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APPROPRIATE TECHNOLOGIES TO COMBAT WATER POLLUTION

Adsorptive removal of endocrine-disrupting compounds and a pharmaceutical using activated charcoal from aqueous solution: kinetics, equilibrium, and mechanism studies

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Abstract

Bisphenol A (BPA), diethyl phthalate (DEP), and carbamazepine (CBZ) have been widely used in chemical and pharmaceutical fields, and their residues are detected in various environments. Therefore, to find a suitable method for removing the compounds from an aqueous solution, an adsorption method by granular activated charcoal (AC) was studied. To investigate the adsorption properties of AC, its kinetics, equilibrium, pH effects, and regeneration of AC were examined. Moreover, its surface properties (i.e., surface area, pore volume, functional groups, and surface charge) were characterized by N_2 adsorption and desorption isotherm, Fourier transform infrared (FTIR), and zeta potential analyses. Experimental results show that AC has high removal efficiencies for the target compounds at the low initial concentration as well as high estimated adsorption capacities (q_m) for DEP, BPA, and CBZ, whose values were 293.4 ± 18.8, 254.9 ± 16.2, and 153.3 ± 1.61 mg/g, respectively. In comparison with other adsorbents based on previously reported results, AC was shown to have generally higher removability for the three compounds than others. Moreover, it was observed that AC's ability to adsorb DEP and BPA was dependent on pH because of hydrolysis and ionization, respectively. Meanwhile, there is no pH effect for CBZ adsorption by AC. After 3 cycles of adsorption/desorption, AC still maintained 92, 100, and 82% of initial adsorption capacities for DEP, BPA, and CBZ, respectively. Therefore, the AC is an effective adsorbent for the removal of endocrine-disrupting chemicals and pharmaceuticals from aqueous solution.

Keywords Endocrine-disrupting compounds · Pharmaceutically active compounds · Activated charcoal · Adsorption · Hydrophobic interaction · Regeneration

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Introduction

Environmental hormones, also called endocrine-disrupting chemicals (EDCs), have already raised public concern with regard to health and the environment (Zhou et al. 2013), because they can mimic the biological activities of natural hormones, allowing them to interfere with the nervous and reproductive systems of wildlife and humans (Pan et al. 2008). In EDCs, bisphenol A (BPA) and diethyl phthalate (DEP) are of major concern. BPA is a toxic compound and is non-biodegradable and highly resistant to chemical degradation (Guo et al. 2011). BPA have been detected in drinking water with the maximum concentration of 0.1 μg/L (Liu et al. 2009). DEP is also toxic and can lead to harmful effect to microorganism during its biodegradation (Cartwright et al. 2000), and it is in large-scale production. The worldwide production of PAEs is already estimated to be 6×10^6 t/year as of 2006 (Xu et al. 2014). Also, pharmaceutically active compounds (PhACs) are considered to be a class of emerging micropollutants (Rivera-Utrilla et al. 2013). Because a variety of pharmaceuticals and their metabolites are persistent and non-biodegradable, they are released to the environment without proper control and treatment. Accordingly, many types of pharmaceuticals are detected in the actual environment. Especially, carbamazepine (CBZ), an antiepileptic pharmaceutical, is one of the 11 most detected pharmaceuticals in drinking water (Benotti et al. 2009). This may be because it is not degradable or adsorbed onto the sewage sludge (Domínguez et al. 2011).

Therefore, removing them from aqueous solution becomes an urgent issue. Until now, several removal techniques have been applied to treat the EDCs and PhACs in aqueous solutions, such as biodegradation (Cartwright et al. 2000), membrane filtration and advanced oxidation (Ganiyu et al. 2015), coagulation sedimentation (Qin et al. 2016), and adsorption (Akhtar et al. 2015). Among these removal methods, adsorption is one of the most promising, due to its numerous advantages, such as being environmental-friendly (Al-Khateeb et al. 2014) and having simpler reactor/absorber design, operational simplicity (Akhtar et al. 2015), and low capital cost (Delgado et al. 2012). To et al. used palm kernel shell as the precursor to prepare activated carbon, and its adsorption capacity for CBZ increased to 170.1 mg/g (To et al. 2017). Liu et al. modified the activated carbon by oxidation and thermal treatment, and its adsorption capacity of BPA were 59.17 and 432.34 mg/g, respectively (Liu et al. 2009). Wang et al. used multi-walled carbon nanotubes (MWCNTs) to adsorb DEP from an aqueous solution with a capacity of 147.9 mg/g (Wang et al. 2010). So, the carbon-based materials as an inexpensive and efficient adsorbent can be used to remove EDCs and PhACs from aquatic environment. However, the adsorption mechanisms have not been clearly elucidated.

Thus, the purposes of this study were to investigate the adsorption properties and mechanisms of AC for removal of EDCs (DEP and BPA) and PhACs (CBZ) from an aqueous solution. The characteristics of AC were analyzed using Fourier transform infrared spectroscopy (FTIR), an N_2 adsorption and desorption isotherm, and zeta potential. The adsorption performance of AC for DEP, BPA, and CBZ were examined by kinetics, isotherm, pH effect, and desorption studies. Furthermore, in order to explore the overall adsorptive effect between the three chemicals and adsorbents, we measured and collected the surface area and pore volume of AC and previously used adsorbents, respectively, and correlated those with the adsorption capacity values for these three compounds.

Materials and methods

Materials

The endocrine-disrupting compounds (BPA and DEP) and a pharmaceutical (CBZ) used in this study, whose purities were over 98% purity, were obtained from Sigma-Aldrich (Seoul, Korea). The stock solutions of the compounds were prepared in deionized water and stored at 4 °C. Their molecular structures and physicochemical properties are provided in Table 1. For HPLC analysis, acetonitrile and sodium dihydrogen phosphate ($NaH_2PO_4 \cdot 2H_2O$) were purchased from Honeywell Burdick & Jackson and Sigma-Aldrich, respectively. Analytical-grade activated charcoal (AC) was purchased from Sigma-Aldrich. AC was prepared by sieving to collect a regular particle, size within 0.18–0.25 mm, and then it was washed several times using distilled water. Next, it was freeze-dried for the following adsorption experiments.

Characteristics of AC

Fourier transform infrared spectroscopy (FTIR, Frontier, Perkin-Elmer, USA) was used to analyze the functional groups on the surface of the AC. The sample was prepared with KBr pellets and marked within the range of 400–4000 cm^{-1}. To analyze the texture properties of AC, N_2 adsorption and desorption isotherm measurements were performed by using Belsorp-mini II (BEL, Japan) at 77 K. Samples were activated by heating at 100 °C for 12 h under high vacuum. The specific surface area and total pore volume of the AC were calculated by the Brunauer-Emmett-Teller (BET) method. The texture properties of AC are shown in Table S1. Point of zero charge (pH_{pzc}) of AC was obtained by the zeta potential-pH curve using a NanoPlus HD zeta potential and nanoparticle size analyzer (particulate systems, USA), and the result is shown in Fig. S1.

Kinetics study

For kinetic experiments, a 250-mL compound solution was put into a conical flask, and the pH was maintained at 6.5. Then, 0.05 g of AC was added and agitated at 120 rpm in a rotary shaker at 25 °C. The samples were taken at regular intervals. The initial concentrations of the compounds were 1 and 100 mg/L. The properties of adsorption kinetics were assessed by measuring the decrease in adsorbate concentration over the time interval from 0 to 24 h.

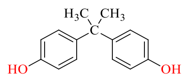
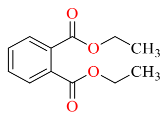
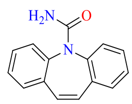
The fitting of kinetic experimental data to three frequently used models was conducted. These were linear pseudo-first-order, pseudo-second-order, and intraparticle diffusion models, whose equations were as follows (Dai et al. 2013; Lv et al. 2006):

$$\text{Pseudo-first-order}: \ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

$$\text{Pseudo-second-order}: \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2}$$

$$\text{Intraparticle diffusion}: q_t = k_{id} t^{0.5} + C \tag{3}$$

Table 1 Physicochemical properties of bisphenol A (BPA), diethyl phthalate (DEP), and carbamazepine (CBZ)

Compound	Structure	MW	pK_a [a]	log K_{ow} [b]	MV(cm^3/mol) [b]	Sw (mg/L) [c,d,e]
BPA		228.3	9.7	3.32	199.6±3.0	300
DEP		222.2	-	2.47	198.2±3.0	1000
CBZ		236.27	0.1, 14.3	2.45	186.6±3.0	125

MW molecular weight, *MV* molar volume, *Sw* water solubility

[a] The pK_a values were provided from the database of ACD/I-Lab

[b] The log K_{ow} and MV were obtained from Chemspider

[c, d, e] (Deng et al. 2013; Gao and Wen 2016; Zhang et al. 2006).

where, q_e (mg/g) is the uptake of solute adsorbed at equilibrium, q_t (mg/g) is the amount adsorbed at time t (min), k_1 (min^{-1}), and k_2 (g/mg·min) are the pseudo-first-order, pseudo-second-order rate constants, respectively. k_{id} (mg/g·$min^{0.5}$) is intraparticle diffusion constant and C (mg/g) is a constant proportional to the thickness of the boundary layer.

Isotherm study

Isotherm experiments of the three compounds were estimated in a batch scale. A series of concentrations of chemicals were added into several conical tubes containing a 30-mL solution. The initial concentrations of BPA and DEP used from 0 to 150 mg/L, and those of CBZ ranged from 0 to 120 mg/L. The amount of AC was 6 mg. The experiments were conducted at pH 6.5 ± 0.15, to simulate the real environmental pH, and shaken at 120 rpm and 25 °C for 24 h. The concentrations of the chemicals were analyzed by HPLC after filtration through a 0.20-μm cellulose acetate membrane filter (Advantec, Japan). Finally, the uptake (q_e) values of AC for the compounds were calculated by the following mass balance (Pehlivan et al. 2012):

$$q_e = \frac{(C_i - C_e)V}{M} \tag{4}$$

where, q_e is equilibrium capacity (mg/g), C_i and C_e represent initial and equilibrium concentrations (mg/L), V is working volume (L), and M is mass of adsorbent (g). The volume used for pH adjustment could be negligible.

Isothermal models

The adsorption isotherm data were fitted to four widely used models: Langmuir, Freundlich, Temkin, and Dubunin Radushkevich models (Ben-Ali et al. 2017). The expressions of these models are shown below.

The Langmuir model assumes that adsorption occurs in a monolayer and describes the adsorbent surface as homogeneous, with identical surface sites. Its linear form is expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{5}$$

where q_m is the maximum adsorption capacity (mg/g) and b is the Langmuir constant that refers to the binding energy of adsorption (L/mg).

The Freundlich model explains the multilayer adsorption process and presumes a heterogeneous adsorbent surface. Its linear form is expressed as follows:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{6}$$

where K_F (mg/g)$(L/mg)^{1/n}$ and n are the Freundlich constants, being indicative of the extent of the adsorption and the degree of non-linearity between solution concentration and adsorption, respectively.

The Temkin isotherm assumes that heat of adsorption decreases for the first layers and then increases with coverage increase. It also assumes a uniform distribution of binding energy up to some maximum binding energy. Its linear form is expressed as Eq. (7):

$$q_e = \frac{RT}{b} lnK_T + \frac{RT}{b} lnC_e \tag{7}$$

where R is the gas constant (8.314 J/mol K), T is the absolute temperature (K), b is the Temkin heat of adsorption (J/mol), and K_T is the Temkin isotherm equilibrium binding constant (L/g).

Dubinin Radushkevich (D-R) model is more general in which assumes the adsorption process according to a pore-filling mechanism. It is commonly used to express the adsorption occurred onto both homogeneous and heterogeneous surfaces. A linear form of D-R model is expressed mathematically as Eq. (8):

$$\ln q_e = \ln q_m - K_{\mathrm{ad}}\varepsilon^2 \tag{8}$$

K_{ad} ($\mathrm{mol^2/J^2}$) is a constant in related to the mean free energy of adsorption E ($E = \frac{1}{\sqrt{2K_{\mathrm{ad}}}}$); and ε is the Polanyi potential ($\varepsilon = \mathrm{RT}\ \ln(1 + \frac{1}{C_e})$).

Effect of pH

To examine the effect of pH on the adsorption uptake by AC, the pH values of solutions were ranged from 2.5 to 10 by adding 0.1 mol/L HCl and NaOH solutions. The other experimental conditions were kept the same as those of the isotherm experiments, whereby the concentrations of adsorbents and adsorbates were maintained at 0.2 g/L and 100 mg/L, respectively. After 24 h, the final concentration of the adsorbate in the solution was measured for calculating the adsorption uptake. The experiment was performed at 25 °C.

Regeneration of AC

Regeneration of AC was investigated using methanol as eluent. First, adsorption of individual EDCs or PhACs (100 mg/L) on AC was conducted. After 24 h, the EDCs- or PhACs-adsorbed AC was centrifuged, separated, and gently washed with distilled water for three times to remove the unbound compounds. The EDCs- or PhACs-adsorbed AC was eluted using 30 ml of methanol at 40 °C for 24 h and then washed by distilled water three times. The regenerated AC was reused in the subsequent adsorption cycles.

Analysis method of micropollutants

Samples were analyzed by HPLC with binary pumps and an ultraviolet (UV) detector (Japan, Shimadzu, LC-20AD). Separations were achieved using an Eclipse XDB-C18 column (250 mm × 4.6 mm) (Agilent, Japan). The HPLC analysis was conducted in a column incubator at 40 °C. The wavelength of UV detector was 211 nm, and the injected volume was 10 μL. The mobile phase for BPA, DEP, and CBZ was a mixture of acetonitrile and buffer solution at the ratio of 40:40 (*v*/*v*). The buffer solution contained 30 mmol/L of NaH_2PO_4. Calibration curves were built using more than six concentration points for DEP, BPA, and CBZ. The estimated calibration curves have acceptable linearity, whose R^2 values are higher than 0.9999. The HPLC detection limits of BPA, DEP, and CBZ were 8.0, 20.0, and 10.0 μg/L, respectively. The peaks of DEP, BPA, and CBZ are show in Fig. S2 and the calibration curves of them are shown in Fig. S3.

Results and discussion

Surface characterization of AC

To investigate the functional groups present on the surface of the AC, FTIR analysis was performed. The analyzed FTIR spectrum is shown in Fig. 1. The broad band at 3300 $\mathrm{cm^{-1}}$ was formed by O-H stretching (Nitayaphat et al. 2009; Zhao et al. 2015), which was consistent with the peak at 1090 $\mathrm{cm^{-1}}$ corresponding to C-O stretching vibration (Tan et al. 2007). The peaks at 1570 and 1455 $\mathrm{cm^{-1}}$ appeared to be due to aromatic C=C ring stretching (Cohen-Ofri et al. 2006). Furthermore, in the spectra of AC, a band at 800 $\mathrm{cm^{-1}}$ was observed, which indicates the existence of C-H out-of-plane bending of aromatics (Pastor-Villegas et al. 2007). Finally, it was confirmed that the AC had a large number of C-OH functional groups connected to aliphatic and aromatic sites.

Adsorption kinetics

Kinetic experiments were performed to evaluate the equilibrium time on the adsorption rate between adsorbates and AC. As seen in Fig. 2, all of the kinetic profiles of AC for DEP, BPA, and CBZ indicated that an initial rapid uptake occurred within 10 min, as followed by a slower, incremental uptake step until the equilibrium state was reached after 2 h at the high initial concentration of 100 mg/L. Moreover, at the low concentration of 1 mg/L, AC can remove almost all of DEP, BPA, and CBZ within 1 h, and after 2 h they could not be detected by HPLC. To further describe the adsorption property, the linear pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were used to fit the kinetic data.

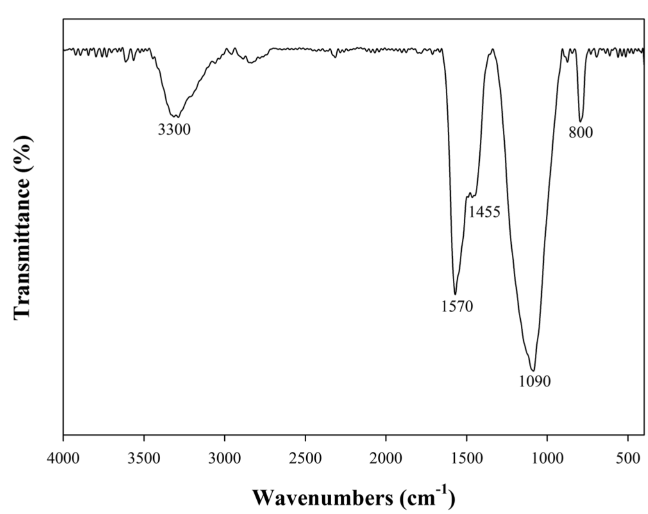


Fig. 1 FTIR spectrum of the activated charcoal

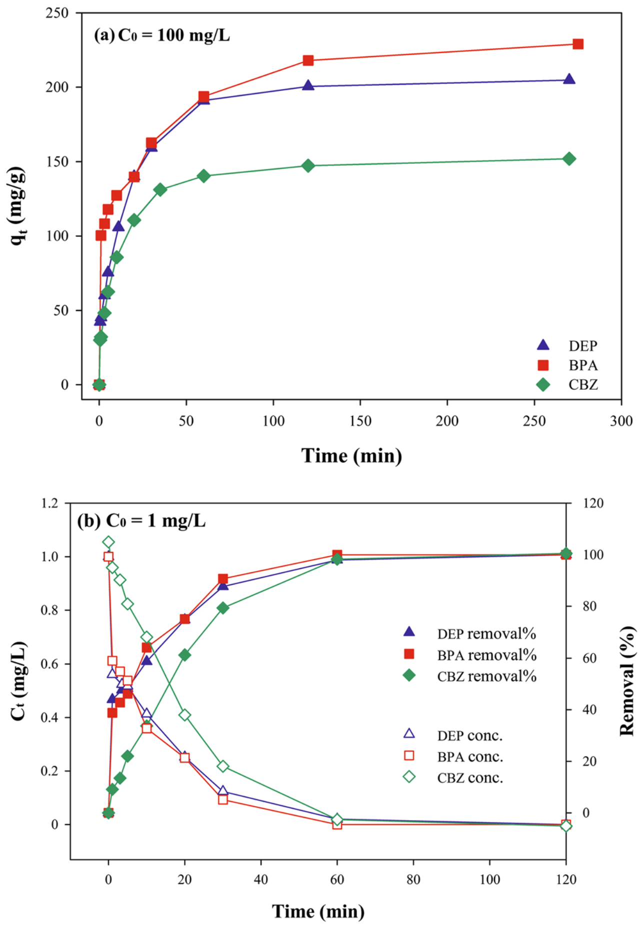


Fig. 2 Effect of contact time on adsorption efficiency of AC for DEP, BPA, and CBZ at high concentration of 100 mg/L (**a**) and low concentration of 1 mg/L (**b**). The experimental conditions were 0.2 g/L of AC dosage, 6.5 ± 0.15 of pH, and 25 °C of temperature

The calculated kinetic parameters for BPA, DEP, and CBZ are given in Table 2, and the fitting curves of BPA, DEP, and CBZ on AC are presented in Fig. 3. The linear pseudo-second-order was greater than the linear pseudo-first-order to describe the adsorption kinetics of BPA, DEP, and CBZ adsorption on AC, which has an excellent R^2 values ($R^2 > 0.999$). Figure 3c shows the straight lines of intraparticle diffusion did not pass through the origin, with a positive intercept of C, indicating that the intraparticle diffusion was not the only rate-controlling step for adsorption of BPA, DEP, and CBZ on AC. Based on the calculated values by linear pseudo-second-order, the adsorption equilibrium uptakes of AC for BPA and DEP were higher than CBZ, while the adsorption rate of CBZ was two times faster than those of BPA and DEP.

The hydrophobic effect plays the most important role in adsorption of hydrophobic organic compounds on AC. The hydrophobic interaction can be characterized by the log K_{ow} value, which can be classified as high ($3.5 < \log K_{ow}$), moderate ($2 < \log K_{ow} < 3.5$), and low ($\log K_{ow} < 2$) (Nam et al. 2014). So, the equilibrium uptake of AC for BPA was higher than DEP and CBZ. While the molecular volume of CBZ was smaller than the other two, which easily goes into the pores of AC and is adsorbed on its surface, it was consistent with the result of intraparticle diffusion model and had a smallest C value. Moreover, Pan et al. (Pan et al. 2008) found that the π-π electron donor-acceptor (EDA) interaction between the benzene-containing chemicals and carbon nanomaterials was consisted with the number of benzene/aromatic rings. So, this approach may also promote the adsorption rate of CBZ.

Adsorption isotherms

Isotherms analysis is an important way to understand the adsorptive interaction between the adsorbent and adsorbate. Moreover, the adsorption capacity of an adsorbent can be predicted by an isotherm experiment. The linear forms of Langmuir, Freundlich, Temkin, and Dubunin Radushkevich models were used to fit adsorption data of BPA, DEP, and CBZ on AC. The calculated adsorption properties are given in Table 3, and the fittings are presented in Fig. 4 and Fig. S4 (Temkin and Dubunin Radushkevich models). The R^2 values for the BPA, DEP, and CBZ show that the Langmuir, Freundlich, and Temkin models fitted well with the adsorption data, but the Dubunin Radushkevich for adsorption of DEP

Table 2 Kinetics parameters of AC adsorption of BPA, DEP, and CBZ

Model	Parameter	Adsorbate		
		BPA	DEP	CBZ
Pseudo-first-order	k_1 (1/min)	0.014(1.2×10^{-3})	0.025 (2.6×10^{-3})	0.036 (2.6×10^{-3})
	q_e (mg/g)	126.6 (13.8)	148.8 (16.9)	102.3 (12.0)
	R^2	0.938	0.923	0.958
Pseudo-second-order	k_2 (g/mg·min)	0.0006 (1.0×10^{-4})	0.0006 (9.6×10^{-5})	0.0012 (2.0×10^{-4})
	q_e (mg/g)	235.7 (2.7)	213.5 (1.6)	152.2 (0.9)
	R^2	0.999	0.999	0.999
Intraparticle diffusion	K_{id} (mg/g·min$^{0.5}$)	13.2 (1.0)	25.8 (0.8)	20.5 (0.9)
	C (mg/g)	86.3 (3.3)	19.8 (2.7)	15.3 (3.1)
	R^2	0.935	0.995	0.990

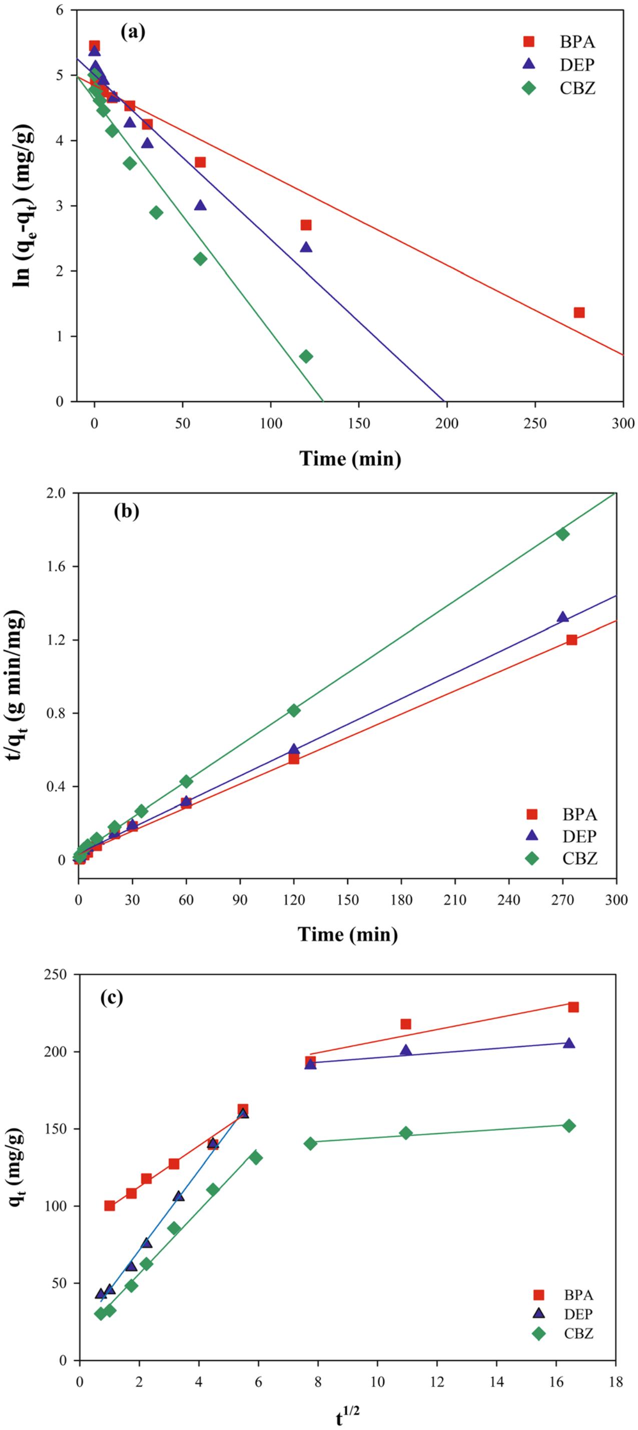


Fig. 3 The fittings of adsorption kinetics of BPA, DEP, and CBZ by AC, (**a**) linear pseudo-first-order model, (**b**) linear pseudo-second-order model, and (**c**) intraparticle diffusion model. The experimental conditions were 0.2 g/L of AC, 100 mg/L of pharmaceutical, 6.5 ± 0.15 of pH, and 25 °C of temperature

and BPA is not good. The Langmuir maximum adsorption capacities q_m were 293.4, 254.9, and 153.3 mg/g for DEP, BPA, and CBZ, respectively. These values are close to the experimental adsorbed amounts, which indicate that the Langmuir model for the adsorption system is acceptable. In detail, the Langmuir model was a slightly better fit for CBZ adsorption data than the Freundlich model, indicating that CBZ was monolayer adsorbed on the AC surface. This is consistent with the kinetic results that the adsorption rate of CBZ was the fastest. On the other hand, the DEP and BPA adsorption data were more suitable for the Freundlich model, in which multilayer adsorption process occurred and the adsorption capacity increased.

However, Dubinin Radushkevich isotherm is usually used to distinguish the physical and chemical adsorption from its mean free energy E (kJ/mol). The value of E in range of 8 and 16 kJ/mol corresponds to a chemical adsorption, while the value of less than 8 kJ/mol means a physical adsorption (Yen et al. 2017). Based on results of K_{ad} shown in Table 3, the E values of these three organic compounds were in a narrow range between 0.60 and 1.15 kJ/mol, indicating a physiosorption process with a certain degree of reversibility. However, this shows an advantage, since it allows recycling the adsorbent in an easier way, thereby extending its working life.

Table S1 compared the adsorption capacities of AC for the target compounds with those of other adsorbents reported in literatures. AC displayed relatively higher adsorption capacities for DEP, BPA, and CBZ than several other adsorbents, such as zeolite, chitosan, silica, resin, single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), and graphene oxide (GO), as well as some kinds of metal-organic frameworks, like UiO-66 and MIL-101. The adsorption properties of AC are facilitated by its large surface area and plentiful cavity construction. Next, to investigate the roles of surface area and pore volume of adsorbents for their maximum adsorption capacity (q_m) in DEP, BPA, and CBZ, we measured and collected the surface area and total pore volume of the adsorbents listed in Table S1. Then, the relationship between each texture property and q_m was built, and the results are shown in Fig. S5. Maximum adsorption capacities of DEP, BPA, and CBZ were positively correlated with the surface area in R^2 of 0.83, 0.58, and 0.88, respectively. Meanwhile, the relationship of q_m with total pore volume does not show a good agreement, except in the case of BPA (in which the data point was only 5), indicating that the pore-filling mechanism does not explain the adsorption between adsorbents and chemicals (i.e., DEP, BPA, and CBZ).

Effect of pH on adsorption capacity

During the adsorption process, the pH value of the solution is an important factor because it can influence the functional groups of adsorbent and properties of chemicals, such as the speciation, degree of ionization, and the surface charge of an adsorbate (Khanday et al. 2017). The species distribution of BPA and CBZ at different pH levels is shown in Fig. S6. When the pH is above 8, BPA starts to have negative charge,

Table 3 Langmuir, Freundlich, Temkin, and Dubunin Radushkevich isotherm parameters for the adsorption of DEP, BPA, and CBZ by AC

Model	Constant $q_{exp.}$ (mg/g)	DEP 296.7	BPA 251.2	CBZ 152.8
Langmuir	q_m (mg/g)	293.4 (18.8)	254.9 (16.2)	153.3 (1.61)
	b (L/mg)	0.136 (0.09)	0.163 (0.09)	0.891 (0.43)
	R^2	0.980	0.984	0.999
Freundlich	K (mg/g)(L/mg)$^{1/n}$	107.8 (2.83)	94.35 (2.17)	81.68 (3.33)
	n	5.090 (0.18)	4.941 (0.16)	6.471 (0.49)
	R^2	0.994	0.996	0.978
Temkin	b	95.37 (11.6)	102.4 (15.1)	174.3 (12.8)
	K_T (L/mg)	0.164 (0.16)	0.104 (0.11)	0.654 (0.44)
	R^2	0.931	0.920	0.988
Dubinin Radushkevich (D-R)	q_m (mg/g)	232.6 (8.81)	206.9 (17.4)	149.7 (1.13)
	$K_{ad} \times 10^{-7}$(mol^2/J^2)	3.772 (1.11)	13.75 (4.20)	11.31 (0.53)
	E (kJ/mol)	1.151	0.603	0.665
	R^2	0.744	0.781	0.993

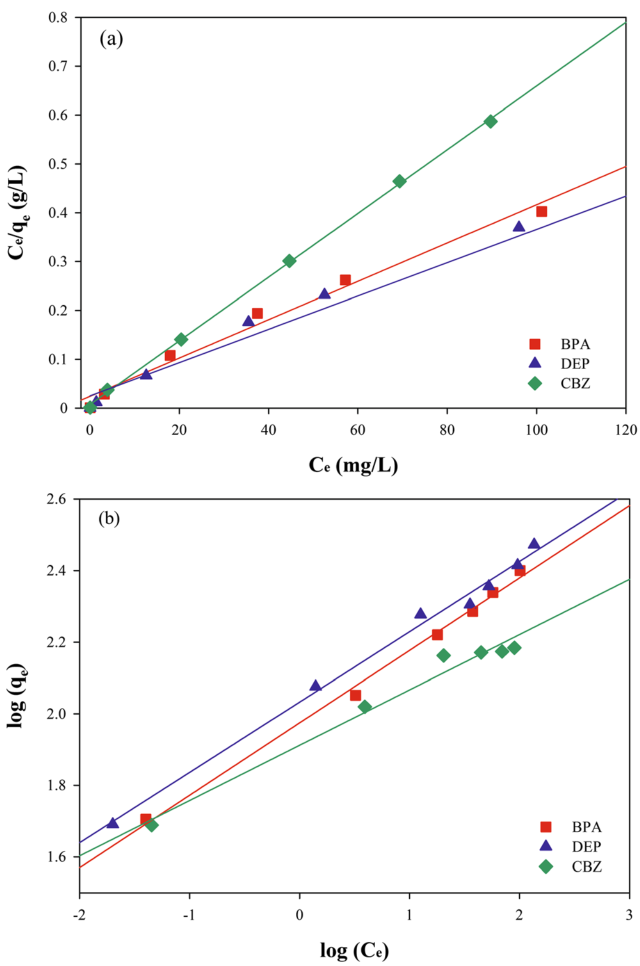


Fig. 4 Isotherms adsorption of BPA, DEP, and CBZ on AC. **a** Langmuir and **b** Freundlich. The experimental conditions were 0.2 g/L of adsorbent, initial concentration of BPA and DEP from 0 to 150 mg/L, initial concentration of CBZ from 0 to 120 mg/L, 6.5 ± 0.15 of pH, and 25 °C of temperature

while CBZ keeps in a neutral form at pH 2–10. In Fig. 5, the equilibrium adsorption capacity values for DEP, BPA, and CBZ is seen to have nearly constant at acid or neutral pH, while DEP and BPA were largely changed at alkaline solution. To better understand the mechanisms during the adsorption process, several adsorption theories regarding the relationship between the adsorbate and carbon materials, such as (i) hydrophobic interactions, (ii) hydrogen bonding, (iii) π-π EDA interactions, and (iv) π-hydrogen bonding should be considered (Wang et al. 2010).

Since the AC's surface is predominantly hydrophobic and favors adsorption of hydrophobic organic compounds, it is assumed that the hydrophobic interactions play an important role in the adsorption process. As seen in Fig. 5, when pH value is lower than 6.5, the adsorption capacity of BPA by AC was not affected by pH, whereas an increase in pH above 6.5 resulted in a gradually decrease of the adsorption. This is

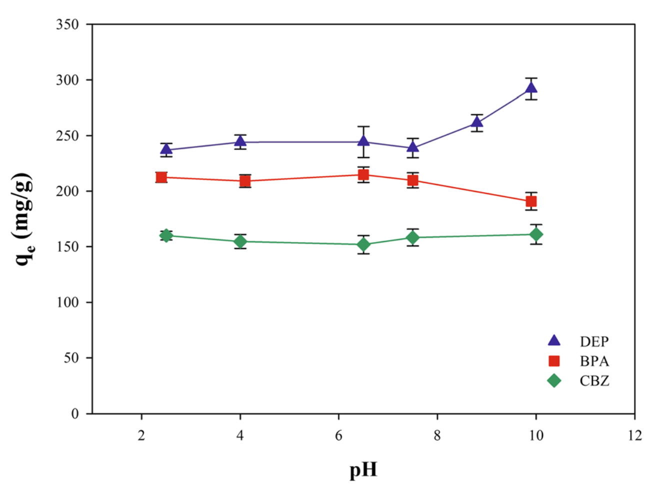


Fig. 5 The effect of pH on the adsorption of AC for DEP, BPA, and CBZ. The experimental conditions were 0.2 g/L of adsorbent, 100 mg/L of initial concentration, and 25 °C of temperature

because of the ionization of BPA as phenolate and bisphenolate with negative charge in the alkali condition, since the pK_a value of BPA is around 9.7 (Zhang et al. 2006). In addition, the pH_{pzc} of AC is 6.5, indicating that it has negative charge when the pH is above 6.5; a higher pH will make the surface negatively charged more. So, the negatively charged AC is difficult to adsorb BPA at pH 8–10 due to the electrostatic repulsion becoming stronger. At the same time, the hydrophobic interaction also reduces due to the ionization of the hydrophobic neutral molecular into hydrophilic negatively charged species. Meanwhile, when -OH dissociates to $-O^-$ at high pH, the electron-donating ability would be further improved, thereby enhancing π-π EDA interaction (Liu et al. 2014). If π-π EDA interaction is the dominant factor, the BPA adsorption capacity should be increased with increasing pH values as the interaction strength increased. In fact, the trend of BPA adsorption with pH was the opposite, which can rule out the π-π EDA interaction as a dominant factor. The reduced adsorption of BPA on the negatively charged AC at higher pH, indicated that electrostatic repulsion plays a major role.

In case of DEP, as solution pH values increased from 8 to 10, the adsorption amount increased. This is mainly due to the hydrolysis of diethyl phthalate. Especially, in alkaline solution, the hydrolysis rate of DEP was accelerated as pH values increased, which is approximately four orders of magnitude faster than acid hydrolysis rate constants, whereas the rate of hydrolysis is the slowest in neutral solution (Yim et al. 2002). In the hydrolysis, the DEP is first converted to the corresponding monoester, namely monoethyl phthalate (MEP), and then the MEP continues to convert to phthalic acid, but this step is slow and can be negligible (Yim et al. 2002). However, the impact of hydrolysis is limited. Lewis et al. (1984) reported that at an initial concentration of 191 μg/L, the decrease of DEP by hydrolysis was only about 5% within 12 h at pH 10. So it seems that the adsorption capacity of AC for DEP is increased with an increase of pH at alkaline solution. In the case of CBZ in the tested pH range (2.5~10), its adsorption capacity on AC was not affected by solution pH because the pK_a values of CBZ are 0.1 and 14.3 (Table 1). It exists as a neutral compound in the wide range of pH. Thus, its binding onto the surface of AC is mainly due to the non-electrostatic interactions involving hydrophobic interaction, π-π interaction, and Van der Waals force (Ghosh et al. 2013; To et al. 2017).

Regeneration of AC

Figure 6 shows the reusability performance of AC for the adsorption of DEP, BPA, and CBZ, which was investigated by repeating the adsorption-desorption process up to three times. The adsorption capacity of AC at third cycle was 92, 100, and 81% of the first uptake for DEP, BPA, and CBZ, respectively. Especially, AC maintained an excellent adsorption performance for BPA during 3 cycles. Furthermore, the application of AC to remove DEP, BPA, and CBZ in sewage water was also examined. The solutions of DEP, BPA, and CBZ were prepared using sewage water collected from the Jeonbuk Sewage Treatment Plant (Jeonju, South Korea). The 6 mg AC was exposed to 30 ml each of 1 mg/L DEP, BPA, and CBZ solutions at pH 6.5, and the results were presented in Fig. S7. The removal efficiencies of AC for DEP, BPA, and CBZ were 99.6, 98.4, and 98.3%, respectively. Compared with those in distilled water (Fig. 2b), the removal efficiencies just slightly decreased; thus, AC still maintains its high adsorption performance in the sewage water.

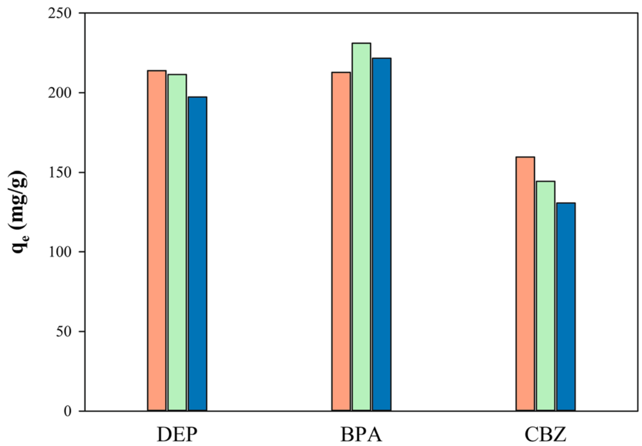


Fig. 6 Regeneration of AC for DEP, BPA, and CBZ in three adsorption-desorption cycles

Conclusions

Activated carbon showed high adsorption capacity for the endocrine-disrupting chemicals DEP and BPA and for the non-biodegradation pharmaceutical CBZ. At low initial concentration of 1 mg/L, AC can remove over 99% of BPA, DEP, and CBZ for 1 h. The adsorption of BPA and DEP on AC exhibited a high dependency on pH. At alkaline solution, the equilibrium adsorption capacity (q_e) of AC for BPA decreased due to the electrostatic repulsion played a major role, while that q_e value for DEP rose because of the hydrolytic effect of DEP, which was accelerated in alkali solution. Meanwhile, the adsorption of CBZ by AC is independent of pH. Compared with other adsorbents, AC has a relatively higher adsorption capacity for DEP, BPA, and CBZ, and the adsorption capacity of an adsorbent is strongly related to its surface area. Furthermore, AC can be regenerated and reused and showed high removal efficiencies in sewage water, showing its potential in practical applications for removing endocrine-disrupting compounds and pharmaceuticals.

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