Adsorption Kinetics of Reactive Brilliant Blue X-BR on Carbon Modified by Urban Greening Waste

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Abstract: In this study, the urban greening waste in Chengdu city was used as raw material. After carbonization, it was modified with zinc chloride modifier under different conditions, and activated carbon was used to adsorb reactive brilliant blue X-BR under different conditions. Combined with the modification conditions and dosage conditions of the prepared activated carbon, the adsorption process data were fitted to the curve with the intra-particle diffusion equation, pseudo first-order kinetic model and pseudo second-order kinetic model. Among them, the correlation coefficient of pseudo first-order kinetic model was 0.931-0.933, and that of pseudo second-order kinetic model was 0.999.The correlation coefficient of intra-particle diffusion equation was low and the fitting degree was poor. By comparing the correlation coefficient R (variance) of the curve, it was found that the adsorption of reactive brilliant blue X-BR by the modified branches conformed to the pseudo-second-order kinetic model.

Keywords: modified carbon; active brilliant blue X-BR; urban greening waste; kinetics

1 Introduction

With the promotion of eco-city construction and the increase of urban greening coverage, the total amount of urban greening waste was increasing. For urban greening waste, burning green waste will also cause certain air pollution, and the environmental problems brought by it were becoming more and more prominent[1]. Therefore, it was bound to become an inevitable trend of social development to reuse green waste as a kind of recycled resource[2].

In the study of adsorption kinetics, the adsorption kinetics of reactive brilliant blue on adsorbents prepared by chemical modification was not deep enough[3-6]. In this study, green waste was used as raw material, and activated carbon was made of zinc chloride modifier. Reactive brilliant blue was treated with modified carbon. The kinetics of reactive brilliant blue was studied.

2 Experimental Part

2.1 Materials, Reagents and Instruments

The selected branches and weeds came from Chengdu city. Zinc chloride, concentrated sulfuric acid, potassium hydroxide, iodine, potassium iodide, sodium thiosulfate and soluble starch, all of which were analytically pure.

Electric heating constant temperature blast drying oven: DHG-9140; Visible spectrophotometer: V-1200; Water bath oscillator: THZ-032; Electronic analytical balance: ESG220-4; pH meter: PHBJ-260; Mesh screen: 20 mesh, 50 mesh and 100 mesh; Universal electric furnace: DL-1.

2.2 Preparation of Modified Carbon from Urban Greening Waste

On the basis of the previous research [7-10], in this experiment, activated carbon was prepared from branches, and the branches were activated by chemical activation method, and the activator was zinc chloride. Rinse repeatedly with distilled water until impurities were removed. Then, it was put into the electrothermal constant temperature air blast drying at 100℃, and the strips with a length of 5cm were cut. The dried raw materials were carbonized in an electric furnace for 90min, heated to 800℃ at a rate of 10℃/min, cooled to room temperature, ground and sieved (40-60 mesh), and carbonized branches were mixed with 3mol/L $ZnCl_2$ in a 100mL conical flask at a mass ratio of 1:3. Closed the bottle stopper and shaked it in a water bath oscillator (temperature: 25℃, speed: 150r/min, time: 120min). After treatment, the modified carbonized waste was obtained by filtration [11-13]. Clean with 1mol/L dilute hydrochloric acid solution, then rinse distilled water repeatedly to neutrality, then dry to constant weight, grind and screen out activated carbon below 200 mesh.

2.3 Drawing of Reactive Brilliant Blue X-BR Standard Curve

Measure the absorbance of different concentrations, as shown in Table 1. Draw the standard curve of reactive

brilliant blue X-BR, as shown in Figure 1.

Table 1. Measurement of absorbance of reactive brilliant blue X-BR with different concentrations

Concentrations (mg/L)	0	4	8	12	16	20	24	28	32
Absorbance	0	0.02	0.036	0.054	0.072	0.09	0.107	0.124	0.145

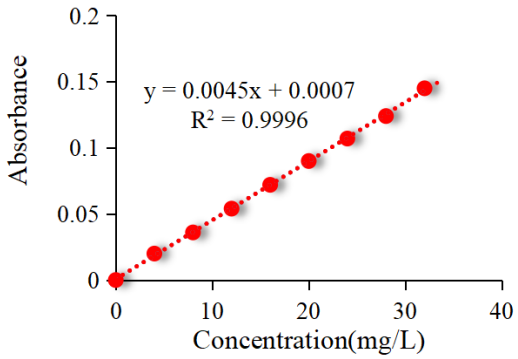


Figure 1. X-BR standard curve of reactive brilliant blue

3 Adsorption Kinetics

3.1 Adsorption Kinetic Model

The adsorption of reactive brilliant blue X-BR[14-16] by modified carbonized branches will be described and analyzed by pseudo first-order kinetic equation, pseudo second-order kinetic equation and intra-particle diffusion equation. Pseudo-first-order model and pseudo-second-order model were widely used to describe adsorption kinetics. They assumed that adsorption was a pseudo-chemical reaction process[17,18]. Pseudo-first-order kinetics held that mass transfer resistance in particles was the limiting factor of adsorption, and the pseudo-first-order kinetic equation was as follows:

$$dq_t/dt=k_1(q_e-q_t) \quad (1)$$

The equation (1) was integrated, and the boundary conditions were: t=0, q_t=0; t=t, q_t=q_t can get:

$$In(q_e-q_t)=lnq_e-k_1t \quad (2)$$

In the formula, q_e— adsorption capacity at adsorption equilibrium, mg/g.

q_t— adsorption capacity at time, mg/g.

K_1— the velocity constant of pseudo-first-order power equation, min^{-1}.

The $ln(q_e-q_t)$ and t curve were a straight line if the fitting result of adsorption process accords with pseudo-first-order model.

The pseudo second-order kinetic equation was:

$$dq_t/d_t=k_2(q_e-q_t)^2 \quad (3)$$

The boundary conditions of the forward integration and utility of equation (3) were t=0, q_t=0; t=t, q_t=q_t can get:

$$1/(q_e-q_t)=1/q_e+k_2t \quad (4)$$

Formula: pseudo secondary adsorption rate constant. The deformation of the pair (4) was obtained:

$$t/q_t=1/k_2qe^2+t/q_e \quad (5)$$

There was a linear relationship with the t, and the k_2, q_e can be obtained from the straight line slope and intercept.

If the fitting result of adsorption process accords with pseudo-second-order kinetic equation, then k/qt and t were a straight line. In the process of transferring adsorbate from solution to solid phase, intra-particle diffusion was a main process, so the intra-particle diffusion process was often the control step of adsorption rate. The linear expression of intra-particle diffusion (formula 6) was:

$$q_t=k_pt^{0.5}+C \quad (6)$$

In the formula, C was related to the thickness of diffusion layer. k_p — diffusion rate constant in particles, $g.mg^{-1}.min^{-0.5}$. The relationship between the diffusion rate constant k_p and the diffusion coefficient D particles was as follows:

$$k_p=(6q_e/R)*(D/\pi)^{0.5} \quad (7)$$

in formula (7), R— particle radius, cm^{-1} .

If q_t and t were a straight line and passes through the origin, then the diffusion process in particles was the only adsorption rate control process.

3.2 Research Methods of Adsorption Kinetics

The adsorption experimental data were plotted as adsorption kinetics curve [19]. The curve was fitted by the diffusion equation in particles, pseudo first-order kinetic equation and pseudo second-order kinetic equation, and the fitting results were studied.

The adsorption kinetics curve of 100mg/L reactive brilliant blue X-BR with different dosage of modified carbon branches (2.0g/L, 2.4g/L) was shown in Figure 2. The reaction conditions were: temperature 25℃; pH 4; oscillation speed was 150r/min. The results showed that the larger the dosage, the longer the adsorption equilibrium time, which may be caused by fewer dye molecules. Moreover, under different dosage of adsorbent, the adsorbent showed similar adsorption kinetics behavior. Each curve can be divided into three stages: taking the dosage of 2.0mg/L as an example, the slope of the first stage was very large, so the rapid adsorption may be caused by the van der Waals force between adsorbent and adsorbate, indicating that the adsorption process was a rapid physical process. The slope of the second stage was small and the growth was slow. In the third stage, when the time was more than 75min, the decolorization rate reached equilibrium. Almost all dye molecules were adsorbed, so the adsorption amount did not increase much.

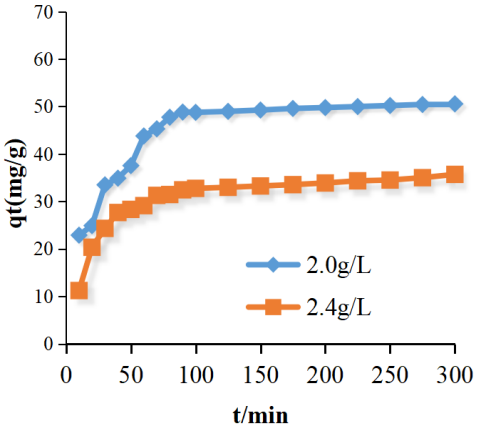


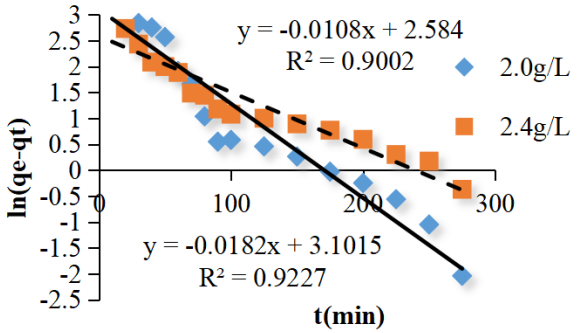
Figure 2. Adsorption kinetics curve

To fit the kinetic experimental data in Figure 2, pseudo first-order kinetic equation, pseudo second-order kinetic equation and intra-particle diffusion equation were used respectively. See Figure 3 (a~c), and the fitting parameters were shown in Table 2.

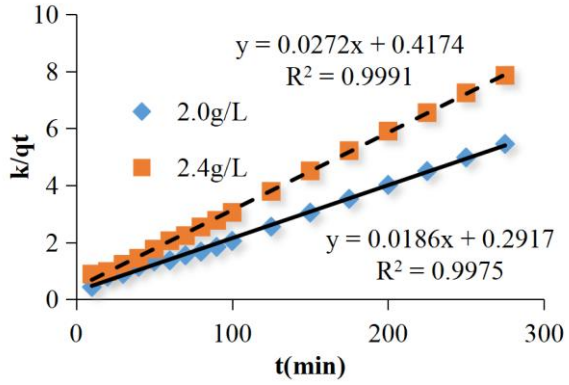
It can be seen from the fitting curve of pseudo first-order kinetic equation (Figure 3(a)) and Table 2 that the correlation coefficient R^2 of pseudo first-order kinetic equation ranged from 0.931 to 0.933, which can describe the initial stage well.

It can be seen from the fitting curve of pseudo second-order kinetic equation (Figure 3(b)) and Table 2 that the correlation coefficient R^2 of pseudo second-order kinetic equation was almost 0.999.

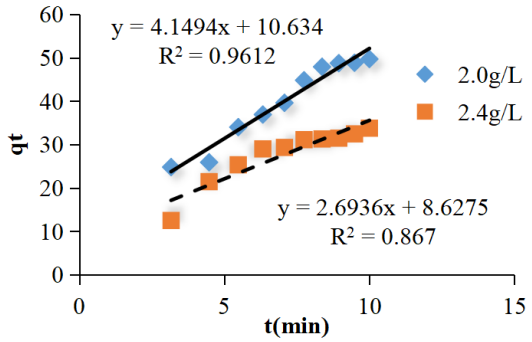
It can be seen from the fitting curve of intra-particle diffusion equation (Figure 3(c)) and Table 2 that the R^2 value of the curve was low and the fitting degree was poor, indicating that the adsorption process was controlled by intra-particle diffusion [20].



(a) pseudo first-order kinetic equation diagram



(b) pseudo-second order kinetic equation diagram



(c) diagram of intra-particle diffusion equation

Figure 3. Fitting curve of adsorption kinetics with different adsorbent dosage

Table 2. Fitting results of reaction rate equation under different adsorbent dosage

M (g/L)	Pseudo-first order dynamic equation		Pseudo-second order dynamic equation		Intra-granular diffusion equation	
	k_1 (min^{-1})	R^2	k_2 ($g.mg^{-1}.min^{-1}$)	R^2	K_p ($mg.g^{-1}.min^{-0.5}$)	R^2
2.0	0.0182	0.923	0.019	0.998	4.149	0.961
2.4	0.0108	0.900	0.027	0.999	2.694	0.867

According to data processing and analysis, this adsorption experiment was a pseudo first-order kinetic equation: with the increase of adsorption capacity, the actual adsorption data gradually deviated from the fitting curve, which can only describe the adsorption process before reaching adsorption saturation. Pseudo-second-order kinetic equation: It can accurately describe the whole adsorption process of this experiment, such as external liquid film diffusion, surface adsorption and intra-particle diffusion. Intra-granular diffusion equation: Although the fitting curve was linear, the curve did not pass through the origin, which indicated that the adsorption process of reactive brilliant blue X-BR on carbonized branches was the control step of the adsorption rate, but it was not the only rate control step, and the adsorption rate was also controlled by the extragranular diffusion process (such as surface adsorption and liquid film diffusion).

4 Conclusion

In this experiment, the correlation coefficient R^2 of pseudo first-order kinetic equation ranged from 0.931 to

0.933, and the correlation coefficient R^2 of pseudo second-order kinetic equation was almost all 0.999, and the R^2 value of intra-particle diffusion curve was even lower. The order of variance of the three curves from large to small was pseudo-second-order kinetic equation, pseudo-first-order kinetic equation and intra-particle diffusion equation, so the fitting degree of second-order kinetic equation was the highest and intra-particle diffusion equation was the lowest. Therefore, the adsorption of reactive brilliant blue X-BR by the modified branches accorded with the pseudo-second-order kinetic model.

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