Study on adsorption of tetracycline by red mud-based ceramsite

Linye Zhang, Zongwu Xin, Xinyu Fei, Heyi Luo, Haiyan Li, Baoxun Lu, Zhongmin Li and Guangtao Wei

ABSTRACT

To understand disposal of antibiotic in wastewater by red mud-based ceramsite (RMBC), a low-cost adsorption material prepared from waste solid red mud, bagasse, powdered glass, and molasses alcohol wastewater, the adsorption of tetracycline from water by RMBC has been studied. Characterization of RMBC was achieved by scanning electron microscope and X-ray diffraction, and the main index parameters of RMBC were tested. Effects of adsorption time, RMBC dosage, initial concentration of tetracycline, temperature, and pH on the adsorption of tetracycline were explored. The adsorption equilibrium isotherms were fitted by Langmuir, Freundlich, and Temkin models. It was found that the Langmuir model described the adsorption process better than the other two isotherm models. Application of Dubinin–Radushkevich adsorption model determined the type of adsorption, which found that the tetracycline adsorption by ceramsite was a physical adsorption. Adsorption kinetics including the pseudo-first order and pseudo-second order kinetic models were investigated and the data fitted better with the pseudo-second order kinetic model than pseudo-first-order kinetic model. The method of regeneration used for RMBC was explored. The results showed that RMBC was an effective and regenerable material used for adsorption treatment of tetracycline.

Key words | adsorption, ceramsite, red mud, regeneration, tetracycline

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INTRODUCTION

Tetracyclines are emerging pollutants of particular concern because of their widespread use in animal and human medicine (Ahmed *et al.* 2017). The high solubility and ubiquitous distribution of tetracyclines in water bodies pose potential ecological risk to the environment (Gao *et al.* 2012). Some researchers have detected various concentrations of antibiotics in municipal wastewater, surface water, and even drinking water (Hirsch *et al.* 1998; Pruden *et al.* 2006). Many studies have shown that even if trace antibiotics are exposed to the environment for a long time, it will do some harm to the ecological environment and human health (Isidori *et al.* 2005). Tetracyclines as one of the most important antibiotic families were widely produced and used in animal husbandry and human medicine (Gu & Karthikeyan 2005). Therefore, more and more researcherrs have expressed concern about the environmental pollutants of tetracyclines. Red mud (RM) is a solid waste discharged from the alumina smelting industry. For one ton of alumina manufactured in the Bayer process, 1.0–1.6 tons (dry weight) of red mud residue are normally generated (Lopes *et al.* 2013). China is the fourth producer of alumina in the world, producing red mud of up to millions of tons a year. A large amount of red mud is piled up, and can take up a great deal of land and cause serious pollution to the environment. Recently, using red mud as the main material to prepare some composites, including adsorbent, catalyst, ceramsite, and so on, has become an effective way to minimize the harm of red mud and realize its resourceful utilization simultaneously (Sglavo *et al.* 2000; Zhang *et al.* 2012a; Wang

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et al. 2016; Kazak *et al.* 2017). The preparation and use of red mud-based ceramsite (RMBC) have been reported by many studies (Yang *et al.* 2008; Guo *et al.* 2014). However, in the preparation of RMBC, using industrial and agricultural waste as auxiliary materials has been rarely reported. In the preparation of RMBC, if sintering aids and pore-forming agents of chemical reagents could be replaced by industrial and/or agricultural wastes, that would further achieve the purpose of saving reagent consumption and reducing the production cost of RMBC.

In this study, RMBC has been prepared using red mud as the main material and molasses wastewater, glass, and bagasse as auxiliary materials. The properties of RMBC were first analyzed and discussed, and then the RMBC was used as adsorbent to explore the disposal of tetracyclines by RMBC. Tetracycline was selected as a model hydrocarbon due to its wide application in clinical medicine processes, aquaculture and stockbreeding, as well as its environmental significance. The effect of adsorption conditions on the adsorption of tetracycline was investigated in detail, and the adsorption behavior of tetracycline on RMBC also has been explored through the study of adsorption isotherm, adsorption kinetics, adsorption mechanism, and adsorption thermodynamics. Lastly, the regeneration experiment of RMBC was also investigated.

EXPERIMENTAL

Materials and chemical reagents

RM in the study was generated by the Bayer process and was obtained from Guangxi Aluminum Corporation in Guangxi Zhuang Autonomous Region, China. Bagasse and molasses alcohol wastewater were obtained from Guangxi East Asia Sugar Group in Guangxi Zhuang Autonomous Region, China. Prior to use, the bagasse was dried at 473 K and then ground to less than 0.15 mm. Glass powder was made by using crushed glass bottles in our laboratory, and the glass powder was less than 0.15 mm. Tetracycline (>96% purity) was obtained from Tianjin Ding Guo Biotechnology Co., Ltd (China). All other chemicals and reagents used in the study, including HNO_3, $AlCl_3$, and NaOH, were of analytical reagent grade.

Preparation of adsorbent

The process of preparing RMBC was roughly divided into three steps. First, 10 g of red mud, 0.25 g of bagasse, 3.5 g of molasses alcohol wastewater, 3 g of glass powder, 0.7 g of $AlCl_3$ were mixed together to make a mixture. Then, the mixture was pressed into pellets (2–5 mm), followed by drying at 425 K for 3 h and then drying at 495 K for 1 h. Finally, the pellets were pre-calcined at 1,223 K in a muffle stove, and then calcined at a suitable temperature. When the calcination finished, RMBC was obtained.

Characterization of RMBC

X-ray diffraction (XRD) analysis of RMBC and red mud were realized using a Bruker D8 ADVANCE X-ray diffractometer equipped with Cu K_α radiation at 40 kV and 40 mA. Scanning electron microscopy (SEM) micrographs of RMBC were recorded with a Hitachi S-3400N scanning electron microscope. Hardness of RMBC was measured by YD-1 type tablet hardness tester. The wear rate of RMBC and the solubility of RMBC in hydrochloric acid were measured according to Chinese National Industrial Standard (CJ/T 299-2008), in which the oscillation frequency was adjusted to 600 times/min for the wear rate measurement. Apparent porosity of RMBC was measured according to Chinese National Standard (GB/T 1966-1996). In order to evaluate the dissolution of alkaline substances from RMBC when it was used in water, 2 g of RMBC was added to 50 mL of deionized water and then constantly stirred for 1 h at the speed of 200 rpm; lastly, the pH of the stirred system was measured by a pH meter to evaluate the dissolution of alkaline substances from RMBC. Water absorption and bulk density of RMBC were calculated according to Equations (1) and (2), respectively:

$$W_a = \frac{m_3 - m_1}{m_1} \tag{1}$$

$$D_a = \frac{m_1 \times D_L}{m_3 - m_2} \tag{2}$$

where m_1 is the dry weight of the sample (g), m_2 is the mass of saturated sample in water (g), m_3 is the mass of the saturated sample in the air (g), W_a is the water absorption (%), D_a is the bulk density ($g{\cdot}cm^{-3}$), and D_L is the density of the immersion liquid at the test temperature ($g{\cdot}cm^{-3}$).

Adsorption and regeneration studies

Adsorption experiments were carried out by using batch techniques. One hundred mL of the tetracycline solution ($c_0 =$ 15 mg/L) was placed in a 250 mL conical flask, and then RMBC (10 g/L) was added. The pH of the solution was adjusted to the desired value by adding 1 mol/L HNO_3 or 4 mol/L NaOH solution. The 250 mL conical flask was fixed in a thermostatic water bath oscillator and stirred at a speed of 200 rpm. At the end of the adsorption, RMBC was separated from the solution. The concentration of tetracycline in supernatant was determined at maximum absorbance wavelength of 368 nm by using a visible spectrophotometer (VIS-722, SHYK, China), and then the removal percentage of tetracycline (η, %) and the amount of tetracycline adsorbed on RMBC (q_t) were calculated, respectively.

Regeneration of RMBC was investigated in a batch mode. The used sorbent was regenerated by calcining in a muffle furnace at different temperatures. The regeneration efficiency (η_r, %) is used to reflect the recycling of RMBC.

RESULTS AND DISCUSSION

Characterization of RMBC

The SEM pictures of RMBC are presented in Figure 1. As shown in Figure 1, there were a number of outer holes with different sizes on the outer surface of RMBC, and a number of holes with different sizes were also found in the inner section of RMBC. In a word, holes are abundant in RMBC, and the external holes partly connected with the inner ones. The SEM results indicated that RMBC was a porous ceramsite and might be a good adsorbent for wastewater treatment.

The XRD pictures of RMBC and RM are presented in Figure 2. As shown in Figure 2, the iron phases of RM and RMBC were both mainly α-Fe_2O_3 (PDF 33-0664). However, compared with that of RM, the diffraction peak of RMBC changed obviously and the diffraction peak of faujasite zeolite (PDF 28-1036) almost disappeared. In addition, many small and widened diffraction peaks were found in the XRD spectrum of RMBC, which might be caused by the amorphous glass phase generated from glass powder after sintering.

The main performance indexes are shown in Table 1. It was found that each evaluation index is good. Especially, the apparent porosity, the average hardness, and the wear rate of RMBC reached 43.04%, 152.8 N, and 1.58%, respectively. In addition, an experiment of the dissolution of alkaline substances from RMBC was carried out, and the result showed that pH was about 6.76, approximately the original pH of water. It indicated that the alkaline substances initially contained in RM had been safely and stably sealed in prepared ceramsite of RMBC.

Effect of adsorption time on adsorption of tetracycline

The adsorption of tetracycline by RMBC at different times was carried out by varying adsorption time from 0 to

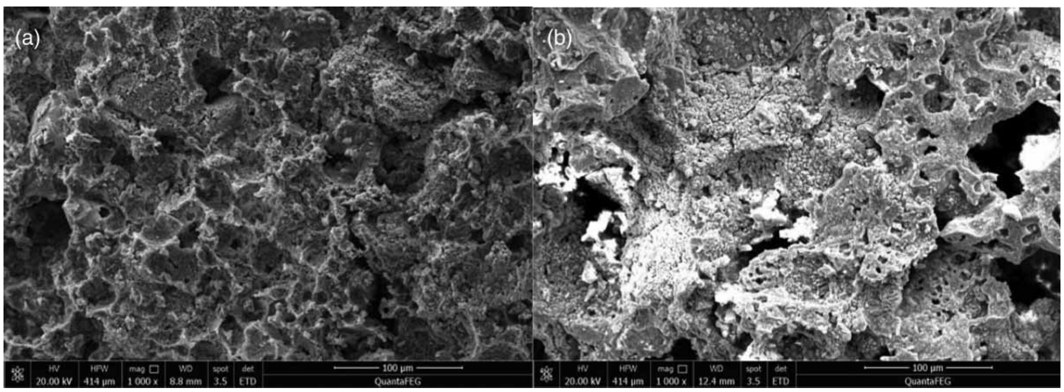

Figure 1 | SEM pictures of the outer surface of RMBC (a) and inner section of RMBC (b).

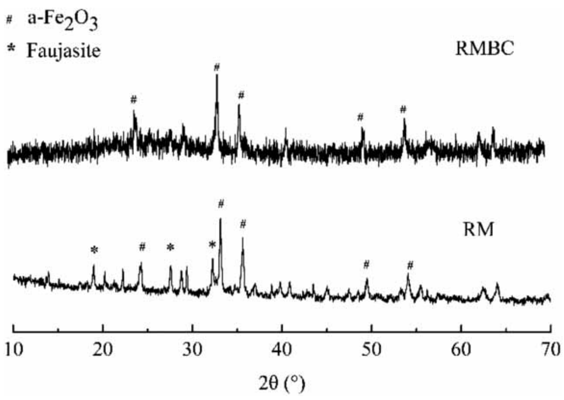

Figure 2 | XRD pictures of RMBC and red mud.

Table 1 | Performance index of RMBC

Index	Value
Solubility in hydrochloric acid (%)	10.59
Apparent porosity (%)	43.04
Average hardness (N)	152.78
Bulk density (g/cm^3)	1.49
Wear rate (%)	1.58
Water absorption (%)	28.95

90 min. As shown in Figure 3, the removal of tetracycline reached adsorption equilibrium at 60 min, and the removal percentage of tetracycline was 55.1%. It was found that the removal efficiency of tetracycline increased in the first 60 minutes, and then the removal percentage of tetracycline stayed almost constant. During adsorption of tetracycline, the available adsorption surface and vacant adsorption site of RMBC could be responsible for excellent adsorption in the first 60 minutes (Wang *et al.* 2016). However, because less adsorption surface and less adsorption site were available after adsorption equilibrium was reached at 60 min, the removal efficiency remained constant with further increase of adsorption time.

Effect of adsorption temperature on adsorption of tetracycline

The effect of adsorption temperature on the adsorption of tetracycline was investigated in the temperature range from 303 K to 333 K. As shown in Figure 4, the removal efficiency of tetracycline decreased with the increase of temperature in the range of 303–333 K, and this indicated that the adsorption of tetracycline by RMBC was exothermic. From Figure 4 it was also found that the time of adsorption equilibrium decreased with the increase of adsorption temperature, which might be attributed to the increased mobility of tetracycline in water at high temperatures (Moussavi & Khosravi 2011).

Effect of pH on adsorption of tetracycline

The effect of solution pH on the adsorption of tetracycline was investigated. As shown in Figure 5, the removal

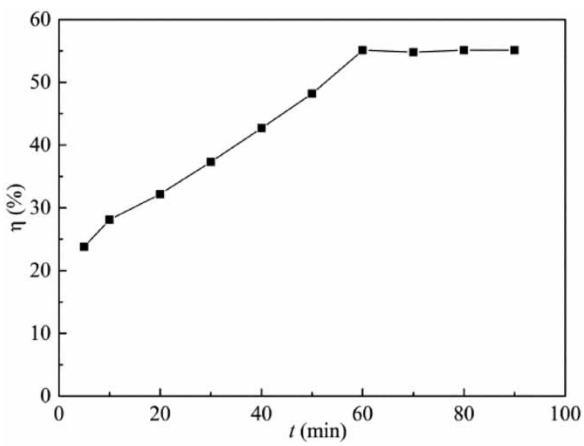

Figure 3 | Effect of adsorption time on adsorption of tetracycline (RMBC dosage = 10 g/L, c_0 = 15 mg/L, initial pH of solution, and room temperature).

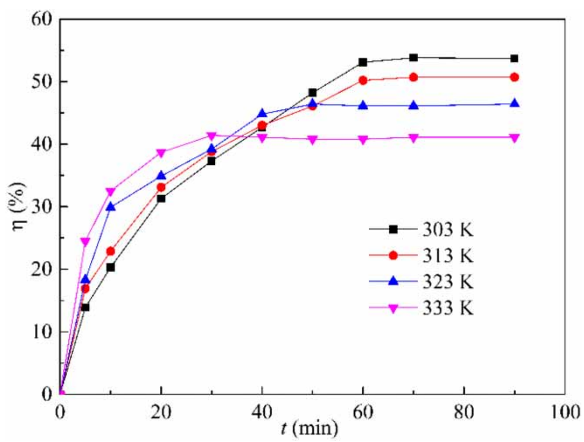

Figure 4 | Effect of adsorption temperature on adsorption of tetracycline (RMBC dosage = 10 g/L, c_0 = 15 mg/L, and initial pH of solution).

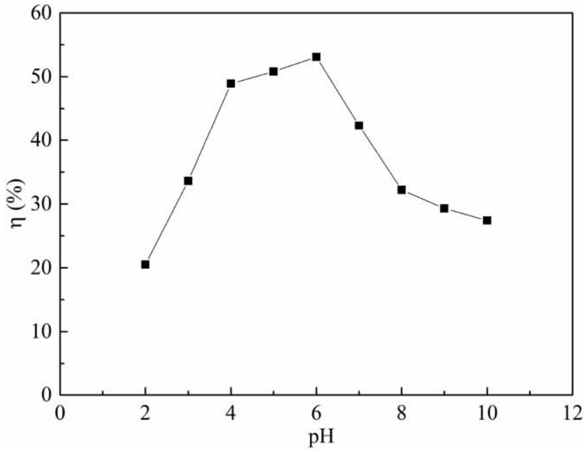

Figure 5 | Effect of pH on adsorption of tetracycline (RMBC dosage = 10 g/L, c_0 = 15 mg/L, and room temperature).

efficiency of tetracycline increased with the increase of pH from 2 to 6, and the removal of tetracycline reached its maximum of about 53.1%. When the initial pH of solution was over 6, the removal efficiency of tetracycline decreased with the further increase of pH from 6 to 10. It was found that the adsorption of tetracycline on ceramsite was obviously affected by the pH of the solution which might be because the form of tetracycline was different at different pH values. When the pH range was 3.3–7.7, the main form of etracycline was zwitterion with a dimethylamino group and a negatively charged phenolic hydroxyl group (And & Lee 2005). There existed a 25% anionic form of the tetracycline molecule at the pH of 7.0 (Pils & Laired 2007). Moreover, the proportion of negative charge in tetracycline molecules increased with the increase of pH. The cationic group on the tetracycline molecule could be combined with the negative charge on the ceramsite by cation exchange. A large amount of H^+ was present in the solution under acidic conditions, which could compete with the antibiotic cation for the adsorption site on the surface of the ceramsite. With the increase of pH, the competition of H^+ gradually decreased, and the adsorption amount of ceramsite to antibiotics gradually increased. When the solution was close to neutral, the amount of ceramsite adsorbed to tetracycline was maximized. The proportion of negative charge in the tetracycline molecule increased with the further increase of pH, which caused an increase in the electrostatic repulsion between the tetracycline molecule and the ceramsite and a decrease in the amount of adsorption.

Effects of initial tetracycline concentration on adsorption of tetracycline

The effect of initial tetracycline concentration on the adsorption of tetracycline was investigated. As shown in Figure 6, the removal efficiency of tetracycline decreased with the increase of initial concentration in the range of 10–30 mg/L. However, as shown in Table 2, the equilibrium adsorption capacity of RMBC increased with the increase of initial concentration. The increase of q_e was ascribed to the change of concentration gradient.

Effect of RMBC dosage on adsorption of tetracycline

The effect of RMBC dosage on the adsorption of tetracycline was investigated. As shown in Figure 7, with the increase of RMBC dosage from 2.5 g/L to 20 g/L, the removal efficiency of tetracycline increased from 23.2% to 53.1%. The removal

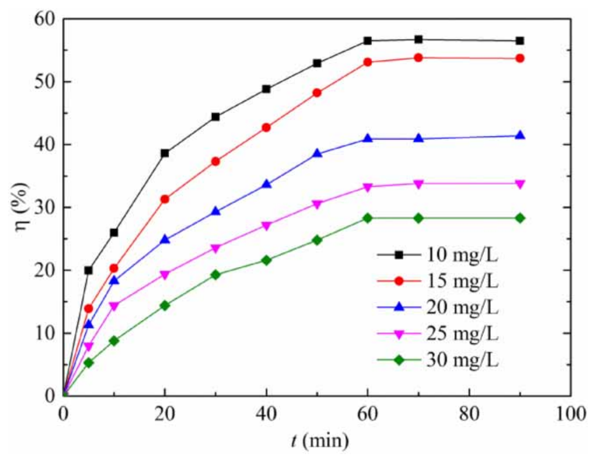

Figure 6 | Effect of initial tetracycline concentration on adsorption of tetracycline (RMBC dosage = 10 g/L, room temperature, and pH = 6).

Table 2 | The equilibrium adsorption capacity of RMBC varies with the initial concentration

c_0 (mg/L)	q_e (mg/g)
10	0.57
15	0.80
20	0.82
25	0.83
30	0.85

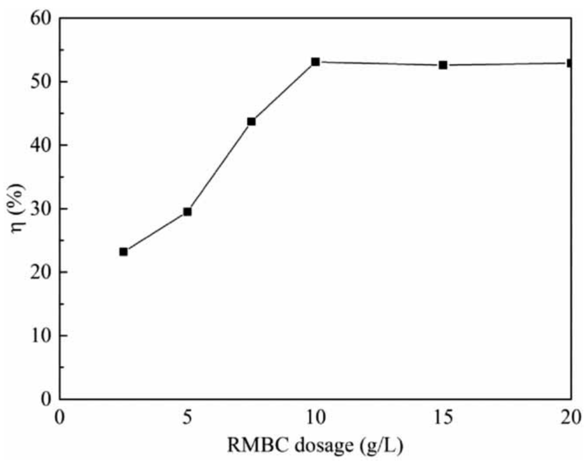

Figure 7 | Effect of RMBC dosage on adsorption of tetracycline ($c_0 = 15$ mg/L, room temperature, and pH = 6).

efficiency of tetracycline revealed a fast increase until the RMBC dosage reached 10 g/L, which was ascribed to more available adsorption surface and vacant adsorption site provided by added RMBC. However, it was found that when the RMBC dosage further increased (>10 g/L), the removal rate of tetracycline almost remained unchanged in our study. Tetracycline molecules exist in different forms at different pH values. In the pH range of 3.3–7.7, the main form of tetracycline molecules is zwitterion ($TCH_2^{\pm}$), but changes to its anion form of TCH^- and TC_2^- when pH >7.7 (Chen *et al.* 2016). In terms of the adsorbent RMBC, it could adsorb some forms of tetracycline molecules but could not adsorb others. When the RMBC dosage exceeded 10 g/L, even though there were tetracycline molecules in the solution, these tetracycline molecules were the forms which could not be adsorbed by the RMBC in fact.

Adsorption isotherm

Langmuir, Freundlich and Temkin isotherm models

In order to explore the relationship between the adsorption capacity of adsorbent and the concentration of adsorbate when the adsorption process reaches equilibrium, the adsorption of tetracycline on RMBC at 303 K was simulated using the Langmuir, Freundlich, and Temkin isotherm models.

The Langmuir adsorption isotherm is the model applied to describe monolayer adsorption (Panday *et al.* 1986). The Langmuir adsorption isotherm can be a good description of the experimental data in a wide range of concentration and is shown as Equation (3):

$$\frac{c_e}{q_e} = \frac{1}{q_m b} + \frac{c_e}{q_m} \tag{3}$$

where q_m is the greatest equilibrium adsorption capacity (mg/g) and b is the adsorption equilibrium constant (L/mg). c_e is the concentration of adsorbate solution when the adsorption reaches equilibrium (mg/L). The values of q_m and b can be calculated from the plot of c_e/q_e against c_e.

The Freundlich adsorption isotherm is an empirical model based on heterogeneous surface and is expressed as Equation (4) (Tabak *et al.* 2010):

$$\ln q_e = \frac{1}{n}\ln c_e + \ln k_f \tag{4}$$

where K_f and n are Freundlich adsorption isotherm constants. The values of K_f and n can be calculated from the plot of $\ln q_e$ against $\ln c_e$.

The Temkin adsorption isotherm describes the energy changed on the surface of non-uniform adsorbents during adsorption, and is shown as Equation (5):

$$q_e = A + B\ln c_e \tag{5}$$

where A and B are the adsorption equilibrium constants. The values of A and B can be calculated from the plot of q_e against $\ln c_e$.

The adsorption results of tetracycline on RMBC at 303 K were fitted by Langmuir, Freundlich, and Temkin adsorption isotherms. They are shown in Figures 8–10. The isotherm parameters from all the models and the correlation coefficients calculated from all linear regression are listed in Table 3. According to the correlation coefficient values of isotherms, the Langmuir adsorption equation fitted well with the equilibrium data. It was concluded that the adsorption process of tetracycline by RMBC was monolayer adsorption. The Langmuir model can be measured by a separate parameter R_L:

$$R_L = \frac{1}{1 + bc_0} \tag{6}$$

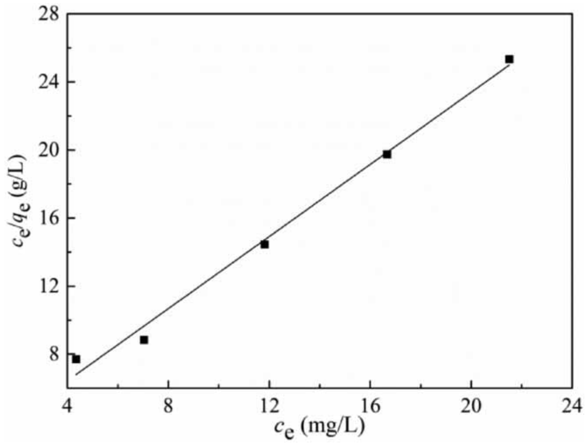

Figure 8 | Plot of Langmuir isotherm model for tetracycline adsorption on RMBC.

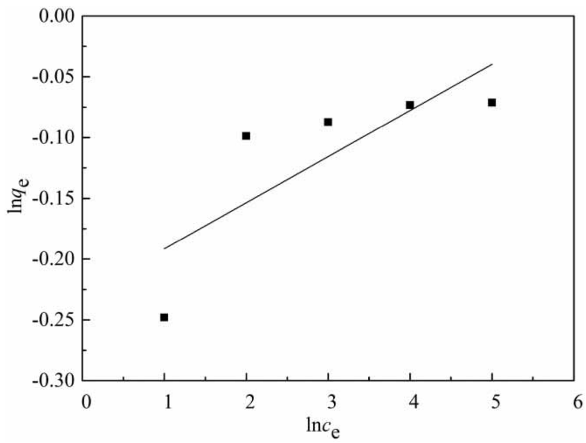

Figure 9 | Plot of Freundlich isotherm model for tetracycline adsorption on RMBC.

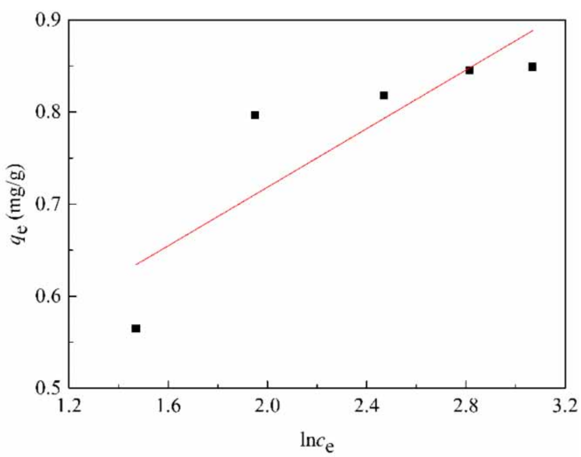

Figure 10 | Plot of Temkin isotherm model for tetracycline adsorption on RMBC.

Table 3 | Isotherm parameters for tetracycline adsorption on RMBC

Isotherm parameter	Value
Langmuir isotherm	
b (L/mg)	1.255
q_m (mg/g)	0.881
R^2	0.999
R_L	0.026–0.074
Freundlich isotherm	
K_F	0.707
N	16.42
R^2	0.630
Temkin isotherm	
A	0.698
B	0.050
R^2	0.663

When the R_L ranges from 0 to 1, favorable adsorption occurs. In this study, the calculated R_L values were in the range of 0.026–0.074, indicating that it was a favorable process.

Dubinin–Radushkevich adsorption model

The Dubinin–Radushkevich adsorption isotherm is usually employed to estimate the porosity apparent free energy and the characteristic of adsorption. Moreover, the Dubinin–Radushkevich isotherm can also be used to determine the type of adsorption (physical or chemical adsorption) (Chowdhury *et al.* 2011). The Dubinin–Radushkevich equation is shown as follows:

$$\ln q_e = \ln q_m + \beta\varepsilon^2 \quad (7)$$

$$\varepsilon = RT \ln(l + 1/C_e) \quad (8)$$

$$E = 1/\sqrt{2\beta} \quad (9)$$

where β is the activity coefficient related to adsorption energy, ε^2 is the Polanyi potential, and E is average adsorption energy.

The plot of the Dubinin–Radushkevich adsorption isotherm for the tetracycline adsorption on ceramsite is shown in Figure 11. The isotherm parameters and the correlation coefficients calculated are listed in Table 4. According to the

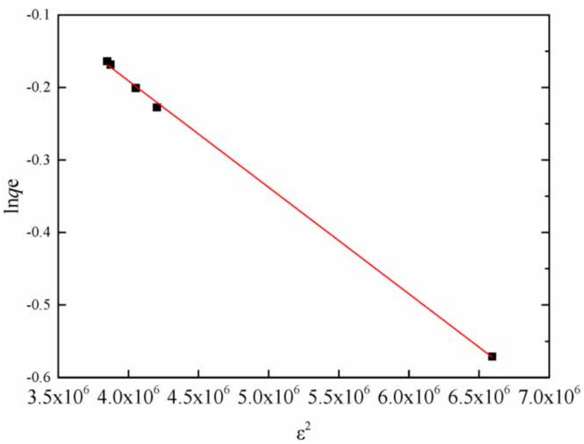

Figure 11 | Plot of Dubinin–Radushkevich isotherm model tetracycline adsorption on ceramsite.

Table 4 | Dubinin–Radushkevich isotherm parameters for tetracycline adsorption on RMBC

Dubinin–Radushkevich adsorption isotherm	RMBC
$\beta \times 10^{-7}$	2
q_m (mg·g^{-1})	1.7
R^2	0.99
E (kJ/mol)	1.58

correlation coefficient values of the isotherm, it was observed that the Dubinin–Radushkevich adsorption equation was a perfect fit for the data. When the average adsorption energy is less than 8 kJ·mol^{-1}, the physical adsorption occurs. The E of tetracycline adsorption on ceramsite was 1.58 kJ/mol (Table 4), which confirmed that the tetracycline adsorption by ceramsite was a physical adsorption.

Adsorption kinetics

For interpreting the controlling theory regarding the adsorption process of tetracycline by RMBC, kinetic experimental data were analyzed and modeled by using two kinetic equations, i.e., pseudo-first-order kinetic equation and pseudo-second-order kinetic equation. The pseudo-first-order kinetic equation can be expressed as Equation (10) (Zhang *et al.* 2012b):

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1 t}{2.303} \quad (10)$$

where q_t is the amount of tetracycline adsorbed (mg/g) at t min, q_e is the amount of tetracycline adsorbed (mg/g) at equilibrium, and k_1 is the rate constant of pseudo-first-order adsorption (L/min).

The pseudo-second-order equation can be expressed as Equation (11) (Daraei *et al.* 2013):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (11)$$

where k_2 is the rate constant of pseudo-second-order adsorption (g/(mg min)).

A pseudo-first-order equation and pseudo-second-order equation were applied to fit the experimental data. Plot of the pseudo-first-order kinetic equation and pseudo-second-order kinetic equation for the adsorption of tetracycline by RMBC are shown in Figures 12 and 13. The values of calculated q_e and R^2 are presented in Table 5. All R^2 of the pseudo-second-order equation were over 0.99. This indicated the good applicability of the pseudo-second-order equation used for fitting the adsorption of tetracycline by RMBC.

Adsorption mechanism

The pseudo-second-order model, containing all the rate controlling processes of adsorption, such as surface adsorption, intraparticle diffusion, and so on, could not truly reflect the mechanism of this adsorption process (Khaled *et al.* 2009).

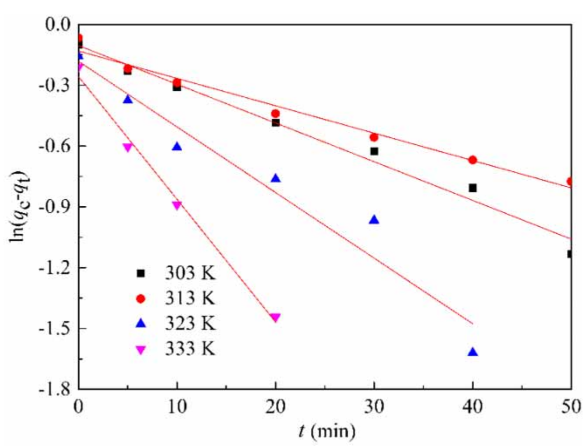

Figure 12 | Plot of pseudo-first-order kinetic equation for tetracycline adsorption on RMBC.

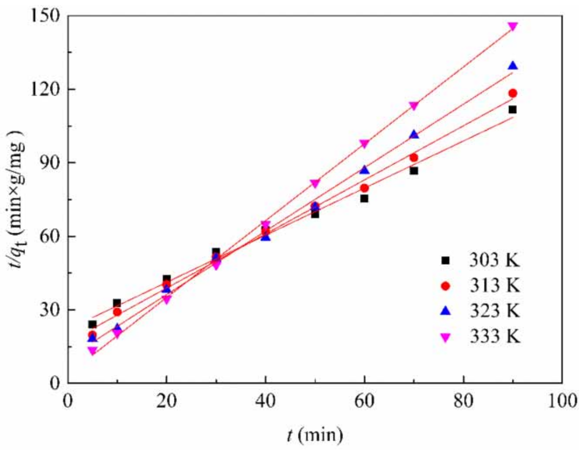

Figure 13 | Plot of pseudo-second-order kinetic equation for tetracycline adsorption on RMBC.

Table 5 | Kinetic constants for adsorption of tetracycline on RMBC

	Temperature			
Kinetic constant	**303 K**	**313 K**	**323 K**	**333 K**
Pseudo-first-order equation				
q_e (mg/g)	0.901	0.877	0.834	0.774
K_1	0.044	0.031	0.746	0.139
R^2	0.979	0.975	0.932	0.989
Pseudo-second-order equation				
q_e (mg/g)	1.041	0.907	0.773	0.638
K_2	0.042	0.073	0.162	0.660
R^2	0.990	0.996	0.996	0.998

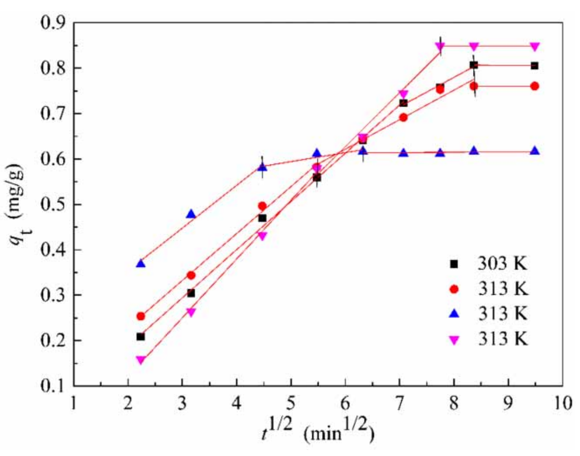

Figure 14 | Plot of intra-particle diffusion model for tetracycline adsorption on RMBC.

In order to further explain the adsorption mechanism, the adsorption of tetracycline on RMBC was studied by intraparticle diffusion equation analysis. Intraparticle diffusion equation can be expressed as Equation (12) (Dursun *et al.* 2013):

$$q_t = k_d t^{0.5} + C \tag{12}$$

where k_d is the intraparticle diffusion rate constant (mg/(g·min$^{1/2}$)) and C is the constant correlation with the thickness of boundary layer.

The intraparticle diffusion equation was applied to fit the experimental data. The plot of q_t vs. $t^{1/2}$ of different temperatures is shown in Figure 14. The values of calculated k_d, C and R^2 are presented in Table 6. As shown in Figure 14, the plots of intraparticle diffusion kinetics were multilinearities and did not pass through the origin, demonstrating that intraparticle diffusion was not the only rate controlling process for the adsorption of tetracycline by RMBC (Lim *et al.* 2013). The adsorption process might be controlled by both membrane diffusion and intragranular diffusion (Vimonses *et al.* 2009). The whole adsorption process was divided into three stages: the first stage was the process by which tetracycline overcame the resistance of the liquid membrane to the surface of the ceramsite, and the initial portion could be attributed to surface adsorption, because the adsorbate diffuses through the solution to the external surface of the adsorbent; the second portion described the gradual adsorption stage, and the second stage diffusion rate constant k_{d2} was smaller than the first stage diffusion rate constant k_{d1}; the last portion refers to the final equilibrium stage, and maximum adsorption was attained (Cheung *et al.* 2007).

Adsorption thermodynamics

The thermodynamic properties of the adsorption process can be characterized by free energy change ΔG, entropy change ΔS, and enthalpy change ΔH, which were obtained from the following equations:

$$\Delta G = \Delta H - T\Delta S \tag{13}$$

$$\ln\left(\frac{q_e}{c_e}\right) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{14}$$

Table 6 | Intraparticle diffusion equation analysis under different temperatures[a]

T	k_{d1}	k_{d2}	k_{d3}	C_1	C_2	C_3	R_1^2	R_2^2	R_3^2
303 K	0.106	0.066	0	−0.024	0.263	0.818	0.996	0.961	1
313 K	0.103	0.065	0	0.022	0.232	0.7605	0.995	0.966	1
323 K	0.165	0.019	0	0.096	0.495	0.610	0.972	0.945	1
333 K	0.130	0.119	0	−0.138	−0.689	0.849	0.996	0.970	1

[a]Subscripts 1, 2 and 3 are for the first, the second and the last stage of adsorption process, respectively.

Table 7 | Thermodynamic parameters for the adsorption process of tetracycline by RMBC

ΔG (kJ/mol)				
303 K	313 K	323 K	ΔH (kJ/mol)	ΔS (J/mol · k)
−0.384	0.059	0.502	−44.326	−14.174

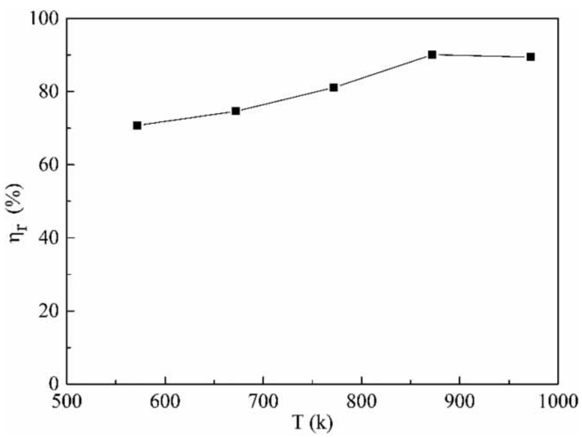

Figure 15 | Effect of regeneration temperature on regeneration of RMBC.

The thermodynamic parameters of the adsorption of tetracycline by RMBC are presented in Table 7. The negative value of ΔG at 303 K suggested the spontaneous nature of the adsorption process of tetracycline by RMBC. The negative value of ΔH indicated the exothermic nature of the adsorption process of tetracycline by RMBC. ΔS was less than zero, indicating that the process was an entropy decreasing process.

The regeneration of RMBC was investigated by varying calcination temperature from 573 to 973 k. As shown in Figure 15, the regeneration efficiency of RMBC increased with the increase of calcination temperature in the range of 573–873 K. The regeneration efficiency of RMBC reached maximum at the calcination temperature of 873 K, and the regeneration efficiency of RMBC was 90.1%.

Furthermore, the effect of calcination time on the regeneration of RMBC was investigated by varying the time from 15 to 90 min. As shown in Figure 16, the regeneration efficiency of RMBC reached maximum at the calcination time of 45 min, and the regeneration efficiency of RMBC was 90.9%. It showed that RMBC had the ability to be regenerated through the method of calcinations and RMBC was a renewable material with excellent mechanical properties, and might be used as an adsorbent for the industrial treatment of tetracycline wastewater.

CONCLUSIONS

RMBC was prepared from waste solid RM, bagasse, powdered glass, and molasses alcohol wastewater. The use of industrial and agricultural wastes as the ceramsite preparation material achieved the purpose of reducing

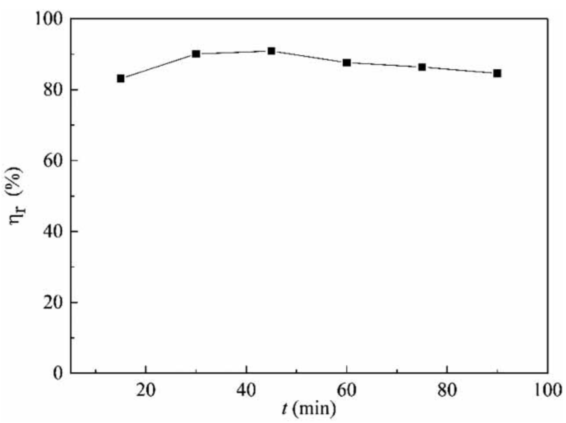

Figure 16 | Effect of regeneration time on regeneration of RMBC.

environmental pollution and lowering the cost of industrial production of ceramsite. RMBC is a porous material, and the external holes of RMBC partly connected with the inner holes of RMBC. The main index parameters of RMBC (apparent porosity, average hardness and wear rate) all in the high performance range, and the alkaline substances initially contained in RM had been safely and stably sealed in prepared ceramsite of RMBC. The adsorption of tetracycline on RMBC was mainly affected by adsorption time, adsorbent dosage, and pH. The adsorption results showed that the Langmuir model described the adsorption process better than the Freundlich isotherm model and Temkin isotherm model. Moreover, it was observed that the pseudo-second-order kinetic model was better fit for the adsorption data than the pseudo-first-order kinetic model. Intraparticle diffusion equation was analyzed, indicating that the adsorption process might be controlled by both membrane diffusion and intragranular diffusion. The adsorption of tetracycline by RMBC was an exothermic process and could be spontaneous at 303 K. In addition, the regeneration results showed that the regeneration efficiency of RMBC reached 90.9% at the calcination time of 45 min under the calcination temperature of 873 K. RMBC was an effective and regenerable material used for adsorption treatment of tetracycline. Moreover, RMBC had a strong average hardness and a small wear rate, which contributed to maintaining its good structure in industrial applications. In addition, ceramsite had low raw material costs and renewable ability. The above shows that ceramsite had the potential to be a column adsorption filler in industrial applications.

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