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Adsorptive removal of 2,4-didichlorophenol and 2,6-didichlorophenol from aqueous solution by β-cyclodextrin/attapulgite composites: Equilibrium, kinetics and thermodynamics

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ABSTRACT

β-Cyclodextrin/attapulgite (β-CD/ATP) composites were prepared for the adsorption of 2,4-didichlorophenol (2,4-DCP) and 2,6-didichlorophenol (2,6-DCP) from aqueous solution. β-CD/ATP composites mainly possessed mesopores, high surface area and big pore volume which were benefit for the adsorption capacity. The batch mode adsorption experiments with respect to pH, temperature, initial concentration, contact time and binary dichlorophenol solution were investigated. Equilibrium data, at various temperatures, were described by the Langmuir, Freundlich and Dubinin–Radushkevich isotherm models. The Langmuir isotherm model was fitted to the experimental data significantly better than the other models. The kinetic data were well fitted to the intraparticle diffusion equation, which indicated that three steps belonged to the pseudo-second-order adsorption process. Intraparticle diffusion increased with the increase of adsorbate concentrations while film and pore diffusion decreased. The initial adsorption factor, R_i, showed that initial adsorption for 2,4-DCP was intermediate while was strong for 2,6-DCP. The thermodynamics parameters (positive values of ΔH° and ΔS°, negative values of ΔG°) indicated that binding systems between β-CD/ATP composites and adsorbates (2,4-DCP and 2,6-DCP) were endothermic, entropy gained and spontaneous in nature.

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1. Introduction

In recent years, contamination of water sources with chlorophenols as a consequence of industrial and agricultural activities has become a serious problem. Discharge of chlorophenol contaminated wastewater into aquatic environment without adequate treatment can lead to negative effect on the water quality. Also, some chlorophenols may be carcinogenic in nature owing to their toxicity, stability and bioaccumulation [1]. Thus, chlorophenols have been listed in the toxic pollutants into the aquatic environment by the U.S. Environmental Protection Agency (U.S. EPA) [2]. As a result, removal of chlorophenols from aquatic environment is an important topic in the fields of environmental science and technology.

Adsorption is an efficient and economically feasible technology for the removal of toxic organic pollutants such as chlorophenols. Activated carbon is the most commonly used adsorbent for the adsorption process in wastewater treatment because it has vast surface area and affinity for many organic chemicals, but it is expensive and necessitates regeneration [3,4]. The need for an alternative low-cost and ecofriendly adsorbent has encouraged the search for novel adsorbents. A variety of low-cost adsorbents have been used for removal of phenolic compounds from aqueous solutions, such as fly ash [5], pumice [6], organophilic bentonite [7], phanerochaete chrysosporium biomass [8], functional chitosan [9], mesoporous MCM-41 [10].

Attapulgite (ATP) is a hydrated octahedral layered magnesium aluminum silicate mineral which has siloxane groups in the bulk and silanol groups on its surface [11]. It is a promising adsorbent because of its special structure, stable chemical properties and large reserves in China. But adsorption of chlorophenols using raw ATP is very limited due to the lack of affinity for many organic chemicals. Organic modification is a useful method to improve this limitation, by which the hydrophobic groups are grafted onto the surface of ATP. The modification by octodecyl trimethyl ammonium chloride [12], ammonium citrate tribasic [13], hyperbranched aliphatic polyester [14], γ-methacryloxypropyl trimethoxysilane [15] and cetyltrimethylammoniumbromide [16] has been reported. β-Cyclodextrin (β-CD) is a doughnut-shape cyclic oligosaccharide

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with a hydrophilic exterior and hydrophobic internal cavity. It has been of considerable interest because it can build inclusion compounds with hydrophobic molecules by various types of intermolecular interactions [17].

In this work, we attempted to modify the ATP with β-CD. And then β-CD/ATP composites were allowed to adsorptive removal 2,4-didichlorophenol (2,4-DCP) and 2,6-didichlorophenol (2,6-DCP) from aqueous solution. The adsorption properties such as equilibrium, kinetics and thermodynamics were demonstrated by batch mode adsorption experiments.

2. Materials and methods

2.1. Instruments and apparatus

Fourier transmission infrared spectra (FT-IR) of the β-CD/ATP composites, ATP and β-CD (4000–400 cm^{-1}) were recorded on a Nicolet NEXUS-470 FT-IR apparatus (USA). The morphology of β-CD/ATP composites and ATP was obtained by scanning electron microscopy (SEM, S-4800). The specific surface area, total pore volume and average pore diameter of the β-CD/ATP composites were determined by nitrogen gas adsorption measurement using Micromeritics TriStar 3000 porosimeter (Norcross, GA, USA). Vario EL elemental analyzer (Elementar, Hanau, Germany) was employed to investigate the surface elemental composition of the β-CD/ATP composites and ATP. Mean particle size of β-CD/ATP composites was carried out by CIS-100 particle-size analyzer (Holand). High performance liquid chromatograph (HPLC, Shimadzu, Japan) equipped with a UV detector was used for the detection of 2,6-DCP and 2,4-DCP. The injection loop volume was 20 μL, and the mobile phase consisted of deionized ultrapure water and methanol with a volume ratio of 45:55. The flow rate of the mobile phase was 1.0 mL min^{-1}. The oven temperature was set at 25 °C and then 2,6-DCP and 2,4-DCP were detected at 277 nm and 285 nm, respectively. All solutions used for HPLC were filtered through a 0.45 μm filter before use.

2.2. Reagents and materials

ATP was supplied by Aotebang International Co. in China. Prior to use, it was activated by calcination at 350 °C for 6.0 h before it was dispersed in 0.1 M NH_4Cl for 4.0 h at room temperature. Dimethylformamide (DMF) and glycidoxypropyltrimethoxysilane (KH-560) were all purchased from Chemical Reagent Corporation (Shanghai, China). β-CD and sodium hydrogen (NaH), 2,4-DCP and 2,6-DCP were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). β-CD was recrystallized with distilled water before use. All chemicals were of analytical reagent grade, except for, methanol which was of HPLC grade. Deionized ultrapure water was purified with a Purelab Ultra (Organo, Tokyo, Japan).

2.3. Preparation of β-CD/ATP composites

β-CD/ATP composites were prepared following the procedure of our recent study. The schematic illustration of synthetic route for β-CD/ATP composites was displayed in Fig. 1a–c [18]. Briefly, β-CD (3.0 g) was dissolved in 100 mL of anhydrous DMF to which NaH (0.3 g) was added. The mixture was stirred at room temperature until no gas was emitted, and the excessive NaH removed by filtration (Fig. 1a). Thereafter, KH-560 (1.0 g) was added and the mixture was magnetically stirred at 90 °C for 5.0 h under nitrogen protection (Fig. 1b). Subsequently, the reaction temperature was increased to 115 °C, and ATP (5.0 g) was added rapidly into the mixture (Fig. 1c). After being stirred for 12 h, the obtained β-cyclodextrin/attapulgite composites were washed with DMF, methanol and distilled water, respectively, and then dried under vacuum at 55 °C.

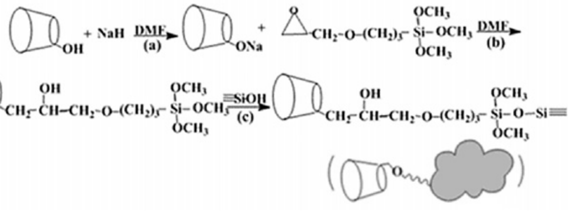

Fig. 1. The schematic illustration of synthetic route for β-CD/ATP composites.

2.4. Effect of solution pH on 2,4-DCP and 2,6-DCP adsorption

Accurately weighted amount (0.01 g) of β-CD/ATP composites were added to eight 10 mL beakers containing 5 mL of 100 mg L^{-1} of 2,4-DCP or 2,6-DCP solution, each adjusted to pH of 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 using 0.1 mol L^{-1} HCl or NaOH solutions. The solutions were stirred at 300 rpm for 12 h at 298 K. The mixtures were centrifuged and HPLC was used to analyze the residual concentrations of 2,4-DCP and 2,6-DCP.

2.5. Equilibrium studies

Equilibrium experiments were carried out by contacting 0.01 g of β-CD/ATP composites with 5.0 mL of 2,4-DCP or 2,6-DCP solution (pH = 8.0 for 2,4-DCP and pH = 9.0 for 2,6-DCP) of different initial concentrations ranging from 20 to 400 mg L^{-1}. A series of such conical flasks were agitated at 300 rpm for 12 h and temperature was maintained at 298 K, 318 K and 338 K, respectively. Moreover, the equilibrium adsorption capacity (Q_e, mg g^{-1}) was calculated according to Eq. (1):

$$Q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial and equilibrium concentrations of adsorbate (2,4-DCP or 2,6-DCP), respectively. V (mL) and W (g) are the solution volume and the weight of adsorbent, respectively.

2.6. Adsorption from binary dichlorophenol solution

The first step was to examine the adsorption of 2,4-DCP at equilibrium (concentration of 2,4-DCP ranging from 100 to 300 mg L^{-1}) in the presence of 100 mg L^{-1} of 2,6-DCP. For the next step, a series of binary solution where the concentration of 2,4-DCP was fixed at 100 mg L^{-1} and concentration of 2,6-DCP was varied from 100 to 300 mg L^{-1}. These binary solutions were also agitated at 300 rpm for 12 h. Equilibrium concentrations of 2,4-DCP and 2,6-DCP in the various binary solutions were determined by HPLC. In this experiment, the adsorption temperature was at 298 K, and the solution pH was 8.0 for the first step and 9.0 for the second step, respectively.

2.7. Adsorption kinetics

Single batch experiments were conducted to assess the adsorption kinetics for 2,4-DCP and 2,6-DCP onto β-CD/ATP composites. 10 mg of β-CD/ATP composites were added to 10 mL beakers containing 5.0 mL of 2,4-DCP or 2,6-DCP solution which the concentration was 100 or 150 mg L^{-1}. And the solution pH was 8.0 for 2,4-DCP and 9.0 for 2,6-DCP, respectively. The solutions were stirred at 300 rpm for the desired time (10–1440 min) at different temperatures (298–338 K). The mixtures were centrifuged and

Table 1
Physicochemical properties of β-CD/ATP composites.

Characteristics	
Specific surface area ($m^2\,g^{-1}$)	92.92
Total pore volume ($cm^3\,g^{-1}$)	3.36
Average pore diameter (Å)	99.92
Mean particle size (μm)	5.42
C (%)	5.2
H (%)	1.2
N (%)	0.15
O (%)	2.8
Main functional groups	
Si–O	$1024\,cm^{-1}$
O–H	$3424\,cm^{-1}$
$-CH_2-$	$1448\,cm^{-1}$
Molecular water	$3580\,cm^{-1}$

HPLC was used to analyze the residual concentrations of 2,4-DCP and 2,6-DCP.

3. Results and discussion

3.1. Physicochemical properties of β-CD/ATP composites

The physicochemical properties of β-CD/ATP composites were shown in Table 1. FT-IR spectra of β-CD/ATP composites (a), ATP (b) and β-CD (c) were shown in Fig. SI (Supporting Information). For the main functional groups of β-CD/ATP composites, typical bands of $-CH_2-$ around $1448\,cm^{-1}$ and O–H around $3424\,cm^{-1}$ from β-CD appeared in β-CD/ATP composites, and the absorption peak at $3580\,cm^{-1}$ was also attributed to the anti-symmetric stretching modes of molecular water coordinated with the magnesium at the edges of the channel for ATP [19]. And there were few differences about the locality ($1024\,cm^{-1}$) and intensity of Si–O characteristic feature for β-CD/ATP and ATP [20]. Moreover, the SEM images of ATP and β-CD/ATP composites were also shown in Fig. SI. Compared with ATP, the surface of β-CD/ATP composites was ruleless and agglomerate. All the results mentioned above suggested that β-CD was bonded onto the ATP, resulting in the grafted β-CD/ATP composites. In our previous work, the elemental analysis of ATP was obtained, which was 1.1%, 0.87% and 0.12% for C, H and N, respectively. And the weight of O in ATP was not detected [18]. The approximate amount of coating (increased weight of C, H, O and N) was 44.71 mg on every gram of the β-CD/ATP particles.

According to the IUPAC definition, β-CD/ATP composites mainly possessed mesopores [21]. And the high surface area and big pore volume were benefit for the adsorption capacity as a adsorbent.

3.2. Effect of pH

Optimization of pH value for adsorption medium plays a vital role in the adsorption studies. The pH of the solution affects the degree of ionization and speciation of dichlorophenols which subsequently leads to a change in adsorption kinetics and equilibrium characteristics [22]. Thus, the chemical characteristics of both the adsorbent and the adsorbate are connected with pH. Then, the effect of pH on the adsorption of 2,4-DCP and 2,6-DCP by β-CD/ATP composites and the effect of initial pH on final pH were shown in Fig. 2. It was observed that adsorption of neutral 2,4-DCP at pH 2.0 and 9.0 (2,6-DCP at pH 2.0 and 8.0) did not cause any change in pH. Fig. 2 also shows that the final pH was generally higher than the initial pH in the blank, i.e. in the absence of 2,4-DCP or 2,6-DCP. Moreover, the fact neutral molecules of dichlorophenol are benefit for the adsorption process has also been reported previously for other adsorbent by Sathishkumar et al. [22]. It is well known that hydrophilic guest molecules are unfavourable to complex with bonded β-CD in β-CD/ATP composites while at low pH, so it was an expected result taking into account that hydrophobic interaction is the only mode between adsorbent and adsorbate at low pH (such as pH 2.0). As a result, the adsorption capacity of β-CD/ATP composites increased with the increase of pH, and reached to maximum value at pH 8.0 for 2,4-DCP and at pH 9.0 for 2,6-DCP, as expected. The results may be bonded β-CD and neutral dichlorophenol molecules could form complexes through the hydrophobic interaction and the hydrogen-bonding interaction simultaneously. At a higher pH, dissociated dichlorophenol molecules may decrease the adsorption effect. At a lower pH, bonded β-CD in β-CD/ATP composites and dichlorophenol molecules positively charged, electrostatic repulsion was not benefit for the adsorption system.

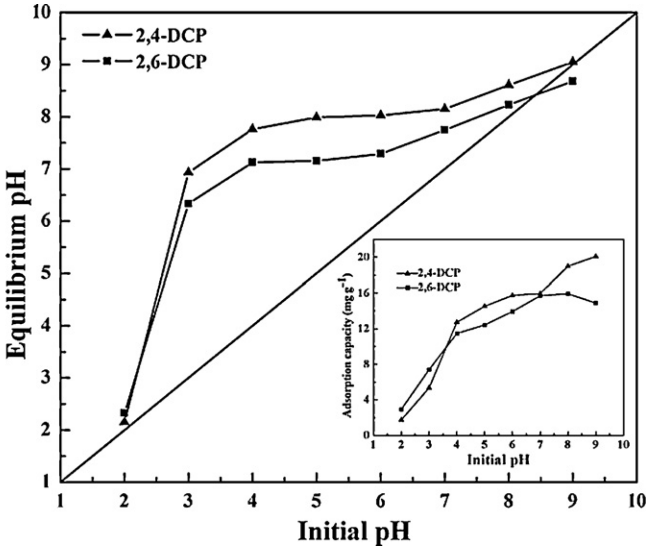

Fig. 2. Effect of initial pH on equilibrium pH. Inset: Effect of pH on adsorptive removal of 2,4-DCP and 2,6-DCP. Temperature: 298 K, adsorbent dose: 0.01 g, solution volume: 5.0 mL, agitation speed: 300 rpm, and contact time: 12 h.

3.3. Equilibrium studies

In order to optimize the adsorption systems for the removal of 2,4-DCP and 2,6-DCP from aqueous solution, it is important to investigate the equilibrium properties of adsorption process. Then the equilibrium data of 2,4-DCP and 2,6-DCP were fitted to the Langmuir [23], Freundlich [24] and Dubinin–Radushkevich [25,26] isotherm models. The applicability of the isotherm models to the adsorption behaviours was studied by judging the correlation coefficient (R^2) and a normalized standard deviation ΔQ(%). ΔQ(%) was calculated using:

$$\Delta Q\,(\%) = 100\sqrt{\frac{\sum[(Q_{exp} - Q_{cal})/Q_{exp}]^2}{N-1}} \quad (2)$$

where Q_{exp} and Q_{cal} are experimental and calculated amount of adsorbate adsorbed onto adsorbent, respectively, and N is the number of measurements made.

The linear and non-linear forms of the Langmuir isotherm model are expressed by the following equations, respectively:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (3)$$

$$Q_e = \frac{K_L Q_m C_e}{1 + K_L C_e} \quad (4)$$

where C_e is the equilibrium concentration of adsorbate ($mg\,L^{-1}$), Q_e is the equilibrium adsorption capacity ($mg\,g^{-1}$), Q_m is the maximum adsorption capacity of the adsorbent, and K_L represents the affinity constant.

Table 2
Adsorption isotherm constants for 2,4-DCP and 2,6-DCP. Sorbent dose: 0.01 g, solution volume: 5.0 mL, agitation speed: 300 rpm, solution pH: 8.0 for 2,4-DCP and 9.0 for 2,6-DCP, and contact time: 12 h.

Adsorption isotherm models	Constants	2,4-DCP			2,6-DCP		
		298 K	318 K	338 K	298 K	318 K	338 K
Langmuir equation	R^2	0.992	0.996	0.992	0.998	0.994	0.993
	$Q_{m,c}$ (mg g^{-1})	41.49	59.88	93.46	29.33	41.84	62.11
	K_L (L mg^{-1})	0.014	0.013	0.032	0.060	0.028	0.026
	R_L	0.153	0.169	0.072	0.040	0.082	0.089
	ΔQ (%)	3.2	0.6	1.2	4.1	3.7	2.4
Freundlieh equation	R^2	0.934	0.971	0.962	0.833	0.918	0.899
	K_F (mg g^{-1})	4.37	2.15	7.02	5.57	4.46	4.50
	$1/n$	0.548	0.568	0.499	0.304	0.395	0.475
	ΔQ (%)	4.0	6.5	7.4	4.1	7.2	5.4
Dubinin-Radushkevich equation	R^2	0.938	0.970	0.946	0.786	0.978	0.979
	$Q_{m,c}$ (mg g^{-1})	34.41	47.45	83.71	28.13	39.04	57.69
	K_{DR} (mol^2 kJ^2)	0.0006	0.0005	0.0002	0.0002	0.0005	0.0005
	E (kJ mol)	28.87	31.62	50.00	50.00	31.62	31.62
	ΔQ (%)	7.4	7.6	6.6	8.2	7.9	6.7

For predicting the favourability of an adsorption system, the Langmuir equation can also be expressed in terms of a dimensionless separation factor R_L defined as follows [23]:

$$R_L = \frac{1}{1 + C_m K_L} \tag{5}$$

where C_m is the maximal initial concentration of adsorbate. The R_L indicates the favourability and the capacity of adsorption system. When $0 < R_L < 1.0$, it represents good adsorption.

The linear and non-linear forms of the Freundlich isotherm model are given as follows, respectively:

$$\ln Q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \tag{6}$$

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

where K_F (mg g^{-1}) is an indicative constant for adsorption capacity of the adsorbent when $C_e = 1.0$ and the constant $1/n$ indicates the intensity of the adsorption. Value of $1/n$ ranging from 0.1 to 1.0 represents a favourable adsorption condition [26].

Moreover, the linear and non-linear forms of the Dubinin–Radushkevich isotherm model are described as follows:

$$\ln Q_e = \ln Q_m - K_{DR}\varepsilon^2 \tag{8}$$

$$Q_e = Q_m \exp(-k\varepsilon^2) \tag{9}$$

where ε can be correlated as:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{10}$$

The constant K_{DR} is related with free energy (E, kJ mol^{-1}) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated by Eq. (8):

$$E = \frac{1}{\sqrt{2K_{DR}}} \tag{11}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature. Value of $K_{DR} < 1.0$ represents the rough surface with many cavities, and the value of E (>40 kJ mol^{-1}) expresses the chemisorption between adsorbent and adsorbate.

The adsorption isotherm constants at three temperatures were listed in Table 2. Moreover, comparison of Langmuir, Freundlich and Dubinin–Radushkevich isotherm models for 2,4-DCP and 2,6-DCP adsorption onto β-CD/ATP composites using non-linear regression was also illustrated in Fig. 3a and b, respectively. From Table 2, it was also found that fitting to the Langmuir isotherm model gave the highest values of correlation coefficients than the other models. Values of $1/n$ also suggested that 2,4-DCP and 2,6-DCP adsorption onto β-CD/ATP composites was favourable at higher temperature. From Fig. 3, when the equilibrium con-

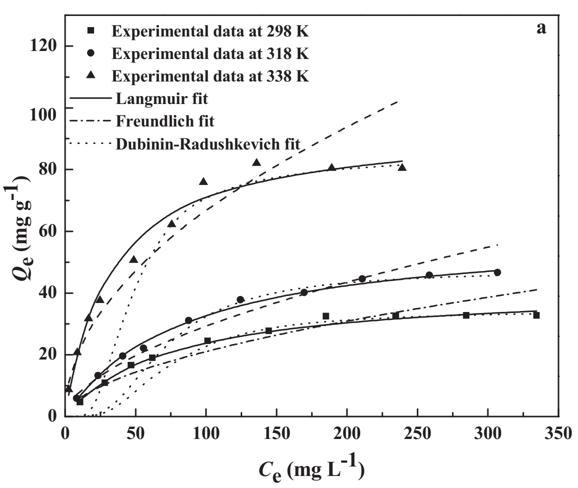

Fig. 3. Comparison of Langmuir, Freundlich and Dubinin–Radushkevich isotherm models for 2,4-DCP adsorption (a) and 2,6-DCP (b) onto β-CD/ATP composites using non-linear regression. Temperature: 298 K, adsorbent dose: 0.01 g, solution volume: 5.0 mL, agitation speed: 300 rpm, solution pH: 8.0 for 2,4-DCP and 9.0 for 2,6-DCP, and contact time: 12 h.

Table 3
Effect of competitive adsorption of 2,4-DCP and 2,6-DCP onto β-CD/ATP composites at different initial concentrations. Temperature: 298 K, sorbent dose: 0.01 g, solution volume: 5.0 mL, agitation speed: 300 rpm, solution pH: 8.0 for 2,4-DCP and 9.0 for 2,6-DCP, and contact time: 12 h.

C_0 (2,4-DCP) (mg L^{-1})	C_0 (2,6-DCP) (mg L^{-1})	Q_e (2,4-DCP) (mg g^{-1})	Adsorbed (%)	Total amount adsorbed (%)
100	0	19.04	38.1	38.1
150	0	24.49	32.7	32.7
200	0	27.78	27.8	27.8
250	0	32.49	26.0	26.0
300	0	32.69	21.8	21.8
100	100	18.19	36.4	60.7
150	100	22.58	30.1	63.7
200	100	24.47	24.5	67.0
250	100	28.29	22.6	68.8
300	100	29.11	19.4	71.5
C_0 (2,6-DCP) (mg L^{-1})	C_0 (2,4-DCP) (mg L^{-1})	Q_e (2,6-DCP) (mg L^{-1})	Adsorbed (%)	Total amount adsorbed (%)
100	0	23.53	47.1	47.1
150	0	25.94	34.6	34.6
200	0	26.00	26.0	26.0
250	0	27.58	22.1	22.1
300	0	27.65	18.4	18.4
100	100	21.08	42.2	60.7
150	100	22.37	29.8	66.3
200	100	23.25	23.3	70.3
250	100	24.18	19.3	72.8
300	100	24.69	16.4	75.0

centration increased, the equilibrium adsorption capacity (Q_e) for 2,6-DCP firstly increased sharply, then increased slightly, and finally reached to maximum point, as expected. Furthermore, with temperature increased from 298 K to 318 K and 338 K, Q_e of 2,4-DCP and 2,6-DCP were both elevated obviously, it was probably because higher temperature provided more chances for dichlorophenol molecules to pass the external boundary layer, and produced the enlargement of pore volume and surface area enabling dichlorophenol molecules to penetrate further [18,27]. Moreover, Langmuir isotherm model fitted the equilibrium data significantly better than the other isotherm models.

3.4. *Effect of initial concentration of adsorbates*

Table 3 shows the adsorption of 2,4-DCP and 2,6-DCP onto β-CD/ATP composites at different initial concentrations. It was observed that increasing the initial concentration of dichlorophenol molecules (2,4-DCP and 2,6-DCP), from 100 to 300 mg L^{-1}, increased the amount of 2,4-DCP adsorbed from 19.04 to 32.69 mg g^{-1} and 23.53 to 27.65 mg g^{-1} for 2,6-DCP. It is possible that the initial concentration of dichlorophenol molecules provides the necessary driving force to overcome the resistances to mass transfer of dichlorophenol molecules between the aqueous phases and the solid phase [23]. Moreover, adsorption ratios were reduced from 38.1% to 21.8% for 2,4-DCP and 47.1% to 18.4% for 2,6-DCP. It could be attributed to the fact that intraparticle diffusions for 2,4-DCP and 2,6-DCP were not impeded to the same extent when the presence of other dichlorophenol molecules [28]. The results also indicated that the initial adsorption rate for 2,6-DCP was higher than that of 2,4-DCP which resulted in the sharp fall of initial concentration of 2,6-DCP.

3.5. *Dichlorophenol molecule solution*

To study the adsorption interaction of both dichlorophenol molecules, the percentage of the binary component systems were also shown in Table 3. It can be observed that the addition of 100 mg L^{-1} of one dichlorophenol to the increasing concentration (from 100 to 300 mg L^{-1}) of the other, also lead to a slight increase in the amount of dichlorophenol molecules adsorbed.

Then the isotherm data of the binary dichlorophenol molecules were analyzed using the Langmuir, Freundlich and Dubinin–Radushkevich models, and the plots were shown in Fig. 4a and b. According to the trend in Fig. 4a, the adsorption of 2,4-DCP from a binary dichlorophenol molecule solution was best described by the Langmuir isotherm model. The trend of the 2,6-DCP adsorption in the presence of 2,4-DCP indicated that the Freundlich was the best fitting model. In this study, the Langmuir and Freundlich model were both successfully applied to the multisolute adsorption systems.

The values of Q_e^b (binary dichlorophenol molecule solution)/Q_e^s (single dichlorophenol molecule solution) for both 2,4-DCP (0.890) and 2,6-DCP (0.906) were found to be less than 1.0, suggesting that simultaneous presence of both dichlorophenol molecules reduced the adsorption through competition for binding sites in the β-CD/ATP composites. Moreover, the value of Q_e^b/Q_e^s for 2,6-DCP was higher than that of 2,4-DCP, indicating that 2,4-DCP adsorption onto β-CD/ATP composites was more affected by the simultaneous presence of competitive dichlorophenol molecules than for 2,6-DCP. Similar effect has been reported by Ofomaja et al. [29]. Some authors attributed this non-equal competition to the heterogeneity of the adsorbent surface and interaction between dichlorophenol molecules in solution [28].

3.6. *Kinetics studies*

3.6.1. *Adsorption kinetic models*

In order to examine the adsorption mechanism such as mass transfer and chemical reaction, the kinetic data obtained were analyzed using pseudo-first-order rate equation and pseudo-second-order rate equation [30,31]. The pseudo first-order equation can be expressed as linear and non-linear forms by Eqs. (12) and (13), respectively:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{12}$$

$$Q_t = Q_e - Q_e\, e^{-K_1 t} \tag{13}$$

The pseudo first-order equation can be expressed as linear and non-linear forms by Eqs. (14) and (15), respectively:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \tag{14}$$

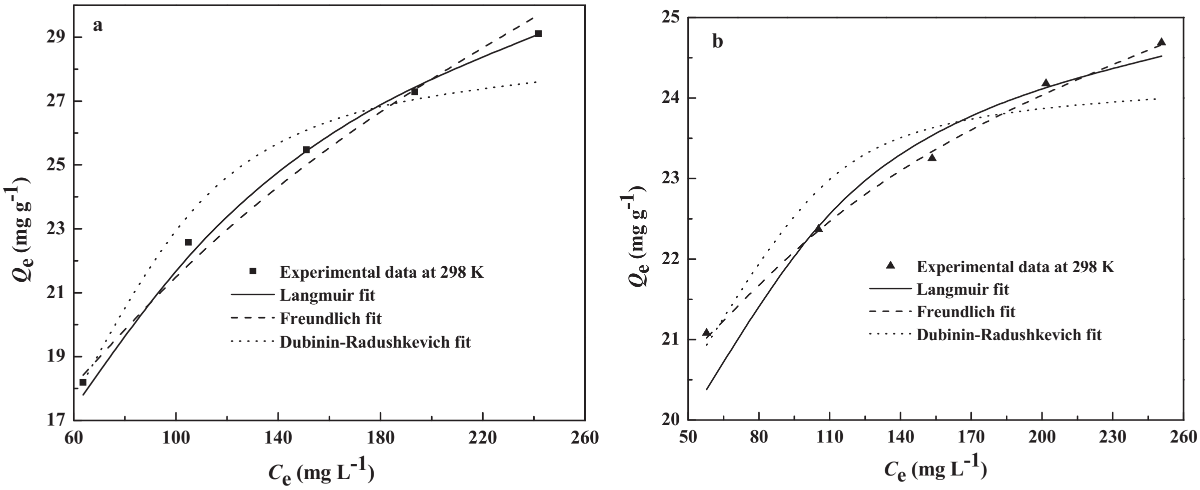

Fig. 4. Isotherm plots of experimental data and for three isotherm models for (a) 2,4-DCP adsorption in the presence of 2,6-DCP and (b) 2,6-DCP adsorption in the presence of 2,4-DCP onto β-CD/ATP composites. Temperature: 298 K, adsorbent dose: 0.01 g, solution volume: 5.0 mL, agitation speed: 300 rpm, solution pH: 8.0 for 2,4-DCP and 9.0 for 2,6-DCP, and contact time: 12 h.

$$Q_t = \frac{k_2 {Q_e}^2 t}{1 + k_2 Q_e t} \tag{15}$$

where Q_e and Q_t are the amount of adsorbate (mg g^{-1}) onto adsorbent at the equilibrium and time t (min), respectively. Values of k_1 (L min^{-1}) and k_2 (g mg^{-1} min^{-1}) are calculated from the plot of $\ln(Q_e - Q_t)$ versus t and t/q_t versus t, respectively.

The adsorption rate constants and linear regression values were summarized in Table 4. The adsorption of 2,4-DCP and 2,6-DCP followed pseudo-second-order kinetics because of the favourable fit between experimental and calculated values of Q_e (R^2 values above 0.99 at different temperatures). And it was assumed that chemical process could be the rate-limiting step in the adsorption process for 2,4-DCP and 2,6-DCP. Fig. 5a and b shows the plots of the experimental data of the amount of 2,4-DCP and 2,6-DCP adsorbed per unit mass of adsorbent against time along the values for two kinetic models, respectively. Non-linear form of pseudo-second-order kinetic model studied at different temperature also showed the better fit than pseudo-first-order kinetic model. From Fig. 5a and b, pseudo-second order kinetics lines deviated substantially from the experimental points around the first 100 min for 2,4-DCP and 2,6-DCP. The observed deviation from experimental data could be attributed to the sharp fall in concentration gradient after the initial rapid adsorption of dichlorophenol molecules onto the large amount of vacant binding sites and not concentration dependent [32,33]. Within this time period, it was believed that there was a switch between mass transfer diffusion control and pore diffusion control, and a change in adsorption mechanism may has occurred after the first 100 min for 2,4-DCP and 2,6-DCP adsorption [34,35].

Basted on the second-order model, the initial adsorption rate (h, mg g^{-1} min^{-1}) and half equilibrium time ($t_{1/2}$, min) were summarized in Table 4 according to the following equations [36]:

$$h = K_2 Q_e^{\mathbf{2}} \tag{16}$$

$$t_{1/2} = \frac{1}{K_{\mathbf{2}} Q_e} \tag{17}$$

The results showed that increasing temperature increased initial adsorption rates of 2,4-DCP and 2,6-DCP, and the rates of 2,6-DCP were also found to be higher than those of 2,4-DCP, as expected.

3.6.2. Intraparticle diffusion

The kinetic data can be used to study the presence or absence of intraparticle diffusion and to determine whether intraparticle diffusion is the rate-limiting step. A functional relationship common to most treatments intraparticle diffusion is described by Weber

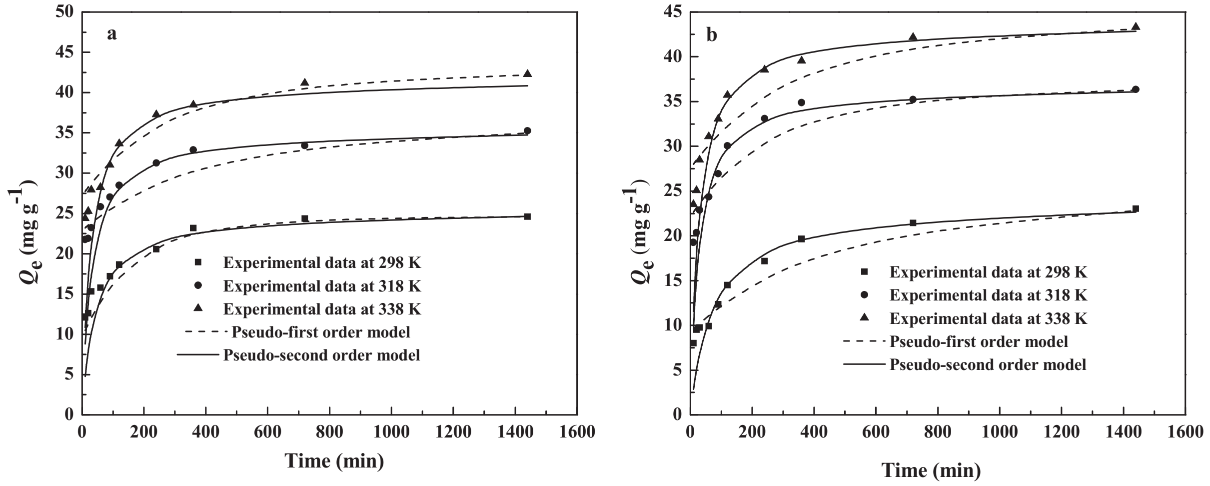

Fig. 5. Kinetic models of the effect of temperature for 2,4-DCP (a) and 2,6-DCP (b) adsorption onto β-CD/ATP composites. Adsorbent dose: 0.01 g, solution volume: 5.0 mL, agitation speed: 300 rpm, and solution pH: 8.0 for 2,4-DCP and 9.0 for 2,6-DCP.

Table 4
Kinetic constants for the pseudo-first-order equation and pseudo-second-order equation. Sorbent dose: 0.01 g, solution volume: 5.0 mL, agitation speed: 300 rpm, and solution pH: 8.0 for 2,4-DCP and 9.0 for 2,6-DCP.

Adsorbates	T (K)	C_0 (mg L^{-1})	$Q_{e,exp}$ (mg g^{-1})	Pseudo-first-order equation			Pseudo-second-order equation				
				$Q_{e,c}$ (mg g^{-1})	k_1 (L min^{-1})	R^2	$Q_{e,c}$ (mg g^{-1})	k_2 ($\times 10^{-4}$ g mg^{-1} min^{-1})	R^2	h (mg g^{-1} min^{-1})	$t_{1/2}$ (min)
2,4-DCP	298	100	24.59	14.93	0.0058	0.985	25.38	9.11	0.997	0.551	44.64
		150	43.39	24.58	0.0029	0.940	44.64	3.65	0.995	0.687	63.20
	318	100	35.26	12.36	0.0026	0.963	35.46	9.32	0.998	1.16	30.43
		150	58.08	26.13	0.0030	0.9863	58.82	4.20	0.997	1.42	40.95
	338	100	42.28	15.05	0.0035	0.933	42.73	9.04	0.999	1.51	27.98
		150	71.00	28.22	0.0025	0.915	71.43	3.99	0.997	2.02	35.23
2,6-DCP	298	100	23.32	13.20	0.0045	0.972	23.98	9.86	0.992	0.566	43.48
		150	43.95	14.89	0.0038	0.932	44.44	10.53	0.999	2.04	21.60
	318	100	36.35	14.24	0.0037	0.955	36.76	10.05	0.999	1.33	27.38
		150	55.22	15.21	0.0059	0.976	55.56	7.89	0.999	2.41	22.94
	338	100	43.31	15.77	0.0030	0.947	43.67	8.24	0.999	1.55	28.04
		150	60.74	18.19	0.0029	0.957	60.98	7.27	0.999	2.68	22.65

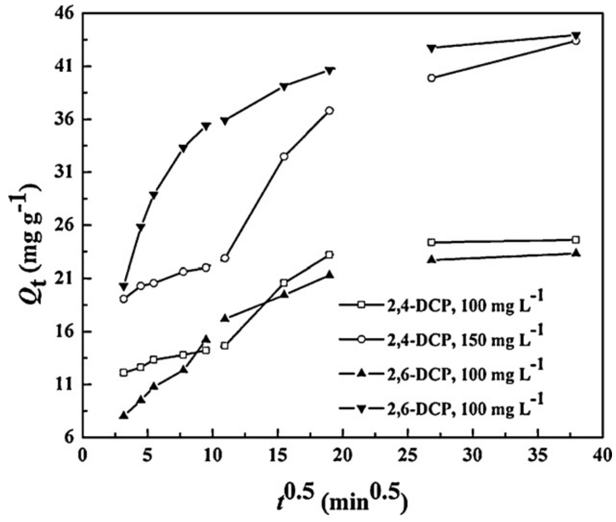

Fig. 6. Intraparticle diffusion treatment of 2,4-DCP and 2,6-DCP onto β-CD/ATP composites at various initial concentrations. Temperature: 298 K, adsorbent dose: 0.01 g, solution volume: 5.0 mL, agitation speed: 300 rpm, solution pH: 8.0 for 2,4-DCP and 9.0 for 2,6-DCP, and contact time: 12 h.

and Morris [37]:

$$Q_t = k_i t^{0.5} + C \tag{18}$$

where k_i is the intraparticle diffusion rate constant (mg g^{-1} min$^{-0.5}$) and the intercept C, obtained by extrapolation of the linear portion of the plot of Q_t versus $t^{0.5}$, is an indicator to express the boundary layer thickness.

The intraparticle diffusion plots multi-linearity indicated that three steps were involved in the process of 2,4-DCP and 2,6-DCP adsorption (Fig. 6). The first, the initial stage can be attributed to the diffusion of adsorbates through the solution to the external surface of β-CD/ATP composites and diffusion of adsorbates through the boundary layer to the surface of β-CD/ATP composites. The second stage described the gradual adsorption of adsorbates and the intraparticle diffusion was the rate-limiting step. The last stage was attributed to the final equilibrium for which the intraparticle diffusion started to slow down due to extremely low concentration of adsorbates left in solution. It was also observed that the adsorption rate for 2,6-DCP in the first step were higher than those of 2,4-DCP, while the values in the second step was lower than those of 2,4-DCP.

In order to further investigate the initial adsorption behaviours, Eq. (18) can be written as:

$$Q_{ref} = k_i t_{ref}^{0.5} + C \tag{19}$$

where t_{ref} is the longest time in the adsorption process and Q_{ref} is the solid phase concentration at time $t = t_{ref}$ for a adsorption system [38]. Subtracting Eq. (19) from Eq. (18), a new equation can be obtained as follows [34]:

$$\left(\frac{Q_t}{Q_{ref}}\right) = 1 - R_i \left[1 - \left(\frac{t}{t_{ref}}\right)^{0.5}\right] \tag{20}$$

where $R_i = K_i t_{ref}/Q_{ref}$, which is expressed as the initial adsorption factor of the intraparticle diffusion model.

According to the description in Ref. [34], the values of R_i for 2,4-DCP (Table 5) which were found to range from 0.662 to 0.697 suggested that the initial adsorption behaviours of 2,4-DCP at two initial concentrations were intermediate initial adsorption. As initial concentration was increased from 100 to 150 mg L^{-1}, the initial adsorption behaviours of 2,6-DCP were strong initial adsorption.

Assuming adsorbent particle to be a sphere of radius '*a*' and that the diffusion follows Fick's law, the corresponding equation is given

Table 5

Intraparticle rate parameters and diffusion coefficients at different initial concentrations. Temperature: 298 K, sorbent dose: 0.01 g, solution volume: 5.0 mL, agitation speed: 300 rpm, solution pH: 8.0 for 2,4-DCP and 9.0 for 2,6-DCP, and contact time: 12 h.

Adsorbates	C_0 (mg L^{-1})	Intraparticle diffusion, K_i (mg g^{-1} min$^{-0.5}$)	Film diffusion, D_1 ($\times 10^{-4}$ μm^2 S^{-1})	Pore diffusion, D_2 ($\times 10^{-3}$ μm^2 S^{-1})	R_i
2,4-DCP	100	0.429	2.17	4.32	0.662
	150	0.798	0.804	2.16	0.697
2,6-DCP	100	0.452	2.41	2.83	0.496
	150	0.553	1.02	1.71	0.478

Table 6

Thermodynamic parameters for 2,4-DCP and 2,6-DCP adsorption onto β-CD/ATP composites. Sorbent dose: 0.01 g, solution volume: 5.0 mL, agitation speed: 300 rpm, solution pH: 8.0 for 2,4-DCP and 9.0 for 2,6-DCP, and contact time: 12 h.

Adsorbates	C_0 (mg L^{-1})	Temperature (K)	Thermodynamic parameters			R^2
			ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	
2,4-DCP	100	298	−0.191	14.11	47.99	0.986
		318	−1.15			
		338	−2.11			
	150	298	−1.79	12.60	48.28	0.999
		318	−2.75			
		338	−3.72			
2,6-DCP	100	298	−0.192	16.38	55.61	0.970
		318	−1.30			
		338	−2.42			
	150	298	−0.880	7.45	27.96	0.969
		318	−1.44			
		338	−1.99			

by [39]:

$$\frac{Q_t}{Q_e} = 6\left(\frac{D_t}{a^2}\right)^{0.5}\left\{\pi^{-0.5} + 2\sum\sum_{n=1}^{\infty} ierfc\frac{na}{Dt^{0.5}}\right\} - 3\frac{Dt}{a^2} \qquad (21)$$

At small times, D is replaced by film diffusion coefficient (D_1) and Eq. (21) reduces to:

$$\frac{Q_t}{Q_e} = 6\left(\frac{D_1}{\pi a^2}\right)^{0.5} t^{0.5} \qquad (22)$$

For moderate and large times, the relation between weight uptake and diffusion equation is [34]:

$$\frac{Q_t}{Q_e} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(\frac{-Dn^2\pi^2 t}{a^2}\right) \qquad (23)$$

As t tends to large times, Eq. (23) can be reduced to as follows:

$$Bt = -0.4997 - \ln\left(1 - \frac{Q_t}{Q_e}\right) \qquad (24)$$

$$B = \pi^2\frac{D_2}{a^2} \qquad (25)$$

where pore diffusion coefficient (D_2) was calculated as Ref. [34].

Both the values of k_i, D_1 and D_2 at different initial concentrations were shown in Table 5. The trends for values of K_i suggested that a higher concentration gradient, produced by an increase in initial concentration of adsorbate, eventually caused faster diffusion and adsorption [34]. And the values of D_1 and D_2 decreased with increasing initial concentrations of adsorbates because of the decreasing available binding sites to adsorption. It was also observed that the pore diffusion was faster than the film diffusion.

3.7. Adsorption thermodynamics

Thermodynamic parameters such as change in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated using the following equations [26]:

$$\ln\left(\frac{Q_e}{C_e}\right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (26)$$

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \qquad (27)$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K). Thus, ΔH° and ΔS° are obtained from the slope and intercept of the line plotted by $\ln(Q_e/C_e)$ versus $1/T$, respectively. The obtained thermodynamic parameters for 2,4-DCP and 2,6-DCP adsorption onto β-CD/ATP composites were listed in Table 6. The negative ΔG° values indicated that the adsorption of 2,4-DCP and 2,6-DCP was spontaneous within the temperature range evaluated, which was the case for many adsorption systems in solution. By adsorption of abundant 2,4-DCP or 2,6-DCP onto the surface of β-CD/ATP composites, the number of water molecules surrounding 2,4-DCP or 2,6-DCP molecules decreased and the degree of the freedom of the water molecules increased. Therefore, the positive values of ΔS° suggested increased randomness at the solid–solution interface during the adsorption of 2,4-DCP or 2,6-DCP onto the surface of β-CD/ATP composites [40]. In fact, the positive value of enthalpy change ΔH° further confirmed the endothermic nature of the processes, so increasing temperature supplied with a more favourable adsorption between 2,4-DCP and 2,6-DCP onto β-CD/ATP composites.

4. Summary

In the present investigation, β-CD/ATP composites were successfully prepared and evaluated as a adsorbent for adsorption of 2,4-DCP and 2,6-DCP in aqueous solutions. β-CD/ATP composites mainly possessed mesopores, high surface area and big pore volume which were both benefit for the adsorption capacity. In a binary dichlorophenol solution, one dichlorophenol adsorption in the presence of the other dichlorophenol reduced the adsorption capacity of either dichlorophenol. The optimum pH for 2,4-DCP adsorption was 8.0 while the 2,6-DCP was 9.0. The proposed binding mechanism may be hydrogen bonding-electrostatic interaction and hydrophobic interaction. Equilibrium data were described by Langmuir isotherm models. Kinetics experiments showed that β-CD/ATP composites offered fast kinetics for adsorption of 2,4-DCP and 2,6-DCP, and the diffusion-controlled process as the essential adsorption rate-controlling step was also observed. Moreover, the initial adsorption rate of 2,6-DCP was faster than that of 2,4-DCP with the increase of temperature and initial concentration. The thermodynamic analysis presented the endothermic, spontaneous and entropy gained nature of the adsorption process.

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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.cej.2010.09.067.

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