

Preparation of polyethersulfone/sulfonated polyethersulfonephenylethane microspheres and its application for the adsorption of bisphenol A

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ABSTRACT: A novel kind of sulfonated polyethersulfonephenylethane (SPESPE) was successfully synthesized firstly in this work. Then the SPESPE was introduced in polyethersulfone (PES) microspheres prepared by the electro spraying technique. The microspheres were applied to adsorbing bisphenol A (BPA) from its aqueous solution. Compared with the PES microspheres, the adsorption capacity of PES/SPESPE microspheres for BPA was increased significantly. Furthermore, the adsorption capacity of PES/SPESPE microspheres was enhanced by increasing the amounts of SPESPE in the microspheres. The pH of solution had influence on the adsorption capacity of PES/SPESPE microspheres. The kinetic data of adsorption were found to follow pseudo-second-order model. The Freundlich isotherm model was suitable to describe the equilibrium adsorption data. The microspheres also showed excellent regeneration and reuse ability. These results indicated that the PES/SPESPE microspheres have the potential to be used in environmental application. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43066.

KEYWORDS: adsorption; applications; nanoparticles; nanowires and nanocrystals

Received 8 July 2015; accepted 18 October 2015

DOI: 10.1002/app.43066

INTRODUCTION

Bisphenol A (BPA) is one of the highest volume chemicals produced worldwide and has been widely used as the raw material for the manufacture of polycarbonates, epoxy resins, polysulfones, polyarylates, phenol resins, and so on.^{1–5} Recently, BPA has aroused extensive attention for its drawbacks of estrogenic activity and abilities of serving as environmental endocrine.^{6,7} For the reported adverse health effects, including liver damage, disrupted pancreatic β -cell function, thyroid hormone disruption, and obesity-promoting effects,^{8–11} the effective removal of BPA has become an urgent issue of requirement.

The conventional processes for the removal of BPA can be divided into three main approaches: physical, chemical, and biological methods.^{12–14} Among these methods, physical adsorption is generally considered as an efficient and economical removal method. For further improving the efficiency of adsorption, extensive attention is focused on improving the specific surface area and surface modification of the physical adsorbents.¹⁵ At present, activate carbonate, zeolite, polyethersulfone (PES) particles modified by montmorillonite, and ultra-

fine fibers have been successfully applied to the removal of BPA from aqueous solution.^{16–20}

Electro spraying technique is a simple and efficient method of fabrication particles with the average diameter ranging from nano-scale to micro-scale.^{21,22} These one-dimensional particles with average diameter ranging from nano-scale to micro-scale have high specific surface area. Therefore, electro spraying technique could be a simple and practical method to produce adsorbent of high specific surface area. In electro spraying process, according to Gañán-Calvo's results, a higher conductivity of solution favors to produce smaller particles.²³ Adding some inorganic salts into the electro sprayed solution could increase the conductivity of solution.²⁴ However, the extra salts may influence the properties of products and complete removal of them is impossible. Hence, incorporation of a certain kind of polymer with ionized functional groups into the electro spraying system is a relatively better way to increase the conductivity of solution. Sulfonation of polymer has been widely applied as an effective method to introduce the ionized functional groups onto the backbone structure of the polymer. The introduction of sulfonic groups could be achieved by either post sulfonation of polymers or direct polymerization of sulfonated monomers.²⁵ It has been widely accepted that the

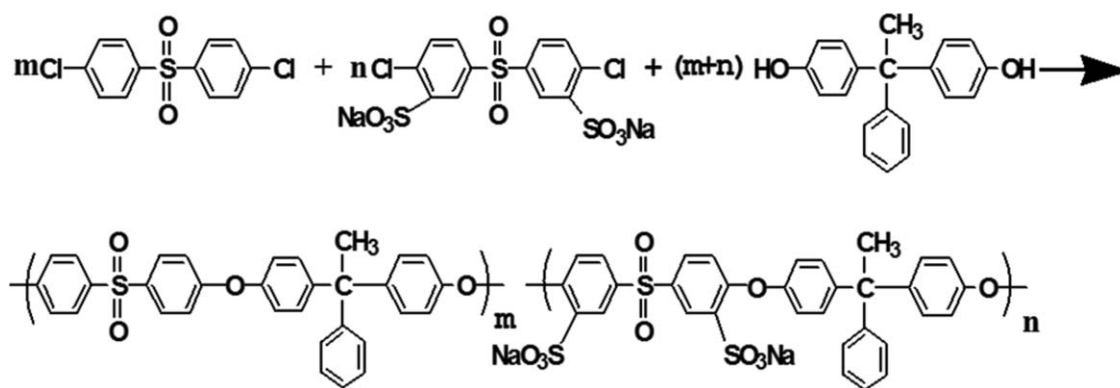


Figure 1. The synthesis of SPESPE.

direct polymerization method has advantages over the postsulfonation method, including easy controlling of the position of sulfonation and the degree of sulfonation as well as minimizing the side reactions.²⁶ Therefore, in this article, the sulfonation polymer of sulfonated polyethersulfonephenylethane (SPESPE) was synthesized by the direct polymerization of sulfonated monomers. To obtain particles with small diameter, SPESPE has been introduced into the electrospaying system. It has been reported that the PES could efficiently remove phenol endocrine disruptors, for example, Peng *et al.* applied porous PES microspheres to the removal of phenol endocrine disruptors, Zhang *et al.* fabricated various structure of PES microspheres for the adsorption of BPA, and Wei *et al.* employed composite ultrafine fibers of PES/PEG to adsorb BPA.^{20,27,28} Based on the reports mentioned above, PES has the potential to be used as efficient adsorbent for the removal of BPA. In this study, PES microspheres were prepared by the electrospaying technique. The prepared microspheres were then used as promising adsorbent for the adsorption of BPA. The adsorption capacity for BPA was increased significantly when SPESPE was introduced in the microsphere. The kinetic and equilibrium isotherm adsorption were investigated in detail.

EXPERIMENTAL

Materials

Phenol, acetophenone, 98% sulfuric acid, anhydrous potassium carbonate, dichloromethane, toluene, N,N-dimethylformamide (DMF), fuming sulfuric acid (30% SO₃), and BPA were all supplied by Chengdu Ke Long Co. Mercaptoacetic acid was purchased from Aladdin. 4,4'-dichlorodiphenyl sulfone (DCDPS) was obtained from Jiangsu Yansheng Chemical Industry Co. N-methyl-2-pyrrolidone (NMP) was obtained from Jiangsu Nanjing Jin Long Chemical Industry Co. PES was supplied by BASF Chemical Co. The disodium 3,3'-disulfonate-4,4'-dichlorodiphenyl sulfone (SDCDPS),²⁹ 1,1-bis(4-hydroxyphenyl)-1-phenylethane (PhBPA) monomer, used in the experiment were synthesized according to the procedure described by the previous literatures.^{30,31} All the chemicals were of analytical grade and used without further purification unless described.

Synthesis of Monomers

3,3'-Disulfonate-4,4'-Dichlorodiphenylsulfone

(SDCDPS). SDCDPS was prepared according to the following procedure: 28.7 g (0.1 mol) DCDPS and 70 mL fuming sulfuric

acid were added into a 500-mL three-necked flask. The reaction mixture was heated to 120°C for 7 h under a nitrogen atmosphere. The reaction solution was then poured into deionized water, which formed the brown solution, and then filtered. The isolation of the product was achieved using a standard procedure at least three times, which include salting out with sodium chloride, neutralization with sodium hydroxide. The white solid was purified by recrystallization with a mixture of deionized water and isopropyl alcohol (1/3, v/v). Then, the SDCDS monomer was dried under vacuum at 100°C. The yield of products was 62%.

1,1-Bis(4-hydroxy phenyl)-1 Phenyl-Ethane (PhBPA). The synthesis of PhBPA followed the following procedure. A 500 mL round-bottom three-necked flask equipped with an overhead mechanical stirrer was used and 56.4 g (0.6 mol) of phenol was added. Then 40 mL of concentrated sulfuric acid (78 wt %) was added with a speed of 10 mL min⁻¹, followed by adding 36 g (0.3 mol) of acetophenone and 0.4 g of mercaptoacetic acid. The reaction mixture was heated to 45°C for 2 h, then raised the temperature up to 57°C and kept for 8 h. The crude product was then obtained and washed with hot water and dichloromethane to remove possible residual salts. The purified product was then dried at 110°C for more than 12 h to yield a white solid. The yield of products was 70%.

Synthesis of SPESPE

As shown in Figure 1, the process for synthesizing SPESPE was as following: SDCDPS (0.01 mol), DCDPS (0.09 mol), PhBPA (0.1 mol), and anhydrous potassium carbonate (0.12 mol) were added to a mixture solution of NMP (100 mL) and toluene (20 mL) in a 250-mL round-bottom three-necked flask which was equipped with a water separator, reflux condenser, mechanical stirrer, thermometer, and nitrogen inlet. The reaction mixture was heated ranging from 140°C to 165°C for 5 h. After the water was being fully removed from the reaction mixture by azeotropic distillation, toluene was distilled out. The temperature of the reaction mixture was then raised to 195°C for 14 h. Afterward, the mixture was cooled to 100°C and poured into methanol, followed by filtration. The residual inorganic materials in the polymer were extracted by deionized water and methanol for 24 h. The products were then dried at 120°C under vacuum for at least 48 h. Finally, the white products of SPESPE were obtained. The yield of products was 97%.

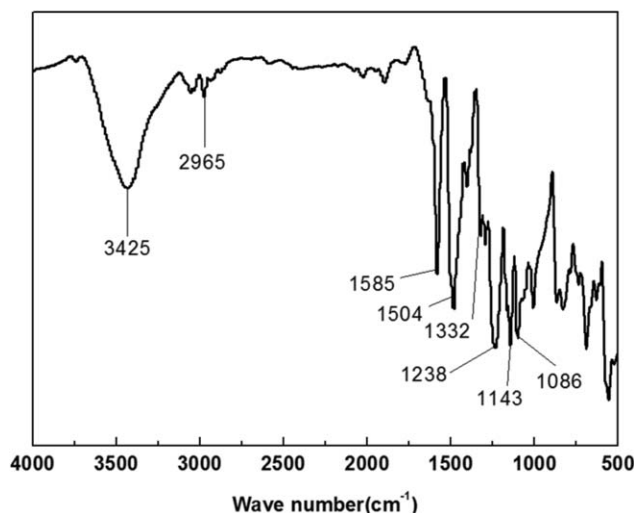


Figure 2. The FIR spectrum of SPESPE.

Electrospraying of Microspheres

Electrospraying technique was used to prepare microspheres. For comparison, a series of PES/SPESPE blend microspheres were prepared. Firstly, the 0.1 g mL⁻¹ solutions were prepared by adding predetermined PES and SPESPE into the solvent of DMF. The weight proportion of SPESPE was 0, 5, 10, and 15% wt, which was labeled as M0, M1, M2, and M3, respectively. With vigorous stirring for several hours, the homogeneous solutions were obtained. In electrospraying process, direct current high-voltage generator (ZGF Chuan Cao electro-tech, China) was used to provide voltage of 10 kV. The solution was placed into a 50-mL syringe, to which a capillary tip of 0.5 mm inner diameter was attached. The positive electrode of high-voltage generator was connected to the capillary tip. The grounded electrode was immersed into water bath. The distance between the tip and the collector was maintained at 6 cm and the flow rate of solution was fixed at 1 mL h⁻¹.

Adsorption Experiments

The adsorption capacity of the microspheres for BPA was determined as following: equal amount of microspheres (0.5 mg mL⁻¹) were distributed into BPA aqueous solution at 25°C with the initial concentration of BPA ranging from 50 to 300 μmol L⁻¹. For the adsorption kinetic study, the concentrations of BPA aqueous solution with the initial concentration of 200 μmol L⁻¹ at different time intervals were detected by UV-Vis spectrophotometer (Beijing Puxi instrument, China). For adsorption isotherms study, the concentrations of BPA aqueous solutions at the saturation adsorption status were measured by the UV-Vis spectrophotometer. The amount of BPA adsorbed onto the microspheres was calculated using the following equation:

$$qt = \frac{C_0 - C_t}{m} V \quad (1)$$

where q_t (μmol g⁻¹) is the adsorption amounts at time t , C_0 (μmol L⁻¹) is the initial concentration of BPA, C_t (μmol L⁻¹) was concentration of BPA at time t , V (L) is the volume of the solution, and m (g) is the weight of the microspheres.

Characterization Methods

The sample of SPESPE was measured with Fourier transform infrared spectroscopic measurements (NEXUS670, USA). The scanning electron microscopy (SEM Inspector F, FEI Co. USA) was employed to characterize the morphology of microspheres. Thermogravimetric analysis measurements (TGA Q500 V6.4 Build 193, USA) were performed under nitrogen atmosphere with a heating rate of 100°C min⁻¹. The static contact angle was conducted on the instrument of surface tension (KrÜss K100, Germany). The conductivities of solutions were measured on conductivity indicator (Leici DDS-307, China). The Brunauer-Emmet-Teller (BET) surface area was measured by nitrogen adsorption-desorption isotherm on Gemini VII 2390 V1.02 (Micromeritics Instrument Corporation).

RESULTS AND DISCUSSION

Characterization of the SPESPE

FT-IR spectra was used to identify the characteristic groups of SPESPE. As shown in Figure 2, the peaks at 1332 cm⁻¹ and 1143 cm⁻¹ were attributed to the asymmetric stretching vibration and symmetric stretching vibration of sulfone group (O=S=O). The characteristic peak of sulfonic acid sodium group appeared at 1086 cm⁻¹ and 1238 cm⁻¹. The peak at 2965 cm⁻¹ was ascribed to the stretching vibration of methyl. The stretching vibration of carbo-oxygen bond appeared at 1241 cm⁻¹. The characteristic peaks for aromatic ring skeleton were observed at 1585 cm⁻¹ and 1504 cm⁻¹.

The intrinsic viscosity of the SPESPE was obtained in NMP at 30 ± 0.1°C, using a Cannon-Ubbelohde viscometer. The result was 0.47 dL g⁻¹.

What's more, the hydrophilicity of SPESPE should be better than PES for the introduction of sulfonate acid sodium groups. As shown in Figure 3, the dynamic contact angle of SPESPE and PES was 77.7° and 92.2°, respectively. It indicated that the hydrophilicity of SPESPE was indeed better than PES. The hydrophilicity has positive influence on the adsorption capacity of the PES blend microspheres in aqueous solution.²⁰

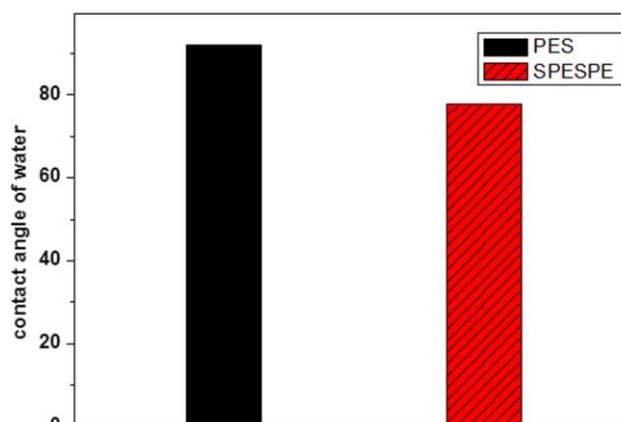


Figure 3. The dynamic contact angle of SPESPE and PES. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

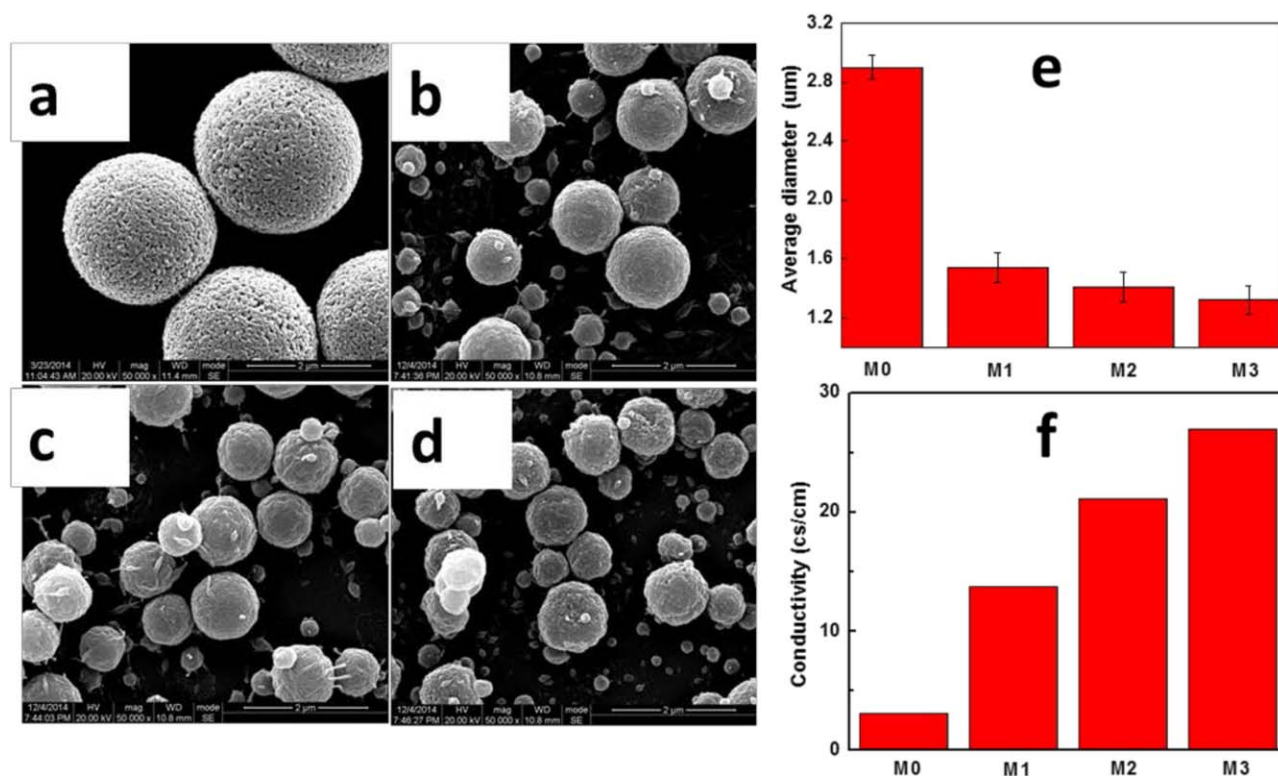


Figure 4. The SEM (50,000 \times) of microspheres: M0 (a), M1 (b), M2 (c) and M3 (d), average diameter of microspheres(e), and conductivity of solution (f). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Morphology of Microspheres

The morphology of microspheres is shown in Figure 4. It can be observed that the surface of microspheres was porous and the porosity was decreased with the introduction of SPESPE. The average diameters of microspheres were 2.9, 1.5, 1.4, and 1.3 μm for M0, M1, M2, and M3, respectively. The decrease of the average diameter of microspheres was mainly due to the increase of conductivity of solution [Figure 4(f)]. The sulfonic acid sodium groups could be ionized, so the SPESPE component could greatly increase the conductivity of solution, which favors to produce microspheres of small average diameter. Therefore, the average diameter of microspheres has a tendency to become smaller with increasing the content of SPESPE. The BET surface areas of microspheres were 59.3, 74.2, 79.8, and 80.6 $\text{m}^2 \text{g}^{-1}$ for M0, M1, M2, and M3, respectively.

Adsorption

The adsorption process of various microspheres for BPA in its aqueous solution at the initial concentration of 200 $\mu\text{mol/L}$ is shown in Figure 5. The rate of BPA adsorption was fast at the beginning; in this case, BPA entered some easy accessible surface pore sites and binding with the microspheres. Afterward, it processed a lower rate. It might be due to the BPA molecular diffusing into some deeper and smaller pores, and finally no further significant adsorption was occurred beyond 120 min. The other reason might be that there was less BPA molecular diffusing after certain time adsorption. Therefore, the optimum contact time was fixed at 120 min for further experiments. The equilibrium adsorption capacity for BPA was increased with increasing the content of SPESPE in microspheres. Compared

with the blend microspheres, the equilibrium adsorption capacity of pure PES microspheres was rather smaller, thus the incorporation of SPESPE into the PES microspheres could enhance the adsorption capacity for BPA.

As seen in Figure 5, the equilibrium adsorption capacity of microspheres for BPA significantly increased by increasing the content of SPESPE. The equilibrium adsorption amounts were 55, 140, 170, and 200 $\mu\text{mol g}^{-1}$ for M0, M1, M2, and M3, respectively. The adsorption capacity of M3 is 3.6 times higher

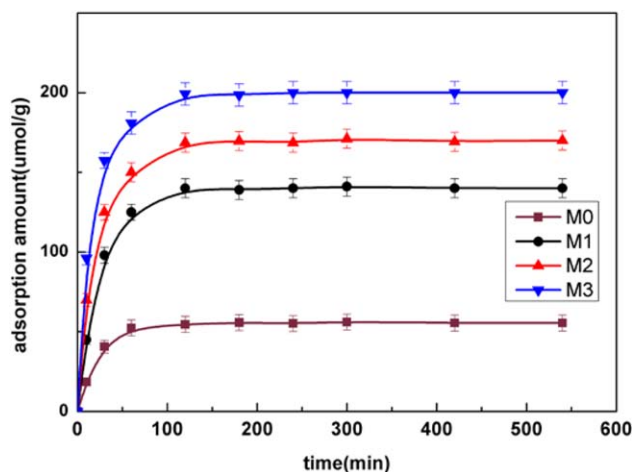


Figure 5. Adsorption kinetic of M0, M1, M2, and M3 for BPA at initial BPA concentration of 200 $\mu\text{mol L}^{-1}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

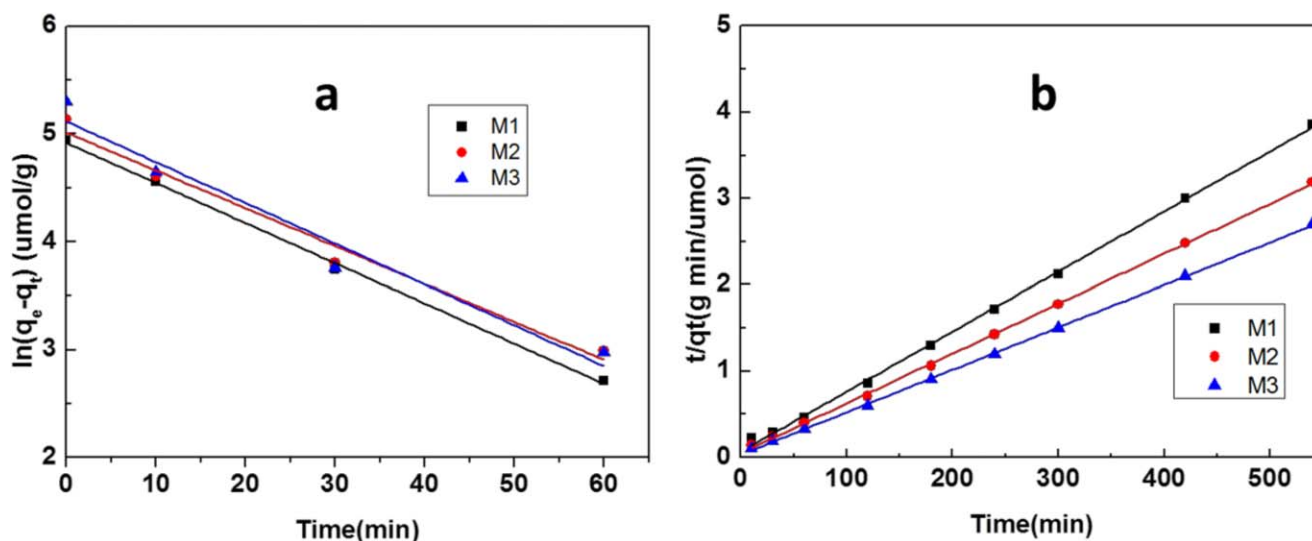


Figure 6. Adsorption of bisphenol A onto various microspheres fitted by kinetic models: (a) pseudo-first-order and (b) pseudo-second-order models. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

than that of M0. The large specific surface area and hydrophilicity are favorable to improving the adsorption capacity for BPA.²⁰ In this work, the average diameters of microspheres became smaller with increasing the content of SPESPE, which enlarged specific surface area. Furthermore, the introduction of sulfonic acid sodium groups in microspheres was favor to improving the hydrophilicity. Therefore, the PES/SPESPE microspheres performed higher adsorption capacity for BPA and the adsorption capacity of PES/SPESPE microspheres for BPA had been further enhanced by increasing the content of SPESPE.

In order to predict the adsorption kinetic behaviors, two kinetic models namely pseudo-first-order models and pseudo-second-order model were employed to analyze the kinetic experimental data and results are shown in Figure 6.

Pseudo-first-order model considers that the rate of occupation of adsorption is proportional to the number of unoccupied site. Its linear form is expressed as following³²:

$$\ln(q_{ex} - q_t) = q_{ec} - k_1 t \quad (2)$$

where q_{ex} and q_t ($\mu\text{mol g}^{-1}$) are the adsorption amount of microspheres at equilibrium and time t (min), respectively; k_1 (min^{-1}) is the rate constant of pseudo-first-order equation.

The slope and the intercept of each linear in Figure 6(a) are used to calculate the first-order constant K_1 and the calculated equilibrium adsorption capacity q_{ec} (see in Table I). The correlation coefficients (R^2) of the first order kinetic model were 0.948, 0.965, and 0.971 for M1, M2, and M3, respectively. The values of q_{ec} were 134, 150, and 175 $\mu\text{mol g}^{-1}$, respectively, which were lower than the data obtained from experiments. These results suggested that the adsorption for BPA onto the PES/SPESPE microspheres were not fitted the pseudo-first-order model very well.

Pseudo-second-order model considers that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites. Its linear form can be given as³³:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{ec}^2} + \frac{t}{q_{ec}} \quad (3)$$

where k_2 ($\text{g}/\mu\text{mol min}^{-1}$) is the rate constant of pseudo-second-order equation; q_{ec} and q_t have the same meaning as those in eq. (2).

The slope and intercept of each line in Figure 6(b) is used to calculate the rate of constant k_2 and q_{ec} , which are summarized in Table I. The correlation coefficients (R^2) of PES/SPESPE microspheres were all up to 0.99. Furthermore, the theoretic values of equilibrium adsorption amount, calculated from the pseudo-second-order kinetic model, were in good accordance with the experimental data. Therefore, the pseudo-second-order kinetic model was suitable to describe the adsorption behavior of PES/SPESPE microspheres for BPA. The results indicated that the rate of occupation of adsorption sites was proportional to the square of the number of unoccupied sites.

Modeling of Equilibrium Data of Bisphenol A Adsorption

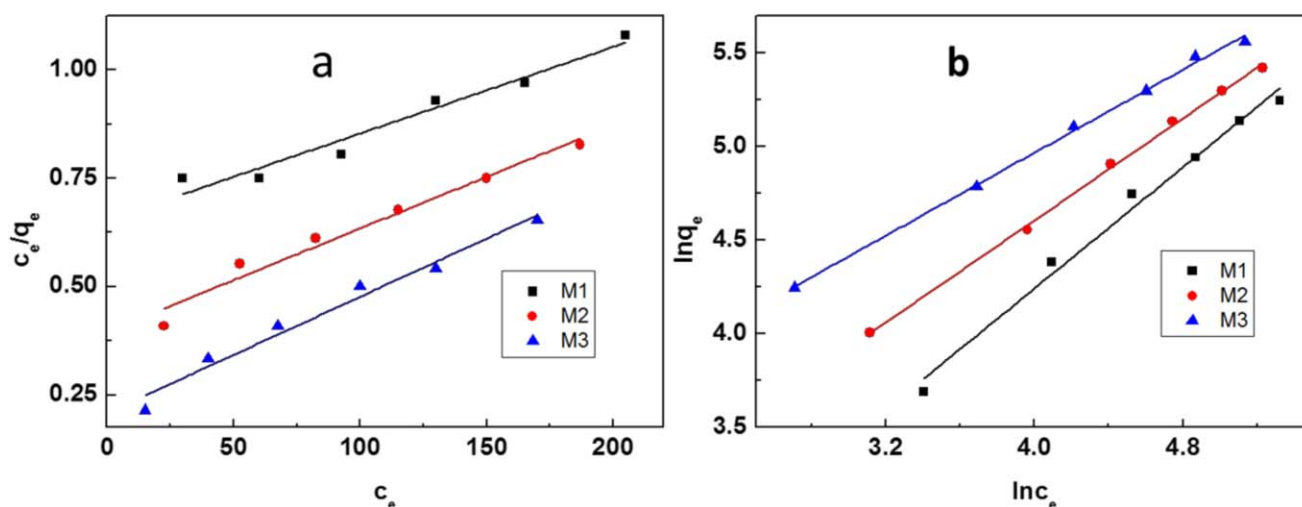
The equilibrium adsorption isotherm is very crucial in the design of adsorption systems, which means that the adsorption process eventually plateaus between the adsorbent phase and the solution phase. Mathematically, the amount or adsorption capacity adsorbed at equilibrium is commonly expressed by an isotherm equation characterized by certain parameters whose values express the surface properties of adsorbent and its affinity to the adsorbate. In this work, the Langmuir and Freundlich isotherm models are applied to analyze the data.

The Langmuir isotherm model is based on the physical hypothesis that the maximum adsorption capacity consists of a monolayer adsorb molecules, and that the adsorption energy is distributed homogeneously over the entire coverage surface. The linear form of Langmuir isotherm model can be expressed as follows³⁴:

$$\frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{k_L q_{\text{max}}} \quad (4)$$

Table I. The Kinetic Parameters of Bisphenol A Adsorption onto Microspheres

	Pseudo-first-order model				Pseudo-second-order model		
	q_{ex} ($\mu\text{mol g}^{-1}$)	q_{ec} ($\mu\text{mol g}^{-1}$)	K_1 (min)	R^2	q_{ec} ($\mu\text{mol g}^{-1}$)	K_2 ($\times 10^6$ g/ $\mu\text{mol min}$)	R^2
M1	140	134	0.040	0.948	144	3.26	0.998
M2	170	150	0.039	0.965	173	1.67	0.999
M3	200	175	0.040	0.971	203	8.12	0.999

**Figure 7.** The equilibrium adsorption isotherm: (a) Langmuir modeling and (b) Freundlich modeling. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where q_e ($\mu\text{mol g}^{-1}$) is the adsorption amount at the equilibrium state, C_e ($\mu\text{mol L}^{-1}$) is the concentration of BPA in solution at the equilibrium state, q_{max} ($\mu\text{mol g}^{-1}$) is the monolayer adsorption capacity of the microspheres, and K_L ($\text{L } \mu\text{mol}^{-1}$) is the Langmuir adsorption constant.

The slope and intercept of each line in Figure 7(a) is used to calculate the value of q_{max} and k_L , which are summarized in Table II.

Freundlich isotherm is an empirical equation based on adsorption on a heterogeneous surface with nonuniform energies of active sites. The linear form of Freundlich isotherm model can be expressed as follows³⁵:

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \quad (5)$$

where q_e and C_e have the same meaning as in eq. (4) and K_F is the Freundlich isotherm constant.

The slope and intercept in Figure 7(b) are employed to obtain the value of n and K_L , which are presented in Table II. It can be seen that the data agree well with the Freundlich model with the value of coefficient (R^2) were all greater than 0.99. Furthermore, the values of n at the equilibrium were 1.238, 1.472, and 1.809 for M1, M2, and M3, respectively. It was noted that the values of n were bigger than 1, which reflected the favorable adsorption.

By comparing the correlation coefficient, it was found that the Freundlich isotherm model ($R^2 > 0.99$) fitted the equilibrium

data better than the Langmuir isotherm model ($R^2 > 0.94$). It indicated that the adsorption behaviors of PES/SPESPE microspheres for BPA were nonmonolayer and the surface energies of active sites were nonuniform.

Effect of pH on Bisphenol A Adsorption

The effect of solution pH on the adsorption capacity of bisphenol A onto blend microspheres at initial BPA concentration of 200 $\mu\text{mol/L}$ was investigated. As shown in Figure 8, in acid condition, the equilibrium adsorption capacity of bisphenol A showed little variation, but it was slightly decreased with the value of pH up to 9 and the worst adsorption capacity of BPA was obtained at the value of pH up to 11.

These results were attributed to the variation of surface charge density of hybrid microspheres and BPA, for both of them mainly depending on the pH of solution. SPESPE is a kind of polyelectrolyte materials, and the net charge density is negative in alkali condition. The pKa of BPA is about 9–10, so the BPA is

Table II. The Isotherm Parameters for Bisphenol A onto Microspheres

	Langmuir isotherm			Freundlich isotherm		
	Q_{max} ($\mu\text{mol g}^{-1}$)	k_L	R^2	n	k_F	R^2
M1	500	0.00306	0.948	1.238	2.753	0.991
M2	420	0.00602	0.963	1.472	6.612	0.998
M3	373	0.0129	0.971	1.809	15.751	0.997

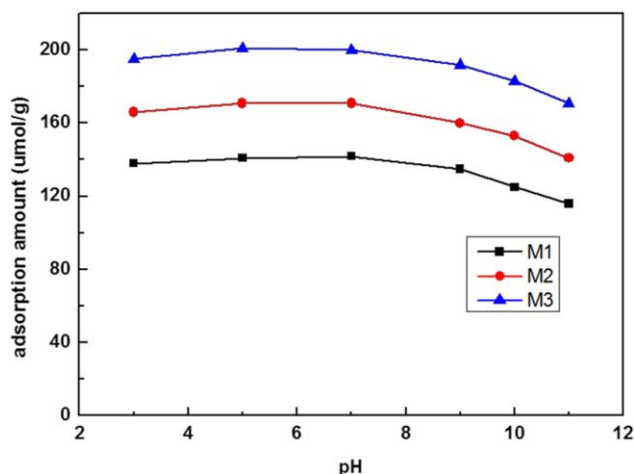


Figure 8. The effect of pH on the adsorption amount of bisphenol A. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

deprotonated in weak basic solution.³⁶ As a result, the repulsive electrostatic interaction is intensified in alkali condition. This is the main mechanism of the worst equilibrium adsorption capacity of BPA onto hybrid microspheres at the value of pH 11.

Reuse of Microspheres

The reuse of adsorbent is crucial in improving the processing economy. Therefore, in this work, the reuse ability of blend microspheres was investigated. Five cycles of adsorption–desorption of blend microspheres for BPA were carried out at initial BPA concentration of $200 \mu\text{mol L}^{-1}$. As shown in Figure 9, after five cycles, the ratio of adsorption capacity for BPA in every cycle to that in the first cycle was all over 85%. It suggested that the PES/SPESPE microspheres could be reused for many times without significant loss of adsorption capacity for BPA and had the potential to be applied in industrial activities.

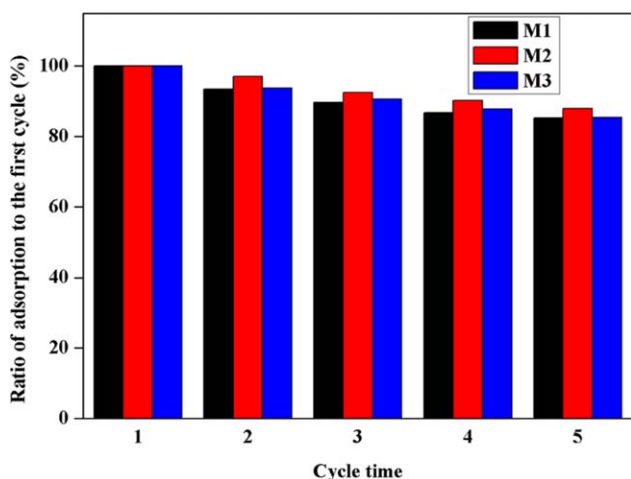


Figure 9. The reuse of hybrid microspheres. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

A novel kind of SPESPE was successfully synthesized. Then, serials of PES/SPESPE microspheres prepared by electro spraying technique were applied to adsorption BPA from aqueous solution. The adsorption capacity of PES/SPESPE microspheres for BPA increased with increasing the proportion of SPESPE in the microspheres. The kinetic data of adsorption were found to follow pseudo-second-order model, which indicated that the rate of occupation of adsorption sites is proportion to the square of the number of unoccupied sites. The equilibrium adsorption isotherm mechanism study showed that the adsorption behaviors of blend microspheres for BPA were nonmonolayer and favorable. Therefore, these results indicated that the PES/SPESPE microspheres could be potentially used as an alternative adsorbent for the removal of BPA from its aqueous solution and could be applied in the environment science field.

ACKNOWLEDGMENTS

We are particularly indebted to Dr. Chaoliang Zhang for assistance of SEM testing in the State Key Laboratory of Oral Diseases.

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