

Preparation of polyethersulfone–organophilic montmorillonite hybrid particles for the removal of bisphenol A

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ABSTRACT

Polyethersulfone (PES)–organophilic montmorillonite (OMMT) hybrid particles, with various proportions of OMMT, were prepared by using a liquid–liquid phase separation technique, and then were used for the removal of bisphenol A (BPA) from aqueous solution. The adsorbed BPA amounts increased significantly when the OMMT were embedded into the particles. The structure of the particle was characterized by using scanning electron microscopy (SEM); and these particles hardly release small molecules below 250 °C which was testified by using thermogravimetric analysis (TGA). The experimental data of BPA adsorption were adequately fitted with Langmuir equations. Three simplified kinetics model including the pseudo-first-order (Lagergren equation), the pseudo-second-order, and the intraparticle diffusion model were used to describe the adsorption process. Kinetic studies showed that the adsorbed BPA amount reached an equilibrium value after 300 min, and the experimental data could be expressed by the intraparticle mass transfer diffusion model. Furthermore, the adsorbed BPA could be effectively removed by ethanol, which indicated that the hybrid particles could be reused. These results showed that the PES–OMMT hybrid particles have the potential to be used in the environmental application.

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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), and biphenyl (BP) [1,2]. It is well known that endocrine disruptor may influence the living system [3,4]. Recently, it has been reported that organoclay [5–11], hydrophobic porous polymer membranes [12], hydrophobic porous polymer beads [13], water-insoluble DNA and DNA matrix materials [14–16] could selectively remove endocrine disruptors. Another method is the degradation of endocrine disruptors. Bacteria distributed in river can degrade some kinds of endocrine disruptors [17], and TiO₂-pillared montmorillonite can also degrade endocrine disruptors [18].

Among these methods mentioned above, clays are widely used as adsorbent [5–11] due to the high-specific surface area, high chemical and mechanical stabilities, a variety of structural properties and low cost. Numerous studies have focused on finding new methods and materials to modify the pristine clay [7,19], studying the kinetic of the sorption process [11,20], and also augmenting the application area of clay, including the removal of heavy metal

ions [21,22], acid dye [23] and trace elements from poultry litter [24]. However, when the clay or the organoclay powder were used directly as in these studies mentioned above, especially used in liquid medium, fine clay powders together with soluble organic compounds in the clay will be eluted. And a centrifugal filtration process should be taken before withdrawing the aqueous samples, which eventually lead the clay adsorbents far from real application.

To resolve the problems mentioned above, clay powders can be encapsulated with a polymer membrane. Moreover, polyethersulfone (PES) shows outstanding thermal and hydrolytic stabilities as well as good mechanical and film-forming properties. Therefore, it is reasonable to predict that by embedding organoclay powder within PES, novel and useful adsorbents may be obtained.

In this paper, PES–OMMT hybrid particles were firstly prepared by using a liquid–liquid phase separation technique, and then used for the removal of BPA from its aqueous solution. The kinetics and equilibrium isotherms of the adsorption of BPA onto the PES–OMMT hybrid particles were investigated.

2. Materials and methods

2.1. Materials

The organoclay (YH-908) modified by using hexadecyl trimethyl ammonium bromide (HDTMA) in an amount equivalent to 100%

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cation exchange capacity (CEC) and abbreviated as OMMT in this article, was supplied by Anji Yuhong Clay Chemical Co., Ltd., China. Clay samples were treated as follows: washed with distilled water three times with constant stirring to remove soluble inorganic salts and any adhering materials. The samples were then left to settle more than 24 h. After decanting the solution, the clay was collected, and dried at room temperature. Polyethersulfone (PES, Ultrason E 6020P, CAS Number: 25608-63-3) was purchased from BASF chemical company (Germany). All the other materials were obtained from the Kelong Chemical Reagent Factory China, which were of analytical grade, and used without further purification.

2.2. Preparation of PES–OMMT hybrid particles

For the sake of comparison, a series of PES–OMMT hybrid particles were prepared by using a liquid–liquid phase separation technique, which was described in detail in our earlier report [13]. Required amounts of PES was dissolved in *N,N*-dimethyl acetamide (DMAC), then required amounts of OMMT powder were added to the polymer solution, and stirred sufficiently. The resultant suspension prepared above was dropped into distilled water by using a 1.2-mm diameter syringe needle at room temperature to prepare hybrid particles. The injection speed was controlled at 60–100 drops/min. The air gap from the syringe needle to the water was 5–8 cm. The particles were placed in ethanol for 24 h followed by incubation in boiling water for over 6 h to elute the solvent, then stored in distilled water until use. Due to the difficulty to prepare smooth-shape particles when the proportion of OMMT is higher than 80% in the particles, the proportion was deemed as the highest proportion for the preparation process. In this study, the mass ratios of PES to OMMT were controlled at 1:0, 1:1, 1:2.5, 1:3 and 1:3.5, and these particles were coded as PO, PO1, PO2, PO3, and PO4, respectively.

2.3. Characterization of the PES–OMMT hybrid particles

The diameter, the porosity and the pore volume of the particles were calculated by using the following formulas [25]:

$$\text{Diameter } (D) = \left\{ \frac{6W_A(1-C\%)/\rho_p + W_A C\%/\rho_c + (W_B - W_A)/\rho_w}{n\pi} \right\}^{1/3} \quad (1)$$

$$\text{Porosity } (P) = \frac{(W_B - W_A)/\rho_w}{W_A(1-C\%)/\rho_p + W_A C\%/\rho_c + (W_B - W_A)/\rho_w} \times 100\% \quad (2)$$

$$\text{Pore volume } (PV) = \frac{n\pi D^3 P}{6W_A} \quad (3)$$

where W_B is the weight of the PES–OMMT hybrid particles before drying (g); W_A is the weight of the hybrid particles after drying (g); ρ_w is the density of water, $\rho_w = 1.0 \text{ g/cm}^3$; and ρ_p is the density of the PES, $\rho_p = 1.43 \text{ g/cm}^3$; ρ_c is the density of the OMMT, $\rho_c = 1.65 \text{ g/cm}^3$; n is the number of the particles, $n = 30$; $C\%$ is the mass percents of the OMMT in the PES–OMMT system.

2.4. Scanning electron microscopy (SEM)

For SEM observation, the samples were dried at room temperature, and then cut by a single-edged razor blade, attached to the sample supports and coated with a gold layer. The SEM images were recorded using an S-2500C microscope (Hitachi, Japan).

2.5. Thermogravimetric analyze (TGA)

Thermogravimetric analysis of the PES–OMMT hybrid particles was carried out by using a WRT-2T instrument (Shanghai Precision & Scientific Instrument Co., Ltd., China) under a nitrogen atmosphere from 50 to 800 °C at a heating rate of 10 °C min⁻¹.

2.6. Adsorption experiments and desorption experiments

Bisphenol A was used as the model endocrine disruptor in our experiment. As it shows small solubility in water, BPA was dissolved in ethanol, and then diluted in distilled water. The adsorption experiments were carried out as follows: about 0.1 g of the PES–OMMT hybrid particles were applied in 20 ml of the BPA solution in conical flasks at a constant temperature 25 ± 0.1 °C. The BPA concentrations were determined at different time intervals by using a UV–vis spectrophotometer U-200A (Shanghai Spectrum Instruments Co., Ltd., Shanghai, China) at the wavelength of 276 nm. The effects of OMMT proportion in the particles were observed among PO, PO1, PO2, PO3, and PO4, in which the proportion of OMMT in the particles increased in order.

In order to analyze the adsorption isotherm, which is very important for design purposes, the saturation adsorption capacity of the particles was studied by applying different weight of the sorbent from about 0.003 to 0.1 g at a fixed BPA concentration (200 μmol/l) at room temperature (25 ± 0.1 °C). After reaching the equilibrium, the BPA concentration was also determined by using the UV–vis spectrophotometer U-200A.

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

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

$$Q_t = \frac{(C_0 - C_t)V}{m} \times 100\% \quad (5)$$

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

The desorption experiments were carried out as follows: after the adsorption, the PO and PO1 particles were immersed into 20 ml ethanol for 12 h, and stirred using a shaker at a speed of 50 rpm at room temperature. Then, the particles were removed out, and applied to another 20 ml ethanol. This process was repeated five times. Each time, the concentration of the BPA was determined by using the UV–vis spectrophotometer U-200A. The desorption ratio (R_d) was obtained as:

$$R_d = \frac{m_d}{m_a} \times 100\% \quad (6)$$

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

2.7. Effect of BPA concentration on the adsorption

Adsorption isotherm experiment was carried out as follows: about 0.1 g of the PO1 hybrid particles were applied to 20 ml of BPA solutions, with the initial concentrations of 100, 150, 200, and 240 μmol/l, respectively, in conical flasks at 25 ± 0.1 °C. The BPA concentration was also determined by using the UV–vis spectrophotometer U-200A.

3. Results and discussion

3.1. PES–OMMT hybrid particles

The liquid–liquid phase separation technique employed for the preparation of the particles resulted in the porous structure of the PES matrix. It was the precipitation of PES in a non-solvent. When the PES solution containing OMMT powder was dropped into water, liquid–liquid phase separation caused by the rapid exchange of the solvent DMAC and non-solvent water occurred, and a skin layer formed due to the rapid phase separation (see Fig. 1b). With the completion of the exchange between the solvent and the non-solvent, the porous PES hybrid particles were prepared (see Fig. 1a and d), and many pores existed in the spheres (see Fig. 1b and c). The OMMT was incorporated into the particles during the process. As shown in Fig. 1, it is clearly observed that the particles exhibit the following features: (1) a finger-like structure was formed near the skin layer, and the diameter of the pores was about 0.5–1.0 μm , which was large enough for the diffusion of the small organic molecules like BPA; (2) the pore size gradually increased from the outer surface to the internal region of the particles; (3) the porous structure led to a very large porosity, which were essential for using as absorbents; (4) with the increase of the OMMT amount in the particles, the porous structure gradually became compact.

The porosity, the diameter and the pore volume of the hybrid particles were calculated; data are shown in Table 1. For the par-

ticles without OMMT (PO), both the porosity and the pore volume were very large; for the PES–OMMT hybrid particles, they became smaller.

3.2. Adsorption and desorption of BPA by the particles

Fig. 2 shows the adsorbed BPA amount by different particles. As shown in the figure, with the increase of the OMMT in the particles, the adsorbed BPA amount per unit mass of the hybrid particles increased. The adsorbed amount of BPA to the pure PES particles is very small, thus the adsorption of BPA largely attributes to the OMMT, while the PES mainly functions as a matrix to embed the OMMT, which agrees with our former research results [25].

Furthermore, the utilization efficiency of the OMMT in the particles, which was calculated as the adsorbed BPA amount per unit mass of the OMMT, is another factor we cared about; the data are shown in Fig. 3. Among the hybrid particles, PO1 has the largest porosity and pore volume (Table 1), while PO2 has the smallest porosity and pore volume. Thus, the OMMT shows the highest utilization efficiency in PO1 and the lowest efficiency in PO2. These results indicate that the porosity and pore volume have great effect on the OMMT utilization efficiency. For the PO3, the OMMT shows higher utilization efficiency than that in the PO4 at the beginning (~ 100 min) due to the larger porosity and pore volume; however, the OMMT in the PO3 shows smaller utilization efficiency than that in the PO4 after 150 min, this may be caused by the larger OMMT

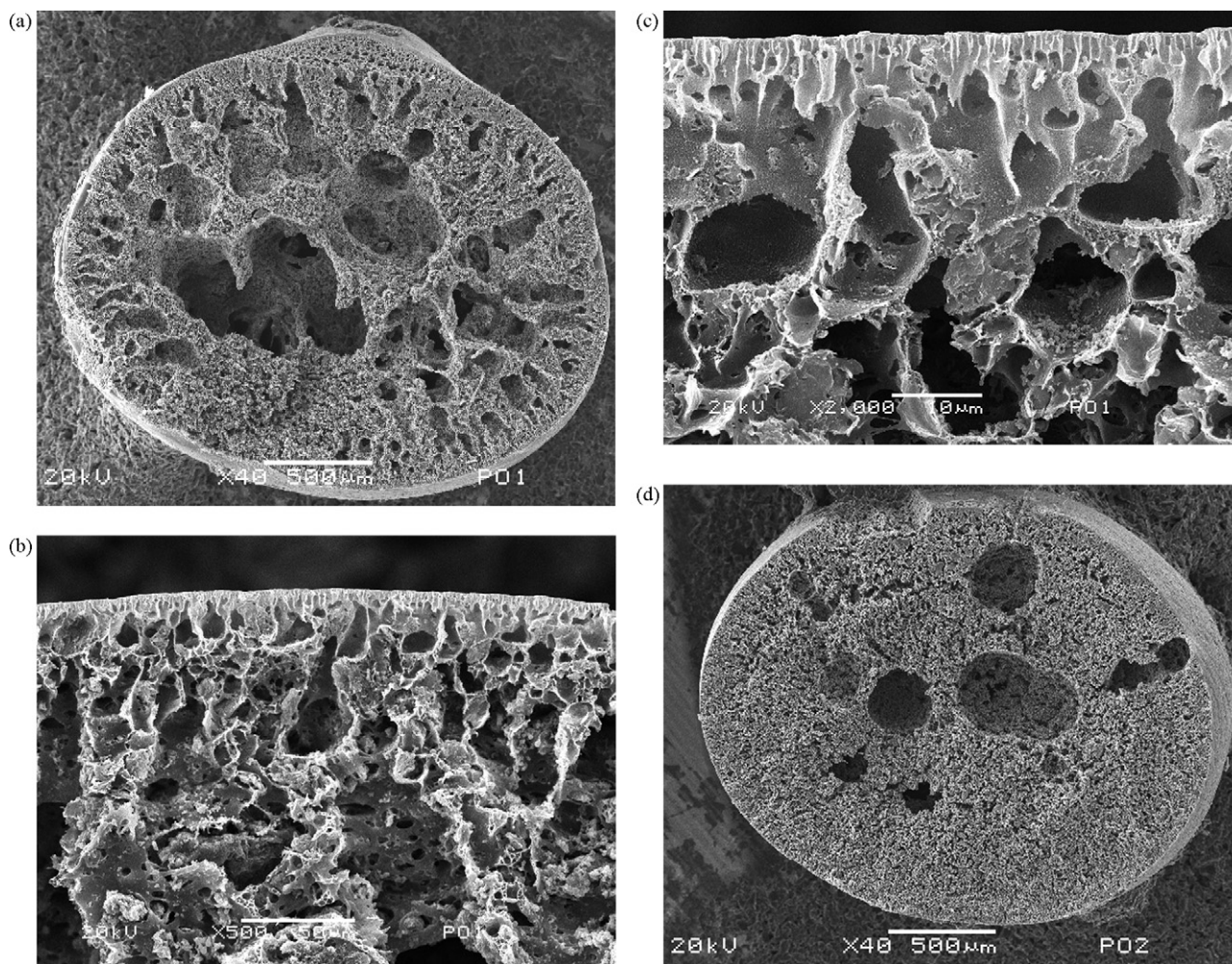


Fig. 1. Cross-section of the PO1 (a), skin layer of PO1 (b and c) and PO2 (d) particles.

Table 1
The porosity, diameter, pore volume value of the PES–OMMT hybrid particles

	PO	PO1	PO2	PO3	PO4
Porosity (%)	89.98 ± 0.15	79.67 ± 0.14	74.49 ± 0.18	76.92 ± 0.15	75.14 ± 0.12
Diameter (mm)	2.95 ± 0.15	3.63 ± 0.15	3.52 ± 0.18	3.54 ± 0.11	3.21 ± 0.17
Pore volume (cm ³ g ⁻¹)	5.47 ± 0.08	2.32 ± 0.14	1.94 ± 0.11	2.19 ± 0.10	1.96 ± 0.15

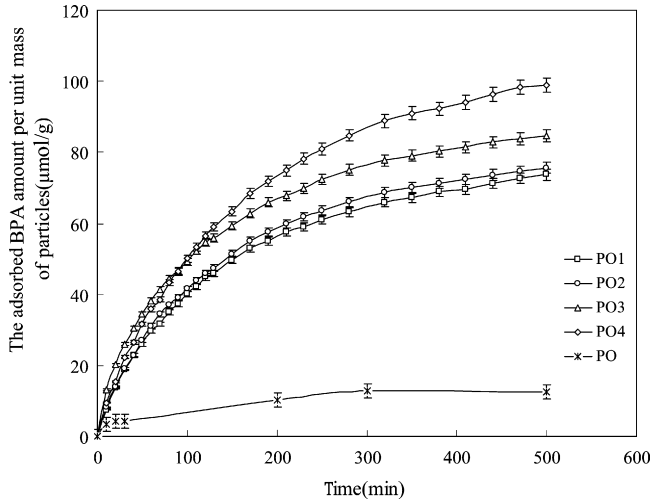


Fig. 2. The adsorbed BPA amount per unit mass of the hybrid particles. Data are expressed as the mean ± S.D. of three independent measurements.

amount in the particle PO4. These results suggested that the OMMT utilization efficiency was affected not only by the porosity and pore volume, but also by the OMMT amount in the particles. Additionally, phenolic compounds [7], herbicide simazine [9], and so on, had been testified by other research groups that these endocrine disruptors could be removed by clay from aqueous solution. The removal of BPA is a good example of the applications of the PES–clay system. So it is reasonable to say that this kind of material might be used as adsorbents for the removal of endocrine disruptors.

Desorption experiment was carried out after the adsorption experiment. The adsorbed BPA by the pure PES particles PO could be removed nearly 100% after immersing into 20 ml ethanol for 12 h at room temperature (data are not shown in the figure). However, the removal ratio of the hybrid particles PO1 was only about 40% after being extracted by 20 ml ethanol for 12 h, as shown in Fig. 4.

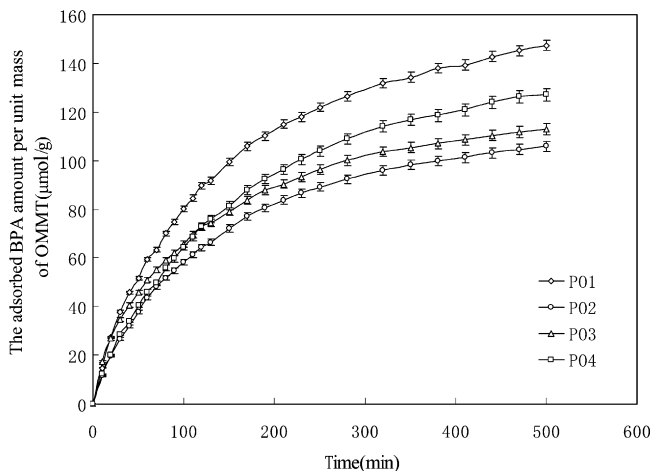


Fig. 3. The adsorbed BPA amount per unit mass of the OMMT. Data are expressed as the mean ± S.D. of three independent measurements.

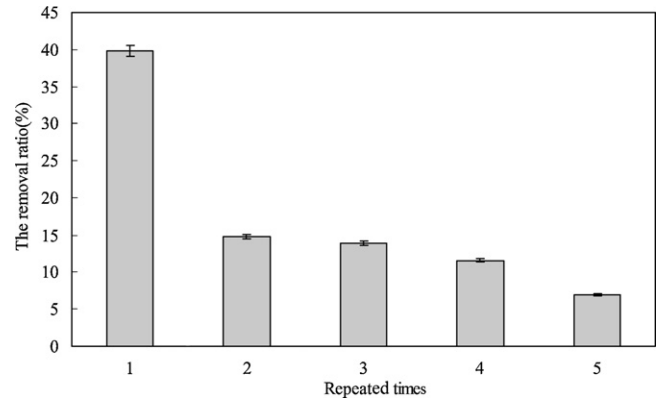


Fig. 4. The removal ratio of the adsorbed BPA by ethanol in the desorption experiment.

After immersing the PO1 into 20 ml ethanol for the second time, about 15% of the adsorbed BPA was removed, and after repeating the process for five times (60 h), nearly 90% of the total adsorbed BPA was removed. These results indicated that the binding ability between OMMT and BPA was stronger than that between PES and BPA; and the PES–OMMT particles could be reused.

Although we did not deal with the obtained BPA–ethanol solution because it is not economy to do that for only 100 ml ethanol, it is not a difficult work to recycle the ethanol by distillation. If the hybrid particles can finally be used for waste water treatment in the industrial field, the obtained BPA–ethanol solution can be managed by distillation.

3.3. Effect of initial concentration on the adsorption

The effects of the initial concentrations on the BPA adsorption by the PES–OMMT hybrid particles (PO1) were investigated; data are shown in Fig. 5. The adsorbed amounts increased with time, and

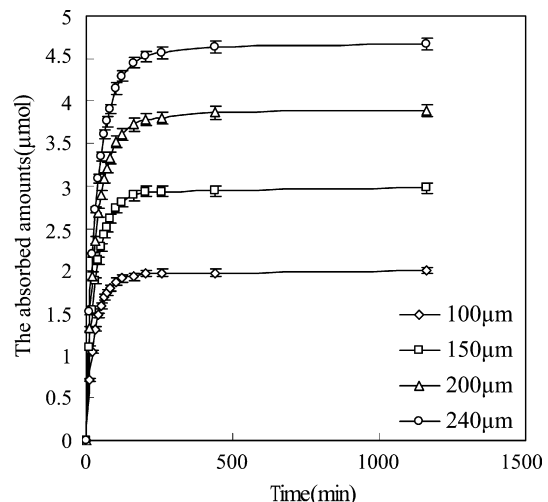


Fig. 5. Effect of BPA concentration on the adsorbed amount by PO1.

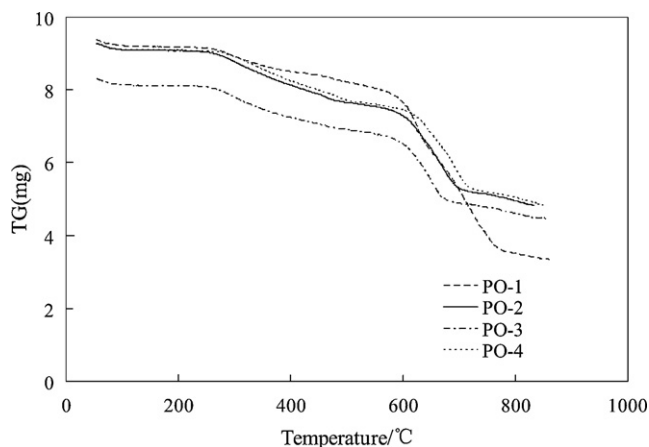


Fig. 6. TG traces of PO1, PO2, PO3, and PO4.

reached an equilibrium value after about 300 min. The equilibrium time was found to be the same for all the concentrations, which means that 300 min could be taken as the optimum contact time for the equilibrium isotherm study. The results also showed that the adsorption of BPA onto the hybrid particles was concentration dependent. These data can be used for the analysis of the mass transfer process, and the details are shown in Section 3.5.

3.4. Thermogravimetric analyze (TGA)

The thermal stability of the hybrid particles was investigated by using TGA; and the weight loss traces, recorded in the range of 50–800 °C, are shown in Fig. 6. These materials lost its weight sharply at three regions. The weight loss between 50 and 120 °C is attributed to the water adsorbed in the particles. In the range of 120 °C to about 250 °C, little weight loss was detected for all the particles. The PES decomposition temperatures of the four materials are 249.7, 253.9, 260.89, and 267.2 °C, respectively. There is a significant increase in the thermal stability resulting from the clay platelets [26], which may be partly due to the kinetic effects, with the platelet retarding the diffusion of oxygen into the polymer matrix. The results showed that these particles hardly release small molecules below 250 °C, which suggested that the hybrids were stable enough for the use at a relative high temperature in environment application.

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 [29], which is the first developed equation describing the adsorption of liquid–solid systems based on solid capacity.

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (8)$$

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. 7 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 0.97, 0.98, 0.97 and 0.93 for PO1, PO2, PO3, and PO4, respectively. The values of q_e are 16.77, 17.71, 18.67, and 26.32 mg/g, respectively, which are mostly smaller than the data obtained from the kinetics study except PO4 (17.89, 18.48, 20.28, 22.64 mg/g for PO1, PO2, PO3 and PO4, respectively). These results

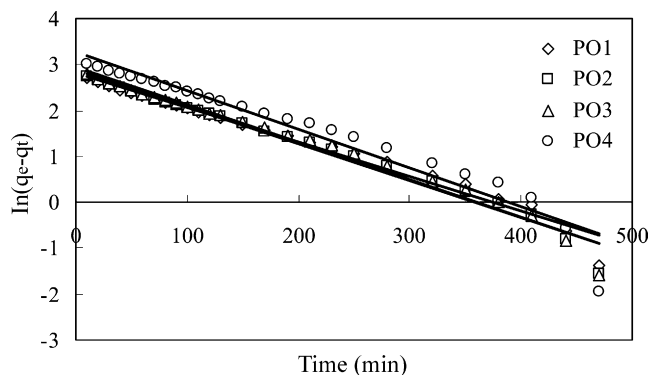


Fig. 7. Application of the pseudo-first-order adsorption model for adsorption of BPA onto PES-OMMT particles.

suggested that the adsorption of BPA onto the PES-OMMT hybrid particles fitted the pseudo-first-order model not very well.

The adsorption kinetics can also be described by pseudo-second-order equation [27,28]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{C_e}{q_e} t \quad (9)$$

where K_2 is the rate constant ($\text{g mg}^{-1} \text{min}^{-1}$), of pseudo-second-order adsorption; q_e and q_t have the same meanings as that in Eq. (8). Fig. 8 shows the curves obtained from the experimental data (t/q_t) vs t . All the correlation coefficients (r^2) are 0.99 (see Table 2), which means that the adsorption of BPA onto the PES-OMMT particles fitted the pseudo-second-order kinetic model very well. But q_e is a little 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 [29] was used. The initial rate of the intraparticle diffusion may be expressed by the following equation:

$$q_t = K_p t^{1/2} \quad (10)$$

where K_p is the rate parameter for the intraparticle diffusion; q_t has the same meaning as that in Eq. (8). By plotting q_t vs $t^{1/2}$ [29], we could justify whether the process of adsorption is controlled by pore diffusion. As can be seen in Fig. 9, there are two regions for the curves. The first one is a straight line passing through the origin, it correlated with the diffusion mechanism [30], 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 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, the pore-size distribution and the degree of mixing [30]. The second region is attributed to the equilib-

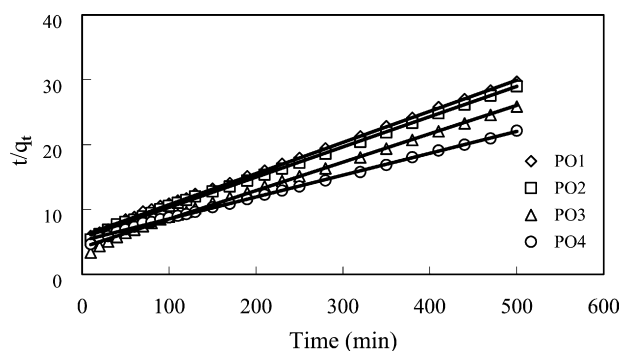


Fig. 8. Application of the pseudo-second-order adsorption model for adsorption of BPA onto PES-OMMT particles.

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

Adsorbent	Pseudo-first-order			Pseudo-second-order		
	$K_1 (\times 10^3 \text{ min}^{-1})$	$q_e (\text{mg/g})$	r^2	$K_2 (\times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1})$	$q_e (\text{mg/g})$	r^2
PO1	7.53	16.77	0.97	3.88	20.83	0.99
PO2	8.04	17.71	0.98	3.87	21.41	0.99
PO3	8.17	18.67	0.97	4.64	22.83	0.99
PO4	8.42	26.32	0.94	2.21	29.59	0.99

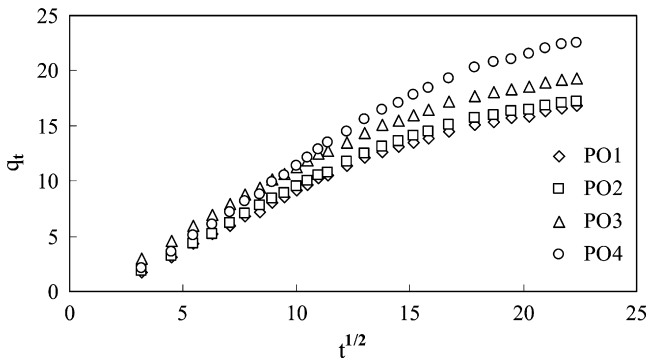


Fig. 9. Application of the intraparticle diffusion model for adsorption of BPA onto PES-OMMT particles.

rium stage, where interparticle diffusion starts, and the adsorption rate slows down due to the extremely low adsorbate concentration in the solution.

The intraparticle mass transfer diffusion is expected to be the rate limiting step due to the porous structure of the adsorbent. In our work, the kinetic model proposed by Urano and Tachikawa was chosen to describe the kinetic data. The relationship between the adsorption amount and the sorption time can be expressed by the following equation [31]:

$$-\ln \left[1 - \left(\frac{q_t}{q_e} \right)^2 \right] = \frac{4\pi^2 D_i}{d^2} t \quad (11)$$

where q_t and q_e are the uptake amounts at time t and equilibrium, respectively; d is the particle diameter and D_i is the diffusion coefficient. The straight line plot of $-\ln[1 - (q_t/q_e)^2]$ vs t for different concentrations (see Fig. 10, all the values of corresponding r^2 are 0.99) indicate the validity of the above equation developed for intraparticle diffusion mechanism. The values of D_i ($10^{-15} \text{ m}^2/\text{s}$) are 10.0682, 10.0135, 8.5112 and 8.0662 for the initial BPA concentration at 100, 150, 200 and 240 $\mu\text{mol/l}$, respectively. The values of D_i decreased slightly with increasing the initial BPA concentra-

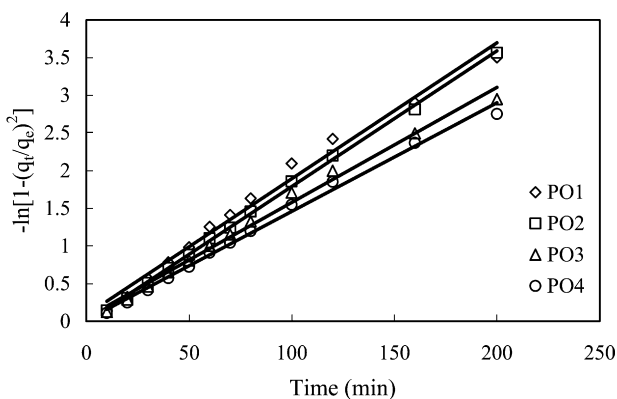


Fig. 10. Urano and Tachikawa intraparticle mass transfer plots for the adsorption of BPA onto PES-OMMT hybrid particles at different initial concentrations.

tions. Increasing the solute concentration in the solution seems to reduce the diffusion of BPA molecules into the boundary layer and to enhance the diffusion into the particles. According to the earlier paper [31,32], diffusion coefficient should be in the range of 10^{-15} to $10^{-17} \text{ m}^2/\text{s}$ for pore diffusion, which indicated that the rate limiting step appears to be the pore diffusion for the present systems.

3.6. Adsorption isotherm

The equilibrium sorption isotherm is very crucial in the design of sorption systems. The equilibrium sorption is usually described by an isotherm equation characterized by certain parameters whose values express the surface properties of the sorbent and its affinity to the adsorbate. In order to investigate the sorption isotherm of the BPA, Langmuir and Freundlich sorption isotherms were examined and in each case the isotherm parameters were determined.

3.7. Langmuir isotherms

The Langmuir adsorption [30], which is a monolayer adsorption, assumed that all the sorption sites are identical and once a BPA molecule occupied a sorption site, no further adsorption could take place at this site. One of the linear forms of the Langmuir equation is shown as:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (12)$$

where q_e is the mass of the BPA adsorbed by the unit mass of the hybrid particles after the concentration reaches equilibrium (mg/g); C_e is the concentration of the BPA in the solutions at the equilibrium (mg/l), q_{\max} is the monolayer adsorption capacity of the particles (mg/g), and K_L is the Langmuir adsorption constant ($1/\text{mg}$). A plot of C_e/q_e vs C_e (see Fig. 11) gives a straight line with the slope of $1/q_{\max}$ and the intercept $1/(q_{\max} K_L)$, and the values are shown in Table 3. The adsorption of BPA onto the hybrid particles exhibited Langmuir behaviour, which indicated the monolayer adsorption. The large values of K_L suggested that the PES-OMMT hybrid particles would be effective as the adsorbent for BPA.

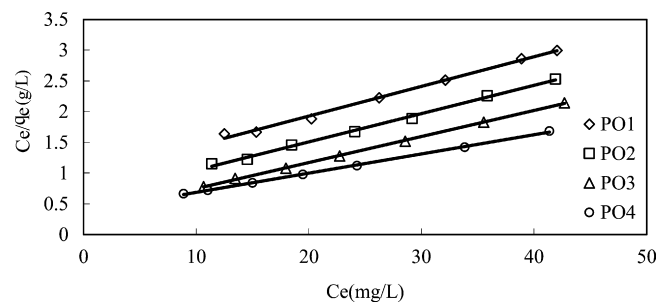


Fig. 11. Langmuir adsorption isotherms of BPA onto PES-OMMT hybrid particles for 300 min contact time.

Table 3
Langmuir and Freundlich isotherm constants for the adsorption of BPA

Hybrid particles	Langmuir			Freundlich		
	q_{\max} (mg/g)	K_L (l/mg)	r_L^2	n	K_F (l/mg)	r_F^2
PO1	20.7039	0.0502	0.99	2.1164	2.4618	0.96
PO2	21.7391	0.0785	0.99	2.6302	4.1491	0.95
PO3	23.5849	0.1307	0.99	3.6258	7.3023	0.96
PO4	32.0513	0.0836	0.99	2.5221	5.9073	0.97

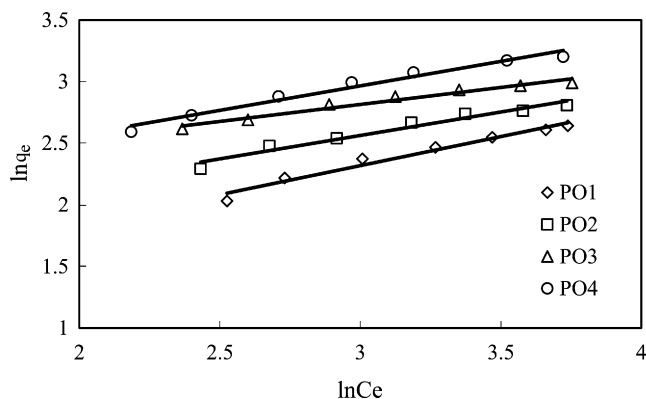


Fig. 12. Freundlich adsorption isotherms of BPA onto PES-OMMT hybrid particles for 300 min contact time.

3.8. Freundlich isotherms

The Freundlich equation [11,30], an empirical equation, is employed to describe heterogeneous systems, describes reversible adsorption, and is not restricted to the formation of the monolayer. The equation was as follows:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (13)$$

where q_e and C_e have the same meanings as in Eq. (12); and K_F is the Freundlich isotherm constant. A linear plot is obtained when $\ln q_e$ is plotted against $\ln C_e$, as shown in Fig. 12, and then the constants are obtained. It can be seen that the data also agree with the Freundlich model though the value of r^2 is smaller than that for the Langmuir model (as shown in Table 3). Furthermore, the value of n at the equilibrium is 2.1164, 2.6302, 3.0658 and 2.5221 for PO1, PO2, PO3 and PO4, respectively. It is noted that the values of n are bigger than 1, reflecting the favourable adsorption.

Both the Langmuir constants K_L and the Freundlich constants K_F reflect the adsorption capacity of the adsorbents. They are follow the order, as shown in Table 3, PO1 < PO2 < PO4 < PO3. Theoretically, the value of PO4 should be bigger than that of PO3. It could be explained as more OMMT powders were enwrapped by PES in PO4 and some of the OMMT could not interact with the BPA solution.

4. Conclusions

Thermal stable PES-OMMT hybrid particles are successfully prepared by using a liquid-liquid phase separation technique. The hybrid particles have a good performance on BPA adsorption, and the adsorption capacity per unit mass of the particles increased with the increase of the OMMT amounts in the particles. The BPA adsorption data are adequately fitted with Langmuir equation. The adsorption kinetics agrees with the pseudo-second-order model and the uptake of BPA onto the PES-OMMT particles involves a pore diffusion process. The intraparticle mass transfer diffusion is expected to be the rate limiting step. The adsorbed

BPA can be effectively removed by ethanol, which indicated that the hybrid particles can be reused. Since the inter-surface chemical structure of montmorillonite can be modified, molecules with different sizes and chemical nature can be removed by the corresponding types of organophilic montmorillonite. These results suggest that the PES-OMMT hybrid particles have potential to be used as adsorbent in devices for environment application.

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References

- [1] J.W.B. Diane, R.E. Speece, Determining chemical toxicity to aquatic species, *Environ. Sci. Technol.* 24 (1990) 284–293.
- [2] K. Christen, Synergistic effects of chemical mixtures and degradation byproducts not reflected in water quality standards, USGS finds, *Environ. Sci. Technol.* 33 (1999) 230A.
- [3] D. Cadbury, *The Feminization of Nature*, Penguin Books, London, 1997.
- [4] T. Colborn, D. Dumanoski, J. Myers, *Our Stolen Future*, The Spieler Agency, New York, through Tuttle-Mori Agency, Inc., Tokyo, 1997.
- [5] S.H. Lin, R.C. Hsiao, R.S. Juang, Removal of soluble organics from water by a hybrid process of clay adsorption and membrane filtration, *J. Hazard. Mater.* B135 (2006) 134–140.
- [6] S. Yapar, V. özbudak, A. Dias, A. Lopes, Effect of adsorbent concentration to the adsorption of phenol on hexadecyl trimethyl ammonium-bentonite, *J. Hazard. Mater.* B121 (2005) 135–139.
- [7] M. AkÇay, G. AkÇay, The removal of phenolic compounds from aqueous solutions by organophilic bentonite, *J. Hazard. Mater.* B113 (2004) 189–193.
- [8] L.S. Lee, T.J. Strock, A.K. Sarmah, P.S.C. Rao, Sorption and dissipation of testosterone, estrogens, and their primary transformation products in soil and sediment, *Environ. Sci. Technol.* 37 (2003) 4098–4105.
- [9] C. Marta, C. Rafael, Adsorption of the herbicide simazine by montmorillonite modified with natural organic cations, *Environ. Sci. Technol.* 38 (2004) 180–186.
- [10] A. Shareef, M.J. Angove, Sorption of bisphenol A, 17 α -ethynylestradiol and estrone to mineral surfaces, *J. Colloid Interf. Sci.* 297 (2006) 68–69.
- [11] Z. Rawajfih, N. Nsour, Characteristics of phenol and chlorinated phenols sorption onto surfactant-modified bentonite, *J. Colloid Interf. Sci.* 298 (2006) 39–49.
- [12] B.O. Yoon, S. Koyanagi, T. Asano, M. Hara, A. Higuchi, Removal of endocrine disruptors by selective sorption method using polydimethylsiloxane membranes, *J. Membr. Sci.* 213 (2003) 137–144.
- [13] C.S. Zhao, Q.R. Wei, K.G. Yang, X.D. Liu, M. Nomizu, N. Nishi, Preparation of porous polysulfone beads for selective removal of endocrine disruptors, *Sep. Purif. Technol.* 40 (2004) 297–302.
- [14] M. Yamada, K. Kato, M. Nomizu, K. Ohkawa, H. Yamamoto, N. Nishi, UV-irradiated DNA matrices selectively bind endocrine disruptors with a planar structure, *Environ. Sci. Technol.* 36 (2002) 949–954.
- [15] C.S. Zhao, K.G. Yang, M. Nomizu, N. Nishi, DNA-modified porous polysulfone microspheres for selective removal of endocrine disruptors, *Chem. J. Chin. Univ.* 26 (2005) 349–352.
- [16] C.S. Zhao, X.D. Liu, M. Nomizu, N. Nishi, DNA-loaded PSF microspheres used in environmental application, *Sep. Purif. Technol.* 39 (2004) 3043–3055.
- [17] J.H. Kang, F. Kondo, Bisphenol A degradation by bacteria isolated from river water, *Arch. Environ. Contam. Toxicol.* 43 (2002) 265–269.
- [18] C. Ooka, H. Yoshida, M. Horio, K. Suzuki, T. Hattori, Adsorption and photocatalytic performance of TiO₂ pillared montmorillonite in degradation of endocrine disruptors having different hydrophobicity, *Appl. Catal. B: Environ.* 41 (2003) 313–321.
- [19] Y. Liu, X. shen, Q.M. Xian, H.D. Chen, H.X. Zou, S.X. Gao, Adsorption of copper and lead in aqueous solution onto bentonite modified by 4'-methylbenzo-15-crown-5, *J. Hazard. Mater.* B137 (2006) 1149–1155.
- [20] H. Koyuncu, A.R. Kul, N. Yıldız, A. Çalımlı, H. Ceylan, Equilibrium and kinetic studies for the sorption of 3-methoxybenzaldehyde on activated kaolinites, *J. Hazard. Mater.* 141 (2007) 128–139.
- [21] U. Neubauer, B. Nowack, G. Furrer, R. Schulin, Heavy metal sorption on clay minerals affected by the siderophore desferrioxamine B, *Environ. Sci. Technol.* 34 (2000) 2749–2755.

- [22] R. Celis, M.C. Hermosín, J. Cornejo, Heavy metal adsorption by functionalized clays, *Environ. Sci. Technol.* 34 (2000) 4593–4599.
- [23] S.H. Lina, R.S. Juang, Y.H. Wang, Adsorption of acid dye from water onto pristine and acid-activated clays in fixed beds, *J. Hazard. Mater.* B113 (2004) 195–200.
- [24] B. Subramanian, G. Gupta, Adsorption of trace elements from poultry litter by montmorillonite clay, *J. Hazard. Mater.* B128 (2006) 80–83.
- [25] X.P. Deng, T. Wang, F. Zhao, L.J. Li, C.S. Zhao, Poly (ether sulfone)/activated carbon hybrid beads for creatinine adsorption, *J. Appl. Polym. Sci.* 103 (2007) 1085–1092.
- [26] G.S. Sur, H.L. Sun, S.G. Lyu, J.E. Mark, Synthesis, structure, mechanical properties, and thermal stability of some polysulfone/organoclay nanocomposites, *Polymer* 42 (2001) 9783–9789.
- [27] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss flat, *Water Res.* 34 (2000) 735–742.
- [28] S.S. Gupta, K.G. Bhattacharyya, Removal of Cd(II) from aqueous solution by kaolinite, montmorillonite and their poly(oxo zirconium) and tetrabutylammonium derivatives, *J. Hazard. Mater.* B128 (2006) 247–257.
- [29] P. Antonio, K. Ihaç, M.E.V. Suárez-Iha, Kinetic modeling of adsorption of di-2-pyridylketone salicyloylhydrazone on silica gel, *J. Colloid Interf. Sci.* 307 (2007) 24–28.
- [30] A.S. Özcan, A. Özcan, Adsorption of acid dyes from aqueous solutions onto acid-activated bentonite, *J. Colloid Interf. Sci.* 276 (2004) 39–46.
- [31] D.M. Manohar, B.F. Noeline, T.S. Anirudhan, Adsorption performance of Al-pillared bentonite clay for the removal of cobalt(II) from aqueous phase, *Appl. Clay Sci.* 31 (2006) 194–206.
- [32] D.M. Manohar, B.F. Noeline, T.S. Anirudhan, Removal of vanadium(IV) from Aqueous solutions by adsorption process with aluminum-pillared bentonite, *Ind. Eng. Chem. Res.* 44 (2005) 6676–6684.