Adsorption of rutin with a novel β-cyclodextrin polymer adsorbent: Thermodynamic and kinetic study

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ABSTRACT

The adsorption properties toward rutin of a cyclodextrin polymer adsorbent CroCD-TuC 3 have been studied. The adsorption capacity is reduced as temperature and pH of solution rises, but increases with the increase of solvent polarity. Compared with Sephadex™ G-15 dextran gel beads, CroCD-TuC 3 shows dramatically higher isosteric enthalpy due to a significant contribution of rutin/β-cyclodextrin inclusion complex formation in CroCD-TuC 3 skeleton. A highlight in our study is that the pore diffusion model has been employed to describe the mass transfer inside the adsorbent pores. It reveals that the diffusion inside the pores is the rate-restricting step in the whole adsorption process. The effective pore diffusivity of rutin in CroCD-TuC 3 calculated is much lower than the diffusivity in diluted solution. The pore diffusion model is an available tool to investigate the profile of mass transfer inside the pores, and provides an effective method to describe adsorption kinetics.

1. Introduction

Cyclodextrin polymers (CDPs) are usually prepared by reaction of cyclodextrins (CDs) with crosslinking reagents such as epichlorohydrin, bis-epoxide and diisocyanate (Mocanu, Vizitiu, & Carpov, 2001; Zhao & Yao, 2012). Unlike other crosslinked polysaccharides such as dextran, agarose, and starch, CDPs can form inclusion complexes with many organic compounds in solution thanks to the dramatic property derived from CDs' hydrophobic hollow cavity (Connors, 1997; Harada, 2001; Li & Purdy, 1992). As a result, CDPs are widely used as adsorbents, particularly in the treatment of waste water (Yamasaki, Makihata, & Fukunaga, 2006), extraction and chromatographic separations (Crini & Morcellet, 2002).

A great many reports have concerned the thermodynamic properties of CDPs. The adsorption isotherms of many molecules adsorbed on CDPs have been measured, including amino acids (Tang et al., 2006), dibenzofuran derivatives (Romo, Penas, & Isasi, 2004), phenols (García-Zubiri, González-Gaitano, & Isasi, 2007; García-Zubiri, González-Gaitano, & Isasi, 2009; Romo, Penas, Isasi,

García-Zubiri, & González-Gaitano, 2008), dyes (Crini, 2008; Crini, Peindy, Gimbert, & Robert, 2007; Yilmaz, Memon, & Yilmaz, 2010) and drugs (Gazpio et al., 2008). They find that the adsorption isotherms generally follow the Freundlich or Langmuir model for most adsorbates, but the line-types are discrepant from different researches due to the diverse adsorbate–adsorbent interactions. Some researchers pay much attention to the adsorption mechanisms with the aid of thermodynamic or spectroscopic methods. García-Zubiri et al. (2007) studied several crosslinked CDPs and sucrose polymers by an isosteric heat approach, and the results showed the evidence that the CD moieties in CDPs were responsible for the striking differences with those of sucrose with a very similar overall chemical composition. Yang, Zhang, Tan, and Rahman (2009) compared polystyrene (PS) resin with oligo-β-cyclodextrin coupled matrix (PS-CDP) in puerarin sorption mechanism through isosteric heat and NMR spectroscopy study, concluding that the higher adsorption capacity of PS-CDP compared with PS was attributed to the complexation between puerarin and β-CD.

Kinetics study is another vital task for CDP adsorbents. There have been large quantities of papers giving the adsorption rate curve of CDPs, *i.e.*, the plot of adsorption capacity *vs.* time (Yamasaki et al., 2006; Zhao, Zhao, Zhu, Huang, & Hu, 2009; Zhao et al., 2009). Unfortunately, these studies are not detailed enough to reflect the intraparticle mass transfer characteristics. Several researchers have made effort on this field. Crini et al. provide good examples of using several kinetic models to investigate the mechanism of cyclodextrin/carboxymethylcellulose (CD/CMC) copolymer adsorbing the dyes C.I. Basic Green 4 (Crini et al., 2007), C.I. Basic Blue 3, Basic

Nomenclature

C	rutin concentration in bulk fluid phase $(mg\,ml^{-1})$
C_0	initial concentration of rutin solution $(mg\,ml^{-1})$
C_{eq}	equilibrium concentration of rutin $(mg\,ml^{-1})$
C_P	rutin concentration in the pore $(mg\,ml^{-1})$
D_{AB}	diffusion coefficient of rutin in free aqueous solution $(m^2\,s^{-1})$
D_e	effective pore diffusivity $(m^2\,s^{-1})$
D_P	diffusivity in particle pores $(m^2\,s^{-1})$
E_T	polarity parameter
$f(\theta)$	distribution function of surface energy
g	acceleration of gravity $(m\,s^{-2})$
K	stability constant of CD-rutin 1:1 complex $(L\,mol^{-1})$
K'	integral constant $(mg\,ml^{-1})$
K_L	Langmuir adsorption equilibrium constant $(ml\,mg^{-1})$
k_f	film mass transfer coefficient $(m\,s^{-1})$
Q	adsorption capacity of rutin $(mg\,g^{-1})$
Q_{eq}	equilibrium adsorption capacity $(mg\,g^{-1})$
Q_{max}	maximum adsorption capacity for Langmuir adsorption model $(mg\,g^{-1})$
Q_P	adsorption amount in the pore $(mg\,g^{-1})$
R	gas constant $(J\,mol^{-1}\,K^{-1})$
R_P	particle radius (m)
T	absolute temperature (K)
V_0	initial volume of rutin solution (ml)
V_{ad}	adsorbent volume (ml)
W	mass of adsorbent (g)

Greek letters

α	surface heterogeneity parameter
ΔH	isosteric enthalpy $(kJ\,mol^{-1})$
ΔH°	isosteric enthalpy at zero loading $(kJ\,mol^{-1})$
δ	solubility parameter
δH	variation of the isosteric enthalpy $(kJ\,mol^{-1})$
ε°	solvent strength parameter
ε_P	particle porosity
γ	pattern parameter characterizing the pattern of surface heterogeneity
μ	liquid viscosity (Pa s)
θ	fractional surface coverage
ρ_l	liquid density $(kg\,m^{-3})$
ρ_P	particle density $(kg\,m^{-3})$

Violet 3 and Basic Violet 10 (Crini, 2008). They found these adsorption process probably simultaneously dominated by surface adsorption and diffusion into the polymer network, and they all followed a pseudo-second-order model, suggesting the rate-limiting step may be chemisorption.

Here we report a novel CDP-based adsorbent named CroCD-TuC 3 potential for the separation and purification of flavonoid compounds. The most dramatic feature of this adsorbent is that it is designed specially for expanded bed adsorption (EBA), as shown in our previous work (Zhao, Lin, Wang, & Yao, 2010). Thanks to the functional β-CD moieties within its skeleton, CroCD-TuC 3 is a promising candidate for the recovery of flavonoids. Although several researches have shown that CDs form inclusion complexes with flavonoids (Ding, Chao, Zhang, Shuang, & Pan, 2003; Schwingel et al., 2008; Shuang, Pan, Guo, Cai, & Liu, 1997; Sri, Kondaiah, Ratna, & Annapurna, 2007; Wang et al., 2009), the interaction between these compounds with CDP adsorbents has been rarely reported yet. In this work, we characterize the adsorption properties of CroCD-TuC 3 toward rutin. Rutin is a flavonol glycoside existing in a variety of plants such as black tea, *Sophora japonica* L., *Ginkgo biloba* L. and many fruits and vegetables. It is a bio-antioxidant to scavenge superoxide radicals in the organism (Cruz et al., 1998). Also it is commonly used as an analytical standard in quantitative analysis of flavonoids, thus it can be regarded as a model molecule of flavonoids. We measure the isotherms and isosteres, and expound the sorption mechanism with the aid of isosteric enthalpy analysis. Sephadex^{TM} G-15 dextran gel is introduced as a comparison since both adsorbents are carbohydrate polymers mainly composed of glucose units and crosslinked with the same reagent epichlorohydrin. Finally, the pore diffusion model is employed at the aim of describing the adsorption kinetics and the mass transfer inside the CDP adsorbent pores.

2. Theoretical descriptions

2.1. Isosteric enthalpy and surface heterogeneity

Isosteric enthalpy shows the relationship between the adsorbate equilibrium concentration and the temperature for a constant equilibrium adsorption. It is calculated with the Clausius–Clapeyron equation (Li, Jiao, Xu, Shi, & He, 2004):

$$\ln C_{eq} = \frac{\Delta H}{RT} + \ln K' \tag{1}$$

where ΔH is isosteric enthalpy, T is absolute temperature, R is gas constant, and K' is integral constant. The isosteric enthalpy can be conveniently obtained from the plot of $\ln C_{eq}$ vs. $1/T$. It varies with the fractional surface coverage θ (it approximatively equals to the adsorbate loading fraction, and $\theta = 1$ means monolayer coverage), also is influenced by the pattern of surface heterogeneity of the adsorbents, which can be described by Do's model (Do & Do, 1997):

$$\Delta H(\theta) = \Delta H^\circ(\theta) - \delta H \cdot f(\theta) \tag{2}$$

where ΔH° is isosteric enthalpy at zero loading, δH represents the variation of the isosteric enthalpy with the loading fraction, and $f(\theta)$ is a distribution function of surface energy used to describe the heterogeneity pattern. It is a function of γ and θ as:

$$f(\theta) = \frac{\Delta H^\circ - \Delta H}{\delta H} = \frac{\gamma\theta}{1 + (\gamma - 1)\theta} \tag{3}$$

where γ in Eq. (3) is defined as pattern parameter characterizing the pattern of surface heterogeneity. By introducing the surface heterogeneity parameter α

$$\alpha = \frac{\delta H}{\Delta H^\circ} \tag{4}$$

Eq. (2) can be rewritten as

$$\Delta H = \Delta H^\circ \left[1 - \frac{\alpha\gamma\theta}{1 + (\gamma - 1)\theta} \right] \tag{5}$$

Higher α value means a more heterogeneity of the surface. The parameters α, γ and ΔH° are obtained from the non-linear fitting with Eq. (5). The heterogeneity pattern corresponding to different γ values is described as: If $\gamma = 1$, the surface energy heterogeneity is a linear pattern; when $\gamma \gg 1$, there is a sharp decay in the energy pattern at low loading, and when $\gamma \ll 1$, there is a slow decay in the energy at low loading but the pattern exhibits a rapid decay when the loading approaches monolayer coverage ($\theta = 1$). If the γ value of the adsorbent is smaller, the fraction of the high-energy adsorption site on the adsorbent surface is greater, according to Do and Do (1997).

2.2. Pore diffusion model

Pore diffusion model deals with the intraparticle mass transfer characteristics. It can be described as follows (Jr Weaver & Carta, 1996; Zhang & Sun, 2002):

$$\varepsilon_P \frac{\partial C_P}{\partial t} + \frac{\partial Q_P}{\partial t} = \frac{D_e}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_P}{\partial r} \right) \tag{6}$$

$$C_P(r, t)\big|_{t=0} = 0 \tag{7}$$

$$\frac{\partial C_P}{\partial r}\bigg|_{r=0} = 0 \tag{8}$$

$$\frac{\partial C_P}{\partial r}\bigg|_{r=R_P} = \frac{k_f}{D_e}(C - C_P|_{r=R_P}) \tag{9}$$

where C_P and C represent rutin concentration in the pore and in the bulk solution, ε_P is the particle porosity, R_P is particle radius, k_f is the film mass transfer coefficient, D_e is the effective pore diffusivity, and Q_P is the adsorption amount in the pore that can be correlated with the adsorption isotherms. It is assumed in this model that intraparticle mass transfer occurs by diffusion in inner pores with a driving force expressed in terms of the pore fluid concentration gradient (Jr Weaver & Carta, 1996). The change of bulk concentration in batch stirred tank is described as:

$$\frac{dC}{dt} = -\frac{3k_f V_{ad}}{R_P V_0}(C - C_P|_{r=R_P}) \tag{10}$$

with the initial condition of

$$C(t)|_{t=0} = C_0 \tag{11}$$

The film mass transfer coefficient k_f in stirred-tank experiments can be estimated as

$$k_f = \frac{D_{AB}}{R_P} + 0.31 \left(\frac{\mu}{\rho_l D_{AB}}\right)^{-2/3} \left[\frac{(\rho_P - \rho_l)\mu g}{\rho_l^2}\right]^{1/3} \tag{12}$$

where V_{ad} and V_0 represent the volume of adsorbent and solution, μ is liquid viscosity, ρ_l and ρ_P represent the density of liquid and particles, and D_{AB} is the diffusion coefficient of solute in free aqueous solution.

Eq. (6) is a non-linear parabolic partial differential equation since the adsorption isotherm is usually non-linear type. This equation is usually solved numerically with orthogonal collocation method (Villadsen & Stewart, 1967).

3. Experimental

3.1. Materials

Sephadex™ G-15 dextran gel beads were provided by Amersham Biosciences Co. (Uppsala, Sweden). The adsorbent CroCD-TuC 3 was prepared as described in our previous work (Zhao et al., 2010). The adsorbent has the porosity (ε_P) of 0.73 and mean pore diameter of 70 nm. Rutin trihydrate ($\geq$97%) was purchased from Alfa-Aesar, A Johnson Matthey Co. (Heysham, UK). Dimethyl sulfoxide (DMSO, $\geq$99%) was obtained from Hangzhou SHUANGLIN Chemical Reagent Industry Co., Ltd. (Hangzhou, China). Deionized water was supplied by Hangzhou WAHAHA Group Co., Ltd. (Hangzhou, China). All other chemicals used were of analytical reagent grade or higher quality, and were used directly except where specified.

3.2. Measurement of adsorption isotherms

In our experiments, rutin trihydrate was selected as a target model molecule. Due to its low solubility, it was dissolved in the minimum quantity of DMSO and diluted to the desired volume with deionized water according to Li and Chase (2009) (the concentration of DMSO is 0.02 g ml^{-1} for all aqueous solutions). However, all the concentrations were kept lower than 0.5 mg ml^{-1} to prevent crystallization.

In order to measure the adsorption isotherms for rutin, 0.8 g wet CroCD-TuC 3 adsorbent were added to 25 ml rutin solutions, and kept in a shaking incubator (150 rpm) for 3 h at set temperature. After equilibrium, the adsorbent was separated by centrifugation (14,500 rpm, 5 min), and the supernatant was analyzed by a spectrophotometer (Ultrospec 3300 pro, Amersham Biosciences) at 355 nm. The adsorption capacity Q (mg g^{-1}) of rutin to the adsorbent was calculated as

$$Q = \frac{(C_0 - C)V_0}{W} \tag{13}$$

where C_0 represented the initial concentration of rutin solution, V_0 (ml) was the initial volume of rutin solution and W (g) was the mass of adsorbent. The adsorption isotherms of rutin adsorbed on Sephadex™ G-15 were measured in the same way.

The adsorption isotherm followed the Langmuir adsorption model:

$$Q = \frac{Q_{max} K_L C_{eq}}{1 + K_L C_{eq}} \tag{14}$$

where K_L represented Langmuir adsorption equilibrium constant, C_{eq} was the equilibrium concentration of rutin, and Q_{max} meant the maximum adsorption capacity. The analysis of the data for isotherms was performed by means of a nonlinear fitting procedure using Origin 7.5.

3.3. Measurement of adsorption kinetics

In adsorption kinetic experiments, 5.0 g hydrated adsorbent CroCD-TuC 3 was mixed with 150 ml rutin aqueous solution in a conical flask. The mixtures were continuously stirred at 200 rpm in the shaking incubator at set temperature. 0.5 ml aliquots was removed every 20 s in the first 2 min and then every 1 min later. The aliquots were immediately centrifuged at 14,500 rpm for 30 s, and the supernatant was diluted and analyzed by a spectrophotometer (Ultrospec 3300 pro, Amersham Biosciences) at 355 nm. The concentration of rutin remaining in supernatant C (mg ml^{-1}) was calculated from Eq. (13).

The kinetics data were fitted by pore diffusion model Eqs. (6)–(9). The diffusion coefficient D_{AB} of rutin in free aqueous solution was estimated as 3.73×10^{-10} m^2 s^{-1} according to Hayduk and Laudie (1974) method. This value was a little higher than that of another reported flavonoid compound naringin (3.09×10^{-10} m^2 s^{-1}) (Singh, Gupta, & Jain, 2008). The pore diffusion model was solved numerically using the program MATLAB 6.5.

4. Results and discussion

4.1. Isosteric heat study and mechanism of rutin adsorbing on CroCD-TuC 3

The adsorption isotherms of rutin adsorbed on CroCD-TuC 3 at a series of set temperatures are measured and fitted with Eq. (14). The correlation coefficient (R^2) is above 0.99, and the results are shown in Fig. 1. Due to low solubility of rutin in aqueous solution, all measured concentrations are approximate within a linear region and thus the equilibrium concentration is not high enough to obtain the accurate values of Q_{max}. However, the difference of adsorption capacity between the two adsorbents is striking enough. The equilibrium adsorption capacity of rutin adsorbed on
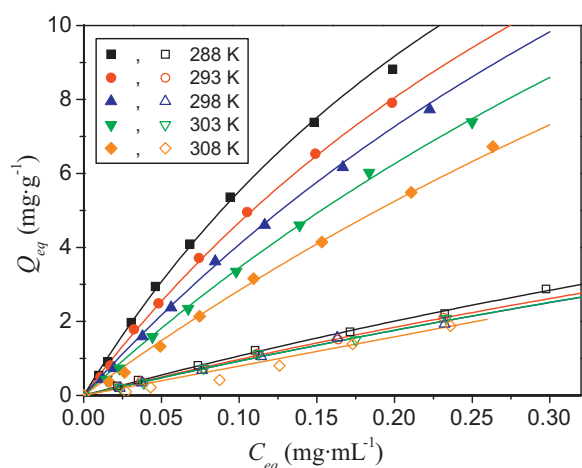
Fig. 1. Adsorption isotherms of rutin adsorbing on adsorbent CroCD-TuC 3 (solid symbols) and Sephadex™ G-15 (open symbols) at different temperatures.

Table 1
The regression results of adsorption isosteres of rutin adsorbed on CroCD-TuC 3 and Sephadex™ G-15.

Q_{eq} (mg g^{-1})	CroCD-TuC 3		Sephadex™ G-15	
	$-\Delta H$ (kJ mol^{-1})	R^2	$-\Delta H$ (kJ mol^{-1})	R^2
0.4	29.15	0.9984	10.72	0.8721
0.8	29.02	0.9983	10.00	0.8886
1.2	28.89	0.9982	9.27	0.9039
1.6	28.75	0.9980	8.51	0.9151
2.0	28.61	0.9979	7.73	0.9177
2.4	28.46	0.9977	6.92	0.9026
2.8	28.31	0.9976	6.10	0.8566
3.2	28.16	0.9974	5.25	0.7612
3.6	28.00	0.9971	–	–
4.0	27.83	0.9969	–	–
5.0	27.40	0.9962	–	–
6.0	26.93	0.9954	–	–
7.0	26.42	0.9943	–	–

CroCD-TuC 3 is higher than that on Sephadex™ G-15 within the measured concentrations. Also it is gradually reduced as temperature rises, revealing an exothermic adsorption process for both two adsorbents.

The adsorption isosteres of the two adsorbents are shown in Fig. 2. The difference comes from the great discrepancy in their structure, although both of them are glucose-based polymers crosslinked by epichlorohydrin. In CroCD-TuC 3 skeleton, the glucoses are linked by α-1,4-glycosidic bond and form regular heptatomic rings; while the glucan skeleton of Sephadex™ G-15 includes α-1,6-, α-1,4-, and α-1,3-glycosidic bonds and the polymer chain is somewhat similar to starch. This discrepancy can be revealed by the values of ΔH (listed in Table 1) fitted by Clausius–Clapeyron equation (1).

As shown in Table 1, ΔH value of CroCD-TuC 3 and Sephadex™ G-15 adsorbing rutin shows decreasing tendency as the increase of adsorption capacity. However, compared with Sephadex™ G-15, ΔH value of CroCD-TuC 3 is much higher, indicating the process of CroCD-TuC 3 adsorbing rutin is more exothermic. Based on the fitting results, we consider the adsorption of rutin on CroCD-TuC 3 obeying the characteristic of chemical adsorption. According to the literatures (Calabrò et al., 2005; Ding et al., 2003; Shuang et al., 1997), rutin forms inclusion complex with β-CD preferring 1:1 stoichiometry and the formation constant is 265 L mol^{-1} at pH 7.5 and 20 °C. The $\Delta H°$ value calculated is −29.31 kJ mol^{-1} and

−11.42 kJ mol^{-1} for CroCD-TuC 3 and Sephadex™ G-15 respectively, and the difference of them is −17.89 kJ mol^{-1}, close to the reported formation enthalpy (−22.2 ± 0.8 kJ mol^{-1}) of rutin/β-CD inclusion complex. Therefore, the formation of rutin/β-CD inclusion complex makes a great contribution to the increase of $\Delta H°$ of rutin adsorbing on CroCD-TuC 3 and thus the increase of adsorption capacity.

The α and γ values regressed with Eq. (5) reflect adsorbent surface heterogeneity. The α and γ values for CroCD-TuC 3 are 3.57 and 0.11 respectively. They are both lower than that of Sephadex™ G-15 (the corresponding values are 6.64 and 0.40 respectively). The lower γ value of CroCD-TuC 3 means there is more fraction of the high-energy adsorption site on its surface than Sephadex™ G-15 according to Do and Do (1997), which is attributed to the CD's inclusion effect. While the higher α value of Sephadex™ G-15 is probably due to more glycosidic-bond types in its glucan skeleton leading to a more heterogeneity of its surface. However, it should be pointed out that all the results above are not quantitative enough, since Do's model could not describe the fine structure of adsorbent surface.

4.2. The adsorption isotherms of rutin on CroCD-TuC 3

4.2.1. Adsorption isotherms of different pH

Rutin presents a polyphenolic structure that can be ionized in alkaline solution, indicating that pH is a significant parameter affecting its adsorption capacity. Fig. 3 gives a comparison of adsorption isotherms of rutin adsorbing on CroCD-TuC 3 in
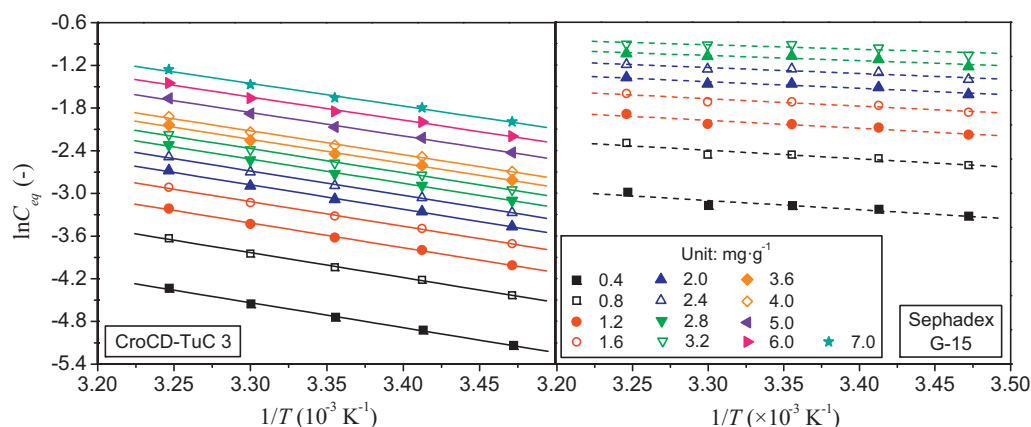

Fig. 2. Adsorption isosteres of rutin adsorbing on CroCD-TuC 3 (solid line) and Sephadex™ G-15 (dashed line) at different equilibrium adsorption capacities.
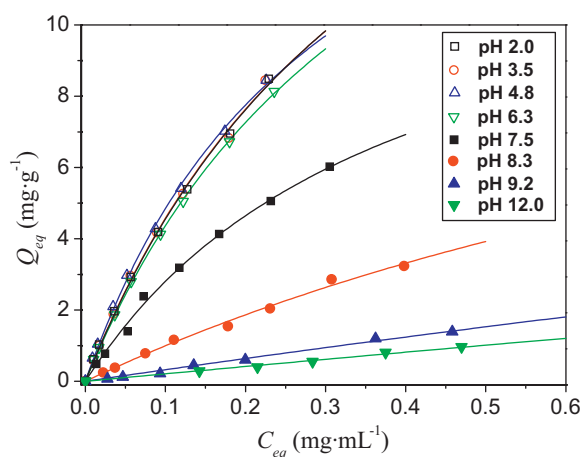
Fig. 3. Comparison of adsorption isotherms of rutin adsorbing on CroCD-TuC 3 in HCl, phosphate buffer, carbonate buffer or NaOH solutions of different pH by Langmuir model.

aqueous solution of different pHs. The isotherms show insignificant discriminations in acidic solutions, probably because rutin keeps the unchanged pattern of neutral molecules in this case. But great discriminations are found when pH > 7 due to the difference of ionization degree in alkaline solutions. As described in Fig. 3, the adsorption capacity decreases rapidly with pH increase. One probable reason is that the ionized rutin molecule shows more hydrophilicity so as not to match the hydrophobic CD cavity very well. Another reason involves the remarkable increase of rutin solubility in the aqueous phase according to the rule "like-dissolve-like" as its gradual ionization, and it is prone to dissolving in the polar liquid phase rather than the hydrophobic CD phase (Guzzo et al., 2006; Tommasini, Calabrò, Raneri, Ficarra, & Ficarra, 2004; Tommasini et al., 2004; Wang et al., 2009). That is why rutin adsorption capacity is much lower in alkaline than that in acidic solutions. Because of this property, weak alkaline solutions may be used as the eluent or regenerating reagent in chromatographic process. However, strong base such as sodium hydroxide is not recommended because of the severe oxidation happens to the polyphenolic structure of rutin found in our experiments.

4.2.2. Adsorption isotherms in organic solution

The adsorption of rutin on CroCD-TuC 3 in organic-aqueous solutions has been determined. Fig. 4(a) is a comparison of isotherms in various organic-aqueous solutions with a fixed concentration of 0.1 g ml^{-1}. It is found that within the solvents investigated, the adsorption capacities in organic solutions are lower than that in water (containing 0.02 g ml^{-1} DMSO). The results of K_L and Q_{max} fitted by Langmuir model are listed in Table 2. Three polarity-related parameters of solvents, solvent strength parameter ($\varepsilon°$), polarity parameter (E_T) and solubility parameter (δ), are also included in Table 2 for comparison (Rohrschneider, 1973). The K_L values generally change in accordance with the varying tendency of the three parameters for most solvents, indicating the adsorption of rutin on CroCD-TuC 3 is promoted by hydrophobic interactions between CD cavity and rutin. The hydrophobic solvent is prone to compete CD cavity with rutin, resulting in a decrease of the cavities occupied by rutin. For the same reason, the adsorption capacity will decrease with the increase of alcohol concentration (confirmed by Fig. 4(b)). The adsorption capacity of rutin in water is nearly 10 times higher than that in 0.3 g ml^{-1} ethanol solution at the same equilibrium concentration. That means increasing the solvent hydrophobicity can improve their elution ability, which is quite similar to the normal phase chromatographic process. However, DMSO is an exception to this general rule that it shows abnormal
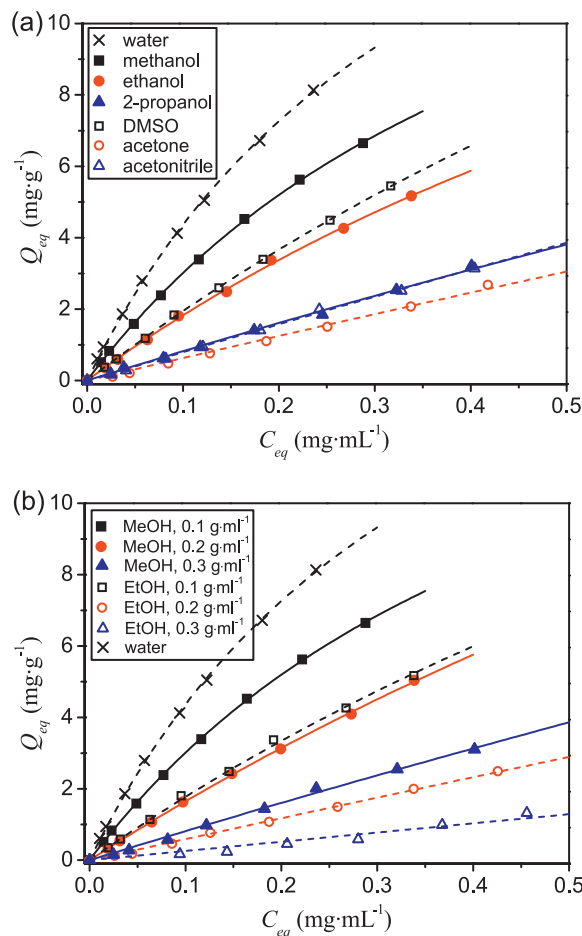

Fig. 4. Comparison of adsorption isotherms of rutin adsorbing on CroCD-TuC 3: (a) in different organic-aqueous solutions with concentration of 0.10 g ml^{-1} for all; (b) in alcohol aqueous solution. MeOH and EtOH represent methanol and ethanol respectively.

K_L close to that of ethanol. It suggests that the adsorption of rutin in DMSO solution may follow other mechanisms not only depends on the hydrophobicity of CD cavity.

4.3. Adsorption kinetics

The adsorption kinetics data are analyzed by the pore diffusion model Eqs. (6)–(9), and solved with orthogonal collocation method. The results are described in Fig. 5. Some parameters obtained by solving Eqs. (6)–(9) are shown in Table 3. As described in Fig. 5, it shows that the adsorption of rutin onto the adsorbent CroCD-TuC 3 is very fast during the initial process of adsorption but becomes a bit slower later. It reaches to equilibrium within 30 min, and more than 90% of the adsorption capacity is achieved within 10 min after the adsorption starts. This adsorption rate is much faster than that of Amberlite XAD7HP resin in rutin aqueous solution reported

Table 2
Some properties of the organic solvents used (Rohrschneider, 1973).

Solvent	$\varepsilon°$	E_T	δ	K_L (ml mg^{-1})	Q_{max} (mg g^{-1})
Water	–	63.1	23.53	1.579	30.54
Methanol	0.95	55.5	14.50	1.205	26.53
Ethanol	0.88	51.9	12.78	0.974	21.32
2-Propanol	0.80	48.6	11.44	0.777	13.00
Acetonitrile	0.65	46.0	12.11	0.748	13.88
Acetone	0.56	42.2	9.62	0.651	12.29
DMSO	0.60	45.0	–	1.078	22.25

Table 3
Parameters for pore diffusion model and the calculation results by numerical method.

C_0 (mg ml^{-1})	D_{AB} ($\times 10^{-10}$ m^2 s^{-1})	k_f ($\times 10^{-5}$ m s^{-1})	D_P [a] ($\times 10^{-11}$ m^2 s^{-1})	D_e ($\times 10^{-11}$ m^2 s^{-1})
0.05	4.0	3.52	8.10	5.94
0.10	4.0	3.52	5.21	3.81
0.20	4.0	3.52	5.08	3.74
0.30	4.0	3.52	5.29	3.88

[a] D_P is the diffusivity of rutin in particle pores given by the relation of $D_e = \varepsilon_P D_P$.
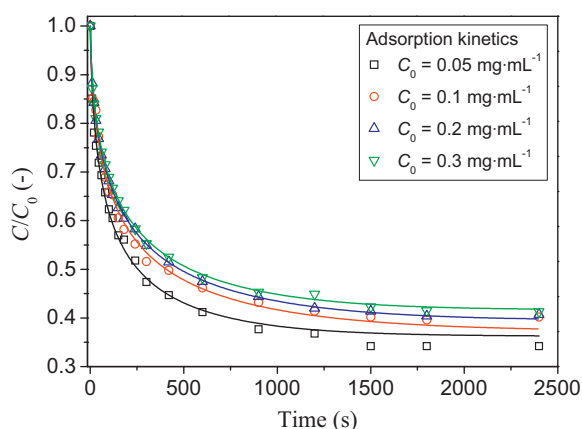
Fig. 5. Adsorption kinetics of rutin on CroCD-TuC 3 with different initial concentrations of rutin. The lines are fitted by pore diffusion model Eqs. (6)–(9) with numerical method.

by Li and Chase (2009). The resin Amberlite XAD7HP they used has the mean pore diameter of 9 nm, whereas the pore diameter of CroCD-TuC 3 (70 nm) is several times larger. It means that the inner diffusion resistance in CroCD-TuC 3 is reduced compared with Amberlite XAD7HP. Therefore, it is more easily for rutin molecule passing through the inner pores of the adsorbent CroCD-TuC 3. However, the D_e value of rutin calculated with this model (3.8×10^{-11} m^2 s^{-1}, listed in Table 3) is much lower than D_{AB} (3.73×10^{-10} m^2 s^{-1}), indicating the inner mass transfer is the rate-restricting step in the whole adsorption process.

It is also shown in Fig. 5 that the increase of rutin concentration hardly changes the time required for adsorption equilibrium, but it does change D_P and D_e according to Table 3, which generally decreases as the increase of rutin concentration. However, D_P and D_e keep almost steady when rutin concentration is above 0.1 mg ml^{-1}. As reported by Singh et al. (2008), D_P and D_e of the flavonoid naringin adsorbed on polymeric non-ionic macroporus resin are 1.032×10^{-10} m^2 s^{-1} and 3.92×10^{-11} m^2 s^{-1} respectively, which are somewhat close to the values we have obtained but a little higher. Therefore, we propose pore diffusion model a significant method to measure the mass transfer in the inner pores of adsorbents. It may provide some beneficial information on the inner pore structure.

5. Conclusions

The flavonoid molecule rutin is adsorbed by a novel CDP adsorbent CroCD-TuC 3. The adsorption isotherms follow the Langmuir adsorption equation, and its adsorption capacity is gradually reduced as temperature and pH of solution rises, but increases with the increase of solvent polarity. The comparisons of CroCD-TuC 3 with Sephadex™ G-15 beads on isosteric enthalpy reveal that the formation of rutin/β-CD inclusion complex in CroCD-TuC 3 skeleton shows significant contribution to the adsorption. The adsorption kinetics data are fitted by the pore diffusion model. It shows that the effective pore diffusivity of rutin calculated with this model (3.8×10^{-11} m^2 s^{-1}) is much lower than its diffusivity

in diluted solution, indicating the diffusion inside the pores is the rate-restricting step in the whole adsorption process.

Isosteric enthalpy determination used in our work is a powerful tool in thermodynamics to expound the adsorption mechanism, and the surface heterogeneity analysis provides an auxiliary method to preliminarily reveal the surface structure of adsorbents. Furthermore, we have obtained the diffusion coefficient by fitting adsorption kinetics data with pore diffusion model, which is considered as an effective method to describe the mass transfer process inside the pores and may show practical application in other adsorption processes. All these results will provide sufficient valuable data as a guide for the separation and purification process of flavonoid compounds in chromatographic operation.

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