

2,4-Dichlorophenol sorption on cyclodextrin polymers

Ning Li · Zheng Mei · Sheguang Ding

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Abstract The sorption of β -cyclodextrin polymer (β -CDP) and γ -cyclodextrin polymer (γ -CDP) toward 2,4-dichlorophenol (2,4-DCP) in aqueous solutions was investigated. The influence of sorption conditions including initial 2,4-DCP concentration, contact time and pH on sorption capability were discussed. Their sorption behaviors for 2,4-DCP were conducted and it was found the sorption kinetics followed the Ho and McKay equation and the film diffusion was the rate-determined step. The sorption isotherm can be correlated to Freundlich model and the sorption capacity on β -CDP was much larger than that on γ -CDP. The maximum sorption capacity of 2,4-DCP for β -CDP was measured to be 0.16 mmol/g with the initial concentration at 0.67 mmol/L at 288 K. The CDPs were easily recovered by ethanol as washing solvent and they could be used as a kind of recyclable sorbents.

Keywords 2,4-Dichlorophenol · β -Cyclodextrin · γ -Cyclodextrin · Sorption

Introduction

Removal of pollutants from water has been a challenge for long time and adsorption technique has been proved perfectly to minimize this task [1]. It is now well established that for the wastewater treatment, adsorption is a much better process than other physical techniques, namely,

flocculation, froth flotation, etc., because of its efficiency and economy [2, 3]. Moreover, adsorption to remove pollutants without disturbing the quality of water or leaving behind any toxic degraded products has competed with electrochemical, biochemical or photochemical degradation processes [4]. Adsorption process has many extraordinary advantages for recovery of valuable pollutants from the wastewater [5]. It has been used for the removal of organics from wastewaters, primarily focusing on the use of activated carbon as the adsorbent. Regeneration of the spent adsorbent material can be an expensive and intensive process [6]. This has resulted in an interest in developing alternative sorbents for the removal of organic pollutants from aqueous waste streams. These sorbents include clay materials [7], zeolites [8], siliceous materials [9], agricultural wastes [10], industrial by-products [11], biomass [12] as well as natural molecules [13, 14].

β -Cyclodextrin (β -CD) and γ -cyclodextrin (γ -CD) are glucose-based molecules derived from the enzymatic degradation of starch by bacteria. They are cyclic oligosaccharides consisted of 7(β) and 8(γ) glucopyranose units, which join together by $\alpha(1-4)$ linkage forming a torus-shaped ring structure. Cyclodextrins (CDs) crosslink with suitable crosslinkers forming insoluble polymers (CDPs) which exhibit specific sorption because of formation of inclusion complex [15–17]. Although high cost and low sorption capacity of CDPs compared with those of activated carbon or other sorbents are important drawbacks, the usefulness of CDPs in treatment applications is available due to several main advantages. The outstanding one of CDs is their ability to form inclusion compounds with various organic molecules through host–guest interactions: the interior cavity of the molecule provides a relatively hydrophobic environment into which a non-polar pollutant can be trapped. The other interesting advantages of CDPs

N. Li (✉) · Z. Mei · S. Ding
College of Environmental and Biological Engineering,
Chongqing Technology and Business University,
Chongqing 400067, China
e-mail: tdljohn@ctbu.edu.cn; tdljohn@yahoo.com.cn

were their chemical stability of the polymers and the reproducible values.

2,4-Dichlorophenol (2,4-DCP) is a toxic organic compound listed in the Environmental Protection Agency (EPA) as priority pollutant [18]. It has been commonly used as pesticide, herbicide, wood, leather and glue preservatives [18, 19]. 2,4-DCP causes respiratory hazard such as cough, chronic bronchitis, chest wheezing, altered pulmonary function, and pulmonary lesions. Adverse effects on the human nervous system have been reported and linked to various health disorders. Due to its high toxicity, carcinogenic effects, and persistence in the environment, attention has been focused on their presence and removal from the environment [19, 20]. There are many methods such as oxidation, precipitation, ion exchange and solvent extraction to remove phenolic species from aqueous solution. However, in water treatment the most widely used method is adsorption onto the surface of sorbents.

In this paper, cross-linked β -cyclodextrin polymer (β -CDP) and γ -cyclodextrin polymer (γ -CDP) has been used as sorbents for removal of 2,4-DCP from its aqueous solution in batch process. The sorption behaviors of the two polymers (CDPs) were compared through experimental investigations. The influence of several operating parameters such as initial concentration, contact time was investigated. Equilibrium isotherms and kinetic models were used to identify the possible mechanism of the sorption process. The recovery of 2,4-DCP from CDPs and their recycle use were also studied. The aim of the present work was to explore the potential of CDPs as sorbents.

Materials and methods

Reagents

β -CD and γ -CD were purchased from Wacker without any further purification before use. 2,4-DCP (analytical grade) has a maximum absorbance at wavelength 286 nm on a UV–vis spectrophotometer. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system. The other chemicals were analytical grade.

Preparation of polymers

CDPs were prepared in one step, by mixing CDs and crosslinking agent epichlorohydrin (EPI) to obtain insoluble polymers. The synthetic procedure had already been described in detail [21]. The CDPs were dried in vacuum for 24 h and then crushed and sieved into different particles sizes. Studies were focused on a size fraction of 150–250 μm . The characteristics of CDPs were reported in

Table 1. These particles have a hydrogel nature with a high capacity for absorbing water. The density of the swollen polymer gel is higher than the density of water. The polymers have a remarkably high swelling capacity in water and, consequently, their networks are sufficiently expanded to allow a fast diffusion process for the studied sorbate. The polymers were stored in a desiccator before use. The Brunauer–Emmet–Teller (BET) surface area of the particles was measured by recording nitrogen adsorption/desorption isotherms at 77 K using a F-Sorb-2400 analyzer (Gold APP Instrument China). The content of the CD moiety in β -CDP and γ -CDP, based on glucose as standard, was determined by the phenol–sulfuric acid method [22].

Sorption studies and kinetics

Experimental data were determined by the following batch method: in each experiment, 100 mg dry CDP was mixed with 50 mL aqueous solution (fixed pH 7, unless otherwise specified) of 2,4-DCP at a known concentration in a tightly sealed flask. The sorption temperature and the concentration of 2,4-DCP were varied according to experiments. The solution was stirred on a shaker (90 times/min) at set constant temperature for 5 h. The sorbents were removed by centrifugation before measurements. The residual 2,4-DCP concentration in solutions was determined by spectrophotometer and absorbance values were recorded at 286 nm for each solution. These data were used to calculate the sorption capacity of the sorbent by Eq. 1:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where, q_e is the amount of 2,4-DCP adsorbed at equilibrium (mol/g); C_0 is the initial 2,4-DCP concentration in liquid phase (mol/L); C_e is the liquid phase 2,4-DCP concentration at equilibrium (mol/L); V is the volume of 2,4-DCP solution used (L); and m is the mass of sorbent used (g). Each experiment was done three times under identical conditions. 2,4-DCP initial concentration in the solution varied to investigate its effect on the sorption capacity. Studies were also conducted for various time intervals to determine when sorption equilibrium was reached and the maximum removal of 2,4-DCP was attained.

Table 1 Characteristics of CDPs

Polymer	β -CDP	γ -CDP
Particle size (μm)	150–250	150–250
Content of CD ($\mu\text{mol/g}$)	49.96	33.71
Swelling capacity (cm^3/g)	5.5	5.0
BET specific surface area (m^2/g)	0.75	0.26

Binding constant

Solutions of 2,4-DCP (10^{-2} mol/L) and β -cyclodextrin or γ -cyclodextrin (10^{-2} mol/L) in aqueous buffer solution ($\text{Na}_2\text{HPO}_4\text{-NaH}_2\text{PO}_4$, pH 6.8) were used for spectrophotometric studies at 298 K. The binding constants were calculated using the Benesi–Hildebrand or its modified formula [23].

$$\frac{1}{\Delta A_i} = \frac{1}{\Delta A} + \frac{1}{\Delta A K} \frac{1}{C_{CD}^i} \quad (2)$$

Hence, plotting $1/\Delta A_i$ versus $1/C_{CD}^i$ gives a slope of $1/(\Delta A K)$ and an intercept of $1/\Delta A$. The ratio of the intercept to the slope can be taken as an estimation of the binding constant K .

Results and discussion

Effect of contact time

For effective designation and representation of the ongoing process, the study of kinetics of the sorption was carried out. The sorption of 2,4-DCP was investigated in the initial concentration 0.6 mmol/L at temperatures 283, 293 and 303 K, respectively. Figure 1 shows the influence of contact time on the sorption of CDPs toward 2,4-DCP. It was shown that sorption was increased instantly at initial stage due to rapid attachment of 2,4-DCP to the surface of the polymers. In the case of β -CDP, above 50% of the equilibrium value occurred in the first 5–10 min. However, in the case of γ -CDP, even more than 70% of the equilibrium value occurred in the first 5–10 min. And thereafter the rate of sorption of 2,4-DCP was found to be slow because the sorbate had to diffuse into the interior of sorbents (CDPs) with the particles of CDPs slowly swelling in the solution, until the equilibrium was reached and remained constant at nearly 120 min contact time.

Sorption kinetics

Time-dependent experimental sorption data (Fig. 1) were used for kinetic modeling. Following kinetic models, commonly used in the literature, were applied to experimental kinetic data in order to investigate the behaviors of 2,4-DCP on CDPs. The model equations used for fitting the data were: 1st order, Lagergren (Pseudo 1st order), 2nd order, Pseudo 2nd order (Ho and McKay), Bhattacharya–Venchobachor model (BV), power function and simple Elovich equations. Except the Ho and McKay equation, the other models were adopted to examine the mechanism of the sorption process, but the straight lines could not be

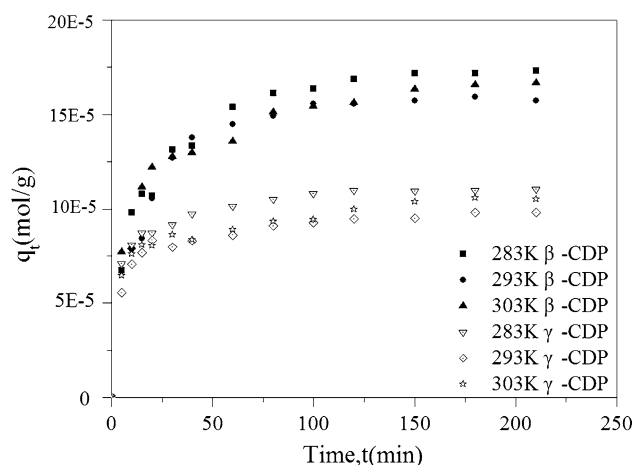


Fig. 1 Effect of contact time on 2,4-DCP sorption (conditions: sorbent: 0.1 g; 2,4-DCP initial concentration: 0.6 mmol/L; volume: 50 mL)

obtained. Then, kinetics of 2,4-DCP on CDPs was analyzed using the Ho and McKay model:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (3)$$

where, q_t and q_e are the amount adsorbed at time t and at equilibrium (mol/g), respectively; k_2 is the rate constant (g/mol/min). The values of k_2 and q_e were calculated from the intercept and slope of the linear plots of t/q_t against t . The results of kinetic fittings and the parameters associated with Ho and McKay model as well as the correlation coefficients is shown in Fig. 2 and Table 2. The high correlation coefficients (r) and the approximate consistency between the calculated $q_{e,cal}$ and experimental $q_{e,exp}$ values suggests that the sorption process is well described by Ho and McKay model. Kinetics of 2,4-DCP sorption on CDPs

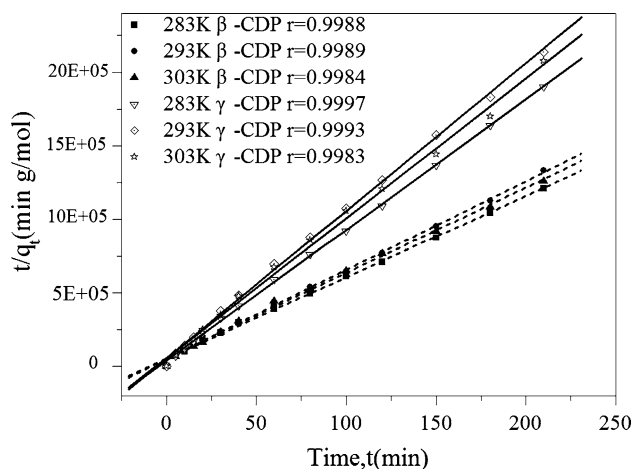


Fig. 2 Ho and McKay plots for sorption of 2,4-DCP on CDPs

Table 2 Ho and McKay sorption kinetic parameters of CDPs for 2,4-DCP (conditions: sorbent: 0.1 g; 2,4-DCP initial concentration: 0.6 mmol/L; volume: 50 mL)

Sorbent	Temperature (K)	$q_{e,exp}/10^{-5}$ (mol/g)	$q_{e,cal}/10^{-5}$ (mol/g)	k_2 (g/mol/min)	r
β -CDP	283	17.3	18.0	598.5	0.9988
	293	15.7	16.5	720.3	0.9989
	303	16.7	17.2	660.0	0.9984
γ -CDP	283	11.0	11.2	1541.0	0.9997
	293	9.8	9.9	1968.5	0.9993
	303	10.1	10.5	1767.0	0.9983

followed the pseudo 2nd order model, confirming that sorption of 2,4-DCP takes place probably via surface exchange reactions until the surface functional sites are fully occupied; thereafter 2,4-DCP molecules diffuse into the polymer network for further interactions (such as inclusion complex, hydrogen bonding, hydrophobic interactions) [24, 25].

Rate limiting step in the process of sorption

In order to interpret the experimental data, it is necessary to identify the step that governs the overall rate of removal in the sorption process. The mathematical treatments of Boyd et al. [26] and Reichenberg [27], that has laid the foundations of sorption/ion exchange kinetics, were used to distinguish between particle and film diffusion mechanism of sorption process.

The kinetics of the sorption processes of β -CDP and γ -CDP were examined at 303 K with 0.6 mmol/L 2,4-DCP and the values of Fractional Attainment of Equilibrium ‘ F ’ were calculated using Eq. 4.

$$F = \frac{q_t}{q_\infty} \quad (4)$$

where, q_t and q_∞ are amounts adsorbed at time t and at infinite time, respectively.

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{\exp(-n^2 Bt)}{n^2} \quad (5)$$

where, F is the fractional factor of equilibrium at time t , and n is the integers defining the infinite series solution obtained by a Fourier type of analysis. $B(=\pi^2 D_i r_i^{-2})$ values are obtained for each F value from Reichenberg’s table [27], D_i is the effective diffusion coefficient of the sorbate in the polymer particle and r_i is sorbent particle radius. The linear validation of Bt versus time (t) plot was employed to find whether the sorption process was film or particle diffusion controlled. If the plot was a straight line passing

through the origin, the sorption process should be dominated by the particle diffusion mechanism, or else, it might be governed by the film diffusion [28]. As is shown in Fig. 3, in all the cases studied, all the lines of relationship between Bt versus t were without passing through the origin, suggesting the film diffusion, not the particle diffusion, dominated the sorption process of CDPs for 2,4-DCP.

Sorption isotherm

Following isotherms, commonly used in the literatures, were applied in the present study. The models were: Langmuir, Freundlich, Dubinin–Radushkevich, Toth and Redlich-Peterson. Applicability of these models was compared by judging the correlation coefficients ($r > 0.975$). However, the correlation coefficients of all models were low except Freundlich model. The Freundlich equation was given below:

$$\text{Freundlich equation: } \ln q_e = \ln k_F + \frac{1}{n} \ln C_e. \quad (6)$$

where, C_e is the equilibrium 2,4-DCP concentration in solution (mol/L), q_e is adsorption capacities at equilibrium (mol/g), k_F (L/mol) and n are the Freundlich constants. The Freundlich model is basically empirical equation suitable for multilayer, heterogeneous sorption sites. It is expected that the Freundlich equation will provide a proper description of the sorption system when different types of interactions (such as interacting with the cavity of the cyclodextrin, i.e., inclusion complex, hydrogen bonding, hydrophobic interactions, with the polymer network) are involved [29]. The Freundlich parameters k_F and n have been determined and they are shown in Table 3.

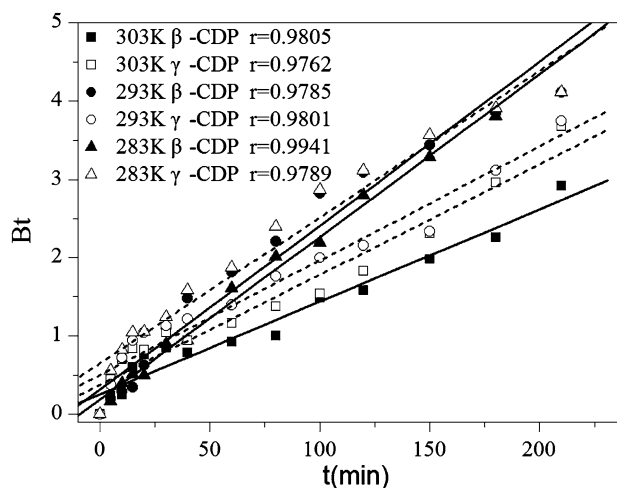


Fig. 3 Bt versus t plots for 2,4-DCP sorption on β -CDP and γ -CDP

Table 3 The different parameters of the Freundlich sorption isotherm on CDPs at different temperature

Sorbent	<i>T</i> (K)	<i>k_F</i> (L/mol)	<i>n</i>	<i>r</i>
β-CDP	283	0.0988	1.2729	0.9872
	288	0.1493	1.1838	0.9654
	293	0.0841	1.2854	0.9811
	298	0.6416	0.9672	0.9947
	303	0.2269	1.0557	0.9855
γ-CDP	283	0.0133	1.5873	0.9723
	288	0.2921	0.9623	0.9977
	293	0.2001	1.0266	0.9827
	298	0.0733	1.1263	0.9961
	303	0.1853	1.0251	0.9840

Our experimental data are found to fit well in the Freundlich model in terms of correlation coefficient (*r*) for 2,4-DCP on β-CDP and γ-CDP. The values of *n_F* > 1 reflected the favorable sorption. Freundlich model suggests that sorption energy exponentially decreases with surface coverage of the sorbent.

Sorption enthalpy

Following van't Hoff equilibrium equation [30], i.e.,

$$\ln C_e = -\frac{\Delta H}{RT} + \ln K, \quad (7)$$

where, *C_e* is the equilibrium concentration of adsorbate, *T* is the sorption temperature, ΔH is the sorption enthalpy, *R* and *K* are constants. The plotting of $\ln C_e$ versus $1/T$ gave a straight line with slope equal to $-\Delta H/R$. The calculated values of ΔH are listed in Table 4.

The Gibbs free energy change (ΔG_i , kJ/mol) of sorption can be calculated using the following equation [31]:

$$\Delta G_i = -nRT_i \quad (8)$$

where, *T* is the sorption temperature (K), *R* is gas constant (J/mol/K), *n* is the Freundlich constant.

The entropy change (ΔS_i , J/mol/K) associated with sorption can be calculated from the Gibbs–Helmholtz equation [31].

$$\Delta S = (\Delta H - \Delta G_i)/T_i \quad (9)$$

Free energy changes and entropy changes of sorption calculated at different temperature are given in Table 4.

The negative ΔG_i values confirm the spontaneous nature and feasibility of the sorption process. The positive values of ΔH indicate that sorption process is endothermic. The apparent endothermic nature of the sorption may contradict the well known criteria of the spontaneity of the adsorption. In fact, the sorption enthalpies adsorbed do not enforce the reversible reaction but are consumed in the dehydration of CD cavities. This is supported by the positive value of ΔS_i that is related to the increased randomness of the system due to the liberation of water from CD cavities during the sorption [32]. The sorption enthalpy is higher at low *C₀*, probably because the sites with higher interaction energies are filled first [33]. However, with the concentration of 2,4-DCP increases, lower sorption enthalpy of CDPs is probably because the concentration difference of sorbate may serve as motive power of sorption. The sorption is more favorable at higher sorbate for both γ-CDP and β-CDP; this was in agreement with the following results of Fig. 4. As can be also seen in Table 4, the sorption enthalpies are always lower for γ-CDP than for β-CDP; this was because the binding constant of 2,4-DCP on γ-CD (the main structural unit of γ-CDP) was higher than on β-CD (the main structural unit of β-CDP).

Binding constant

In order to evaluate the inclusion ability of the β-CD and γ-CD, the binding constant was tested. The evaluation of binding constants by spectrophotometric method relies on analytical differences between the free 2,4-DCP and the inclusion complex. Changes in the absorption intensity of 2,4-DCP at 286 nm were monitored as a function of β-CD or γ-CD to measure the binding constant. The binding

Table 4 Estimated thermodynamic parameters of 2,4-DCP sorption on β-CDP and γ-CDP

Sorbent	<i>C₀</i> (mmol/L)	ΔH (kJ/mol)	$-\Delta G_i$ (kJ/mol)					ΔS_i (J/mol/K)				
			283 (K)	288 (K)	293 (K)	298 (K)	303 (K)	283 (K)	288 (K)	293 (K)	298 (K)	303 (K)
β-CDP	0.3	10.3 ± 1.12	2.99	2.83	3.13	2.40	2.66	46.87	45.50	45.74	42.50	42.67
	0.5	6.76 ± 1.21						34.47	33.31	33.76	30.73	31.09
	0.7	1.65 ± 0.42						16.41	15.57	16.32	13.58	14.22
γ-CDP	0.3	8.36 ± 1.02	3.73	2.30	2.50	2.79	2.58	42.75	37.04	37.08	37.43	36.12
	0.5	5.28 ± 0.44						31.85	26.33	26.56	27.08	25.95
	0.7	1.01 ± 0.11						16.77	11.51	11.98	12.75	11.86

constant determined for 2,4-DCP with β -CD and γ -CD was 102 and 171 L/mol, respectively. The values of binding constant revealed that the inclusion effect of 2,4-DCP on γ -CD was stronger than on β -CD.

Influence of the initial 2,4-DCP concentration

The influence of various initial 2,4-DCP concentration on sorption was investigated (Fig. 4). The quantity of CDP was kept constant while the concentration of 2,4-DCP varied between 0.3 and 0.7 mmol/L. The results showed an increase in the sorption capacity with the initial concentration of 2,4-DCP increase. At the same conditions, the sorption capacity of β -CDP was higher than that of γ -CDP. This different sorption capability may be explained from the BET specific surface area, the content of CD units in the CDPs, and inclusion effect between the sorbent and the sorbate. The BET specific surface area of β -CDP is larger than the corresponding γ -CDP (Table 1), so the sorption capacity of 2,4-DCP on β -CDP is higher than that on γ -CDP. However, the BET specific surface area does not play an important role. In previous works [33, 34], it was reported that the sorption mechanism of CDP was complex, probably simultaneously dominated by surface sorption (physical adsorption, hydrogen bonding) and diffusion into the polymer network, chemisorptions via the formation of an inclusion complex due to the presence of the CD sites. CD molecules have a remarkable capacity to form inclusion complexes, and the CDPs retain the inclusion properties of CD molecules. So the inclusion capacity is influenced by the content and the variety of CD units in the CDPs. The molar content of CD units in the β -CDP was larger than that in the γ -CDP (Table 1), so the sorption capacity of 2,4-DCP on β -CDP is higher than that on

γ -CDP even though the value of binding constant of 2,4-DCP on γ -CD was stronger than on β -CD. In one word, the main reason that causes the differences in sorption capacity between β -CDP and γ -CDP are the differences of the molar content of CD units in the CDPs.

Effect of pH

To evaluate the influence of the pH on the sorption of the 2,4-DCP, tests were carried out in buffer solutions with 0.3 mmol/L 2,4-DCP solution at 288 K. A series of working solutions with different pH values were prepared from stored solution. pH of these working solutions were adjusted by using 1 mol/L NaOH and 1 mol/L HCl from the range of pH 1–10. The values of the sorption capacity for 2,4-DCP on β -CDP and γ -CDP were almost no change until pH 7 (figure omitted). However, the sorption capacities decreased rapidly at pH > 7 for the two sorbents, which maybe due to ionization and hydrophilic increase of 2,4-DCP. It is well known that the hydrophilic guest molecules are unfavorable to complexing with cyclodextrins. Thus all the studies were performed at pH 7.

Recovery of 2,4-DCP and recycle use of CDPs

To recover the adsorbed 2,4-DCP and to reuse the CDPs, 0.3 g β -CDP or γ -CDP, with previously adsorbed equilibrium 2,4-DCP, was shaken for 2 h at 40 °C with 10 mL absolute alcohol. The recovery ratio was defined as the ratio of the 2,4-DCP amount in alcohol to the amount previously adsorbed on β -CDP or γ -CDP. The recovery ratio (first time) of 2,4-DCP on γ -CDP was greater than 75%, however, which even reached 90% on β -CDP. It was observed that the sorption capacity was not changed after this treatment. Even after 5 times regeneration tests were performed, the CDPs have almost the same sorption ability in contrast to original CDPs. This suggested that recyclable values of the CDPs were more advantageous than activated carbon in practical use. Compared with some recent data in the literatures [33–35], the result also revealed the potential of CDPs to be effective sorbents for removing pollutants in the water.

Conclusions

Results of sorption showed that both β -CDP and γ -CDP exhibited good sorption behavior and acceptable sorption time toward 2,4-DCP. Sorption kinetics of β -CDP and γ -CDP for 2,4-DCP followed the Ho and McKay model. Equilibrium isotherm data were consistent with the Freundlich equation for β -CDP and γ -CDP. Rate limiting step in the process of sorption was film diffusion.

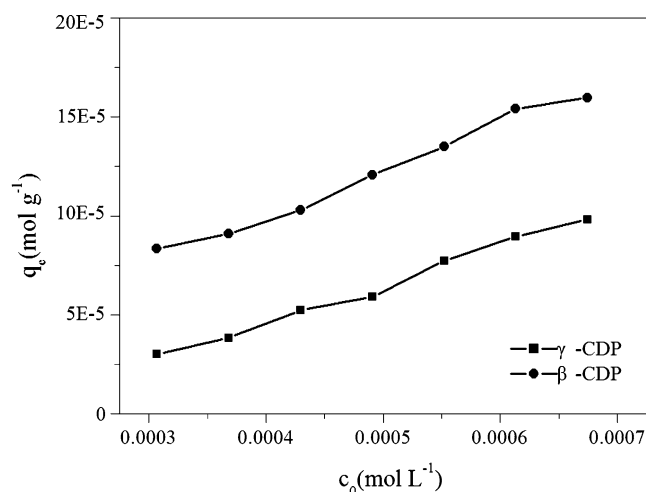


Fig. 4 Effect of initial concentration on 2,4-DCP sorption (conditions: sorbent: 0.1 g; volume: 50 mL; temperature: 288 K)

Furthermore, the regeneration of β -CDP and γ -CDP was so easy that CDPs could be used as a kind of recyclable sorbents. However, taken into account the factors of cost, sorption capacity and regeneration capacity, the β -CDP will be more suitable as a sorbent than γ -CDP. In order to verify whether the observed behavior is generally accepted, some additional work is in progress in subsequent studies.

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