Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Polyethersulfone-Modified Montmorillonite Hybrid Beads for the Removal of Bisphenol A

Yin Chen[a]; Tian Chen[a]; Fuming Cao[a]; Zehua Yin[a]; Xiaojun He[a]; Jian Gao[a]; Anqi Zhang[a]; Changsheng Zhao[a]
[a] State Key Laboratory of Polymer Materials Engineering, Sichuan University, College of Polymer Science and Engineering, Chengdu, China

To cite this Article Chen, Yin , Chen, Tian , Cao, Fuming , Yin, Zehua , He, Xiaojun , Gao, Jian , Zhang, Anqi and Zhao, Changsheng(2008) 'Polyethersulfone-Modified Montmorillonite Hybrid Beads for the Removal of Bisphenol A', Separation Science and Technology, 43: 6, 1404 — 1420
To link to this Article: DOI: 10.1080/01496390701885869
URL: http://dx.doi.org/10.1080/01496390701885869

Separation Science and Technology, 43: 1404–1420, 2008

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701885869

Polyethersulfone-Modified Montmorillonite Hybrid Beads for the Removal of Bisphenol A

Yin Chen, Tian Chen, Fuming Cao, Zehua Yin, Xiaojun He, Jian Gao, Anqi Zhang, and Changsheng Zhao

State Key Laboratory of Polymer Materials Engineering, Sichuan
University, College of Polymer Science and Engineering, Chengdu,
China

Abstract: Na-Montmorillonite (Na-MMT) was modified by cetyltrimethylammonium bromide first, then polyethersulfone (PES)-MMT hybrid beads were prepared using a liquid-liquid phase separation technique for the removal of bisphenol (BPA). The interlayer spacing of the MMT increased after the modification. Adsorption data showed that the modified MMT had excellent adsorption ability to BPA due to the hydrophobic interaction and large porosity. An adsorption dynamics model for the beads was constructed using concentration decrease data. Also, the experimental data of BPA adsorption were adequately fitted with both Langmuir and Freundlich equations. These results indicated that the PES-MMT hybrid particles have the potential to be used in the environmental application.

Keywords: Montmorillonite, organic modification, polyethersulfone, hybrid beads, bisphenol A, adsorption

INTRODUCTION

Many industrial chemicals have been introduced into the environment; some of them have potential hormonal activities and may affect the endocrine

Received 2 June 2007, Accepted 19 November 2007

Address correspondence to Changsheng Zhao, State Key Laboratory of Polymer Materials Engineering, Sichuan University, College of Polymer Science and Engineering, Chengdu 610065, China. Tel.: +86-28-85400453; Fax: +86-28-85405402. E-mail: zhaochsh70@163.com or zhaochsh70@scu.edu.cn

system, thereby affecting health, reproduction, and development of humans and animals (1). Bisphenol A (BPA) is a chemical compound and widely used in the manufacture of polycarbonate plastic products, including many types of food and beverage containers (2). For many years, BPA has been one of the highest-volume chemicals in worldwide production, with annual production capacity in the excess of six billion pounds in 2003 and continued growth in production expected (2). The effluent of polycarbonate plastic product has been contaminating water and soil, and finally will affect the health of humans. However, wastewater containing BPA from those industrials is difficult to treat using traditional treatment methods, such as coagulation, ultrafiltration, oxidation, sedimentation, etc., due to economic considerations and some other reasons (3). Adsorption has gained favor in recent years due to proven efficiency in the removal of pollutants from effluents to stable forms for the above conventional treatment methods (4).

Montmorillonite (MMT) is a kind of clay stone which disperses widely in the world. Because of the large specific surface area, low price, special mechanical property, and some other special properties, MMT has been widely studied. Most of the studies focused on polymer-MMT composites to improve the glass transition temperature and the storage modulus of the polymers (5–7). MMT or organic modified MMT could also be used for the removal of endocrine disrupting chemicals (8–10). However, when the MMT or modified MMT is used directly, cations together with soluble compounds will be eluted. Thus MMT should be coated with a polymer film similar to activated carbon when used in hemoperfusion.

Polyethersulfone (PES) is a well-known polymeric material, which shows outstanding thermal and hydrolytic stabilities as well as good mechanical and film-forming properties. PES-DNA and PES-activated carbon hybrid particles were prepared in our recent study (11–13), and used for the removal of endocrine disruptors. In this study, Na-MMT was modified using etyltrimethylammonium bromide; then PES-MMT hybrid beads were prepared using a liquid-liquid phase separation technique for the removal of BPA.

MATERIALS AND METHODS

Materials

Na-Montmorillonite (Na-MMT), whose chemical formula is $Na_XAl_2\text{-}_XMg_X Si_4O_{10}(OH)_2 \cdot nH_2O$ ($X \approx 0.33$), was purchased from Chengdu Bentonite Plant, China, and filtrated by a sieve with 300 mesh/inch^2, after which the average particle size is about 48 μm. Cetyltrimethylammonium bromide (CMAB) was obtained from Chengdu Kelong Inc, China. Polyethersulfone (PES) was obtained from BASF chemical company, Germany. Bisphenol A (BPA) was obtained from the Tianjin Damao Chemical Reagent, Inc., China. Dibenzofuran (DBF) and Ethidium Bromide (EB) were purchased from Wako Pure Chemical Industry Ltd., Japan. Other chemicals were obtained from Chengdu Kelong Inc., China, and used without further purification.

Organic Modification of Na-MMT

Organic Na-MMT was prepared using a modified method according to the references (14, 15): 10 g CMAB was dissolved in 50 g ethanol-distilled water (1:1) mixture; then 10 g Na-MMT was added and diluted to 1000 ml using distilled water. After the dilution, the mixture was kept at 70°C, and stirred at the rate of about 300 r/min for 4 h. And then the mixture was filtrated and washed by distilled water for several times until no bromine ions could be detected by silver nitrate solution (2%). The modified Na-MMT (m-Na-MMT) was dried in an oven to constant weight and then filtrated by a sieve (300 mesh/inch^2) for further use.

The X-ray diffraction (XRD) and Fourier transform infrared (FTIR) were used to characterize the m-MMT. The X-ray diffraction (XRD) experiment was performed using a diffractometer (Bruker, D8-Advace, 40 kV and 20 mA, CuKa, $\lambda = 0.154$ nm, Philips, Netherland) at room temperature. The scanning step was 0.02° and the scanning range of 2θ was 1°–18°. The FTIR spectra were obtained using the Perkin Elmer 1000 Infrared Spectrometer, USA.

Preparation and Characterization of the Hybrid Beads

PES-MMT hybrid beads were prepared using a liquid-liquid separation technique as our previous study (11). Polyethersulfone (PES) was dissolved in N,N-dimethyl acetamide (DMAc) to obtain PES solution (10 wt%). Then, required amount of MMT was added into the PES solution, and stirred sufficiently to obtain the well-distributed suspension solution. The resultant polymer solution was dropped into distilled water by using a 0.6-mm-diameter syringe needle at room temperature to prepare the hybrid beads. The injection speed was controlled at about 80 drops/min. The air gap from the needle head to the water was 15–20 cm. The hybrid beads were then incubated in distilled water for over 72 h to elute the solvent from the beads. For the sake of comparison, non-modified MMT was also used to prepare hybrid beads.

For the SEM observation, the bead samples were dried at room temperature. Then the beads were quenched by liquid nitrogenous gas, cut with a single-edged razor blade, attached to the sample supports and coated with a gold layer. A scanning electron microscope (JSM-5900LV, JEOL) was used for the morphology observation of the outer surface and the cross-section of the beads.

The average diameter and porosity of the hybrid beads can be calculated using the following formulas (12):

$$\text{Diameter } (D) = \left\{ \frac{6[W_A(1 - C\%)/\rho_P + W_A \times C\%/\rho_M + (W_B - W_A)/\rho_W]}{n\pi} \right\}^{1/3} \tag{1}$$

$$\text{Porosity } (P) = \frac{(W_B - W_A)/\rho_W}{W_A(1 - C\%)/\rho_P + W_A \times C\%/\rho_M + (W_B - W_A)/\rho_W} \times 100\% \tag{2}$$

where W_B is the weight of the hybrid beads before drying (g); W_A is the weight of hybrid beads after drying (g); ρ_p is the density of PES (1.43 $\mathrm{g/cm^3}$); ρ_M is the density of MMT (2.23 $\mathrm{g/cm^3}$) and m-MMT (1.65 $\mathrm{g/cm^3}$); ρ_W is the density of water (1.0 $\mathrm{g/cm^3}$); n is the number of the beads (25) and $C\%$ is the mass percentage of the MMT in the PES-MMT system.

The densities for MMT and m-MMT were the bulk densities in the formula above. A simple method was used to determine the bulk densities for MMT, as described following: About 1 g dried MMT (or m-MMT) powder was immersed into 10 mL distilled water. After the adsorption of water at the equilibrium value, the bulk volume of the MMT could be obtained by the volume change of the water. And then the bulk density of MMT (or m-MMT) could be calculated.

Accumulation and Removal of BPA by the Hybrid Beads

As BPA shows very low solubility in water, therefore, we dissolved BPA in ethanol, and then diluted in distilled water. The removal of BPA was examined by the following procedures: The PES-MMT hybrid beads (about 40 mg) were applied to the prepared BPA solutions (25 mL) at room temperature. The BPA concentrations were determined at the planned time intervals by using an UV-VIS spectrophotometer (SP-752 Shanghai Spectrum Instruments Co. Ltd., Shanghai, China) at the wavelength of 276 nm. The effect of ethanol in the BPA solution on the adsorption was also studied.

The BPA adsorbed amount by the hybrid beads was calculated by using the following formula:

$$A_t = \frac{(C_0 - C_t) \times V \times M}{m} \times 100\% \tag{3}$$

where A_t is the adsorbed amount of BPA to the hybrid particles per gram at the time t, mg/g; C_0 is the original BPA concentration in the solution, μmol/L; C_t is the concentration at the time t, μmol/L; V is the volume of the BPA solutions, ml; $M = 228.29$ g/mol, is the molecular weight of BPA; m is the weight of the dried hybrid particles, g.

Accumulation and Removal of Organic Compounds by the Hybrid Beads

To investigate the application of the hybrid beads, dibenzofuran (DBF), hydroquinone (HQ), and ethidium bromide (EB) were also used to test their accumulation into the hybrid beads. The accumulation of these reagents was examined by the following procedures. The beads (about 40 mg) were put into the respective aqueous solutions (25 mL, 100 μmol/L; for DBF, 5% ethanol in the solution) and incubated for 48 h at room temperature. The accumulation of these reagents was confirmed by the absorption spectra of their aqueous solutions in the absence or presence of the hybrid beads.

RESULTS AND DISCUSSION

Characterization of the Modified Na-MMT

It is normal that the persuasive evidence for the intercalation of a modifier into the interlayer of MMT can be obtained from XRD patterns. By monitoring the position, shape, and intensity of the diffraction peaks, the intercalated structure can be identified. For the intercalated MMT, the finite layer expansion associated with the modifier intercalation usually results in the appearance of a new basal reflection corresponding to the larger gallery height. Figure 1 shows the XRD patterns of the MMT and CMAB modified MMT (m-MMT). The interlayer spacing was calculated to be 1.577 nm for the MMT, while that was 4.106 nm for the m-MMT. This was caused by the intercalation of the

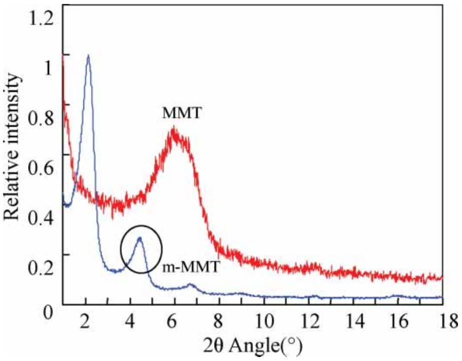

Figure 1. XRD patterns of MMT & m-MMT.

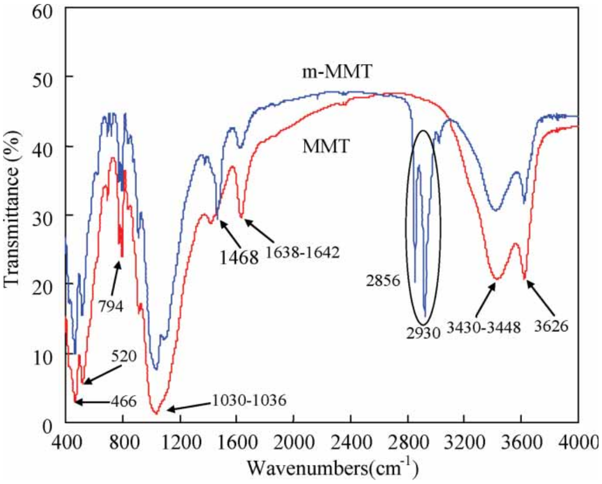

Figure 2. FTIR spectra of MMT and m-MMT.

CMAB, and the formation of intercalated structure. The interlayer spacing of MMT and is somewhat high, this may be caused by the origination from the specific geologic and climatic environment (16). Thus, the d(001) value calculated from the XRD pattern for the modified MMT was high, and the data was consisted with the result in the reference (14).

Figure 2 shows the FTIR spectra of the MMT and m-MMT. As shown in the spectra, the absorption bands (3626, 3430–3448, 1638–1642 cm^{-1}) attributed to the hydroxyl stretching of the silicate lattice, water in the interlays, and the hydroxyl bending of adsorbed water, respectively which also suggested the presence of some adventitious adsorbed water (17). The broad bands at 1030–1036 cm^{-1} and a weak band at 794 cm^1 can be assigned to the stretching of Si-O-Si and Si-O-Al in the MMT lattice, respectively. No significant changes in the bands (520 and 466 cm^{-1}), which correspond to the bending of Si-O-Si and Si-O-Al, respectively, were found for the material modified by the adsorption of the CMAB; these indicated that the modification did not cause obvious changes in the lattice structure of the MMT. Two sharp bands at 2930 and 2856 cm^{-1} were observed in the FTIR spectrum of the CMAB modified MMT, corresponding to the symmetrical and asymmetrical vibration of the $-CH_2$ group in the CMAB, respectively. The band at 1468 cm^{-1} is assigned to the C-C stretching bands of the modifier (18).

Characterization of the Hybrid Beads

The liquid–liquid phase-separation technique employed for the preparation of the beads results in a porous structure for the PES matrix. Figure 3 shows the

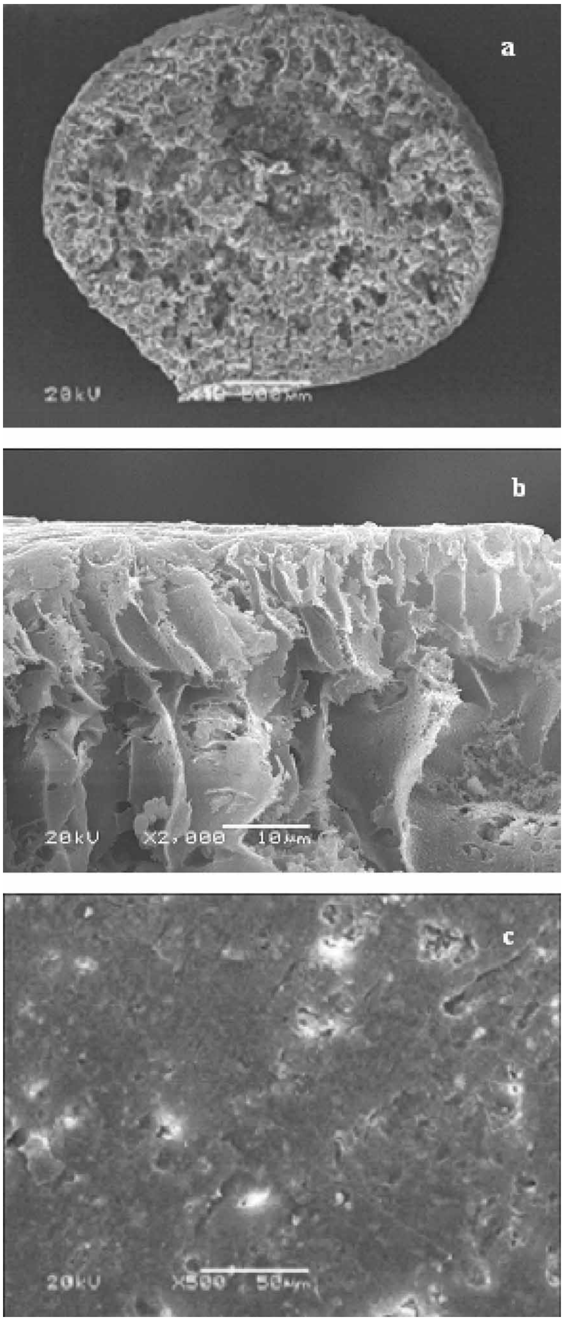

Figure 3. SEM pictures of the PES-m-MMT (60% m-MMT) hybrid beads (a) Cross-section with a magnification ×40; (b) Cross-section with a magnification ×2000; and (c) outer surface with a magnification ×500.

Table 1. Average diameters and porosities for different hybrid beads

Kinds of hybrid beads	Average diameter (mm)	Average porosity (%)
PES-MMT (60%)	2.20 ± 0.06	77.3 ± 0.4
PES-m-MMT (60%)	2.26 ± 0.06	78.3 ± 0.4
PES-m-MMT (40%)	2.45 ± 0.07	84.6 ± 0.5
PES-m-MMT (20%)	2.56 ± 0.08	82.9 ± 0.5

cross-section (Fig. 3a, b) and the outer surface (Fig. 3c) of the hybrid beads. First, because of the rapid phase separation, a skin layer is formed on the outer surface of the beads. It is obvious that the outer surface is more compact than the internal of the beads. Second, the pore size gradually increased from the outer surface to the internal region of the beads. No significant difference was found between the hybrid beads with MMT and m-MMT. The structure is similar to that for the other PES hybrids in our earlier reports (11–13), and is useful for using as adsorbents.

The average diameter and porosity were calculated using the formulas mentioned above, and are shown in Table 1. Though traditionally BET is used to determine the specific areas and porosities of porous materials, we failed to gain them from our hybrid beads due to the compact skin layers. For the PES-MMT hybrids, the diameter and the porosity were 2.20 mm and 77.3% respectively. And no significant differences in the diameter and porosity were found for all the beads. In fact, the diameter of the bead is mainly depending on the needle diameter used to prepare the beads.

Accumulation and Removal of BPA by the Hybrid Beads

Figure 4 shows the concentration decrease in the BPA solution when the PES-MMT hybrid beads and the PES-m-MMT hybrid beads were incubated in the solutions, respectively. As shown in the figure, there was no notable decrease in the BPA concentration for the PES-MMT hybrid beads, even after for 80 hours. For the PES-m-MMT hybrid beads, the BPA concentration rapidly decreased when the beads were applied to the BPA solutions. And the concentration reached an equilibrium value at about 70 h. These results suggested that the accumulation of BPA was contributed to the modified MMT.

Analysis of the dynamic is important in order to develop an equation that accurately represents the results, and which would be useful for application and design purposes. Here, we developed a dynamic model to describe the adsorption and the concentration change.

The BPA adsorption is a dynamic process. Assume the PES-m-MMT had enough adsorption sites, thus the BPA adsorption rate only depended on the

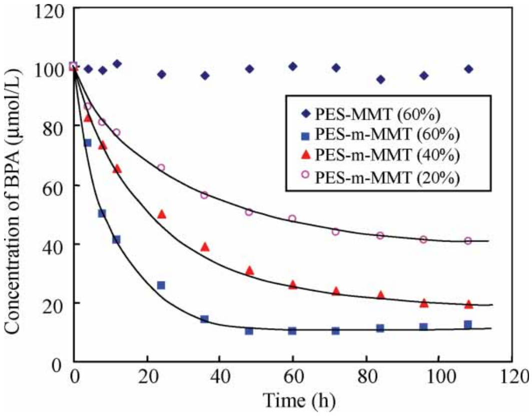

Figure 4. BPA concentration decrease when the beads were incubated in BPA solutions. Duplicate experiments gave the similar results.

BPA concentration and the BPA molecules transport through the bead surface. According to the assumptions and the surface mass action law (19), the BPA adsorption rate, R_a, to the PES-m-MMT hybrid beads could be expressed as:

$$R_a = k_1 c \tag{4}$$

where c is the concentration of the BPA solution and k_1 is the adsorption velocity constant.

The BPA desorption rate, R_d, can be expressed as:

$$R_d = K_2' N \tag{5}$$

where K_2' is the desorption velocity constant; N is the amount of the BPA adsorbed to the beads. Since N is proportional to the concentration decrease ($c_0 - c$), Equation (5) can be transformed as:

$$R_d = k_2(c_0 - c) \tag{6}$$

where, k_2 is the apparent desorption velocity constant.

Thus, the total BPA adsorption rate can be expressed as following:

$$R_t = -dc/dt = R_a - R_d = k_1 c - k_2(c_0 - c) \tag{7}$$

According to the initial condition that $t = 0$, $c = c_0$ (100 µmol/L), the differential Equation (7) can be solved:

$$c = \frac{k_2}{k_1 + k_2} c_0 + \frac{k_1}{k_1 + k_2} c_0 e^{-(k_1+k_2)t} \tag{8}$$

When $R_t = 0$, the adsorption reaches equilibrium, and the equilibrium BPA concentration can be calculated as:

$$c_m = \frac{k_2}{k_1 + k_2} c_0 \tag{9}$$

Thus, the Equation (8) can be rewritten as:

$$c = c_m + (c_0 - c_m)e^{-(k_1+k_2)t} \tag{10}$$

The parameters k_1 and k_2 could be calculated using nonlinear simulation with the help of a mathematical software, i.e., Matlab 7.01. The parameters of PES-m-MMT hybrid beads with different mass percentage of m-MMT in this model are shown in Table 2. The results showed that the Equation (10) could describe the concentration decrease well, as shown in Fig. 4. When the amount of the m-MMT increased, the adsorption constant k_1 increased, which indicated that the adsorption ability mainly attributed to the m-MMT. There was no obvious difference in the desorption constant k_2 for the hybrid with 40% and 60% m-MMT in the hybrids. But due to the higher adsorption constant k_1 for the hybrid with 60% m-MMT, the BPA concentration decreased rapidly, and a large amount of BPA was adsorbed to the hybrid.

Adsorption Isotherms to BPA

Analysis of the isotherm is also important for design purposes. Figure 5 shows the original adsorption isotherms of BPA onto the PES-m-MMT hybrid beads. The results indicated that PES-m-MMT hybrid beads with higher m-MMT proportion had better adsorption ability on BPA.

There are several adsorption isotherm equations, two of which used widely are the Langmuir and Freundlich equations.

The Langmuir adsorption, which is the monolayer adsorption, depends on the assumption that there are many adsorption sites on the adsorbent dispersing evenly on the surface, every site has the same energy and can just adsorbs one molecule. Therefore, a saturation value is reached beyond which no further sorption can occur (3). One of the linear forms of the

Table 2. Values of parameters in Equation (10)

Kind of hybrid beads	k_1 (h^{-1})	k_2 (h^{-1})	c_m (μmol/L)	r^2
PES-m-MMT (60%)	0.0810	0.0100	10.99	0.9953
PES-m-MMT (40%)	0.0353	0.0090	20.32	0.9961
PES-m-MMT (20%)	0.0250	0.0160	39.02	0.9925

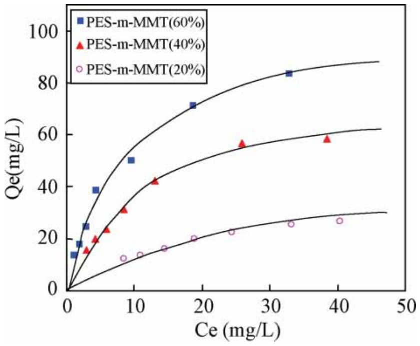

Figure 5. Original adsorption isotherms of BPA onto the PES-m-MMT hybrid beads.

Langmuir equation is shown as:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max}K_L} + \frac{C_e}{Q_{\max}} \tag{11}$$

where Q_e is the mass of BPA adsorbed by unit mass of the hybrid beads after the concentration reaches equilibrium (mg g^{-1}); C_e is the concentration of BPA in the aquatic solutions at equilibrium (mg L^{-1}), $Q_{\max}$ is the monolayer capacity of the beads (mg g^{-1}), and K_L is the Langmuir adsorption constant (L mg^{-1}). A linear plot was obtained when C_e/Q_e plotted aganist C_e as shown in Fig. 6. The Langmuir constant K_L and $Q_{\max}$ could be calculated from the intercept and the slope of the linear plot of the experiment data, the values were exhibited in Table 3.

The maximum adsorption amount $Q_{\max}$, which is a measure of the capacity of the adsorbent to retain the adsorbed solute, suggested that the hybrid particles could adsorb BPA effectively. Our results showed that

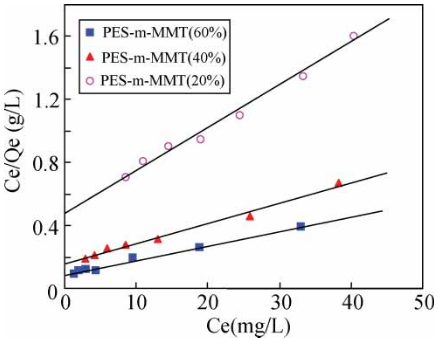

Figure 6. Langmuir adsorption isotherms of BPA onto the PES-m-MMT hybrid beads.

Table 3. Values of parameters in Langmuir Equation (11)

Kind of hybrid beads	K_L (L/mg)	Q_{max}(mg/g)	r^2
PES-m-MMT (60%)	0.1464	103.92	0.9978
PES-m-MMT (40%)	0.1142	69.69	0.9939
PES-m-MMT (20%)	0.0592	36.6	0.9911

the adsorption isotherms of BPA onto the PES-m-MMT the hybrid beads could be described by Langmuir model well based on the large correlation coefficients. And the beads with the largest amount of m-MMT had the best adsorption.

The Freundlich equation is an empirical equation employed to describe heterogeneous systems, characterized by the heterogeneity factor $1/n$, describes reversible adsorption, and is not restricted to the formation of the monolayer (3). A linear form of the Freundlich expression is as following:

$$\ln Q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{12}$$

where Q_e and C_e have the same meanings and units as in the Langmuir equation. K_F is the Freundlich constant (Lg^{-1}), and $1/n$ is the heterogeneity factor. The plot can be seen in Fig. 7. Values of the parameters in Freundlich equation were exhibited in Table 4.

The results showed that with the decrease of the amount of m-MMT in the hybrid beads, K_F decreased dramatically; while there was no change in the heterogeneity factor n. The larger Freundlich constant K_F for the higher amount of m-MMT in the hybrids indicated better adsorption ability. We also noted that the value of n in the Freundlich equation is larger than 1, which reflecting the favorable adsorption (3).

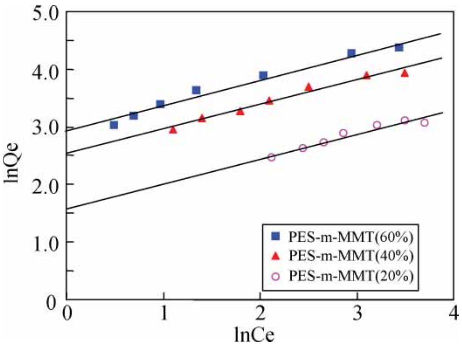

Figure 7. Freunlich adsorption isotherm of BPA onto the PES-m-Na-MMT hybrid beads.

Table 4. Values of parameters in Freundlich Equation (12)

Kind of hybrid beads	K_F (L/g)	n	r^2
PES-m-MMT (60%)	18.51	2.143	0.9791
PES-m-MMT (40%)	12.41	2.276	0.9718
PES-m-MMT (20%)	4.62	2.102	0.9729

BPA Adsorption in Ethanol-Water Mixture

Since BPA shows low solubility in water and for further utilization of the hybrid beads, the effect of ethanol in the BPA solution on the adsorption was examined. Figure 8 shows the BPA removal ratio by the hybrid beads in different ethanol-water mixture after incubating for 72 h.

It is clear that there was no effect on the BPA removal when the volume fraction of the ethanol in the BPA solution was low (the volume ratio was lower than 10%). However, when the ratio was higher than 10%, the BPA removal ratio decreased dramatically. And with the increase of ethanol in the solution, the BPA removal ratio decreased, which indicated that a smaller amount of BPA was adsorbed to the hybrids. When the ethanol ratio increased to 30%, the BPA removal ratio decreased from about 90% to about 40%. As we know, BPA is soluble in ethanol; the results suggested that the adsorption was caused by the hydrophobic interaction between the BPA and the hybrid beads due to the intercalation of CMAB.

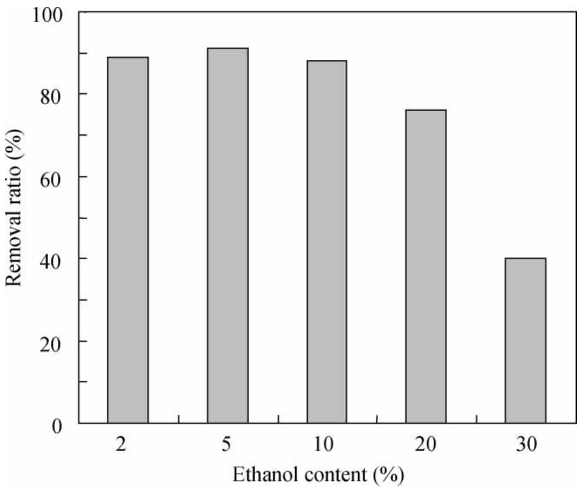

Figure 8. BPA removal ratios in the solutions with different volume fractions of ethanol. Duplicate experiments gave the similar results.

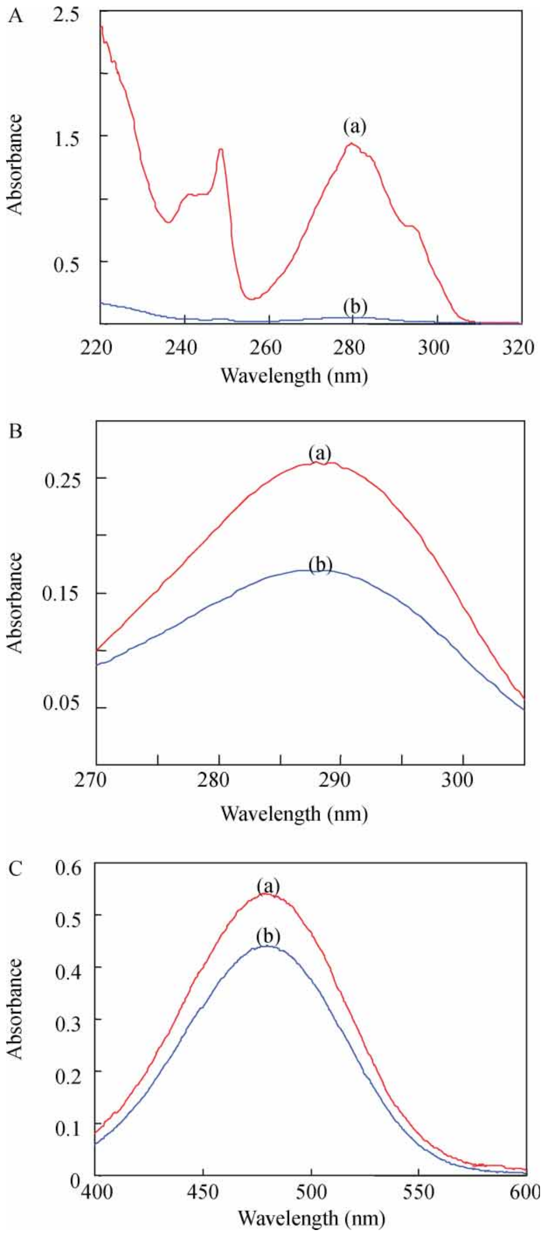

Figure 9. Absorption spectra of aqueous solutions of dibenzofuran (DBF), hydroquinone (HQ) and ethidium bromide (EB) in the absence (a) and presence (b) of the PES/m-MMT hybrid beads microspheres. (A) Aqueous DBF solution (100 μmol/L, containing 5% ethanol); (B) aqueous HQ solution (100 μmol/L) and (C) aqueous EB solution (100 μmol/L). Duplicate experiments gave the similar results.

Furthermore, when the ethanol ratio was over 80%, there is almost no BPA adsorption to the beads. In fact, when the hybrid beads after the adsorption experiments were applied to ethanol, the adsorbed BPA would be eluted; and about 90% of the adsorbed BPA would desorbed to ethanol after incubating for 24 h. These indicated that the hybrid beads could be reused after the incubation in ethanol.

Accumulation and Removal of Other Organic Compounds by the Hybrid Beads

To study the application of the hybrid beads, the PES-m-MMT hybrid beads with 60% m-MMT were also used in the accumulation and removal of other organic compounds, including dibenzofuran (DBF), hydroquinone (HQ), and ethidium bromide (EB). The water solubility for BPA, DBF, HQ, and EB are 120 mg/L, 4.75 mg/L, 70 g/L, and 50 g/L respectively at room temperature (20–22). Figure 9 shows the absorption spectra of their aqueous solutions before and after the application to the hybrid beads for 72 h, respectively.

The absorption peak of DBF dissipated with the application to the hybrids, and the DBF were almost completely removed by the beads. About 40% of the HQ was removed by the beads. Not more than 20% of the EB was adsorbed in the beads. The results showed that the PES-m-MMT hybrid beads have excellent adsorption ability to DBF, but poor adsorption ability to HQ and EB due to their high water solubility, which indicated that the adsorbed amount (or removal ratio) in the aqueous solutions corresponded to the water solubility of the chemical compounds. Water soluble compounds, such as HQ and EB could also be partly removed by the hybrids. Thus, the accumulation and removal of chemical compounds by the PES-m-MMT hybrid beads might attribute to the hydrophobic interaction, large porosity and specific surface area.

CONCLUSION

In this study, Na-montmorillonite (Na-MMT) was modified by cetyltrimethylammonium bromide for the removal of bisphenol A (BPA). For the application, PES-MMT hybrid beads were prepared using a liquid-liquid phase separation technique. It was demonstrated that the modified MMT (m-MMT) showed excellent adsorption ability to BPA. This may be caused by the m-MMT which has a larger interlayer spacing, which leads to a larger porosity and specific surface areas, and better hydrophilicity. An adsorption dynamics model for the beads was constructed, and can be used to predict the concentration decrease data. Also, the experimental data of the BPA adsorption were adequately fitted with both Langmuir and Freundlich equations. Furthermore, the effect of ethanol in BPA solutions on the adsorption and the removal of other organic compounds by the hybrid beads were investigated. The results indicated that the hybrid particles may be a potential adsorbent to be used in the environmental application.

ACKNOWLEDGMENT

This work was financially sponsored by the National Natural Science Foundation of China (No. 50403028, 50673064), State Education Ministry of China (Project-sponsored by SRF for ROCS, No. 2004527-16-14, and Program for New Century Excellent Talents in University, NCET-05-0791) and Innovation Fund of Sichuan University (G2006004).

REFERENCES

1. Ryoko, K., Yumiko, T., Yasuteru, U., and Ryushi, N. (2007) Measurement of bisphenol A concentrations in human colostrums. *Chemosphere*, 6 (66): 1160.
2. Vom Saal, F.S. and Welshons, W.V. (2006) Large effects from small exposures. II. The importance of positive controls in low-dose research on bisphenol A. *Environmental Research*, 1 (100): 50.
3. Zcan, S. and Zcan, A. (2004) Adsorption of acid dyes from aqueous solutions onto acid-activated bentonite. *Journal of Colloid and Interface Science*, 1 (276): 39.
4. Sun, Q.Y. and Yang, L.Z. (2003) The adsorption of basic dyes from aqueous solution on modified peat-resin particle. *Water Research*, 37 (7): 1047.
5. Choi, Y.S., Choi, M.H., Wang, K.H., Kim, S.O., Kim, Y.K., and Chung, I.J. (2001) Synthesis of exfoliated PMMA/Na-MMT nanocomposites via soap-free emulsion polymerization. *Macromolecules*, 34: 8978.
6. Chang, Y.W., Yang, Y.C., and Ryu, S.H. (2002) Preparation and properties of EPDM/organo-montmorillonite hybrid nanocomposites. *Polymer International*, 51 (4): 319.
7. Choi, Y.S., Choi, M.H., Wang, K.H., Kim, Y.K., and Chung, I.J. (2002) Synthesis of exfoliated PS/Na-MMT nanocomposites via emulsion polymerization. *Chemistry Materials*, 14: 4990.
8. Shareef, A., Angove, M.J., Wells, J.D., and Johnson, B.B. (2006) Sorption of bisphenol A, 17α-ethynylestradiol and estrone to mineral surfaces. *Journal of Colloid and Interface Science*, 297: 62.
9. Cruz-Guzman, M., Celis, R., Hermosin, M.C., and Cornejo, J. (2004) Adsorption of the herbicide simazine by montmorillonite modified with natural organic cations. *Environmental Science and Technology*, 38: 180.
10. Akcay, M. and Akcay, G. (2004) The removal of phenolic compounds from aqueous solutions by organophilic bentonite. *Journal of Hazardous Materials B*, 113: 189.
11. Mao, M., Liu, Z.B., Wang, T., Yu, B.Y., Wen, X., Yang, K.G., and Zhao, C.S. (2006) Polysulfone-activated carbon hybrid particles for the removal of BPA. *Separation Science and Technology*, 41 (3): 515.
12. Zhao, C.S., Sun, S.D., Yang, K.G., Nomizu, M., and Nishi, N. (2005) DNA-loaded porous polyethersulfone particles for environmental applications I. Preparation. *Journal of Applied Polymer Science*, 98 (4): 1668.

13. Zhao, C.S., Liu, X.D., Nomizu, M., and Nishi, N. (2004) Preparation of DNA-loaded polysulfone microspheres by liquid-liquid phase separation and its functional utilization. *Journal of Colloid and Interface Science*, 275 (2): 470.
14. Wang, Y.Y., Liu, J.P., Tian, J., and Qian, C. (2006) Preparation and properties characterization of organophilic montmorillonite. *Henan Chemical Industry*, 23: 17.
15. Pospíšil, M., Čapková, P., Měřínská, D., Maláč, Z., and Šimoník, J. (2001) Structure analysis of montmorillonite intercalated with cetylpyridinium and cetyltrimethylammonium: molecular simulations and XRD analysis. *Journal of Colloid and Interface Science*, 236: 127.
16. Wu, P.X. and Ming, C.B. (2006) The relationship between acidic activation and microstructural changes in montmorillonite from Heping, China. *Spectrochimica Acta, Part A*, 63: 85.
17. Zhang, L.M., Xu, J., Hou, G.J., Tang, H.R., and Deng, F. (2007) Interactions between Nafion resin and protonated dodecylamine modified montmorillonite: A solid state NMR study. *Journal of Colloid and Interface Science*, 311 (1): 38.
18. Kozak, M. and Domka, L. (2004) Adsorption of the quaternary ammonium salts on montmorillonite. *Journal of Physics and Chemistry of Solids*, 65 (2–3): 441.
19. Morrissey, F.A. and Grismer, M.E. (1999) Kinetics of volatile organic compound sorption/desorption on clay minerals. *Journal of Contaminant Hydrology*, 36 (3–4): 291.
20. Zhao, C.S., Wei, Q.R., Yang, K.G., Liu, X.D., Nomizu, M., and Nishi, N. (2004) Preparation of porous polysulfone beads for selective removal of endocrine disruptors. *Separation Science and Technology*, 40 (3): 297.
21. http://www.inchem.org/documents/hsg/hsg/hsg101.htm
22. http://www.jtbaker.com/msds/englishhtml/e2410.htm