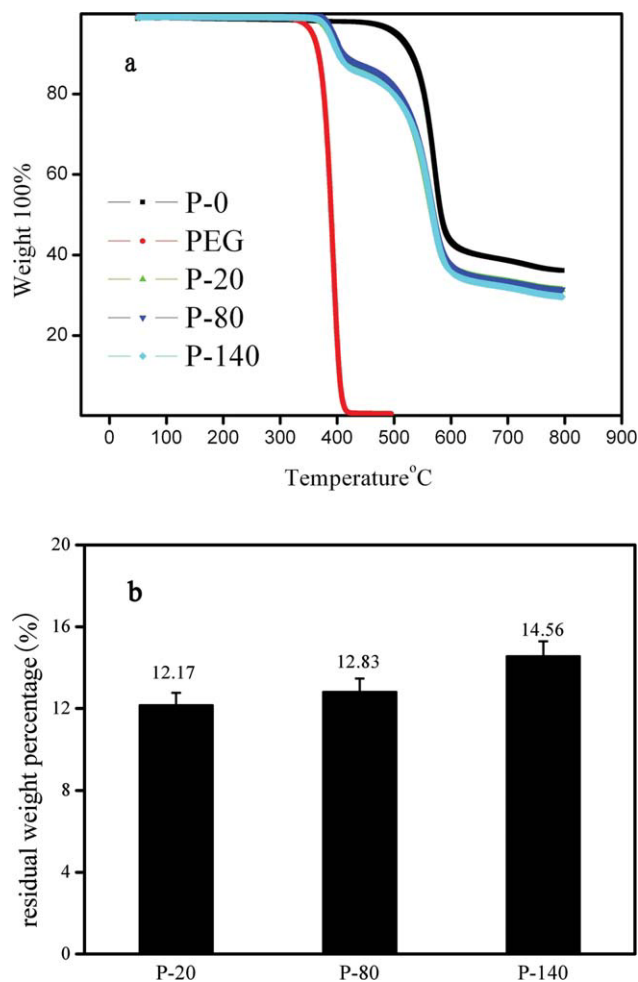


Figure 2 (a) TGA traces of P-0, P-20, P-80, P-140, and PEG (b). The residual weight percentage of PEG for P-20, P-80, and P-140. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It suggests that the microsphere surface is porous [Fig. 1(a,b)]. To study the internal structure, the microspheres were cut by a method.²⁴ Macrovoids throughout the cross section of the microsphere which display a uniform cellular structure can be seen [Fig. 1(c)], adding PEG, the skin layers become much thicken [Fig. 1(d)]. The formation process of porous microspheres can be divided into two steps. The first step is electrospinning which was accompanied with rapid evaporation of solvent while the second step is the figuration of microspheres. Nonsolvent water was selected as the coagulation medium. Here, water showed high solubility for DMSO but not for PES. When PES/DMSO droplet was sprayed into water, liquid-liquid phase separation occurred by rapid exchange of the solvent DMSO and water. With the completion of the exchange, the porous microspheres were formed.

The thermal stability of electrospayed microspheres was investigated with TGA, and the weight

loss traces are shown in Figure 2(a). The decomposition temperatures of pure PES microspheres and pure PEG are 515.4 and 360.5°C, respectively. When PEG was added into the electrospayed solution, the microspheres lost its weight sharply at two regions. The first weight loss is attributed to the decomposition of PEG while the second weight loss is PES. Because the water was selected as the coagulation medium, PEG would be dissolved into water. But part of PES and PEG molecular chains might be in entanglement, so there was residual PEG in the microspheres.²³ The maximum fraction of chains entanglement between PES and PEG content was limited by PES amount, so the fraction of PEG does not increased significantly with the increase of initial PEG [shown in Fig. 2(b)].

Adsorption of BPA in various concentration solutions

It was carried out firstly in BPA solutions with various concentrations (100, 200, and 300 μM BPA aqueous solutions) at room temperature to study the adsorption capacity of electrospayed pure PES microspheres. Figure 3 shows the adsorption kinetic curve of Pure PES microspheres in BPA aqueous solutions. The adsorption amounts 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 33.7, 60.0, and 81.3 $\mu\text{mol/g}$ for microspheres in 100, 200, and 300 μM BPA solutions, respectively. With the increase of BPA concentration in aqueous solutions, the adsorbed amounts increased. These can be explained by the adsorption theory reported earlier.²⁵

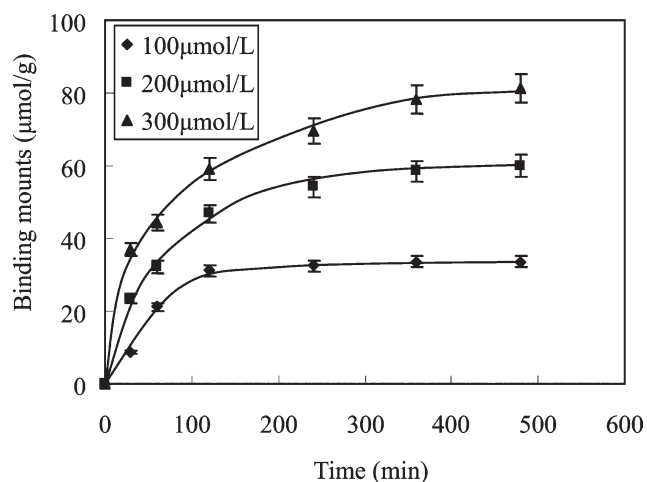


Figure 3 The binding amounts per unit mass of the electrospayed PES microspheres (P-0) in BPA aqueous solutions of different concentrations.

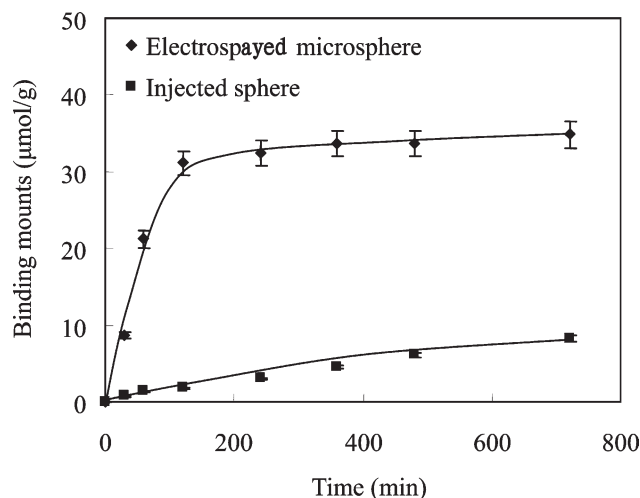


Figure 4 Binding amounts of electrospayed microspheres (P-0) and injected spheres in 100 μM BPA aqueous solutions.

As shown in Figure 3, the adsorption was fast at the beginning; in this case, BPA might enter some easy accessible pore sites and bind with microspheres. After 120 min, the adsorption speed decreased, the most reason may be that the BPA molecules diffuse into deeper and smaller pores.

Adsorption of BPA by electrospayed microspheres and injected spheres

In this study, the adsorption capacity of PES injected spheres which had been reported²⁶ and electrospayed microspheres was investigated. Figure 4 shows the adsorption kinetics of the two kinds of spheres to BPA. The saturated adsorption amounts of BPA were about 8.3 and 33.7 $\mu\text{mol/g}$ for injected spheres and electrospayed microspheres, respectively. The adsorption amount for electrospayed microspheres is much larger than that for injected spheres, and the time for more than 90% of the

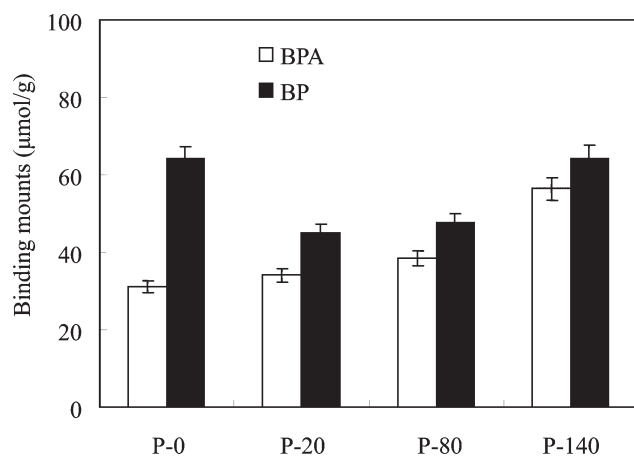


Figure 5 Binding amounts of BPA and BP for P-0, P-20, P-80, and P-140.

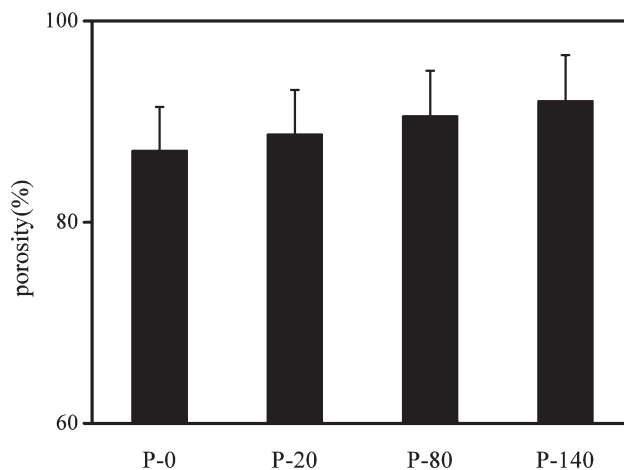


Figure 6 The porosity of P-0, P-20, P-80, and P-140.

amount of saturated adsorption for electrospayed microspheres was 2 h but it was more than 10 h for injected spheres. These can be explained by the larger specific surface area caused by the much smaller diameter and porous structure of the electrospayed microspheres.

Effect of PEG on the adsorption behavior

The affinity to adsorbent molecule and the porosity of microspheres matrix could affect the adsorption behavior. As we know, the PEG is a common additive that used to improve the hydrophilicity and porosity of PES membrane. The binding amounts of BPA to porous microspheres with different fractions of PEG were investigated and the results were shown in Figure 5. The binding amounts of BPA gradually increased with the increase of PEG. It may be due to the increase of hydrophilicity or porosity of electrospayed microspheres (shown in Fig. 6). To further study the effect of PEG on the adsorption behavior of microspheres, BP that more hydrophobic than BPA was used to study the adsorption mechanism. As seen in Figure 5, the adsorption amount was decreased by adding PEG. The most reason was that the interaction between hydrophobic BP molecules and microspheres was weakened by increasing the hydrophilic property. However, with the increase of the amount of PEG, the binding amount increased gradually. With the amount of PEG excess 20% in the electrospaying solution, the residual PEG amount in microspheres did not changed significantly [Section 3.1 and Fig. 2(b)], so it almost did not improve the hydrophilic property of microspheres, but improved the porosity of microspheres (Fig. 6), which increased the binding amount of microspheres. These results demonstrated that both the hydrophilic properties and porosity of microspheres which altered by

adding PEG would affect the adsorption behavior optimistically.

CONCLUSION

The PES microspheres successfully prepared via electro spraying technique, and the surface and the internal structures of microspheres were porous. Then their application for removal of endocrine disrupters was studied. It showed that the porous PES microspheres have a good performance on adsorption of endocrine disrupters such as BPA and BP. Compared with injected spheres, electro sprayed microspheres exhibited much great capacity and fast kinetics of uptaking target species. The experiments also showed that both the hydrophilic properties and porosity of electro sprayed microspheres would affect the adsorption behavior optimistically, meanwhile the hydrophilic properties and porosity of electro sprayed PES microspheres could be controlled by changing the amount of hydrophilic PEG.

These results showed that the electro sprayed microspheres have the potential to be used in the water treatment and environmental depuration.

NOMENCLATURE

W_B	The weight of microspheres before drying (g).
W_A	The weight of microspheres after drying (g).
ρ_W	The density of water (g/cm^3).
ρ_P	The density of the PES (g/cm^3).
$C\%$	The additive ratio in the microspheres.
ρ_C	The density of the additive (PEG).
m_B	The weight of PEG in microspheres (g).
m_A	The weight of PES/PEG microspheres (g).
C_C	The weight loss percentage of PEG in microspheres.
C_B	The weight loss percentage of pure PEG.
ω_B	The residual weight percentage of PEG in microspheres
R_t	The removal ratio of BPA by microspheres at time t .
C_0	The initial concentration of BPA solutions ($\mu\text{mol}/\text{L}$).
C_t	The concentration at time t ($\mu\text{mol}/\text{L}$).
Q_t	The adsorbed BPA amount per gram of microspheres at time t ($\mu\text{mol}/\text{g}$).

V	The volume of the BPA solution (L).
m	The weight of the microspheres (g).

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