

Adsorption of bisphenol-A from aqueous solution onto minerals and carbon adsorbents

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Received 8 September 2005; received in revised form 24 October 2005; accepted 25 October 2005

Available online 15 December 2005

Abstract

The adsorption behaviors of bisphenol-A, which has been listed as one of endocrine disrupting chemicals, from aqueous solution onto four minerals including andesite, diatomaceous earth, titanium dioxide, and activated bleaching earth, and two activated carbons with coconut-based and coal-based virgins were examined in this work. Based on the adsorption results at the specified conditions, the adsorption capacities of activated carbons are significantly larger than those of mineral adsorbents, implying that the former is effective for removal of the highly hydrophobic adsorbate from the aqueous solution because of its high surface area and low surface polarity. The adsorption capacities of bisphenol-A onto these mineral adsorbents with different pore properties are almost similar in magnitude mainly due to the weakly electrostatic interaction between the mineral surface with negative charge and the target adsorbate with hydrophobic nature. Further, a simplified kinetic model, pseudo-second-order, was tested to investigate the adsorption behaviors of bisphenol-A onto the two common activated carbons at different solution conditions. It was found that the adsorption process could be well described with the pseudo-second-order model. The kinetic parameters of the model obtained in the present work are in line with the pore properties of the two adsorbents.

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Keywords: Bisphenol-A; Adsorption; Activated carbon; Mineral adsorbent; Kinetic modeling

1. Introduction

In recent years, the environmental pollution of endocrine disrupting chemicals (EDCs) in water sources and factory effluents has aroused the public concerns. Among these anthropogenic chemicals, bisphenol-A, which has been listed as one of EDCs [1], is widely used in the plastic industry as a monomer for the production of polycarbonate and epoxy resin [2]. Its annual production capacity in Taiwan has now exceeded 390,000 metric tonnes in response to the increasing needs in the compact discs and construction materials [3]. As expected, its environmental distribution will be highly widespread. Because of its reported threats to human health and reproductive biology [4], an environmental technology for the rapid removal of bisphenol-A from the water body is required.

Conventional methods for the removal of organic pollutants in effluents may be divided into three main categories:

physical, chemical, and biological [5]. Among them, physical adsorption is generally considered to be an effective method for quickly lowering the concentrations of organic molecules in an effluent because common adsorbents including mineral clay and activated carbon generally possess large accessible internal surface and/or external surface. It is well known that the unique surface property of activated carbon, in contrast to the other non-carbon adsorbents (e.g., clay), is that its surface is non-polar or only slightly polar [6]. In this regard, activated carbon is now the most widely used adsorbent for removal of organic molecules. However, the published information on the adsorption of bisphenol-A onto mineral and carbon adsorbents is limited. Nakanishi et al. [7] investigated the adsorption characteristics of bisphenol-A onto the carbonaceous adsorbents produced from a variety of wood chips. Based on the adsorption isotherms at 25 °C onto the carbonaceous materials by the Freundlich model, the results indicated that the affinity between bisphenol-A and the carbonaceous material was similar. Asada et al. [8] pointed out that porous carbon produced from the carbonization of bamboo could be used as an effective adsorbent for removal of bisphenol-A from the aqueous solution.

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According to the results from the adsorption isotherm, the adsorption amount of bisphenol-A increased as the carbonization temperature increased, which is in line with the corresponding BET surface area. They also found that carbon adsorbent with a low surface polarity would be more effective for the adsorption of a high hydrophobic substance like bisphenol-A. Choi et al. [9] examined the removal performances of three endocrine disrupting chemicals (e.g., bisphenol-A) using activated carbons with three different base materials in the column test, showing that bisphenol-A can be effectively adsorbed onto all carbons, and the pore volume was found more significant to adsorption capacity than the specific surface area based on the adsorption isotherm, but the surface charge was also profound probably due to the electrical interaction between the nearly non-polar carbon surface and highly hydrophobic molecule. Bautista-Toledo et al. [10] studied the adsorption of bisphenol-A from water on activated carbon, showing that the system fundamentally depends on the chemical nature of the carbon surface and the pH of the solution. The presence of mineral matter in carbons reduces their adsorption capacity because of the hydrophilic nature of the matter.

With respect to the adsorption characteristics of bisphenol-A in the aqueous solution onto the mineral materials, and the adsorption kinetics and its modeling in the case of the activated carbon, the information is scarce. Thus, the objectives of this work were to (1) determine the extent of the adsorption of bisphenol-A onto various minerals and activated carbons at the specified conditions, (2) evaluate the usefulness of pseudo-second order model for analyzing the adsorption system between the hydrophobic adsorbate and the carbon adsorbent, and (3) investigate the applicability of common isotherm models (i.e., Langmuir and Freundlich) based on the adsorption capacities from the fittings of the adsorption rate model.

2. Methods

2.1. Materials

The endocrine disrupting chemicals used as target adsorbate in the present study is bisphenol-A (99+% purity), which was purchased from Aldrich Chemical Co. (Milwaukee, USA). Its CAS identification information and molecular weight are 80-05-7 and $228.29 \text{ g mol}^{-1}$, respectively. The molecular structure of this adsorbate is shown in Fig. 1. Two different kinds of the materials were used as adsorbents, including minerals and activated carbons. The former included andesite from local clay manufacturer (Taitung, Taiwan) with the particle size of $<0.074 \text{ mm}$ ($<\text{mesh no. } 200$), diatomaceous earth from Celite Co. (Santa Bar-

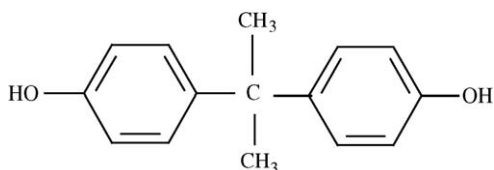


Fig. 1. Molecular structure of bisphenol-A used as adsorbate in the study.

Table 1

Main physical properties of minerals and activated carbons used as adsorbents in the present study^a

Sample	$S_{\text{BET}}^{\text{b}}$ ($\text{m}^2 \text{g}^{-1}$)	S_{L}^{c} ($\text{m}^2 \text{g}^{-1}$)	V_{t}^{d} ($\text{cm}^3 \text{g}^{-1}$)
Andesite ^a	2.7	17.1	0.0098
Diatomaceous earth	3.8	21.2	0.0155
Titanium dioxide	50.1	408	0.247
Activated bleaching earth	257	388	0.374
Activated carbon-PCB ^a	916	1606	0.576
Activated carbon-BPL ^a	1060	1958	0.714

^a Particle size is less than 0.074 mm.

^b BET surface area.

^c Langmuir surface area.

^d Total pore volume.

bara, USA) with the Product Grade 577 [11], titanium dioxide (photocatalyst P-25) from Degussa AG Co. (Frankfurt, Germany) with 80% anatase, 20% rutile and BET area of about $50 \text{ m}^2 \text{g}^{-1}$, and activated bleaching earth from Mizusawa Co. (Tokyo, Japan) with the main components of 75.8 % SiO_2 , 8.8 % Al_2O_3 and 3.0 % Fe_2O_3 [12]. The later were two different kinds of the commercial granular activated carbons from Calgon Carbon Co. (Pittsburgh, USA) with the notations of PCB (coconut shell-based) and BPL (bituminous coal-based), respectively. The activated carbons were ground and sieved to mesh no. ranges of 60–120 (0.125–0.250 mm), 120–200 (0.074–0.125 mm), and <200 ($<0.074 \text{ mm}$). These adsorbents were dried at about 100°C and then stored in a desiccator, before being used in the analytical measurements and adsorption experiments. The main pore properties of these adsorbents using an automated nitrogen adsorption/desorption analyzer (Model No.: ASAP 2010; Micromeritics Co.; Atlanta, USA) are given in Table 1. H_2SO_4 and NaOH were used for adjusting initial pH value of aqueous solution to obtain the extent of the adsorption of bisphenol-A.

2.2. Adsorption studies

All the experiments of adsorption kinetics were carried out in a ca. 3-dm^3 stirred batch adsorption apparatus with four baffles as similarly described in our previous studies [11–16]. All the bisphenol-A solutions were prepared with de-ionized water. The effect of agitation speed at 200, 400 and 600 rpm on the adsorption uptake was first tested and depicted in Fig. 2, showing that it seemed to be negligible. The adsorption uptake of the adsorbents under the initial bisphenol-A concentration of 60 mg dm^{-3} , mixing rate of 400 rpm, temperature of 25°C , pH of 7.0 and dosage of $0.5 \text{ g } 2.0 \text{ dm}^{-3}$ was first investigated for the purpose of studying the effectiveness of adsorbents. From the results in Table 2, it was found that the adsorption capacities of activated carbons are significantly superior to those of the minerals at the same conditions. Thus, the activated carbons were further used to study the variation of adsorption at various initial bisphenol-A concentrations (i.e., $60\text{--}100 \text{ mg dm}^{-3}$), pH (i.e., 3–11), adsorbent dosage (i.e., $0.05\text{--}0.25 \text{ g dm}^{-3}$), and adsorbent size (i.e., <0.074 , $0.074\text{--}0.125$, and $0.125\text{--}0.250 \text{ mm}$). The solution sample (about 10 cm^3) was taken at specified time up to 2 h and then filtrated with fiber membrane (Cat. No.: A045A025A;

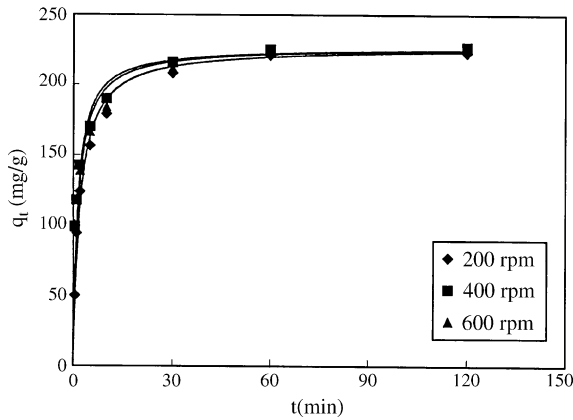


Fig. 2. Plots of adsorbed bisphenol-A amount versus time onto the activated carbon (BPL) at various agitation speeds (adsorption conditions: adsorbent dosage = 0.5 g 2.0 dm⁻³, initial concentration = 20 mg dm⁻³, pH 7.0, particle size ≤ 0.074 mm, and temperature = 25 °C; symbols: experimental data, full lines: calculated from pseudo-second order kinetics model).

ADVANTEC MFS, Inc.). The bisphenol-A concentration analysis of filtrate solution was immediately measured with UV/Visible spectrophotometer (Model: U-2001; Hitachi Co., Japan) at a 221 nm wavelength [7]. The amount of bisphenol-A adsorbed (q_t , mg g⁻¹) was determined as follows:

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

where C_0 and C_t are the initial and liquid-phase concentrations of the bisphenol-A solution at t time (mg dm⁻³), respectively, V is the volume (ca. 2.0 dm³) of aqueous solution containing bisphenol-A, and m is the mass of dry adsorbent used (g). In order to evaluate the statistical significance of data in the kinetic experiments, a preliminary experiment was also repeated under identical conditions, showing that the reproducibility of the measurements is within 5% in the adsorption experiments.

3. Adsorption kinetic model

The adsorption process in a stirring chamber generally involves several transport stages [6]; i.e., external diffusion, internal diffusion and actual adsorption process. The model of the separation process should adequately account for the mass balance and the adsorption equilibrium if the system is isothermal. In most cases, the resistance to internal diffusion can be significant. However, the local rate of adsorption is assumed to be relatively fast and the resistance to external diffusion is exper-

imentally controlled to be negligible, compared to the intra-particle diffusion. Although many theoretical model equations have been proposed for describing the adsorption kinetics based on mass balance, pore diffusion rate and initial/boundary conditions. These equations are not only complicated and impractical while using them, but also require detailed data such as the characteristics of adsorbate and adsorbent.

In order to investigate the adsorption characteristics of bisphenol-A onto minerals and activated carbons, the pseudo-second order kinetics model was used to test the adsorption dynamics in this work because of its good applicability in most cases in comparison with pseudo-first order model and intra-particle diffusion model [17–20]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (2)$$

where k is the pseudo-second order rate constant (g mg⁻¹ min⁻¹), q_e is the amount of bisphenol-A adsorbed at equilibrium (mg g⁻¹), q_t is the amount of bisphenol-A adsorbed at time t (mg g⁻¹). Integrating Eq. (2) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \quad (3)$$

Eq. (3) can be rearranged to obtain a linear form of:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \left(\frac{1}{q_e}\right)t \quad (4)$$

Rate parameters, k and q_e , can be directly obtained from the intercept and slope of the plot of (t/q_t) against t . The equilibrium concentration (i.e., C_e) can be further determined by the mass balance principle as the value of q_e has been obtained from the fitting of Eq. (4). Also, half of the adsorption time, $t_{1/2}$, is the time required for the adsorbent to take up half as much paraquat as it will at equilibrium (i.e., $t = t_{1/2}$ as $q_t = q_e/2$). This period of time is often used as a measure of the rate of adsorption and is given from the rearrangement of Eq. (3) as follows:

$$t_{1/2} = \frac{1}{kq_e} \quad (5)$$

On the other hand, the initial adsorption rate, h , can be further obtained using Eq. (2) at the initial adsorption time (i.e., $t = 0$ as $q_t = 0$) as the value of q_e has been determined from the fitting of Eq. (3) as follows:

$$h = kq_e^2 \quad (6)$$

Table 2

Pseudo-second order parameters for the adsorption of bisphenol-A onto the minerals and activated carbons^a

Sample	k (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	$t_{1/2}$ (min)	h (mg g ⁻¹ min ⁻¹)	C_e (g dm ⁻³)	R^2
Andesite	12.00	0.53	0.16	3.36	19.87	1.000
Diatomaceous earth	7.46	0.73	0.18	3.95	19.82	1.000
Titanium dioxide	48.01	0.33	0.06	5.23	19.92	1.000
Activated bleaching earth	4.02	0.86	0.29	2.98	19.78	1.000
Activated carbon-PCB	0.08	78.13	0.16	476	0.47	1.000
Activated carbon-BPL	0.23	78.13	0.05	1429	0.47	1.000

^a Adsorption conditions: initial concentration = 20 g dm⁻³, adsorbent dosage = 0.5 g 2.0 dm⁻³, agitation rate = 400 rpm, pH 7.0, and temperature = 25 °C.

The equilibrium concentration (i.e., C_e) can be further calculated from Eq. (1) as the value of q_e has been obtained from the fitting of Eq. (3) as follows:

$$C_e = (C_0 - q_e) \frac{m}{V} \quad (7)$$

In the present study, the effects of the initial bisphenol-A concentration, pH, adsorbent mass, and particle size on the rate and extent of adsorption were presented and discussed as below.

4. Results and discussion

4.1. Adsorption characteristics of bisphenol-A onto minerals and activated carbons

Adsorption studies of bisphenol-A onto minerals and activated carbons were carried out at initial concentration of 20 g dm^{-3} , adsorbent dosage of $0.5 \text{ g } 2.0 \text{ dm}^{-3}$, agitation rate of 400 rpm, pH of 7.0, adsorption time of 2 h, and temperature of 25°C . Table 2 lists the results of adsorption kinetics of each adsorbent using the fittings of pseudo-second order model. Several noteworthy features may be obtained from the results shown in Table 2.

- (1) Using the regression analysis (least square method), the model obviously appears to fit the experimental adsorption data reasonably well.
- (2) The adsorption capacities of bisphenol-A onto mineral adsorbents (i.e., andesite, diatomaceous earth, titanium dioxide, and activated bleaching earth) are significantly smaller than those of carbon adsorbents (i.e., BPL and PCB) showing that carbon adsorbent with a low surface polarity will be more effective than mineral adsorbent for the adsorption of bisphenol-A since it has a high value (i.e., 3.1) of octanol–water partition coefficient (K_{ow}) and thus possesses a highly hydrophobic property [9].
- (3) It was observed that the adsorption capacities of bisphenol-A below 1 mg g^{-1} were obtained for all mineral adsorbents, not in proportion to their pore properties listed in Table 1. It revealed that the pore volume and/or particle surface area in the cases of these mineral adsorbents are not determining factors for the removal of bisphenol-A from the aqueous solution probably due to the repulsive interaction between the mineral surface with negative charge and the target adsorbate with hydrophobic structure.
- (4) It was observed that the total amount of the acidic groups of carbon-BPL is larger than that of carbon-PCB as studied previously [21]. Therefore, the pore property of carbon-BPL is slightly superior to that of carbon-PCB but the q_e of carbon-PCB is exactly same as that of carbon-BPL due to the electrostatic repulsion between the bisphenol-A and the negatively charged surface as a result of organic functional groups containing oxygen.
- (5) Consequently, the initial adsorption rates of carbon adsorbents are more rapid than those of mineral adsorbents. In other words, the activated carbon adsorbs more nonpolar and

weakly polar organic molecules than mineral adsorbents do [6].

From the results described above, the most significant factors in determining adsorption capacity are not only the physical characteristics of adsorbents including pore volume and surface area but also their chemical characterizations (i.e., surface polarity). Although the activated bleaching earth possesses a mesoporous structure with high BET surface area of ca. $260 \text{ m}^2 \text{ g}^{-1}$, for example, its adsorption capacity (0.88 mg g^{-1}) for bisphenol-A is so low in comparison with those (0.53 and 0.73 mg g^{-1} , respectively) of other mineral adsorbents (i.e., andesite and diatomaceous earth) with low BET surface areas (ca. 3 and $4 \text{ m}^2 \text{ g}^{-1}$, respectively) as a result of electrostatic repulsion between the negatively charged surface and hydrophobic adsorbate (i.e., bisphenol-A). As expected, the activated carbon could adsorb significant quantity of bisphenol-A because of its large accessible internal surface (ca. $1000 \text{ m}^2 \text{ g}^{-1}$) and its very low polarity in the surface.

4.2. Adsorption kinetics of bisphenol-A onto activated carbon

4.2.1. Effect of initial concentration

The adsorption uptake and its kinetics using pseudo-second order kinetics model at different initial bisphenol-A concentrations onto the activated carbons BPL and PCB are presented in Table 3. As seen from Table 3, it is evident that the kinetic modeling of the bisphenol-A adsorption onto the carbon adsorbent well follows this model with the correlation coefficients of higher than 0.999 for all the system in the present work. The equilibrium adsorption capacity (i.e., q_e) increased as the initial bisphenol-A concentration (i.e., C_0) increased from 60 to 100 mg dm^{-3} , showing that the initial concentration provides a powerful driving force to overcome the mass transfer resistance between the aqueous and solid phases [22]. As expected from the results in Table 1, the maximum loading capacities of the activated carbon BPL were higher than those of the activated carbon PCB. For example, 357.1 mg g^{-1} for the activated carbon BPL, and 270.3 mg g^{-1} for the activated carbon PCB at 100 mg dm^{-3} initial bisphenol-A concentration. Further, it was found that the variations of rate constant (i.e., k) seem to have a decreasing trend with initial bisphenol-A concentration increased, which is consistent with similar studies [16,18,19,22].

4.2.2. Effect of initial pH

Using the fittings of pseudo-second order kinetics model, the variations of equilibrium adsorption capacities of both carbon adsorbents with initial pH are given in Table 4. Again, the kinetics of the adsorption follows this model with the regression coefficients of higher than 0.999, as listed in Table 4. Obviously, the adsorption capacity (i.e., q_e) exhibits a constant extent as the pH was increased from 3 to 9, while the bisphenol-A adsorption shows a decreasing trend at a higher pH ranging from 9 to 11. These results are consistent with those studied by Bautista-Toledo et al. [10]. The result could be attributed to the pK_a value of bisphenol-A ranging 9.6–10.2 [23], implying

Table 3

Pseudo-second order parameters for the adsorption of bisphenol-A onto the activated carbons at various initial concentrations^a

Activated carbon	Initial concentration (mg dm ⁻³)	Pseudo-second order		
		k (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2
BPL	60	10.25×10^{-3}	238.0	1.000
	70	5.95×10^{-3}	270.3	1.000
	80	4.36×10^{-3}	303.0	1.000
	90	3.21×10^{-3}	333.3	1.000
	100	2.70×10^{-3}	357.1	0.999
PCB	60	3.28×10^{-3}	227.3	0.999
	70	2.21×10^{-3}	243.9	0.999
	80	2.19×10^{-3}	250.0	0.999
	90	2.12×10^{-3}	263.2	0.999
	100	1.93×10^{-3}	270.3	0.999

^a Adsorption conditions: adsorbent dosage = 0.5 g 2.0 dm⁻³, agitation rate = 400 rpm, pH 7.0, particle size ≤ 0.074 mm, and temperature = 25 °C.

Table 4

Pseudo-second order parameters for the adsorption of bisphenol-A onto the activated carbons at various initial pH^a

Activated carbon	Initial pH	Pseudo-second order		
		k (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2
BPL	3	10.28×10^{-3}	237.6	1.000
	5	10.32×10^{-3}	238.6	1.000
	7	10.25×10^{-3}	238.0	1.000
	9	9.05×10^{-3}	239.1	1.000
	11	3.51×10^{-3}	196.1	0.999
PCB	3	3.04×10^{-3}	238.1	0.999
	5	3.30×10^{-3}	232.6	0.999
	7	3.28×10^{-3}	227.3	0.999
	9	3.03×10^{-3}	227.3	0.999
	11	4.38×10^{-3}	140.8	0.999

^a Adsorption conditions: dosage = 0.5 g 2.0 dm⁻³, initial concentration = 60 mg dm⁻³, agitation rate = 400 rpm, particle size ≤ 0.074 mm, and temperature = 25 °C.

that the ionization of bisphenol-A occurred at around pH 9–10 to form the bisphenolate anion. Therefore, the reduction in the adsorption capacity of the activated carbons at very basic pH range (>10.0) may be probably due to the electrostatic repulsion between the bisphenolate anion from the ionization of bisphenol-A and the slightly negatively charged surface

Table 5

Pseudo-second order parameters for the adsorption of bisphenol-A onto the activated carbons at various adsorbent dosages^a

Activated carbon	Adsorbent dosage (g dm ⁻³)	Pseudo-second order		
		k (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2
BPL	0.05	1.78×10^{-3}	400.0	0.999
	0.10	1.93×10^{-3}	384.6	0.999
	0.15	2.63×10^{-3}	344.8	0.999
	0.20	4.71×10^{-3}	285.7	1.000
	0.25	10.25×10^{-3}	238.0	1.000
PCB	0.05	1.65×10^{-3}	270.3	0.999
	0.10	1.60×10^{-3}	277.8	0.999
	0.15	1.85×10^{-3}	263.2	0.999
	0.20	2.03×10^{-3}	250.0	0.999
	0.25	3.28×10^{-3}	227.3	0.999

^a Adsorption conditions: initial concentration = 60 mg dm⁻³, pH 7.0, agitation rate = 400 rpm, particle size ≤ 0.074 mm, and temperature = 25 °C.

as a result of organic functional groups containing oxygen [21].

4.2.3. Effect of adsorbent dosage

The effect of varying the activated carbon mass on bisphenol-A adsorption at the initial concentration of 60 mg dm⁻³, pH of 7.0, agitation rate of 400 rpm, particle size of <0.074 mm, and temperature of 25 °C has been carried out. The values of parameters for the adsorption system are listed in Table 5. Evidently, the correlation between the experimental and theoretical results is also good. As expected, the bisphenol-A concentration in the solution rapidly decreased and the rate constant, k , thus increased at a larger value as the adsorbent dosage increased. This implies that the number of adsorption sites increases in parallel with increasing adsorbent dosage. But the adsorption capacity (i.e., q_e) decreased as the adsorbent dosage increased. Such a phenomenon is similar to those of Ho and Chiang [19] and Hue et al. [24] for the adsorption of dye onto activated clay. This leads to make a suggestion that, in order to obtain the optimal adsorbent dosage, higher initial bisphenol-A concentrations should be tested in conjunction with appropriate adsorbent dosage [18].

4.2.4. Effect of adsorbent size

The effect of varying the activated carbon particle size on bisphenol-A adsorption has been investigated, and the results

Table 6
Pseudo-second order parameters for the adsorption of bisphenol-A onto the activated carbons at various adsorbent sizes^a

Activated carbon	Adsorbent size (mm)	Pseudo-second order		
		k ($\text{g mg}^{-1} \text{min}^{-1}$)	q_e (mg g^{-1})	R^2
BPL	<0.074	10.25×10^{-3}	238.0	1.000
	0.074–0.125	0.63×10^{-3}	188.7	0.995
	0.125–0.250	0.71×10^{-3}	137.0	0.994
PCB	<0.074	3.28×10^{-3}	227.3	0.999
	0.074–0.125	0.88×10^{-3}	137.0	0.996
	0.125–0.250	1.66×10^{-3}	80.0	0.996

^a Adsorption conditions: initial concentration = 60 mg dm^{-3} , pH 7.0, dosage = $0.5 \text{ g } 2.0 \text{ dm}^{-3}$, agitation rate = 400 rpm, particle size $\leq 0.074 \text{ mm}$, and temperature = 25°C .

are listed in Table 6. It can be seen that the adsorption capacity (i.e., q_e) of the activated carbon BPL decreased from 238.0 to 137.0 mg g^{-1} as the adsorbent particle size increased from 0 – 0.074 to 0.125 – 0.250 mm , while in the case of the activated carbon PCB, the adsorption capacity decreased from 227.3 to 80.0 mg g^{-1} . This behavior can demonstrate that larger surface area of adsorbent particle for a given mass of activated carbon is associated with smaller particle size [13,19,24], resulting in the adsorption availability increased. The results obtained from this section of experiments also indicated that the rate constant (k) seemed to be significantly decreased as the adsorbent size increased from 0 – 0.074 to 0.074 – 0.125 mm .

4.3. Adsorption isotherm

Two common isotherm equations have been applied to model the isotherms in the present study: the Langmuir and Freundlich models [25–27].

$$\text{Langmuir : } \frac{1}{q_e} = \frac{1}{(K_L q_m) C_e} + \frac{1}{q_m} \quad (8)$$

$$\text{Freundlich : } q_e = K_F C_e^{1/n} \quad (9)$$

In Eq. (8), C_e and q_e are the concentration (mg dm^{-3}) and amount (mg g^{-1}) of bisphenol-A adsorbed at equilibrium, respectively, K_L is a direct measure of the intensity of the adsorption process ($\text{dm}^3 \text{mg}^{-1}$), and q_m is a constant relating to the surface area occupied by a monolayer of adsorbate, reflecting the adsorption capacity (mg g^{-1}). Based on the data of q_e from the fittings of the pseudo-second order adsorption rate model, q_m and K_L can be determined from its slope and intercept from a typical plot of $1/q_e$ versus $1/C_e$. In Eq. (9), K_F is a constant for the system, related to the bonding energy. K_F can be defined

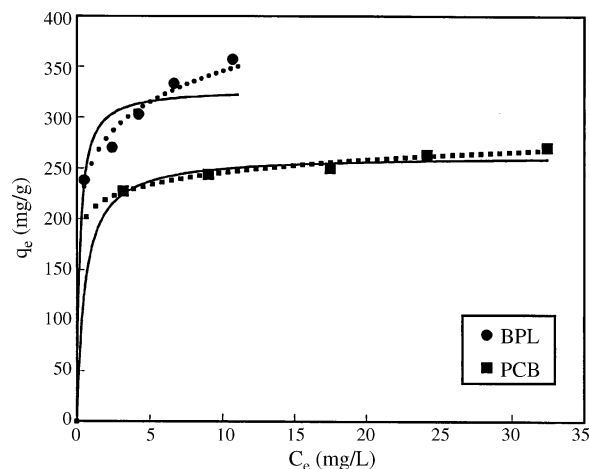


Fig. 3. Adsorption isotherms of bisphenol-A in aqueous solution onto the activated carbons (i.e., BPL and PCB) at 25°C (adsorption conditions: dosage = $0.5 \text{ g } 2.0 \text{ dm}^{-3}$, agitation rate = 400 rpm, particle size $\leq 0.074 \text{ mm}$, and pH 7.0; symbols (●/■): experimental data, full lines: calculated from the Freundlich model, dotted lines: calculated from the Langmuir model).

as adsorption or distribution coefficient and represents the general capacity of bisphenol-A adsorbed onto adsorbents for a unit equilibrium concentration (i.e., $C_e = 1 \text{ mg dm}^{-3}$). The slope $1/n$, ranging between 0 and 1, is a measure for the adsorption intensity or surface heterogeneity.

The results of the Langmuir and Freundlich isotherms fitted by using the data of adsorption capacity from the regression of Eq. (2) at 25°C are presented in Table 7. Obviously, it can be seen in Fig. 3 that the Freundlich model yields a somewhat better fit than the Langmuir model [7,8], as reflected with correlation coefficients (R^2) of 0.951 versus 0.770 and 0.963 versus 0.854 for the activated carbons BPL and PCB, respectively. It has been known that the magnitudes of K_L and K_F indicate a measure of

Table 7
Parameters in the Langmuir and Freundlich adsorption isotherm models of bisphenol-A onto the activated carbons at 25°C ^a

Activated carbon	Langmuir			Freundlich		
	q_m (mg g^{-1})	K_L ($\text{dm}^3 \text{mg}^{-1}$)	R^2	K_F [$\text{mg g}^{-1} (\text{dm}^3 \text{mg}^{-1})^{1/n}$]	$1/n$ (-)	R^2
BPL	328.3	4.97	0.770	253.8	0.140	0.951
PCB	263.2	1.81	0.854	206.1	0.072	0.963

^a Adsorption conditions: initial concentration = 60 – 100 mg dm^{-3} , adsorbent dosage = $0.5 \text{ g } 2 \text{ dm}^{-3}$, agitation speed = 400 rpm, particle size $\leq 0.074 \text{ mm}$, and pH 7.0.

the adsorbent capacity. As indicated in Table 7, the values of K_L and K_F of adsorbent BPL are larger than those of adsorbent PCB. This is consistent with the results based on their pore properties in Table 1. The adsorption isotherms revealed that the activated carbon can uptake over 200 mg g^{-1} in relatively low concentration of the bisphenol-A in aqueous medium. As also illustrated in Table 7, the values of $1/n$ are significantly less than unity indicating a favorable adsorption system.

5. Conclusions

The uses of minerals and carbon adsorbents for the adsorption of bisphenol-A from aqueous solution have been examined. The results showed that the adsorption capacities of bisphenol-A onto mineral adsorbents are significantly smaller than those of carbon adsorbents. It seemed that carbon adsorbent with a low surface polarity would be more effective than mineral adsorbent for the removal of the hydrophobic adsorbate from the aqueous solution. Furthermore, the adsorption kinetics of bisphenol-A onto the activated carbon can be well described by pseudo-second order reaction model. The kinetic parameters thus obtained from the fittings of the model were dependent on initial adsorbate concentration, pH, adsorbent dosage and adsorbent particle size. From the isotherm data obtained from the fittings of the pseudo-second order model, the Freundlich model yields a somewhat better fit than the Langmuir model in the adsorption of bisphenol-A onto activated carbon.

Acknowledgement

This research was supported by NSC (National Science Council, Taiwan) under contract number NSC 93-2211-E-041-008.

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