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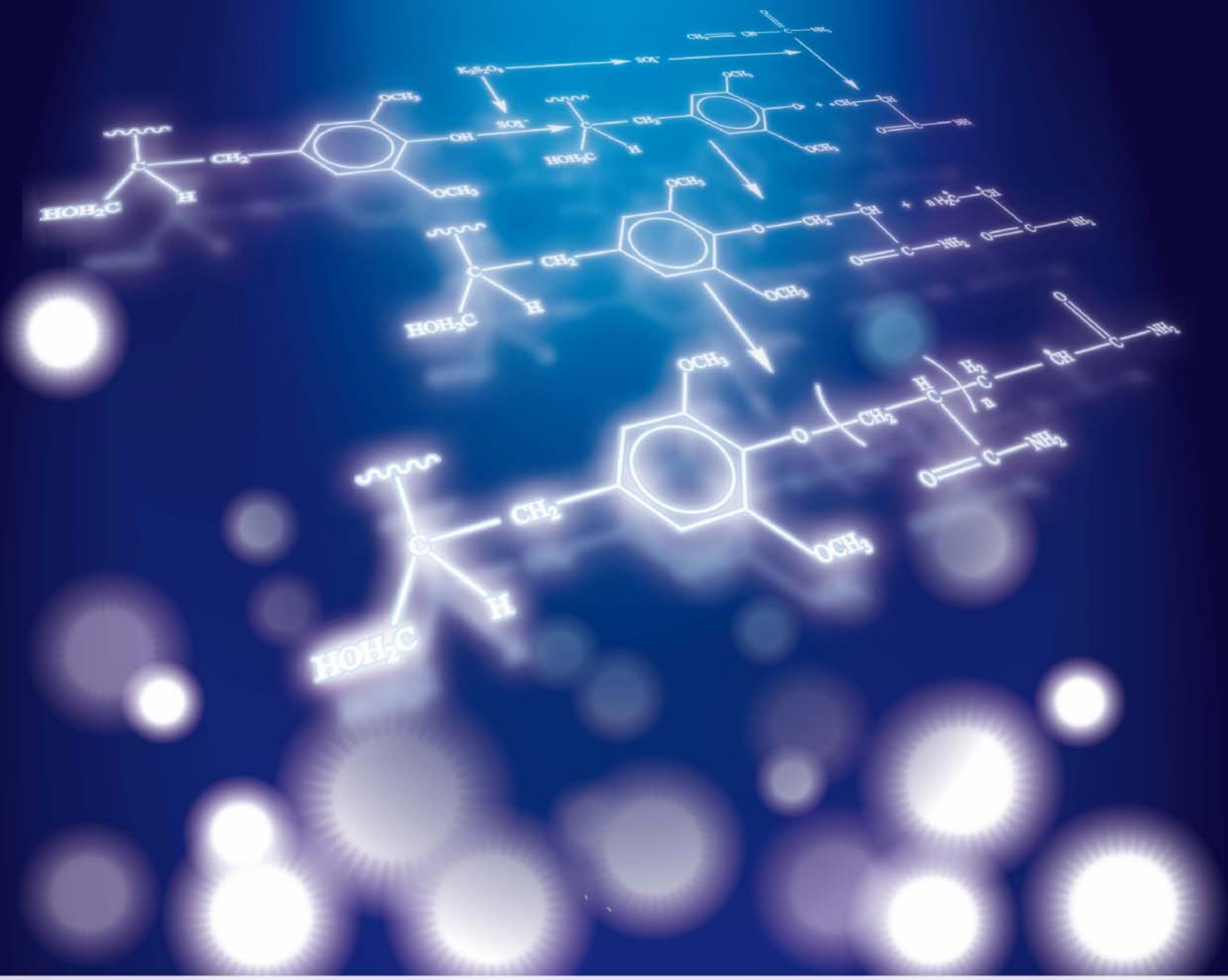

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Biosorption of clofibric acid and carbamazepine in aqueous solution by agricultural waste rice straw

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Abstract

Due to their widespread use, clofibric acid (CA) and carbamazepine (CBZ) have been frequently detected simultaneously at relatively high concentrations in aquatic environments. In this study, agricultural waste rice straw was employed as a potentially low-cost, effective and easy-to-operate biosorbent (RSB) to remove CA and CBZ. The adsorption of both pharmaceuticals followed pseudo second-order kinetics, and intraparticle diffusion was an important rate-limiting step. The adsorption isotherms of both drugs were fit well with Freundlich model. The adsorption of CA onto RSB was exothermic and was more likely to be dominated by physical processes, while the adsorption of CBZ was endothermic. Solution pH was determined to be the most important factor for CA adsorption, such that the adsorption capacity of CA onto RSB increased with the decline of solution pH. In the lower range of solution pH below 3.1, the CA removal efficiency was enhanced with the increase of biosorbent dosage. The CBZ removal efficiency was enhanced with the increase of RSB dosage without pH control. The maximum adsorption capacities were 126.3 mg/g for CA and 40.0 mg/g for CBZ.

Key words: biosorption; clofibric acid; carbamazepine; rice straw; agricultural waste; uniform design

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Introduction

Both human and veterinary pharmaceuticals and their metabolites, especially those that have been found to be resistant in water and wastewater treatment processes (Heberer, 2002; Zhou et al., 2010), can be continually introduced to the environment primarily via sewage systems, and could accumulate slowly for decades to cause unexpected effects on aquatic organisms (Fent et al., 2006). Clofibric acid (CA) and carbamazepine (CBZ) have been studied because of their widespread use, recalcitrance in most sewage treatment plants (STPs) and frequent simultaneous detection in the environment.

CA is the metabolite and active principle of the blood lipid regulators clofibrate, etofyllin clofibrate, and tofibrate (Buser et al., 1998) and has been one of the most routinely reported drugs found in treated water, surface water, groundwater, and even drinking water (Buser et al., 1998; Dębska et al., 2004). The concentration of CA can be up to 1.6 μg/L in the effluent of STP (Ternes, 1998), and as high as 7.3 μg/L in groundwater samples (Heberer et al., 1995). Moreover, clofibric acid has an estimated persistence of 21 years in the environment (Winkler et al., 2001). The removal efficiency of CA by STPs was only between 5% and 34% (Stumpf et al., 1999; Castiglioni et al., 2006). The structure and pH-dependent speciation of CA is shown in **Fig. 1a**. Important physicochemical properties of CA are the following (Bui and Choi, 2009; Löffler et al., 2005): logK_{ow}, 2.57; water solubility, 583 mg/L; K_d, < 30 L/kg.

CBZ is a widely used antiepileptic, mood-stabilizing drug, and was also one of the drugs detected most frequently. The concentration of CBZ could be up to 6.3 μg/L in STP wastewater (Ternes, 1998), and 1.1 μg/L in surface water (Zhou et al., 2010). CBZ is reported as a persistent compound with poor removal efficiency, which was only 7% in the study of Ternes (1998), or even not degraded or adsorbed at all during wastewater treatments (Clara et al., 2004). The structure of CBZ is shown in **Fig. 1b**. Important physicochemical properties of CBZ are the following (Bui and Choi, 2009; Jones et al., 2002): logK_{ow}, 2.45; water solubility, 17.7 mg/L; K_d, 25.52 L/kg.

Because of their resistance to biodegradation, several treatments that might improve the efficacy of CA and CBZ removal have been developed, such as advanced oxidation processes (AOPs), molecular imprinting technology, and activated carbon adsorption. Most of the AOPs do not

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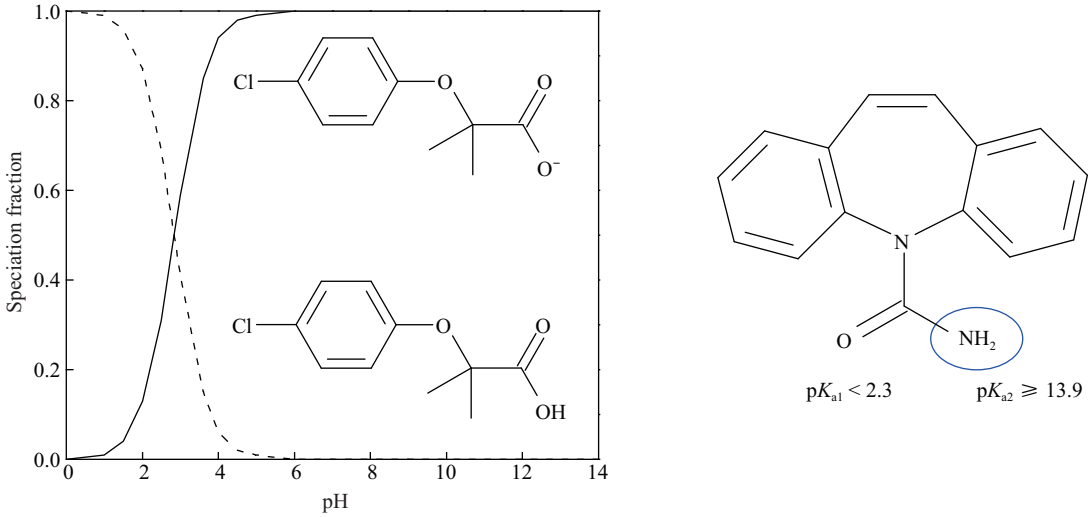

Fig. 1 (a) pH-dependent speciation of CA and (b) chemical structure of CBZ (Bui and Choi, 2009).

completely mineralize the compounds of interest (Ternes et al., 2002; Andreozzi et al., 2003), and their stable transformation products may be more toxic and worsen the environmental and health impacts (Ternes et al., 2002). Furthermore, AOPs normally increase the cost of wastewater treatment. Molecularly imprinted polymer (MIP) was proved to be of high affinity and selectivity to CBZ even in surface water or STP effluent (Dai et al., 2010). However, the application of MIP on large volumes of water with trace drug residues may be cost-intensive and potentially cause environmental risk. Adsorption on activated carbon based adsorbents was effective in removing some pharmaceuticals (Ternes et al., 2002; Nowotny et al., 2007). However, the adsorption of CA on granulated activated carbon may be difficult (Ternes et al., 2002). Moreover, activated carbon is difficult to regenerate, requiring high pressure and/or temperature (Le Noir et al., 2009). Besides activated carbon, some traditional adsorbents, such as mesoporous silica (Bui and Choi, 2009), and smectite clays (Zhang et al., 2010) were also used for potential adsorption of CA and CBZ.

Alternatively, biosorption processes using dead biomass can be considered as a promising technique to remove pharmaceutical products, with some advantages such as high selectivity and efficiency, cost effectiveness and good removal performance (Aksu, 2005). Dordio et al. (2011) evaluated the possibility of using granulated cork as a support matrix for a constructed wetlands system to remove some pharmaceuticals, including CA and CBZ.

Agricultural waste rice straw is a more important biomass resource in China and has been employed as a natural biosorbent for removal of heavy metals (Rocha et al., 2009), dyes (Gong et al., 2007), and anion salts (Zhang and Frankenberger, 2003; Cao et al., 2011). In China, the annual production of waste crop straw was as high as approximately 0.7 billion tons, of which 70% was composed of rice straw, wheat straw, and corn stalk. Nevertheless, only a small part of crop straw is recovered as resource utilization, such as energy production (Chen and Zhu, 2007). On the other hand, abundant rice straw would be a potentially cheap natural biosorbent with less environmental risk compared to conventional adsorbents. In addition, due to their low cost, at the end of their lifetime they can be disposed of without expensive regeneration (Rocha et al., 2009). However, there is very limited information relative to the adsorption of CA and CBZ using rice straw.

The objective of this study was to assess the feasibility of employing agricultural waste rice straw as a natural biosorbent for CA and CBZ removal. Firstly, the adsorption kinetics, isotherms, and thermodynamics of CA and CBZ onto rice straw biosorbent (RSB) were evaluated. Secondly, the adsorption influence factors, primarily solution pH and RSB dosage, were investigated. Finally, an evaluation of rice straw as a biosorbent was presented.

1 Materials and methods

1.1 Chemicals

CA (purity ⩾ 97%) and CBZ (purity ⩾ 99%) were purchased from Sigma-Aldrich. HPLC grade acetonitrile (ACN), methanol, and acetic acid were purchased from Tedia Company (USA). Ultra-pure water was produced by a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Standard stock solutions of CA 1# (2 g/L) and CBZ 1# (2 g/L), which were prepared in a methanol:millipore water (1:1, *V*/*V*) mixture, were employed for adsorption isotherm study. Stock solutions of CA 2# (0.1 g/L) prepared in millipore water and CBZ 2# (0.1 g/L) prepared in a methanol:millipore water (1:99, *V*/*V*) mixture were used in other batch assays. All the stock solutions were stored at 4°C.

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1.2 Preparation of rice straw biosorbent

The rice straw used in this study was collected from Jiangsu Province, China. The collected straw was dried by natural spreading and cut into shorter sections. The cut dry straw was then pulverized by a pulverizer (JP-350-A8, Shanghai Jiupin, China). The particles that passed through a 100 mesh sieve (< 150 μm) were selected for the adsorption study. All the selected RSB particles were initially dried at 60°C for 24 hr and stored in a desiccator. Before every batch adsorption experiment, the RSB was dried again at 60°C for 1–2 hr.

1.3 Rice straw biosorbent characterization

Fourier transform infrared (FT-IR) measurement of the RSB samples before and after adsorption of drugs was carried out on a Nicolet 5700 FT-IR spectrometer. The spectra were recorded in the transmission mode in the range of 4000–400 cm^{-1}. The drug-adsorbed RSB samples were prepared with 1 g/L of RSB contacted with 600 mg/L of CA or CBZ for 2 hr.

1.4 Batch adsorption assays

The batch adsorption assays were performed in 30 mL capped amber glass flasks with 10 mL of working volume. After loading with a certain amount of RSB and the target pharmaceutical solution, the flasks were then stirred in a constant temperature rotary shaker (TS 2102, Shanghai Tensuclab, China) at 180 r/min. The liquid phase concentration of pharmaceutical was measured using HPLC analysis. Each of the batch assays was run in duplicate.

1.4.1 Adsorption kinetics study

In the adsorption kinetics assay, the initial concentration of drugs was 100 mg/L and the temperature was controlled at 28°C. There was no pH adjustment in the kinetics assays and the initial pH in the flasks amended with CA and CBZ was 3.5 and 6.8, respectively. The biosorbent dosage for CBZ adsorption was 1.0 g/L. Considering the adsorption of CA was greatly influenced by solution pH, a lower RSB dosage of 0.5 g/L was applied for CA adsorption since higher RSB amounts would lead to higher solution pH for CA adsorption system in the preliminary study. The solution concentrations of CA and CBZ were measured as a function of time.

1.4.2 Adsorption isotherm study

For adsorption isotherm experiments, different concentrations of CA and CBZ (5–100 mg/L) were reacted with 1 g/L of RSB at 28°C, 37°C and 50°C, respectively. The uptake of both drugs could reach equilibrium quickly and the adsorption efficiency was relatively stable within 2 hr after equilibration was achieved in the kinetics assay. The contact time was hence determined to be 2 hr in the isotherm assay, considering the practical operation of this biosorbent for pharmaceuticals removal. There was no pH adjustment in isotherm experiments except that an additional CA adsorption assay was conducted at constant pH of 3. The solution pH was adjusted with 10% HCl solution if needed.

1.4.3 Uniform design assay for CA adsorption

In contrast with CBZ, the adsorption of CA was greatly influenced by solution pH. In addition, solution pH would change with the variation of biosorbent dosage and CA concentration. The adsorption system of CA was much more complicated than that of CBZ. Therefore, three factors with different levels, namely solution pH 2.0–4.5, biosorbent dosage 0.5–10 g/L and CA concentration 20–500 mg/L, were evaluated for the adsorption of CA onto RSB using a uniform design method. The solution pH was adjusted with 10% HCl solution. A $U_6{}^*$ (6^4) table was applied to arrange these factors (**Table 1**). After being shaken at 180 r/min under 28°C for 2 hr, pH was measured immediately and the liquid phase CA concentration in the filtrate was determined by HPLC.

1.4.4 Batch assay for RSB dosage effect

Four batch assays were performed to investigate the effect of biosorbent dosage on the adsorption of drugs. For CA adsorption, 100 mg/L of CA was first reacted with 0.1–10 g/L of RSB at the natural initial pH of 3.5. A lower concentration of 5 mg/L of CA was then employed to react with 0.5–50 g/L of RSB at initial pH 2.0. For CBZ adsorption, 50 and 5 mg/L of CBZ was reacted with a range of RSB amounts, respectively. All the flasks were capped and shaken at 180 r/min at 28°C for 2 hr.

1.5 Equations and calculations

To assess the potential rate-controlling steps involved in the process of adsorption of CA and CBZ onto RSB, the pseudo second-order (Eq. (1)) and intraparticle diffusion kinetic models (Eq. (2)) were applied to analyze the experimental data.

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

$$q_t = k_i t^{1/2} + c \quad (2)$$

where, q_t (mg/g) and q_e (mg/g) are the amounts of pharmaceuticals adsorbed at t (min) and at equilibrium, respectively, k_2 (g/(mg·min)) and k_i (mg/(g·$min^{1/2}$)) are the rate constants of pseudo second-order and intraparticle diffusion models, respectively. The initial adsorption rate

Table 1 Uniform design table derived from $U_6{}^*$ (6^4)

Test number	1	2	3	4	5	6
Solvent pH	2.0	2.5	3.0	3.5	4.0	4.5
Biosorbent dosage (g/L)	1	4	10	0.5	2	6
CA concentration (mg/L)	100	500	20	500	20	100

Uniformity deviation D = 0.2656

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h (g/(mg·min)) at time approaching 0 is calculated as $h = k_2 q_e^2$.

Freundlich and Langmuir isotherm models were employed to describe the adsorption isotherm experimental data. The linearized forms of the Freundlich and Langmuir isotherm models are given as Eq. (3) and Eq. (4), respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{3}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where, C_e (mg/L) is the equilibrium concentration of liquid phase pharmaceutical, q_e (mg/g) is the amount of adsorbed pharmaceutical, q_m (mg/g) is the maximum adsorption capacity, K_L (L/mg) is the Langmuir constant, K_F ($mg^{1-1/n}L^{1/n}/g$) and n are the Freundlich constants.

To investigate the effect of temperature on pharmaceutical adsorption, standard free energy change (ΔG^0, kJ/mol), standard enthalpy change (ΔH^0, kJ/mol) and standard entropy change (ΔS^0, J/(mol·K)) were calculated from Eq. (5) and Eq. (6), respectively.

$$\Delta G^0 = -RT \ln K_F \tag{5}$$

$$\ln K_F = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{6}$$

where, R (8.314 J/(mol·K)) is the ideal gas constant, and T (K) is the adsorption temperature. ΔH^0 and ΔS^0 were calculated according to the slope and intercept of the linear plot of Eq. (6).

1.6 Analytical methods

The liquid phase concentration of CA and CBZ was measured on an Agilent 1200 series HPLC system equipped with a G1315D diode array detector and a Shimadzu C_{18} reversed-phase column (250 mm × 4.6 mm id, particle size 5 μm). The UV detection wavelength was 230 nm and the column temperature was set at 30°C. The mobile phase consisted of 60% methanol and 40% millipore water (0.1% acetic acid). The flow rate was 1.0 mL/min, and the injection volume was 20 μL. The samples were filtered using 0.2 μm PTFE syringe filters before HPLC analysis. The limit of detection was 0.01 mg/L and the limit of quantitation was 0.1 mg/L for CA and CBZ. The dissolved organic carbon was measured on a Shimadzu TOC-VCPN TOC analyzer equipped with a non-dispersive infrared detector.

2 Results and discussion

2.1 Characterisation of rice straw biosorbent

The RSB was prepared with a minimum of pretreatment in consideration of its evaluation for easy-to-operate and low-cost adsorption of drugs. The FT-IR spectrum of RSB before adsorption of drugs is given in **Fig. 2 line a**. As shown in **Fig. 2 line a**, a broad band at around 3420 cm^{-1} is attributed to hydroxyl (OH) stretching of cellulose and lignin in macro-molecular association. The bands at 2920 and 2860 cm^{-1} are assigned to the asymmetric and symmetric stretching, respectively, of the CH_2-group, which constitutes the majority of the aliphatic fractions of the waxes on the rice straw surface (Inglesby et al., 2005). The strong band at around 1650 cm^{-1} could be assigned to the substituted aromatic group of lignin on the surface of rice straw. The carboxylate anion stretching vibration and free C=O stretching mode of carboxyl group should also overlap in the band around 1650 cm^{-1} (Bouanda et al., 2002). The absorption bands at 1050 and 460 cm^{-1} could be attributed to Si–O stretching and Si–O bending, indicating the presence of silica (Rocha et al., 2009).

The FT-IR spectra of RSB samples after adsorption of drugs are given in **Fig. 2 line b** and **c**. It can be seen in **Fig. 2 line b** that the spectrum of CBZ-loaded RSB is significantly different from that of pure RSB. The sharp band at 1400 cm^{-1}, which could be assigned to the acidamide group in CBZ, as well as the two adjacent bands at around 800 cm^{-1}, are in accordance with the spectrum of pure CBZ (Sethia and Squillante, 2004). As shown in **Fig. 2 line c**, the absorption bands in the spectrum of CA-loaded RSB is almost the same as that of pure RSB because the characteristic functional groups in CA, such as phenyl and carboxyl groups, also can be found in the complex organic components of rice straw. However, the bands at around 3420 cm^{-1} and 1650 cm^{-1} were slightly strengthened, indicating the adsorption of CA onto RSB.

2.2 Adsorption kinetics

As shown in **Fig. 3a**, in the batch adsorption kinetics assay, the adsorption of CA and CBZ reached equilibrium within 1 min and 40 min, respectively. The rapid

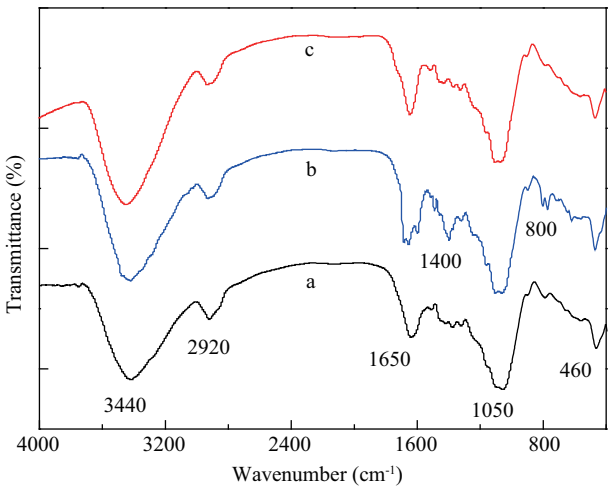

Fig. 2 FT-IR spectra of pure RSB (line a) and RSB samples after adsorption of CBZ (line b) and CA (line c).

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adsorption of drugs enables the RSB to treat large volumes of wastewater. The equilibrium time for RSB is similar to that (< 15 min) for adsorption of 100 μg/L drugs on mesoporous silica (Bui and Choi, 2009), but significantly shorter than activated carbon (Nowotny et al., 2007) or granulated cork (Dordio et al., 2011). As it was directly pulverized and screened from rice straw, RSB was actually a complex system, so that all of its components, such as cellulose, hemicellulose, lignin and even silica could be exposed to the pharmaceuticals in aqueous solution. Furthermore, some of these components would release dissolved organics when RSB is dispersed in aqueous solution, and thus may influence the adsorption of drugs if the RSB dosage was extremely high. Therefore, the reaction time was selected as 2 hr in the following batch adsorption assays even though the equilibrium time was relatively short in the adsorption kinetics study.

The pseudo second-order model was applied to investigate the kinetics of CA and CBZ adsorption processes. By plotting (t/q_t) versus t for drugs, straight lines were obtained as shown in **Fig. 3b**. The linear correlation coefficients (R^2) for CA and CBZ were 0.9984 and 0.9978, respectively. The values of k_2, q_e and h presented in **Table 2** were determined from the slopes and intercepts of the plots in **Fig. 3b**. As indicated in **Table 2**, the initial adsorption rate of CA is much higher than that of CBZ, showing that the adsorption of CA is more likely to be dominated by physical processes. Furthermore, the theoretical values of $q_{e,calculated}$ also agreed well with the experimental data, indicating good compliance with the pseudo second-order model for CA and CBZ.

The intraparticle diffusion model was further employed to assess the potential rate-controlling steps involved in the process of adsorption of CA and CBZ onto RSB. **Figure 3c** shows the intraparticle diffusion plots of q_t versus $t^{0.5}$ for the adsorption of CA and CBZ onto RSB. There were two different stages in the adsorption process. The first sharper portion was the external surface adsorption or instantaneous adsorption stage. The second portion was the equilibrium stage, where the intraparticle diffusion was slow, possibly due to the absence of effective adsorption sites. It can be seen that intraparticle diffusion was an important rate-controlling step, especially for the CA adsorption process. However, considering that the first linear portions of the plots did not pass through the origin, intraparticle diffusion was not the only rate-controlling step (Kannan and Sundaram, 2001).

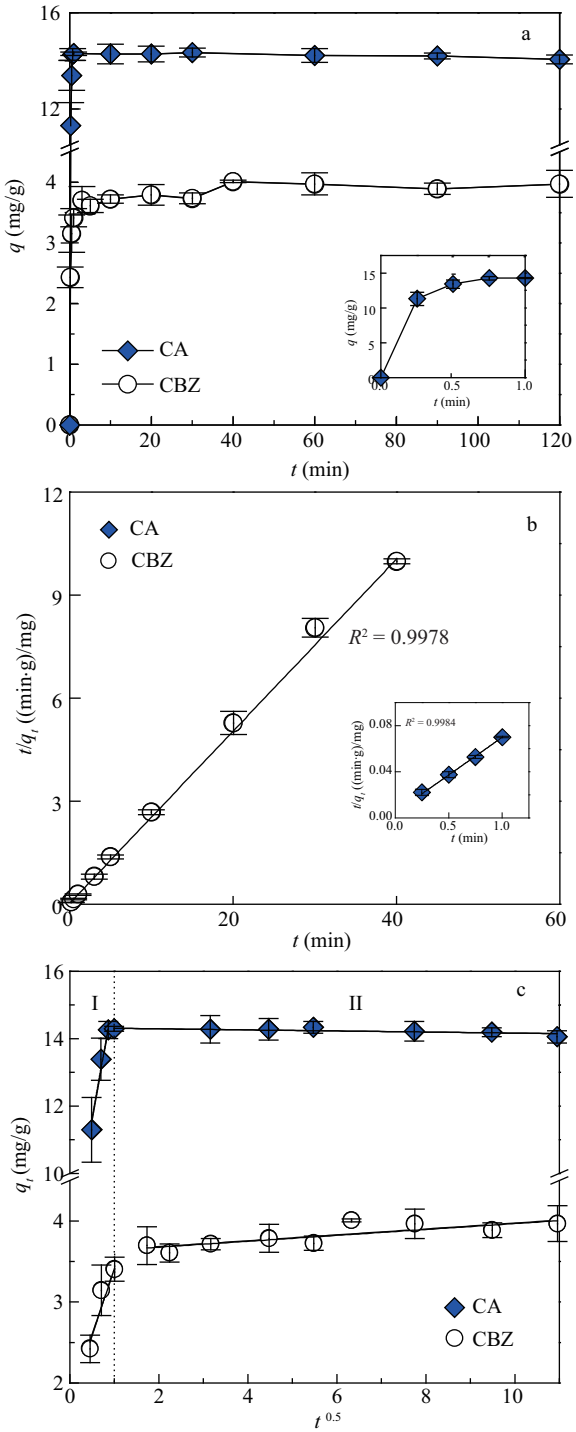

Fig. 3 (a) Kinetics plot, (b) pseudo second-order and (c) intraparticle diffusion kinetics for adsorption of CA and CBZ onto RSB.

2.3 Adsorption isotherms

The adsorption isotherms of CA and CBZ obtained at different temperatures were nonlinearly fitted according to the Freundlich equation using the Origin® 8 software package. The data fit according to the Freundlich isotherm model is shown in **Fig. 4**. In addition, for the purpose of comparison, the data were fitted according to linearized Langmuir and Freundlich equations. All the fitting parameters are given in **Table 3**.

As indicated in **Table 3**, the adsorption of both drugs fit the Freundlich model much better at all temperatures as shown by the higher R^2, indicating the complex surface characteristics of RSB. The empirical Freundlich isotherm is always used for describing adsorption onto heterogeneous surface sites. The nonlinear Freundlich

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Table 2 Pseudo second-order kinetics parameters for adsorption of CA and CBZ onto RSB

Pharmaceuticals	k_2 (g/(mg·min))	h (mg/(g·min))	$q_{e,calculated}$ (mg/g)	$q_{e,measured}$ (mg/g)
CA	0.69	171.43	15.76	14.3
CBZ	0.71	11.73	4.07	4.01

Table 3 Isotherm parameters for adsorption of CA and CBZ onto RSB at different temperatures

Pharmaceuticals	Temperature (K)	Langmuir			Freundlich		
		q_m (mg/g)	K_L (L/mg)	R^2	K_F	$1/n$	R^2
CA	301	11.38	4.12E-3	0.6201	3.94E-2	1.11	0.9811
	310	8.27	4.81E-3	0.8652	2.85E-2	1.17	0.9947
	323	6.81	5.01E-3	0.8337	2.28E-2	1.20	0.9913
CBZ	301	28.57	2.26E-3	0.8990	5.55E-2	1.08	0.9992
	310	37.59	2.02E-3	0.3933	6.35E-2	1.08	0.9972
	323	65.79	1.23E-3	0.3575	7.12E-2	1.06	0.9993

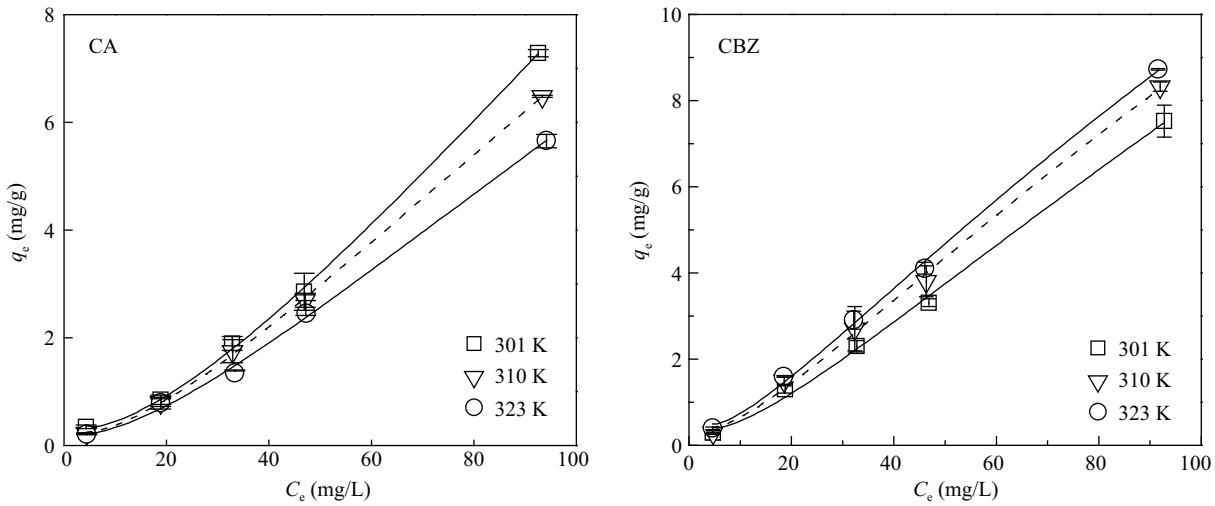

Fig. 4 Adsorption isotherms of CA and CBZ according to the Freundlich model at different temperatures.

fitting results in **Fig. 4** confirmed that a complicated adsorption mechanism was involved in the process. Rice straw generally contains about 40% crystalline cellulose and 45% amorphous components, such as hemicellulose and lignin (Reddy and Yang, 2006). After pulverization pretreatment, crystalline cellulose as well as amorphous hemicellulose and lignin could be exposed to the pharmaceuticals directly. Thus, the adsorption of drugs onto RSB fit the Freundlich isotherm model better because of the heterogeneous surface sites in these different rice straw components.

2.4 Effect of temperature

It can be seen in **Fig. 4** that the adsorption capacity of CA slightly decreased with increasing temperature, while the adsorption of CBZ slightly increased with increasing temperature. To investigate the effect of temperature on pharmaceutical adsorption, the thermodynamic parameters were calculated from Eqs. (5) and (6) based on the Freundlich constants given in **Table 3**. The linear fit R^2 values for CA and CBZ adsorption according to Eq. (6) were 0.964 and 0.983, respectively. The calculated parameters are given in **Table 4**. It can be seen that all the values of ΔG^0 were negative, indicating that the adsorption of drugs onto RSB is a spontaneous process. The ΔG^0 values of CA adsorption were almost the same at different temperatures. However, the negative value of ΔH^0 revealed the exothermic nature of the CA adsorption. Thus, lower temperature is still more favorable for the adsorption of CA and this process is more likely to be dominated by physical processes. For the adsorption of CBZ, the negative ΔG^0 value slightly decreased with increasing temperature. Furthermore, the positive ΔH^0 value also indicated that the adsorption of CBZ is endothermic and higher temperature is more advantageous, even though the decrease of ΔG^0 was not significant. In addition, chemical adsorption may be important for CBZ adsorption onto RSB. The difference between CA and CBZ should be governed by different interactions of carboxyl groups and amino groups with the anionic groups on the RSB surface.

2.5 Effect of solution pH

The pH variation before and after the adsorption of drugs on RSB is shown in **Fig. 5a**. Since the pK_a of CA is

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Table 4 Thermodynamic parameters for the adsorption of CA and CBZ onto RSB

Pharmaceuticals	Temperature (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/(mol·K))
CA	301	–22.63	–19.8	9.2
	310	–22.47		
	323	–22.81		
CBZ	301	–23.73		
	310	–24.78		
	323	–26.13	9.1	109.0

as low as 2.84, the initial pH of CA aqueous solutions decreased quickly with increasing CA concentration. It can be concluded from the speciation plot of CA (**Fig. 1a**) that about 60% of CA exists in the negatively charged form at pH 3, but the portion of dissociated CA quickly increases to about 95% when pH increases to 4. Meanwhile, because of the dissociation of anionic groups, such as hydroxide and carboxylic groups on the surface of RSB (Inglesby et al., 2005), the solid–liquid interface of rice straw was also negatively charged in the pH range of the isotherm experiments. Actually, the anticipated iso-electric point, particularly for cellulosic fiber systems, is typically located at a pH below 3.0 (Bismarck et al., 2002). Thus, electrostatic interaction was probably an important factor that resulted in the saturation of adsorption after initial uptake of CA was completed, especially in the lower CA concentration range where the pH values were higher than 4. As indicated in **Fig. 5a**, the pH experienced a significant increase after CA was adsorbed on RSB, confirming the effect of electrostatic interaction. The interaction of RSB with different concentrations of CA at a constant initial pH of 3 was then evaluated to investigate the effect of solution pH. The comparison of adsorption capacity with the result obtained in the isotherm assay conducted at initial pH > 3.5 is shown in **Fig. 5b**. All other experimental conditions were the same. It can be seen that the adsorption capacity of CA at constant pH 3 was significantly higher than that at pH > 3.5. More uncharged CA can be released and adsorbed onto RSB at lower solution pH, thus enhancing the adsorption capacity of CA. Furthermore, as shown in **Fig. 5b**, the increase of q_e at the concentration of 100 mg CA/L significantly decreased, since the solution pH at the highest CA concentration was significantly lower (**Fig. 5a**). Actually, the adsorption of CA may be co-influenced by initial solution pH, CA concentration, and RSB dosage considering that all of these factors could change the final solution pH.

Different from CA, CBZ with $pK_{a1} < 2.3$ and $pK_{a2} \geqslant 13.9$ exists entirely in the neutral form in the pH range of 1.9–11.9 (Bui and Choi, 2010). It also can be seen in **Fig. 5a** that the pH was almost the same in solutions with different CBZ concentrations. The pH of CBZ solutions slightly decreased after reaction possibly due to the $–NH_2$ groups involved in the adsorption of CBZ onto RSB. Actually, CBZ adsorption as a function of initial pH between 1 and 13 was investigated in this study, but the removal efficiency of CBZ was not significantly changed.

2.6 Co-influence factors for solution pH

A uniform design (UD) method was employed to arrange the initial solution pH and CA concentration as well as RSB dosage in this study. UD is capable of producing samples with high representativeness with lower experiment time, especially for those experiments that have many levels for each factor (Fang et al., 2000). A U_6^* (6^4) table was employed to arrange these factors. The final pH values and adsorption capacity (q_e) of each test in **Table 1** are shown in **Fig. 6**.

It can be seen that the initial pH in Tests 4 and 6 was lower than the corresponding solution pH due to higher CA concentration. Meanwhile, the final pH significantly increased in Tests 3, 5, and 6 because of the effect of higher RSB amount. Thus, the solution pH was a function of both CA concentration and RSB amount. Nevertheless, it should be noted that the effect of CA concentration

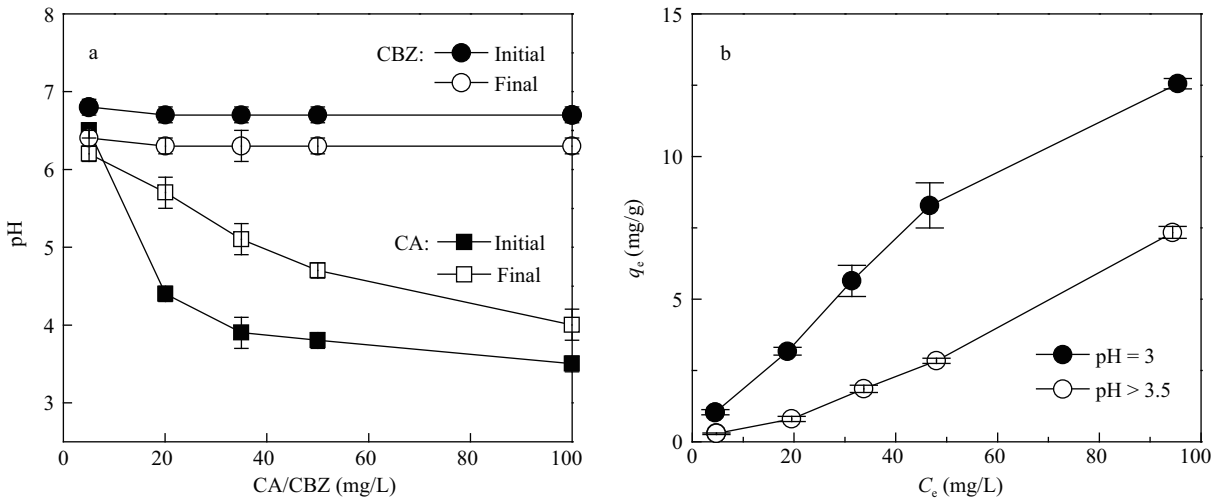

Fig. 5 (a) pH values before and after different concentrations of drugs adsorbed on RSB and (b) adsorption capacity of CA in different pH ranges.

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and RSB amount on solution pH and adsorption efficacy was actually dependent on the sensitive variation of CA in terms of speciation, which directly influences the adsorption efficiency of CA. Actually, as shown in **Fig. 6a**, the final pH in Test 2 performed with the relatively high dosage of 4 g/L was not significantly changed because a lower initial solution pH 2.5 was applied. Thus, the effect of RSB should be dependent on the initial solution pH, and the initial pH hence should be the most important factor to determine the final solution pH. The effect of RSB dosage will be further investigated in the following section 2.7.

In the relatively high CA concentration range (20–500 mg CA/L) used in the UD assay, a new parameter K_R was defined as the biosorbent amount divided by the CA concentration. The calculated values of K_R, along with the adsorption capacity are given in **Fig. 6b**. q_e was even lower than 0.2 mg/g in Tests 3, 5, and 6, in which final pH values were determined to be about 5, indicating the adsorption of CA was directly influenced by solution pH, which is characterized as final pH here. Meanwhile, it can be observed from the other three tests, in which final pH values were between 2 and 3.1, that higher biosorbent dosage would be more advantageous for CA adsorption when pH was lower than 3.1. As reported by Mestre et al. (2010), the highest removal of CA by cork-based activated carbons were obtained at solution pH 2.0 and decreased at higher pH. Otherwise, the complex parameter K_R, which combined the effect of CA concentration and RSB amount, can be employed to predict the adsorption efficiency in a specified concentration range. However, one should be very cautious in using this parameter in different CA concentration ranges, because the solution pH is highly sensitive to the concentration of CA.

2.7 Effect of RSB dosage

The effect of RSB dosage on the adsorption of CA and CBZ was further investigated under different pH and drug concentrations. The final pH and adsorption capacity (q_e) of CA that interacted with various dosages of RSB at different initial pH conditions are presented in **Fig. 7a** and **b**. With the same initial pH, the final pH increased with increasing RSB dosage while the adsorption capacity of CA significantly decreased with increasing final solution pH. It can be seen in **Fig. 7a** that the value of q_e was dramatically decreased to less than 1 mg/g when the final pH increased to 4.5. Furthermore, with the same RSB dosage of 0.5 g/L, the q_e value for 5 mg CA/L at initial pH 2 reached 126.2 mg/g, while the q_e was only 11.6 mg/g for 100 mg CA/L at initial pH 3.5. Therefore, solution pH was extremely important for CA adsorption, and the initial pH should be as low as possible, especially in field operation where the RSB dosage can be adjusted flexibly. As shown in **Fig. 7b**, when the initial pH was adjusted to 2, the increase rate of solution pH and the final pH values were both much lower than that with initial pH 3.5, even though the initial CA concentration was low (5 mg/L). Thus, it is also confirmed that the effect of RSB dosage on solution pH was highly dependent on initial pH. Meanwhile, once the initial pH was determined, the solution pH should be more dependent on the increasing biosorbent dosage while the CA concentration was within 100 mg/L. In addition, the increment of pH at each RSB dosage was higher and higher with increasing amounts of RSB.

The removal efficiencies of CA corresponding to **Fig. 7b** are shown in **Fig. 7c**. It can be seen that the CA removal efficiency increased more and more slowly as the pH became higher and higher with increasing amounts of RSB. The highest CA adsorption of 42.5% was obtained at an RSB dosage of 30 g/L, while the pH was about 3.1. With further increase of pH, the CA adsorption began to decrease with increasing RSB dosage. These results confirmed that higher RSB dosage had a positive effect on the adsorption of CA when solution pH was lower than 3.1. In addition, at a certain CA concentration, the optimal RSB dosage can be determined by the maximum biosorbent dosage at the corresponding initial solution pH.

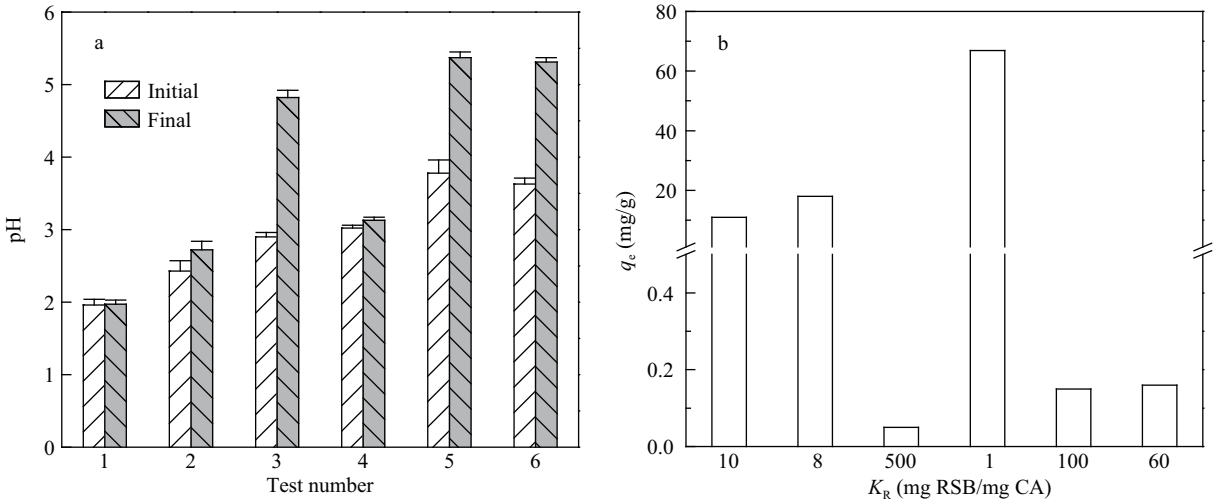

Fig. 6 (a) pH and (b) adsorption capacity in each test of the uniform design assay for CA adsorption onto RSB.

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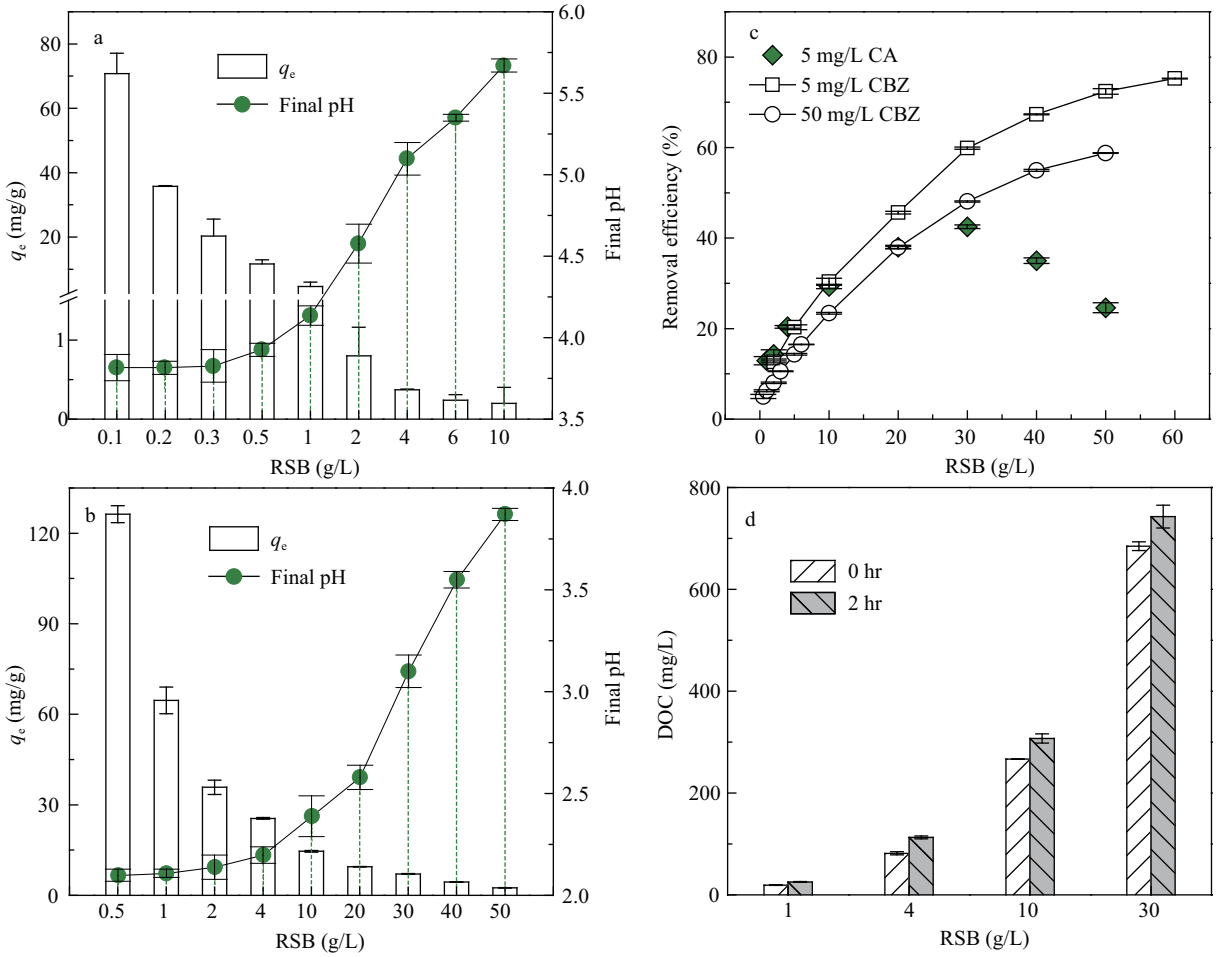

Fig. 7 Adsorption capacity and final pH in the RSB dosage assays with (a) 100 mg/L of CA at initial pH 3.5, and (b) 5 mg/L of CA at initial pH 2; (c) removal efficiency of CA and CBZ and (d) dissolved organic carbon content with increasing RSB dosage.

Table 5 Comparison of the adsorption of CA and CBZ onto various adsorbents

Drugs	Adsorbents	q_m (mg/g)	pH	Temperature (K)	References
CA	Cork-based activated carbon	139–295	3.6	303	Mestre et al., 2010
	Ni-Al-HDTMA modified bentonite	0.64	3.2	–	Rivera-Jimenez et al., 2011
	Mesoporous silica SBA-15	0.07	3	298	Bui and Choi, 2009
	Granulated cork	0.06	–	293	Dordio et al., 2011
	RSB	126.3	2	301	This study
CBZ	Multiwalled carbon nanotube	41.1–7910	7.0	296	Oleszczuk et al., 2009
	Powdered activated carbon	287	–	298	Li et al., 2011
	CBZ-MIP	86	–	–	Dai et al., 2010
	Ni-Al-HDTMA modified bentonite	0.61	6.2	–	Rivera-Jimenez et al., 2011
	Granulated cork	0.37	–	293	Dordio et al., 2011
	Mesoporous silica SBA-15	0.16	5	298	Bui and Choi, 2009
	RSB	40.0	6–7	301	This study

–: Data not available.

The CBZ removal efficiencies under different RSB dosages with initial concentrations of 5 mg CBZ/L and 50 mg CBZ/L are also given in **Fig. 7c**. The pH was not controlled here as the adsorption of CBZ was not affected by solution pH. It can be seen that the CBZ removal efficiency was enhanced with the increase of RSB dosage. Furthermore, the increase rate of CBZ adsorption was linearly correlated with the amount of RSB (R^2 > 0.99) when the RSB dosage was lower than 30 g/L. The increase rate of the CBZ removal efficiency gradually slowed when the RSB dosage further increased because relatively less CBZ was available. The maximum CBZ removal efficiency of 75.3% was achieved at an RSB dosage of 60 g/L. In addition, due to the swelling property of rice straw, it can be seen in **Fig. 7d** that the concentration of dissolved organic carbon (DOC) was enhanced with

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increasing amounts of RSB. The release of DOC would change the surface characteristic of rice straw and further influence the adsorption of pharmaceuticals. Higher DOC in the water also would arouse a concern about secondary environmental pollution and thus need to be treated properly.

2.8 Evaluation of rice straw as a biosorbent

Biomass materials that are either abundant or easy to obtain could be used as biosorbents to remove residual pharmaceuticals in aqueous solution (Volesky, 2001). China is rich in agricultural crop straw waste, which would be a potentially low-cost natural biosorbent with less environmental risk compared to conventional adsorbents. **Table 5** compares the maximum adsorption capacity of CA and CBZ onto different adsorbents, including the rice straw biosorbent used in this study. For the purpose of comparison, the values of q_m presented in **Table 5** were obtained from either experimental data or Langmuir isotherm parameters if available. As shown in **Table 5**, the q_m for CA adsorption onto RSB at pH 2 was of the same order of magnitude as that for activated carbon, but greatly higher than that for modified bentonite, mesoporous silica, or granulated cork. Meanwhile, it has been found that the adsorption of CA onto activated carbon and modified bentonite decreased with the increase of solution pH (Bui and Choi, 2009; Mestre et al., 2010). The relatively lower values of q_m for CA adsorption onto granulated cork and mesoporous silica may be due to higher solution pH and lower initial CA concentration, respectively. For the adsorption of CBZ, it can be seen that the q_m for CBZ adsorption onto RSB was comparable with that for CBZ-MIP but lower than that for carbon nanotubes and powdered activated carbon. Therefore, RSB can be used as a biosorbent with relatively high efficiency for CA and CBZ removal.

More importantly, considering that activated carbon is difficult to regenerate and energy-intensive (Le Noir et al., 2009), RSB presents great advantages for removal of pharmaceuticals in that it can be disposed of without expensive regeneration due to its low cost (Rocha et al., 2009). For practical application of a biosorbent, the biomass processing should be limited to a minimum. In this study, the rice straw was only pulverized and screened to ensure adequate dispersion of biosorbent in the aqueous solution. Furthermore, the rapid adsorption of drugs enables the RSB to treat large volumes of wastewater. Meanwhile, the adsorption of CBZ was not pH dependent and thus also enabled the application of rice straw as a practical support matrix in constructed wetlands designed for simultaneous removal of CA and CBZ from wastewaters (Dordio et al., 2011). In addition, as a biomass adsorbent with proper pretreatment, the spent RSB could be easily separated from aqueous solution with appropriate moisture content and then sent for fermentative biogas production. All these show that rice straw is a potentially cheap, effective and easy-to-operate biosorbent for the removal of residual pharmaceuticals.

3 Conclusions

The agricultural waste rice straw was employed for adsorption of CA and CBZ in this study. The adsorption of both CA and CBZ followed a pseudo second-order kinetic model. Intraparticle diffusion was the rate-limiting step. However, intraparticle diffusion was not the only rate-controlling step. The adsorption of both drugs can be fit well by a nonlinear Freundlich isotherm. Lower temperature was advantageous to the adsorption of CA on RSB and the process of CA adsorption onto RSB was more likely to be dominated by physical processes than CBZ adsorption. Different from CA, the adsorption of CBZ was endothermic, showing that chemical adsorption may be important for CBZ adsorption onto RSB. Solution pH was the most important factor for the adsorption of CA, such that the adsorption capacity of CA onto RSB increased with the decline of solution pH. Furthermore, solution pH was co-influenced by initial solution pH, CA concentration and RSB amount. Nevertheless, for 100 mg/L of CA, the initial pH was the most important factor to determine the final solution pH. In a proper range of solution pH below 3.1, the CA removal efficacy was enhanced with increasing biosorbent dosage. The CBZ removal efficiency was enhanced with the increase of RSB dosage. Moreover, the increase rate of CBZ adsorption was linearly correlated with the RSB amount when the RSB dosage was lower than 30 g/L.

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