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Synthesis of β-cyclodextrin/mesoporous attapulgite composites and their novel application in adsorption of 2,4,6-trichlorophenol and 2,4,5-trichlorophenol

Xudong Zheng, Jiangdong Dai, Jianming Pan*

School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China, Tel. +86 0511 88791800; emails: zhengks@outlook.com (X. Zheng), aiwo254@126.com (J. Dai), zhenjiangpjm@126.com (J. Pan)

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ABSTRACT

In this work, mesoporous attapulgite (mATP) was firstly prepared in the presence of the cetyltrimethylammonium bromide using attapulgite (ATP) as the matrix materials. Then, it was modified by β-cyclodextrin (β-CD) to obtain the β-cyclodextrin/mesoporous attapulgite composites (β-CD/mATP). The characterization of the composites showed that β-CD/mATP composites remained excellent channel structure and the value of the specific surface area was 300.30 m^2/g. As-prepared β-CD/mATP was evaluated as sorbents to adsorption of 2,4,6-trichlorophenol (2,4,6-TCP) and 2,4,5-trichlorophenol (2,4,5-TCP). The results of the batch mode experiment revealed that the Langmuir isotherm model fitted the equilibrium data better, while the kinetic data could be described by pseudo-second-order model perfectly. Furthermore, 2,4,5-TCP adsorption onto β-CD/mATP was more affected than that of 2,4,6-TCP in the presence of competitive phenolic compound. In addition, β-CD/mATP possessed excellent regeneration property.

Keywords: Mesoporous attapulgite; β-cyclodextrin; 2,4,6-trichlorophenol (2,4,6-TCP); 2,4,5-trichlorophenol (2,4,5-TCP); Adsorption

1. Introduction

Chlorophenols are widely used in the production of herbicide's pesticides, fungicides, and wood preservatives. They are discharged into the environment and pollute water and soil seriously because they are not easily biodegradable. Trichlorophenol, because of its phenolic ring structure, has three chlorine atoms making it one of the biggest toxicity of chlorophenol compounds. Among them, 2,4,6-trichlorophenol (2,4,6-TCP) has been listed as "priority pollutants" by the United States Environmental Protection Agency (EPA), and 2,4,5-trichlorophenol (2,4,5-TCP) was identified by the EPA as persistence bioaccumulation and toxic pollutants [1].

Mesoporous materials with open channel structure, narrow pore size distribution, high specific surface area, and mesopore diameter were widely used in the environmental, chemical, or other fields [2]. At present, people used four oxygen alkane silane as a silicon source to prepare mesoporous materials, such as tetraphenylborate (TMSO) and tetraethyl orthosilicate (TEOS). Using them for large production of mesoporous silica, it could cause serious environmental pollution. Therefore, in order to solve this problem,

*Corresponding author.

researchers began to look for natural silicon mineral to replace toxic organic silicon for preparing mesoporous materials. Zhang et al. [3] using natural minerals, plagioclase as silicon source and aluminum source, white carbon black as an added silicon source (change the silica alumina ratio), hexadecyl trimethyl ammonium bromide (CTAB) as template, hydrothermally synthesized mesoporous molecular sieve with micropores in alkaline condition. The mean mesopore diameter of the as-synthesized sample is 2.82 nm and the BET surface area is 847.13 m^2/g. Attapulgite (ATP), the chemical formula is $Mg_5Si_8O_{20}(OH)_2(OH_2)_4{\cdot}4H_2O$, and the structure was first proposed by Bradley in 1940 [4]. Its chemical compositions should be: SiO_2 56.96%, (Mg, Al, Fe)O 23.83%, H_2O 19.21% [5]. Because of the original attapulgite's lack of various chemical adsorption forces, the adsorption capacity of direct chlorine phenol adsorption is very limited. β-cyclodextrin (β-CD) is a kind of internal cavity hydrophobic and hydrophilic hydroxyl groups outside the annular oligosaccharides. Because of this kind of special structure, it can make the hydrophobic molecules by molecular interactions within the cavity to form host–guest package material [6].

In this research, a novel mesoporous material is prepared by hydrothermal method using cationic surfactant CTAB as a structure-directing agent, ATP as the silicon source, following modified by β-CD. The obtained composite material was characterized by different means. The effects of temperature, initial concentration, and contact time on adsorption performance were studied by static adsorption experiment study, also its dynamic behavior and the regeneration performance was investigated.

2. Experimental

2.1. Chemicals

ATP was provided by the Jiangsu Autobang International Co., Ltd. Analytically pure β-cyclodextrin (β-CD), sodium hydride(NaH), 2,4,5-TCP, and 2,4,6-TCP were provided by the Aladdin reagent Co., Ltd; analytically pure γ-(2,3-epoxypropoxy) propytrimethoxysilane (KH-560), dimethyl formamide (DMF), CTAB were provided by the Sinopharm Chemical Reagent Co., Ltd (Shanghai, China); double-distilled water was used for preparing all aqueous solutions and cleaning processes.

2.2. Instruments

Infrared spectra (4,000–400 cm^{-1}) were recorded on a Nicolet NEXUS-470 FT-IR apparatus (USA) using KBr disks. The morphology was observed by a transmission electron microscope (TEM, JEOL IEM-200CX). UV–vis spectrophotometer (UV–vis spectrophotometer), Japan, Shimadzu UV-2450. Surface area and porosity were determined using the US, Micromeritics TriStar3000. Samples were outgassed for 6 h at 100℃ prior to the N_2 adsorption analysis, which was carried out at liquid nitrogen temperature (−196℃). Surface area was obtained by a multi-point analysis of the volume of nitrogen adsorbed as a function of relative pressure. Muffle (Shanghai Shi Yan Electric Furnace Co., Ltd); centrifuge (Shanghai Analysis Instrument Factory Co., Ltd); ultrasonic cleaner (Kunshan Ultrasonic Instruments Co., Ltd); electronic balance (Beijing Sartorius Instrument System Co., Ltd); DZF-6051 vacuum drying oven (Shanghai Yiheng Instruments Co., Ltd).

2.3. Preparation of mesoporous attapulgite

Synthesis process of mesoporous attapulgite is as follows [7]: 1.0 g of ATP (after ground) reacted with 8.0 mol/L HCl for 2.0 h under 80℃, and then cooled down at room temperature. ATP was filtered from the product, washed thoroughly with distilled water to be neutralized and then dried under 80℃. 0.2 g of CTAB was dissolved in 10-ml deionized water, then 0.2 g of acidified ATP was added to form complexes, a drop of 0.5 mol/L NaOH was added to bring the complex system's pH to 12, reacted under 100℃ for 24 h, and then cooled down at room temperature, filtered, washed with distilled water and anhydrous ethanol three times to neutralize and dried under 80℃ for 12 h. The compound underwent calcination in the muffle furnace, with the temperature at a rate of 5.0℃/min to 540℃ for 6 h and the mesoporous attapulgite (mATP) was obtain.

2.4. Synthesis β-CD/mATP composites

β-CD/mATP was synthesized as follows [8]: after recrystallizing 3 times, 3.0 g of β-CD was dissolved in 100 ml of DMF, then 0.3 g of NaH was added and stirred for 30 min. Solid was filtered off, 1.0 g of KH-560 was added to the filtrate, reacted under 90℃ for 5.0 h with N_2 protection, and then 4.0 g of mATP was added reaction was maintained under 110–120℃ for 24 h. Product was cooled down at room temperature, filtered, washed in DMF, distilled water, methanol and acetone several times. Then, the white solid product was obtained after drying at 100℃ for 24 h in vacuum drying oven.

2.5. Single adsorption study

In the process of a single adsorption study, the experimental parameters such as pH, temperature, initial concentration, and contact time were studied. The experiment was carried out in a 10-mL plastic centrifuge tube, by adding 0.01 g of sorbent. The above solution was placed in a constant temperature shaking water bath, oscillating at a rate of 300 rpm after a defined range of adsorption times for adsorption experiments. And the same tests were done under the same conditions without adding sorbent as a blank test for eliminating error caused by the adsorption of the plastic tube. After centrifugation, the supernatant was observed using a UV spectrophotometer detector, corresponding to the maximum absorption wavelength of 289.4 nm (2,4,5-TCP) and 293 nm (2,4,6-TCP), using Eq. (1) to calculate the final equilibrium adsorption capacity (Q_e mg/g), and draw the adsorption isotherms and kinetic curves.

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

Among them, C_0 (mg/L) and C_e (mg/L), respectively, stand for TCP initial concentration and equilibrium concentration. V (mL) is the volume of solution. W (g) is sorbent mass.

2.6. Binary adsorption studies

To configure a series of solutions: (1) fix 2,4,5-TCP concentration as 100 mg/L, add 2,4,6-TCP so that the concentration of 2,4,6-TCP in the solution is, respectively, 20, 50, 80, 100, and 150 mg/L, and the pH is adjusted to 5; (2) fix 2,4,6-TCP concentration as 100 mg/L. Add 2,4,5-TCP so that the concentration of 2,4,5-TCP in the solution is 20, 50, 80, 100, and 150 mg/L, the pH is adjusted to 4, and the adsorption temperature is set to 298 K. Put this dihydric solution for oscillation in the rate of 300 rpm for 12 h, the binary solution of 2,4,5-TCP and 2,4,6-TCP's equilibrium concentration was detected with a UV spectrophotometer, the maximum absorption wavelength of the resulting absorbance A_1 and A_2 was 289.4 and 293 nm, respectively. $k_{293}^{6\text{-TCP}}$, $k_{289.4}^{6\text{-TCP}}$, $k_{293}^{5\text{-TCP}}$, $k_{289.4}^{5\text{-TCP}}$ stand for the molar absorption coefficients of the 2,4,6-TCP and 2,4,5-TCP at the maximum adsorption wavelength (293 and 289.4 nm). The concentration is calculated by the following formula [9]:

$$C_{5\text{-TCP}} = \frac{k_{293}^{6\text{-TCP}} A_1 - k_{289.4}^{6\text{-TCP}} A_2}{k_{289.4}^{5\text{-TCP}} k_{293}^{6\text{-TCP}} - k_{289.4}^{6\text{-TCP}} k_{293}^{5\text{-TCP}}} \tag{2}$$

$$C_{6\text{-TCP}} = \frac{k_{289.4}^{5\text{-TCP}} A_2 - k_{293}^{5\text{-TCP}} A_1}{k_{289.4}^{5\text{-TCP}} k_{293}^{6\text{-TCP}} - k_{289.4}^{6\text{-TCP}} k_{293}^{5\text{-TCP}}} \tag{3}$$

3. Results and discussion

3.1. Characterization

By transmission electron microscopy, the characterization results of ATP, mATP, and β-CD/mATP structures are presented in Fig. 1. As can be seen from the figure, compared to the original ATP, mATP has neat pore structure, a similar structure as reported [7], which indicates that mesoporous materials synthesize successfully. Compared with mATP, β-CD/mATP materials retain the pore structure. Compared to the mATP, pore shapes are not so structured.

Infrared spectra of ATP, mATP, and β-CD/mATP are shown in Fig. 2. The absorption peak at 3,617 cm^{-1} corresponded to the internal structure of tetrahedral and octahedral structures between Mg and Al as a result of hydroxyl stretching vibration.

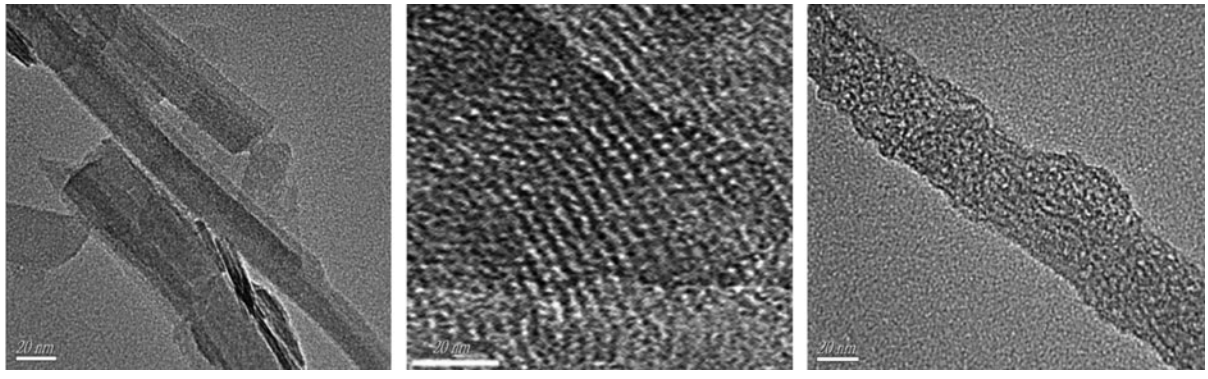

Fig. 1. TEM images of ATP (left), mATP (middle), and β-CD/mATP (right).

The peak at 3,546 cm^{-1} is with Mg, Al, on the edge of the ATP channel connected to the octahedral structure of hydroxy symmetric stretching vibration of water and the Si–O keys of Si–O–Si at 1,031 cm^{-1} asymmetric stretching vibration characteristic peak. The peak at 1,456 cm^{-1} is corresponded with carbonate vibration of CO_3^{2-} of the minerals [10]. Compared with the original ATP, the peak of mATP at 1,031 cm^{-1} slightly changes in intensity and location; a broad peak at 3,440 cm^{-1} may be produced by acidification in the amorphous phase structure due to additional hydroxyl groups' stretching vibration peak; a new peak of 797 cm^{-1} is Si–OH vibration peak and shows that the surface properties of modified ATP change [7]. And the peak at 1,650 cm^{-1} shifts to 1,630 cm^{-1} and indicates that β-CD grafts onto the surface of mATP. β-CD/mATP is prepared successfully [11,12].

BET surface area, pore volume, and mesopore diameter of the mATP and β-CD/mATP are shown in Table 1. BET surface area, pore volume, and mesopore diameter of β-CD/mATP composite material are 300.30 m^2/g, 0.33 cm^3/g, and 21.86 Å, which are higher than the surface area of mATP due to β-CD partially cross-linking on the surface of the mATP. Also significantly higher than Pan's group [12] synthesized β-CD/ATP specific surface (92.92 m^2/g).

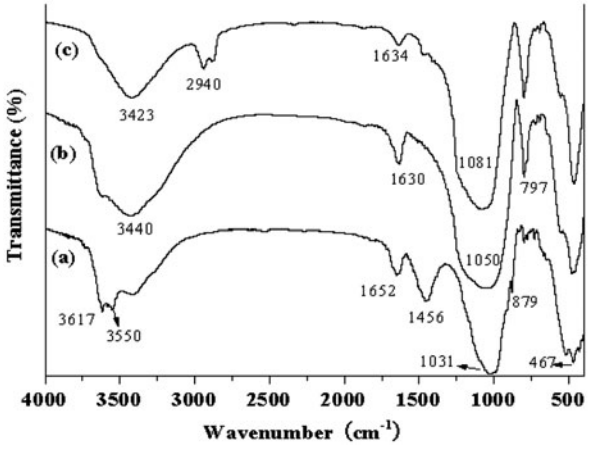

Fig. 2. FT-IR spectra of ATP (a), mATP (b), and β-CD/mATP (c).

3.2. The effect of pH on the adsorption

The pH of the solution has a significant influence on the adsorption of 2,4,5-TCP and 2,4,6-TCP β-CD/mATP. In the static adsorption, temperature is 25°C, and the initial concentration of the solution is 100 mg/L. The experimental results are shown in Fig. 3. As is seen from Fig. 3, for 2,4,5-TCP, the initial pH is in the range of 2–5, the adsorption capacity of β-CD/mATP increases slightly, achieving the maximum adsorption capacity at 5 (25.541 mg/g). In the initial pH at the range of 5–8, with the TCP ionization, the adsorption capacity of β-CD/mATP decreases significantly. 2,4,5-TCP exists mainly in the form of neutral molecules, which are beneficial for adsorption [13,14] and this may be due to the pH range 2–5. When pH is higher than 5, the negatively charged 2,4,5-TCP and functional groups of sorbent dissociation emerge electrostatic repulsion, so the adsorption capacity decreases. Therefore, pH 5 is chosen as the optimal initial pH value of 2,4,5-TCP in this paper. Similarly, pH 4 is chosen as the best initial pH value of 2,4,6-TCP.

3.3. Effect of contact time at different initial concentrations and temperatures

Different initial concentrations, temperatures, and contact time have a certain effect on the adsorption, as

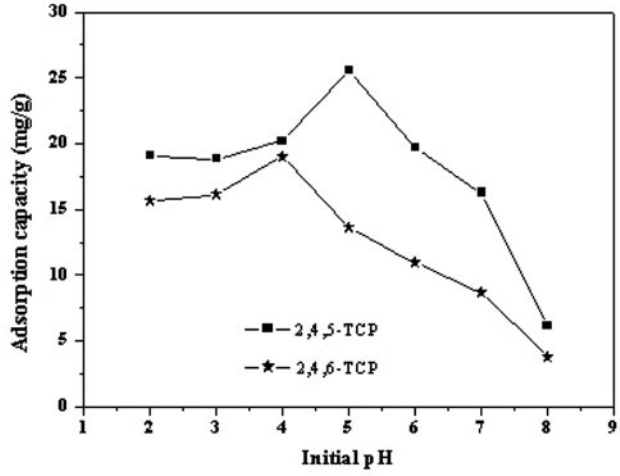

Fig. 3. Effect of pH on adsorptive removal of 2,4,5-TCP and 2,4,6-TCP.

Table 1
Data of mATP (b) and β-CD/mATP (c) from nitrogen adsorption–desorption analysis

Material	BET surface area (m^2/g)	Pore volume (cm^3/g)	Mesopore diameter (Å)
mATP	95.95	0.36	34.14
β-CD/mATP	300.30	0.33	21.86

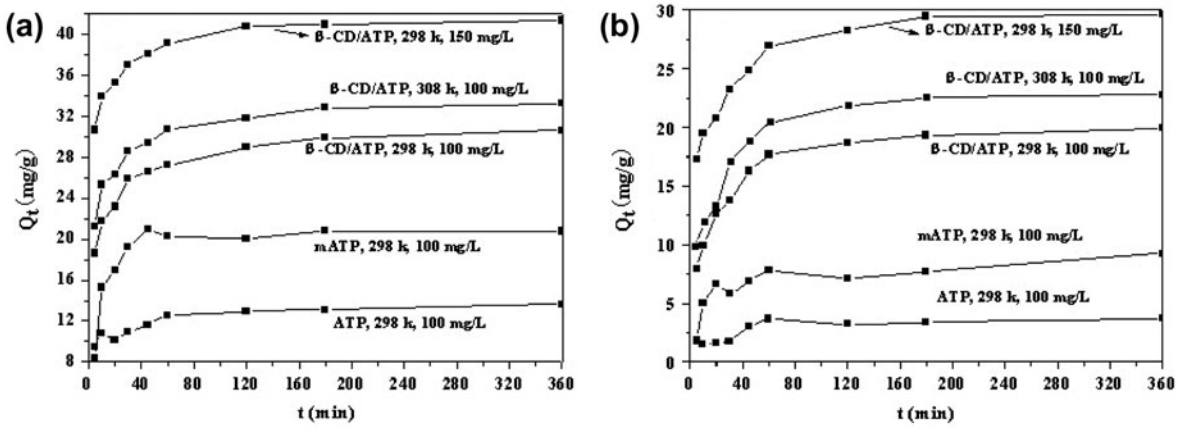

Fig. 4. Effect of contact time at different initial concentrations and temperatures on adsorptive removal of 2,4,5-TCP (a) and 2,4,6-TCP (b).

shown in Fig. 4. As a comparison, choose ATP and mATP as sorbents to adsorb 2,4,5-TCP (4a) and 2,4,6-TCP (4b). As can be seen from the figure, along with the increase in temperature and the initial concentration, the adsorption capacity increases, and the initial concentration of TCP may provide dynamics to overcome the aqueous and solid phase mass transfer resistance [14]. A higher temperature may provide TCP, through the sorbent surface liquid film, more opportunities also to expand the pore volume and specific surface area of sorbent. So it provides the TCP molecule the opportunity for further penetrating [15]. Meanwhile, compared with ATP and mATP, β-CD/mATP adsorption capacities are increased obviously. This result also shows the excellent property of modified materials.

3.4. Adsorption kinetics

In this paper, we use a quasi-first-order kinetic and quasi-second-order kinetic equation to fit the experimental kinetic data. The pseudo-first-order kinetics of linear and nonlinear equations are as follows [16]:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{4}$$

$$Q_t = Q_e - Q_e e^{-k_1 t} \tag{5}$$

Quasi-second-order kinetics of linear and nonlinear equations are as follows [17]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{6}$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \tag{7}$$

Q_e (mg/g), Q_t (mg/g) respectively stand for balance and time t (min) when the adsorption capacity of TCP; K_1 (L/min), K_2 (g/mg min) is the adsorption rate constant, the corresponding values through graph $\ln(Q_e - Q_t)$ on T and t/Q_t to intercept t on the calculation.

Based on the second-order rate equation, the initial adsorption rate h (mg/g min) and half adsorption time $t_{1/2}$ (h) are obtained using the following equation [18,19]:

$$h = k_2 Q_e^2 \tag{8}$$

$$t_{1/2} = \frac{1}{k_2 Q_e} \tag{9}$$

where $t_{1/2}$ (h) represents the need to reach half the time when adsorption balance, therefore, h and $t_{1/2}$ can be used to evaluate the adsorption rate. Usually a larger h value and a smaller $t_{1/2}$ value indicate the faster adsorption rate. Calculated kinetic parameters are listed in Table 2. The pseudo-first-order kinetics and quasi-second-order kinetics of nonlinear fitting are shown in Fig. 5. From Table 2, two TCP adsorptions are in line with the quasi-second-order kinetic process; the value of the experimental Q_e and calculated Q_e is consistent; while fitting a straight line, the correlation coefficient (R^2) value exceeds 0.999, indicating that the quasi-second-order kinetic equation is well used to describe the applicability of the adsorption dynamics of β-CD/mATP, two chlorophenols, as well as the

Table 2
Kinetic constants for the pseudo-first-order model and pseudo-second-order model

				Pseudo-first-order kinetic model			Pseudo-second-order kinetic model				
Adsorbates	T (K)	C_0 (mg/L)	Q_{erexp} (mg/g)	$Q_{e,c}$ (mg/g)	k_1 (L/min)	R^2	$Q_{e,c}$ (mg/g)	$k_2 \times 10^{-2}$ (g/mg min)	h (mg/(g min))	$t_{1/2}$ (min)	R^2
2,4,5-TCP	298	100	30.65	9.46	0.0147	0.980	31.056	0.5126	4.944	6.282	0.9998
	298	150	41.78	8.29	0.0149	0.962	41.736	0.7501	13.07	3.194	0.9998
	308	100	33.26	9.43	0.0175	0.984	33.659	0.5978	6.772	4.970	0.9999
2,4,6-TCP	298	100	19.92	9.81	0.0169	0.971	20.521	0.4353	1.833	11.20	0.9998
	298	150	29.64	13.5	0.0232	0.988	30.276	0.4533	4.155	7.287	0.9998
	308	100	22.79	12.6	0.0226	0.992	23.524	0.4141	2.292	10.27	0.9997

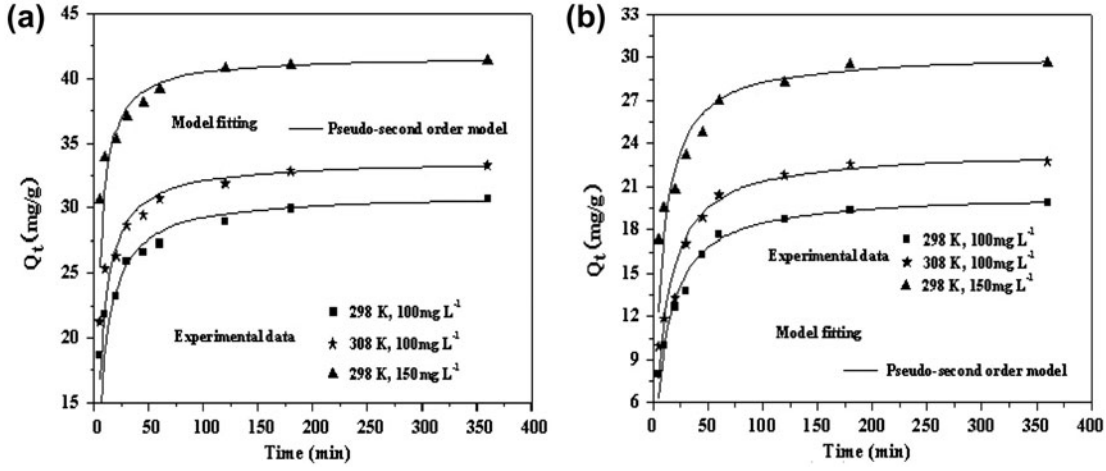

Fig. 5. Kinetic modeling of the effect of initial concentration and temperature for adsorption of 2,4,5-TCP (a) and 2,4,6-TCP (b) onto β-CD/mATP.

chemical process which is the rate-controlling step of the adsorption of two chlorophenols [20]. At the same time, from the h and $t_{1/2}$ values, with the increase of temperature and concentration of the solution, the initial adsorption rate become faster, and the initial adsorption rate of 2,4,5-TCP is significantly higher than that of β-CD/mATP β-CD/mATP 2,4,6-TCP, in a short period of time to the adsorption of 2,4,5-TCP more easily. From Fig. 5, in the beginning, the rate is fast in which β-CD/mATP adsorbs two chlorophenols, then slowlyreaches equilibrium after 60 min. This may be at the beginning of adsorption, adsorption agent within lots of the empty binding site, so that TCP is fast adsorption, after a period of time, sorbent adsorption sites on the less, and the lower concentration, the adsorption rate decreases and finally achieves the balance.

3.5. Adsorption equilibrium

The adsorption isotherm model is the chief method to describe the nonlinear dynamic balance of the solute and the solution which is adsorbed by the sorbent at a constant temperature of the main method [21]. The analysis of adsorption equilibrium plays a vital role on the optimal sorbent. Adsorption equilibrium data of a single component system fitted by Langmuir adsorption isotherm model and Freundlich isotherm model, in accordance with the correlation coefficient (R^2) and standard deviation ΔQ (%), determine the applicability of the adsorption behavior. Q (%) by Eq. (10) is used to calculate.

$$\Delta Q\ (\%) = 100\sqrt{\frac{\sum [(Q_{exp} - Q_{cal})/Q_{exp}]^2}{N-1}} \tag{10}$$

The Q_{exp} and Q_{cal} are the sorbent of sorbate experimental values and the calculated value (mg/g); Langmuir adsorption isothermal model of linear and nonlinear equations are as follows [14]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \tag{11}$$

$$Q_e = \frac{K_L Q_m C_e}{1 + K_L C_e} \tag{12}$$

where the C_e (mg/L) represents adsorption equilibrium concentration in the solution, Q_e (mg/g) is equilibrium adsorption capacity; Q_m (mg/g) represents the maximum adsorption capacity of sorbent; K_L (L/g) is affinity constant. Langmuir isotherm equation can also be defined as the dimensionless equilibrium parameter R_L, which is calculated as follows [22]:

$$R_L = \frac{1}{1 + C_m K_L} \tag{13}$$

C_m is the largest in the initial concentration of TCP (mg/L); there are four possibilities of the R_L value: (1) $0 < R_L < 1.0$, favorable adsorption; (2) $R_L > 1.0$, negative adsorption; (3) $R_L = 1.0$, the linear adsorption; and (4) $R_L = 0$, irreversible adsorption.

Freundlich isotherm model of linear and nonlinear equations are as follows [23]:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \tag{14}$$

$$Q_e = K_F C_e^{1/n} \tag{15}$$

K_F (mg/g) represents sorbent adsorption capacity direction constants and $1/n$ of values between 0.1 and 1.0 indicates favorable adsorption conditions [24].

In experiment, the solution of the initial concentration is 10, 30, 50, 80, 100, 150, 200, 250, 300, and 400 mg/L to adjust the pH of the solution to the optimal pH value. Under different temperatures, the adsorption isotherm of the sequence is shown in Table 3; the nonlinear Langmuir and Freundlich isothermal models' regression fitting is shown in Fig. 6. As can be seen from Table 3, R_L and $1/n$ value less than 1.0 show that the experimental conditions are conducive to the two TCP adsorptions. Adsorption equilibrium data of β-CD/mATP of two TCPs are more suitable for the Langmuir isotherm model, which show that the adsorption of two kinds of TCP is a single molecular layer adsorption. From Fig. 6, with the increase in the equilibrium concentration, the adsorption amount of β-CD/mATP increases greatly, and then slows down until balance; as the temperature increases from 298 to 318 K, two kinds of chlorophenols in Q_e are improved significantly, which may be attributed to the high temperature of TCP. The sorbent surface film layer provides more chances and can also expand the pore volume and specific surface area of the sorbent, and hence provides the TCP molecule [15] the opportunity for further penetration.

3.6. Competitive adsorption of the binary solution system

In order to study the interaction of 2,4,5-TCP and 2,4,6-TCP, at different initial concentrations, the effect of β-CD/mATP competitive adsorptions of two chlorophenols is given in Table 5. Adsorption agent of two TCPs, Q_e^b (binary solution system)/Q_e^s (single solution system) is less than 1: for adsorbing 2,4,5-TCP, the concentration of adding 2,4,6-TCP is 50 and

Table 3
Adsorption isotherm constants for 2,4,5-TCP and 2,4,6-TCP

		2,4,5-TCP			2,4,6-TCP		
Adsorption isotherm models	Constants	298 K	308 K	318 K	298 K	308 K	318 K
Langmuir equation	R^2	0.9942	0.9939	0.9941	0.9872	0.9909	0.9938
	$Q_{m,c}$ (mg/g)	65.19	74.96	85.03	56.88	65.62	70.92
	K_L (L/mg)	0.0117	0.0121	0.0148	0.0070	0.0086	0.0116
	R_L	0.176	0.171	0.146	0.263	0.225	0.177
	ΔQ (%)	2.53	1.64	0.572	1.42	0.291	1.04
Freundlich equation	R^2	0.9742	0.9656	0.9573	0.9868	0.9866	0.9851
	K_F (mg/g)	1.680	1.844	2.604	0.8342	1.281	1.990
	$1/n$	0.6353	0.6492	0.6224	0.6980	0.6612	0.6133
	ΔQ (%)	7.39	7.36	9.34	3.00	2.93	3.02

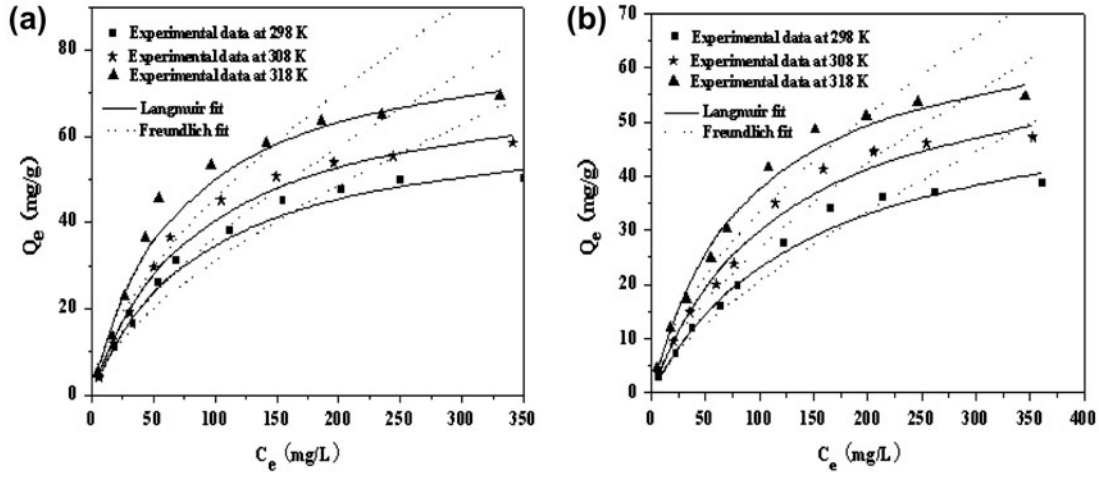

Fig. 6. Comparison of Langmuir and Freundlich isotherm models for 2,4,5-TCP (a) and 2,4,6-TCP (b) adsorption onto β-CD/mATP using nonlinear regression.

Table 4
The Q_m values and selectivity of β-CD/mATP and other adsorbents

Adsorbent	Adsorbent (mg/g)	Selectivity	Refs.
β-CD/mATP	41.74	High	This work
Modified single-walled carbon nanotubes	110.3	Low	[25]
Activated carbon	140.8	Low	[26]

100 mg/L, and their values are 0.3198 and 0.2681; while for adsorbing 2,4,6-TCP, values are 0.4272 and 0.3665, respectively, with the concentration of adding 2,4,5-TCP being 50 and 100 mg/L. This shows that the adsorption of two kinds of chlorophenols through competition for binding sites will reduce the adsorption effect of β-CD/mATP [21]. Moreover, the 2,4,6-TCP Q_e^b/Q_e^s value is greater than the value of 2,4,5-TCP and shows that in the presence of competition of chlorophenols, adsorption effect of β-CD/mATP on 2,4,5-TCP is larger than it is on 2,4,6-TCP [12]. Because the structure of the 2,4,5-TCP and 2,4,6-TCP is very similar, this property of β-CD/mATP could make it a further potential application in selective adsorption of 2,4,5-TCP from the mixed system.

And the comparison between β-CD/mATP composites and other adsorbents on the adsorption of trichlorophenol is listed in Table 4. The adsorption capacity of β-CD/mATP is lower than modified single-walled carbon nanotubes and activated carbon. But our material has higher selectivity for 2,4,5-TCP than other adsorbents due to modified by β-CD.

Table 5
Effect of competitive adsorption of 2,4,5-TCP and 2,4,6-TCP onto β-CD/mATP particles at different concentrations

	C (2,4,5-TCP) = 100 mg/L			C (2,4,6-TCP) = 100 mg/L	
C_0 (2,4,6-TCP)	Q_e (2,4,6-TCP) (mg/g)	Q_e (2,4,5-TCP) (mg/g)	C_0 (2,4,5-TCP)	Q_e (2,4,6-TCP) (mg/g)	Q_e (2,4,5-TCP) (mg/g)
20	3.107×10^{-2}	10.01	20	8.628	2.532×10^{-2}
50	1.981	9.930	50	8.448	3.384
80	4.527	9.793	80	8.160	7.008
100	9.032	8.326	100	7.248	10.36
150	17.66	4.288	150	5.888	15.39

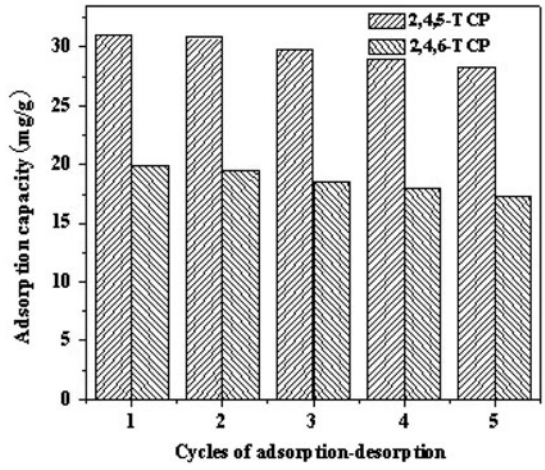

Fig. 7. Adsorption–desorption cycles for β-CD/mATP.

3.7. Regeneration performance study

The regeneration performance of the sorbent is one of the important factors of use value for the sorbent. It reaches the saturation adsorption in 298 K by static adsorption experiment, and centrifugal separation after the collection of the sorbent. 2.0 mL of acetonitrile washes 2 times. Then, use the 2.5 mL volume ratio, methanol: acetic acid 9:1, to elute TCP; ultrasonic oscillation for 30 min obtains TCP from β-CD/mATP. Five regeneration adsorption capacities of β-CD/mATP for two chlorophenols are shown in Fig. 7. As is seen from the figure, after five-time regeneration, β-CD/mATP on 2,4,5-TCP and the adsorption capacity of 2,4,6-TCP only decrease a little (reduce by 8.78 and 13.07%). It shows β-CD/mATP has excellent regeneration performance.

4. Conclusions

Using the Langmuir and Freundlich isothermal models for fitting the isothermal adsorption process, the Langmuir isotherm model can fit the balance data better. And at 298 k, the sorbent for 2,4,5-TCP and 2,4,6-TCP monolayer adsorption capacity is 31.049 and 19.775 mg/g. Pseudo-second-order model can be used to match β-CD/mATP two chlorophenols' adsorption kinetics data mainly. In the binary system, when there is a competition between phenolic compounds, 2,4,5-TCP on β-CD/mATP adsorption than 2,4,6-TCP is more likely to be affected. And β-CD/mATP has an excellent regeneration property.

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