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Application of natural biosorbent and modified peat for bisphenol a removal from aqueous solutions

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ABSTRACT

The sorption behaviour of bisphenol A (BPA) from aqueous solutions onto a biosorbent such as peat, rice husk, bagasse, and sawdust was evaluated. The effects of various parameters, including sorbent dose, solution pH, ionic strength, temperature, and competitive adsorption, were determined. The sorption capacity of peat notably increased to a level even higher than that of activated carbon after modification with a quaternary ammonium surfactant. The sorption process fitted the pseudo-second-order model well. The sorption of BPA onto modified peat is preferred in the presence of phenol as a competitor. Hydrophobic interactions play an important role during the sorption process. These observations indicate that the BPA sorption capacity of natural peat can be significantly promoted via surfactant modification and is of great potential for environmental application.

1. Introduction

Endocrine-disrupting chemicals (EDCs) are substances that mimic natural hormones in the endocrine system and thus cause adverse effects on humans and wildlife. Bisphenol A [2,2-bis(4-hydroxyphenyl)propane] or BPA is an EDC that has caused great concern because of its potential risk to human health (European Food Safety Authority, 2006). BPA is an important industrial chemical whose consumption is primarily driven by the increasing demand for epoxy resins and polycarbonate plastics, which are widely used in different products. BPA can enter a body of water during manufacturing, leach from plastic products, and be disposed in landfills after use (Sala, Kitahara, Takahashi, & Fujii, 2010). Several studies have contributed to the detection and analysis of BPA in the aquatic environment. In general, BPA concentrations vary in surface waters from <0.1 $\mu g L^{-1}$ to 2.0 $\mu g L^{-1}$ (Huang et al., 2011), and the concentrations are significantly higher in some rivers located in highly developed industrial and commercial regions, such as the Huang-Pu River (near Shanghai) and Kao-Pin River (near Gaoxiong), with levels reaching 4 $\mu g L^{-1}$ (Ding & Wu, 2000; Ma et al., 2006). Wastewater from paper recycling plants in Shizuoka (Japan) contained a rather high level of BPA (up to 370 $\mu g L^{-1}$) (Fukazawa, Hoshino, Shiozawa, Matsushita, & Terao, 2001). In addition, several studies demonstrated that the BPA concentrations in hazardous waste landfill leachates are extremely high compared with the level in environmental waters. The BPA concentration of raw leachate from a landfill in West Germany was 3.61 $mg L^{-1}$ (Coors, Jones, Giesy, & Ratte, 2003), whereas the maximum concentration reported by Yamamoto, Yasuhara, Shiraishi, and Nakasugi (2001) from a plastic landfill leachate is 17.2 $mg L^{-1}$. Consequently, the leaching of chemicals such as BPA from plastics in landfills has the potential to contaminate the environment; therefore, chemical leaching may be an important source of BPA found in environmental water (Vandenberg, Hauser, Marcus, Olea, & Welshons, 2007).

Accordingly, an environmental technology for the effective removal of EDCs is needed. From the technical and economic points of view, sorption technologies for EDC removal are very promising (Basile et al., 2011; Nakanishi, Tamai, Kawasaki, Nakamura, & Tanada, 2002). Recently, environmental scientists and engineers have considered some natural biosorbents to be effective as low-cost sorbent alternatives. A variety of natural biosorbents has been proposed for the removal of pollutants from aqueous solutions, including bark and wood chips, chitosan, peat, sugarcane bagasse, straw and rice husks, activated bamboo, and others (Asada et al., 2004; Bhatnagar & Sillanpaa, 2009; Brandao, Souza, Ferreira, Hori, & Romanielo, 2010; Chakraborty, Chowdhury, & Das Saha, 2011; Ibrahim, Wang, & Ang, 2010). Natural biosorbents are widely available and renewable. Several biological materials are used to remove heavy metals. Meanwhile, interest in the use of biosorbents in organic pollutant removal from solutions has also increased (Brandao et al., 2010).

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However, the capacities of these materials are comparable to but slightly lower than those of activated carbon. Extensive research is needed to enhance the sorption capacities of these biosorbents for various pollutants after an appropriate treatment. Li, Chen, and Zhu (2010) recently investigated the sorption of phenanthrene and pyrene onto raw and modified pine bark prepared via Soxhlet extraction, saponification, and acid hydrolysis. The sorption capacity of the pine bark fractions notably increased (4–17 folds) after polysaccharide consumption via acid hydrolysis, suggesting that pine bark can be significantly improved via acid hydrolysis for polycyclic aromatic hydrocarbon (PAH) removal.

Aside from Soxhlet extraction, saponification, and acid hydrolysis, a number of less complex modification processes are also available. In recent years, surface modification via ion exchange with quaternary ammonium cations has been successfully conducted. The use of organically modified clay for the removal of organic pollutants from water is also well known (Alkaram, Mukhlis, & Al-Dujaili, 2009). Based on the results from our previous research, the sorption of hydrophobic pollutants on natural sorbents can be significantly enhanced by grafting quaternary ammonium surfactants with long alkyl groups (Zhou, Tang, Xu, & Lu, 2010). Modified biosorbents are potential candidates for EDC removal from wastewater.

Several studies have reported on BPA removal as a single solute using various sorbents (Asada et al., 2004; Choi, Kim, Kim, & Kim, 2005; Pan, Lin, Mashayekhi, & Xing, 2008). However, only a few researchers have reported on a binary system that involves the competitive adsorption of BPA and other organic pollutants. Some researchers investigated the effect of adding a certain concentration of another chemical on BPA removal; however, no attempt to analyse the system in terms of binary sorption isotherms was made (Kim, Lee, Choo, & Choi, 2011; Li, Zhou, Liu, Yang, & Cai, 2008). BPA is produced by the condensation of phenol and acetone in the presence of an acid catalyst or a cation exchange resin. Phenol commonly coexists with BPA and can be easily detected in a contaminated body of water (Chavan & Mukherji, 2010). Therefore, the effects of competitive sorption on BPA removal must be explored.

The main factors affecting the sorption of BPA onto modified biosorbents remain to be determined. A series of experiments must therefore be conducted to determine the effect of various operating parameters on the BPA removal performance of these sorbents for potential engineering applications.

The objective of the current study are (1) to screen and evaluate a series of candidate sorbents, including peat, activated carbon, and other biosorbents, for BPA removal from aqueous solutions; (2) to examine the effects of sorbent dose, temperature, solution pH, and ionic strength on the BPA sorption onto two peat samples exhibiting good sorption efficiencies; and (3) to study the BPA sorption capacities of peat in a binary system containing phenol as a competitor.

2. Materials and methods

2.1. Materials

Natural sorbents (sawdust, bagasse, and rice husks) were collected from the local market of Shanghai for comparison of the sorption capacities. The natural fibric peat used to prepare the modified sorbent was obtained from Jixiang Peat Co. (Jilin, China). All raw materials were sequentially pretreated with hot distilled water and 0.01 mol/L NaOH solution. After soaking for 2 h, the pretreated material was separated from the solution, thoroughly washed in distilled water several times to remove soluble impurities, dried in an oven at 90 °C for 24 h, and then stored in desiccators at 25 °C. A commercial coal-based granular activated carbon (GAC) from Calgon Carbon Corp. was used as the control. The materials were ground and sieved to a particle size of 300–400 μm prior to the sequential modification process and sorption tests.

Table 1
Ultimate analysis and specific surface area of sorbent used in the present study.

Sorbent	Ultimate analysis			BET surface area (m^2 g^{-1})
	C%	H%	N%	
Peat	43.4	4.5	1.8	1.02
Sawdust	47.1	5.6	1.4	0.72
Bagasse	45.7	4.8	1.1	1.67
Rice husk	42.9	5.3	1.9	0.24
GAC	86.3	0.7	0.4	896
Modified peat	51.9	7.9	2.7	0.66

Methanol was of HPLC grade; all other chemicals and reagents were of analytical grade. Hexadecyltrimethylammonium bromide (HTAB) was purchased from Lingfeng Chemical Co. (Shanghai, China) and used as a modifier. A 50 mg L^{-1} stock solution (pH 7.0) was prepared by dissolving BPA powder or phenol (Tokyo Chemical industry Co., Japan) in double-distilled water.

The modified peat was prepared via ion exchange between HTAB cations and polar functional groups in a peat matrix. In brief, pretreated peat (5 g) was mixed with 200 mL 50 mmol L^{-1} HTAB solution in a water bath oscillator (HHS-4 Boxun Shanghai, China) at 35 °C for 8 h. Afterwards, the modified peat was separated via suction filtration, washed until all foam was removed, and dried at 80 °C for 24 h. The characteristics of these sorbents are listed in Table 1.

2.2. Sorption experiments

Batch sorption experiments were conducted to evaluate the BPA sorption potential of the natural sorbents, modified peat, and GAC. Approximately 0.05 g sorbent was added into glass flasks containing 50 mL of 2.0 mg L^{-1} BPA solution (pH 7.0). The flasks were then sealed and agitated at 200 rpm in a water bath oscillator (25 °C). The samples were collected at appropriate time intervals to determine the residual BPA concentration and calculate the removal efficiency. From the results in Table 2, the sorption capacity of peat is significantly superior to those of the other natural sorbents under the same conditions. Thus, the variations in the sorption capacity of modified peat at various pH, sorbent dosages, temperatures, and ionic strengths were further examined. The effect of the sorbent dosage was determined by mixing 0.01–0.1 g peat with 50 mL of 2 mg L^{-1} BPA solution for 4 h at 25 °C. The effects of pH and the ionic strength on BPA adsorption ability were subsequently determined using a certain amount of peat and a fixed BPA concentration. The original pH was adjusted from 3 to 11 using 0.1 mol/L HCl and 0.1 mol/L NaOH. The ionic strength was controlled by adding 0.1 mol/L to 1.0 mol/L NaCl or $CaCl_2$. The isotherm study was conducted at different temperatures (298, 308, and 318 K) to obtain the equilibrium isotherms. A 0.05 g peat was thoroughly mixed with 50 mL of a 0.5–20 mg L^{-1} BPA solution at a constant temperature for 24 h.

Phenol was used as a competitor to evaluate the effects of a coexisting pollutant on BPA sorption onto the modified peat. The experiments were performed following the procedure used for the single-solute sorption experiments. A series of binary-solute solutions containing 0.5–20 mg L^{-1} (m_{BPA}:m_{phenol} = 1:1) BPA and phenol were prepared. The binary-solute solution (50 mL) was thoroughly mixed with 0.05 g peat at 25 °C for 24 h. The equilibrium concentrations of BPA and phenol were then determined. All experiments were conducted in duplicate to ensure the reproducibility of the results. BPA loss via volatilisation or degradation was

Table 2
Pseudo-second order kinetic parameters for BPA sorption onto various sorbent.

Sorbent	C_0 (mg L^{-1})	q_e (mg g^{-1})	K_2 g (mg min)$^{-1}$	$t_{1/2}$ (min)	h mg (g min)$^{-1}$	R^2
Rice husk	2	0.18	1.007	5.52	0.03	0.997
bagasse	2	0.41	1.061	2.28	0.18	0.999
Sawdust	2	0.58	0.150	11.48	0.05	0.996
Peat	2	0.81	0.149	8.33	0.10	0.999
Modified peat	2	1.71	0.119	4.92	0.35	0.999
GAC	2	1.67	0.347	1.72	0.97	0.999

negligible (within 2%), which was confirmed via control tests without the addition of a sorbent.

2.3. Analytical methods

The BPA and phenol concentrations were determined using a Hitachi (Tokyo, Japan) L2000 high-performance liquid chromatography system with an Alltima C_{18} reverse phase column (3.2 mm × 150 mm, 5 μm) at 30 °C. Aqueous methanol (80%, v/v) was used as the mobile phase at a rate of 1.0 mL/min. The detector wavelength was 280 nm. The linearity was good for both compounds, with correlation coefficients (R^2) always above 0.999 over the studied concentration range. All samples were analysed in triplicate. The relative standard deviations (RSD) of this method for the BPA and phenol standard solutions (5.0 mg L^{-1}) were 0.9% and 0.6%, respectively.

The removal efficiency (R%), amount of BPA and phenol adsorbed per unit mass of sorbent at time t (q_t, mg g^{-1}) and at equilibrium (q_e, mg g^{-1}) were calculated using the following mass balance relationships:

$$R\% = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{1}$$

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{2}$$

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{3}$$

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium pollutant concentrations in the solution, respectively, and C_t (mg L^{-1}) is the residual concentration at time t. V represents the volume of the solution (L), and m is the mass of the dry sorbent used (g).

3. Kinetic and isotherm studies

3.1. Sorption kinetics

The pseudo-second-order kinetic model has been widely used to describe biosorption data obtained under non-equilibrium conditions (Ho & McKay, 1999). As noted by Kumar and Sivanesan (2006), the nonlinear method is a better way of obtaining the parameters involved in the kinetic equations. The nonlinear equation of the pseudo-second-order kinetic model used in the current study, the initial sorption rate (h, mg g^{-1} min^{-1}), and the half-sorption time ($t_{1/2,}$ min) are obtained using Eqs. (4)–(6), respectively.

$$\frac{1}{q_e - q_t} = k_2 t + \frac{1}{q_e} \tag{4}$$

$$h = k_2 q_e^2 \tag{5}$$

$$t_{1/2} = \frac{1}{k_2 q_e} \tag{6}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second-order sorption, and $t_{1/2}$ is the time needed to adsorb half of the equilibrium value of BPA.

3.2. Sorption isotherm

Based on our previous study, the Freundlich isotherm is more suitable in describing the sorption behaviour of the modified peat. Hence, the equilibrium sorption data obtained in the current study were fitted to a Freundlich isotherm equation, as shown in a nonlinear form in Eq. (7), as follows:

$$q_e = K_F {C_e}^{1/n} \tag{7}$$

where K_F [(mg g^{-1}) (L g^{-1})$^{1/n}$] and $1/n$ are the Freundlich constants related to the sorption capacity and intensity, respectively.

4. Results and discussion

4.1. Characteristics of BPA sorption onto various sorbents

The BPA removal performances of various sorbents were compared. The sorption studies were performed at 25 °C and pH 7.0 using an initial BPA concentration of 2 mg L^{-1}, a sorbent dosage of 0.05 g, an agitation rate of 200 rpm, and a sorption time of 4 h. The BPA removal efficiencies of all investigated materials are presented in Fig. 1. The kinetic parameters of the pseudo-second-order kinetic model, including k_2, q_e, and R^2 for each fit, are listed in Table 2.

The BPA removal capacities of the natural sorbents (i.e., rice husk, bagasse, sawdust, and unmodified peat) are significantly lower than those of activated carbon (Fig. 1). In all cases, the sorption kinetics can be satisfactorily fitted using the pseudo-second-order equation ($R^2 > 0.99$). GAC showed the best BPA removal efficiency (75.6%) at 10 min, showing that a carbon sorbent with a high surface area exhibits a faster and more effective BPA adsorption than natural sorbents. BPA removal linearly increased with time, and a pseudo-equilibrium BPA removal state was established within 120 min for all sorbents. The transport of BPA from the solution to the sorbent occurred in two stages, namely, the external surface sorption or faster sorption stage, and the interior surface sorption or gradual sorption stage. Most of the BPA mass transfers

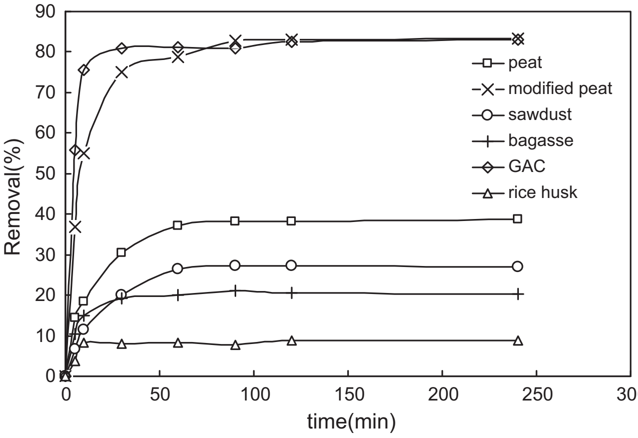

Fig. 1. BPA removal efficiency of various sorbent (BPA concentration = 2 mg L^{-1}; sorbent dose = 0.05 g; pH = 7.0; 25 °C).

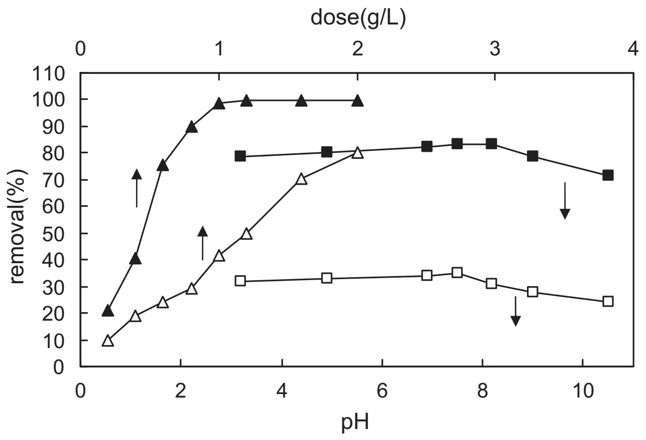

Fig. 2. Effect of peat dose and pH on the BPA removal (peat: open symbols, modified peat: solid symbols. BPA concentration = 2 mg L^{-1}; 25 °C).

to the sorbent particles occurred during the first stage, which possibly corresponds to macropore and mesopore diffusion. On the other hand, the second stage may be related to micropore diffusion.

The GAC sorption rate is faster than those of the other sorbents based on the h and $t_{1/2}$ values (Table 2). However, the BPA removal of peat was remarkably enhanced through modification. The h and q_e values of the modified peat were more than two times higher compared with those of the unmodified peat. At 240 min, the amount of BPA removed by R-CTAB was slightly higher than that removed by GAC, with removal efficiencies of 83.4% and 82.9%, respectively. A comparison of these adsorbents with those reported in literature shows that the adsorptive capacities of the modified peat are superior to those of other low-cost adsorbents and equal to those of commercial activated carbon and hybrid particles (Cao et al., 2009; Dong, Wu, Chen, & Lin, 2010; Tsai, Lai, & Su, 2006).

The most significant factors that determine the sorption capacity include not only the physical characteristics of the sorbent, such as pore volume and surface area, but also their chemical characteristics (i.e., surface polarity). In this case, activated carbon adsorbed organic pollutants through its huge surface area. However, its sorption efficiency quickly drops in the presence of high-concentration pollutants. By contrast, modified peat, having no huge surface area, retained organic pollutants through a synergistic interaction involving partition, adsorption, and hydrogen-bonding. Partition and adsorption are related to the organic matter content and sorbent surface, respectively (Zhu & Chen, 2000). The grafted organic layer created by the cationic surfactants on the internal or external surface of peat increased the BPA partitioning into the sorbent. The increased organic matter content of the modified peat and the formation of specific graft sites on the surface facilitated BPA binding with the sorbent. In addition, modified peat contains numerous hydroxyl groups. Hence, hydrogen-bonding between the hydrophilic hydroxyl groups of peat and the two hydroxyl groups of BPA is another possible interaction (Kim et al., 2011).

Among the low-cost biosorbents, modified peat may be an ideal choice for environmental application. The optimal operating conditions for BPA removal using modified peat were investigated in the subsequent sections.

4.2. Effect of sorbent dose

The effect of the sorbent dose on BPA removal at an initial concentration of 2 mg L^{-1}, pH of 7.0, agitation rate of 200 rpm, and temperature of 25 °C was determined, and the results are presented in Fig. 2. The increase in the sorbent dose resulted in a greater surface area and an increased amount of available binding sites for BPA, resulting in increased BPA percentage removal. However, the sorption capacity per unit mass of the sorbent (i.e., q_e) decreased as the sorbent dose increased because of the reduction in the amount of BPA adsorbed onto a unit mass of a sorbent with increasing sorbent mass concentration. Similar trends have been reported for BPA sorption onto activated carbon (Tsai et al., 2006) and malachite green sorption onto clayey soil (Saha, Chowdhury, Gupta, & Kumar, 2010).

Hence, evaluating the sorbent performance from q_e alone is not sufficient. Comparison with other sorbents should be conducted under the same conditions (i.e., dose, initial concentration, temperature, etc.). An increase in the sorbent dose did not significantly change the adsorption yield because of the establishment of an equilibrium between the BPA molecules on the sorbent and in the solution. Fig. 2 shows that a relatively low dose (approximately 1 g L^{-1}) is sufficient for the modified peat to achieve a reasonably good removal performance, whereas a much higher dose is needed for the unmodified peat. Therefore, the optimum sorbent dose is 1 g L^{-1}, which was used for the subsequent experiments for economic purposes.

4.3. Effect of pH

The effect of the initial pH on sorption provides an insight on the nature of the physicochemical interaction between the sorbate and the sorbent adsorptive sites. The initial pH of the solution can change the sorbent surface charge and the degree of ionisation of the sorbate molecule (Yu, Deng, & Yu, 2008). Fig. 2 illustrates the effect of the initial pH on the sorption of BPA onto peat at a given experimental condition.

The BPA removal efficiency slightly changed when the pH values changed from 2 to 7, indicating that the binding affinity between BPA and the binding sites did not significantly change under acidic conditions. The protonation of the functional groups present on the biosorbent surface easily occurs at low pH values, and the H^+ ions can compete with BPA for appropriate sites on the biosorbent surface. The maximal BPA removal efficiency was reached within the pH range of 6–8, with its value fluctuating between 97% and 99%. The removal efficiencies of both peats clearly decreased when the pH was increased to above 8. A similar behaviour was observed in other adsorbents, such as activated carbon (Bautista-Toledo, Ferro-Garcia, Rivera-Utrilla, Moreno-Castilla, & Fernandez, 2005), mainly because BPA has a pKa of 9.90–10 and behaves as an anion at high pH values (Yoon, Westerhoff, Snyder, & Esparza, 2003). Thus, the concentration of negative BPA anions increased with increasing pH. Although the results from the BPA removal by a modified zeolite show that anionic species may have higher affinity towards modified zeolites than neutral ones (Dong et al., 2010; Li, Dong, Wu, Peng, & Kong, 2011), the results of the current study indicate that the increase in the negative charge of BPA did not result in an increase in the sorption capability. The overall surface charge becomes more negative as the pH increases, and the electrostatic repulsion between BPA and the sorbent becomes increasingly stronger and overcomes the binding affinity. These combined effects resulted in the reduction in the amount of BPA adsorbed onto the peat at alkaline conditions.

4.4. Effect of the ionic strength on BPA sorption

The sorption of BPA onto peat at different NaCl and $CaCl_2$ concentrations was studied, and the results are shown in Fig. 3. The sorption of BPA onto the modified peat shows negligible ionic strength-dependence on the electrolyte concentrations compared with that on the sediment and activated carbon (Li et al., 2007; Reddad, Gerente, Andres, & Le Cloirec, 2002). The increase in the ionic strength induced a slight increase in the modified peat

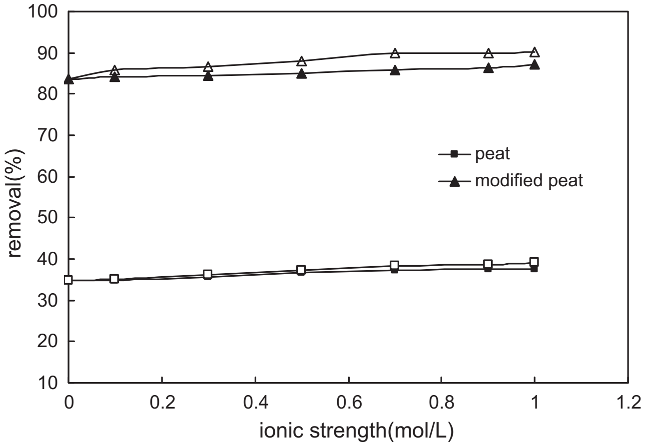

Fig. 3. Effect of ionic strength on the BPA removal (Na^+: solid symbols, Ca^{2+}: open symbols; BPA concentration = 2 mg L^{-1}; sorbent dose = 0.05 g; pH = 7.0; 25 °C).

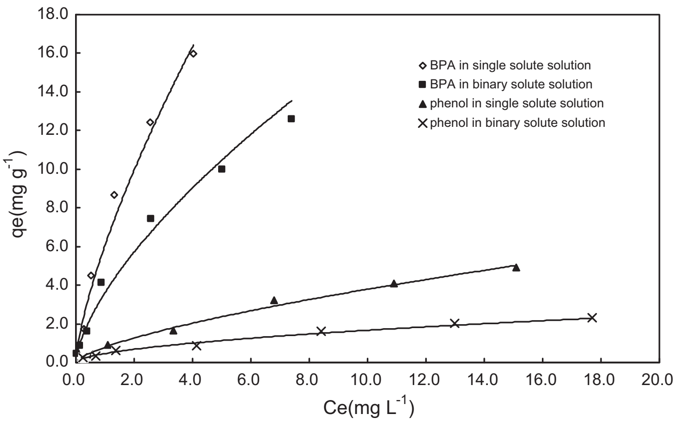

Fig. 4. Single-solute and binary-solute sorption isotherms of BPA and phenol to modified peat (sorbent dose = 0.05 g; pH = 7.0; 25 °C).

sorption capacity by approximately 5%. These results indicate that the BPA removal, which was enhanced by the addition of Ca^{2+} and Na^+, is limited; however, the effect of Ca^{2+} is more obvious than that of Na^+ because of the stronger ionic strength.

The slight increase in BPA sorption is attributed to several reasons. First, Ca^{2+} and Na^+ react with the negatively charged group of the peat surface, thereby decreasing the repulsion between BPA and the negatively charged surface (Kyriakopoulos, Doulia, & Hourdakis, 2006). Second, Ca^{2+} and Na^+ can reduce the water solubility of BPA (i.e., salting-out effect), which can lead to an increase in BPA removal. Given that the experiment was conducted at a neutral condition, the enhancement of the sorption was mainly due to the salting-out effect of the electrolytes resulting from the decrease in BPA solubility, not the electrostatic attraction.

Liu, Ma, Li, and Qin (2009) found that the q_e of BPA onto activated carbon decreased after a small amount of NaCl was added into the solution; Na^+ may have occupied the active sites. The fluctuations in q_e were not observed in the current study. For the modified peat, the presence of competing ions did not result in a significant difference in the sorption performance, indicating that the primary sorption mechanism of the modified peat is different from that of activated carbon.

4.5. Sorption isotherm

Sorption isotherms under different temperatures (298, 308, and 318 K) were obtained (Appendix A) to study the thermodynamic process and parameters for the sorption of BPA molecules on the modified peat. The results, which were fitted using a Freundlich model, are listed in Table 3.

The q_e values increased with increasing initial BPA concentrations and were also affected by temperature changes. The initial concentration and temperature plays a significant role in determining the maximum sorption capacity of the modified peat for BPA. As shown in Table 3, the isotherm data fit the Freundlich model well ($R^2 = 0.97$). The value of $1/n$ is less than 1, which indicates a favourable sorption. Both the K and q_e values decreased as the temperature increased, indicating the exothermic nature of BPA molecule sorption on peat. The negative ΔG° value (−5.492, −4.792, and −4.640 kJ mol^{-1} at 298, 308, and 318 K, respectively) and negative ΔH° value (−13.75 kJ mol^{-1}) indicate that the sorption of BPA molecules onto the modified peat was a spontaneous and exothermic process. The negative value of ΔS° possibly corresponds to a decrease in the degree of freedom of the sorbate during the sorption process (Ozcan, Oncu, & Ozcan, 2006).

4.6. Competitive sorption in binary solution systems

Knowledge of the competitive sorption characteristics is critical for the application of these modified sorbents in wastewater treatment because organic pollutants usually coexist with one other (Pan et al., 2011). The q_{eb}/q_{es} ratio represents the extent of sorption competition in a binary-solute solution system; q_{eb} and q_{es} are the equilibrium sorption amount of BPA or phenol adsorbed per unit mass of the sorbent in binary and single-solute solutions, respectively. The q_{eb}/q_{es} values for BPA and phenol must be less than 1.0, according to the results in Fig. 4. In addition, the competitive sorption behaviours were enhanced at higher concentrations of the competitive phenolic compound. Meanwhile, the sorption coefficients (K_F) of the modified peat for BPA and phenol obtained from the Freundlich model (Appendix B) decreased in the binary-solute solution compared with the single-solute system, suggesting that the presence of both phenolic compounds reduced the sorption via competition for the binding sites.

The competitive sorption between phenol and BPA at low concentrations (under 2 mg L^{-1}) was not noticeable. The BPA sorption capacity in the binary-solute solution was only lower than that of the single-solute solution by 5%. Moreover, the q_{eb}/q_{es} values for phenol were much lower than those of BPA, indicating that phenol sorption onto the modified peat was more sensitive to the presence of competitive adsorbate molecules compared with that of BPA. A similar phenomenon was observed by Yang, Wang, Zhu, and Xing (2006). These results indicate that the modified peat is an effective sorbent for the remediation of BPA-contaminated water.

This difference in behaviour is attributed to the different octanol–water partitioning coefficients (log K_{ow}) of each compound, which results in different hydrophobic interaction densities

Table 3
Thermodynamic parameters and Freundlich isotherm constants for sorption of BPA onto modified peat.

Temperature (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° J $(mol\,K)^{-1}$	K_F (mg g^{-1}) (L $mg^{-1})^{1/n}$	$1/n$	R^2
298	−5.492			6.064	0.715	0.974
308	−4.792	−18.095	−42.6	4.603	0.724	0.989
318	−4.640			4.226	0.727	0.990

with the modified peat. BPA is more hydrophobic, and its log K_{OW} value (3.32) is significantly higher than that of phenol (1.46) (Staples, Dome, Klecka, Oblock, & Harris, 1998). In addition, BPA is moderately soluble in water, with approximately 12 mg dissolving in 100 mL at room temperature, whereas phenol is far more water-soluble, with approximately 8–9 g dissolving in 100 mL. The differences between the hydrophobic and hydrophilic regions of BPA and phenol determine the extent of the sorption affinity, resulting in the preferential sorption of the modified peat for BPA.

5. Conclusion

The performance of peat and other natural sorbents in the removal of BPA from aqueous solutions have been examined. The results show that the BPA removal efficiencies of the natural sorbents are significantly lower than that of activated carbon. Peat shows great potential as a natural sorbent material compared with the other materials investigated. The introduction of alkyl ammonium onto the peat surface led to a high sorption affinity and selectivity for BPA. Moreover, the sorption capacity of the modified peat ($1.71\,\mathrm{mg\,g^{-1}}$) was slightly higher than that of activated carbon ($1.67\,\mathrm{mg\,g^{-1}}$) under certain conditions (BPA concentration = $2\,\mathrm{mg\,L^{-1}}$; sorbent dose = 0.05 g; pH = 7.0; 25 °C). The strong hydrophobic interaction between the hydrophobic phenyl groups and the grafted HTAB groups is the most important factor that determines the sorption capacity. Furthermore, BPA was preferred over phenol in a binary solute system, and the increase in the sorbent dose and ionic strength in a neutral solution facilitated the removal of BPA.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbpol.2011.12.034.

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