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Adsorption of Dye Reactive Brilliant Red X-3B by Rice Wine Lees from Aqueous Solutions

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ABSTRACT

In this study, the adsorption performance of rice wine lees on reactive brilliant red (X-3B) was studied. Five aspects of SEM, FTIR characterization of rice wine lees, initial X-3B pH, rice wine lees dosage and initial dye concentration were studied. The characterization of rice wine lees indicated that it was a good adsorbent due to its larger specific surface area. And the experiment results showed that pH had a great influence on the adsorption effect of rice wine lees, and the adsorption performance decreased with the increase of pH. At the same time, the removal rate of reactive brilliant red X-3B increased with the increase of the dosage of rice wine lees and decreased with the increase of initial concentration of dyes. In the meanwhile, the experimental data were fitted to find that the adsorption of Reactive Brilliant Red X-3B by rice wine lees followed the Langmuir isotherm model. The adsorption kinetics was consistent with the intraparticle diffusion model and the maximum adsorption capacity was 12.376 mg/g.

INTRODUCTION

In the textile industry, various textile chemicals, such as dyes, surfactants, fixing agents, softeners and many other additives, are used in the production process (Sundrarajan et al. 2007). Therefore, the textile wastewater discharged during the production process is extremely loaded, in which dye sewage is the main component of the wastewater. Reactive Brilliant Red (X-3B) is a kind of azo dye which is widely used in the textile industry due to its unique colour. However, this kind of brilliant red dye wastewater is subject to the change of water quality, water quantity and water temperature, and its chromaticity and COD value are extremely high (Yong et al. 2008). Besides, due to the -N=N- double bond in their molecular structure, dye wastewater is very stable in water and is not easily biodegraded, toxic degradation is really slow, causing damage to aquatic organisms and some terrestrial organisms. Therefore, these dyes are classified as environmentally harmful materials (Lu et al. 2009). To avoid polluting the river channel, it must be treated to discharge emission standards before discharging the dye wastewater.

At present, the methods for treating dye wastewater mainly include adsorption method (Annadurai et al. 2002), biological treatment method (Tantak & Chaudhari 2006), chemical oxidation method (Arslan et al. 2000), electrolysis method (Bechtold et al. 2010) and photocatalytic degradation method (Konstantinou & Albanis 2004). However, these methods have some disadvantages such as the high adsorbent price, generation of large amounts of sludge, difficulty in the regeneration of adsorbents, and membrane fouling. Among them, the adsorption method is one of the economical and efficient methods for treating dye wastewater. To solve the problem of expensive industrial adsorbents, in recent years, researchers have used non-living biomass to adsorb dyes in wastewater and achieved remarkable results. Wang et al. (2008) successfully removed methylene blue from aqueous solution by using the nonliving-biomass of seaweed and freshwater plants. And another researcher modified the peanut shell with citric acid and successfully adsorbed methylene blue in aqueous solution (Peng et al. 2015). Some researchers have also discovered that orange peel is a good adsorbent to adsorb the acid dyes in aqueous solution (such as Acid Violet 17) (Sivaraj et al. 2001). In addition to using agricultural waste to treat dye wastewater, researchers have found that distiller's grains may also be a good adsorbent.

Rice wine lees are the main by-products of southern yellow wine enterprises. The annual output of 10 kt rice wine produces about 727 t of rice wine lees every year. As a by-product of the rice wine brewing process, the rice wine grains are rich in a large amount of protein, amino acid and other nutrients and contain a large number of microorganisms including mould, yeast, etc. (Zheng & He 2007), which may be a good adsorbent. It has been reported by many researchers about the adsorption of dyes in wastewater by rice wine lees. For example, Xiaolian et al. (2016) used white distiller's grains to degrade Congo red and malachite green in aqueous solution. However, a large amount of rice distiller's grains is mainly used for feed, and some of them are directly discarded, which pollutes the environment. If a large amount of rice wine grains can be treated with dye wastewater, the effect of 'disused waste' can be achieved, which not only saves energy but also provides a new idea for the degradation of dye wastewater.

In this study, rice wine lees was used as non-living biosorbent, and X-3B was used as the adsorption target. The effects of initial pH, initial concentration and adsorbent dosage on the adsorption performance of rice wine lees adsorbed X-3B were studied. Through the adsorption of isothermal adsorption equation and the kinetic fitting analysis, the adsorption and removal mechanism of rice wine lees on X-3B in wastewater was discussed.

MATERIALS AND METHODS

Materials

All the chemicals were of analytical grade including X-3B, HCl and NaOH. During the experiment, the corresponding dye was dissolved in ultra-pure water produced by the Milli-Q water purification system.

Advanced Treatment by the Adsorbent Rice Wine Lees

The lees used in this experiment was produced during the brewing process of rice wine. A certain amount of rice wine lees was washed with tap water repeatedly until the water flow was excellent and nearly colourless followed by rinsing again 3-4 times with distilled water. It was then wrapped with gauze and squeezed to flush out the water, and later put on a clean tin foil in a tray and spread evenly and loosely. The tray was later placed in an oven for drying. The rice wine lees was turned over for every 5-6 hours to make it properly drier.

SEM Characterization

The original rice wine lees was characterized by SEM and the

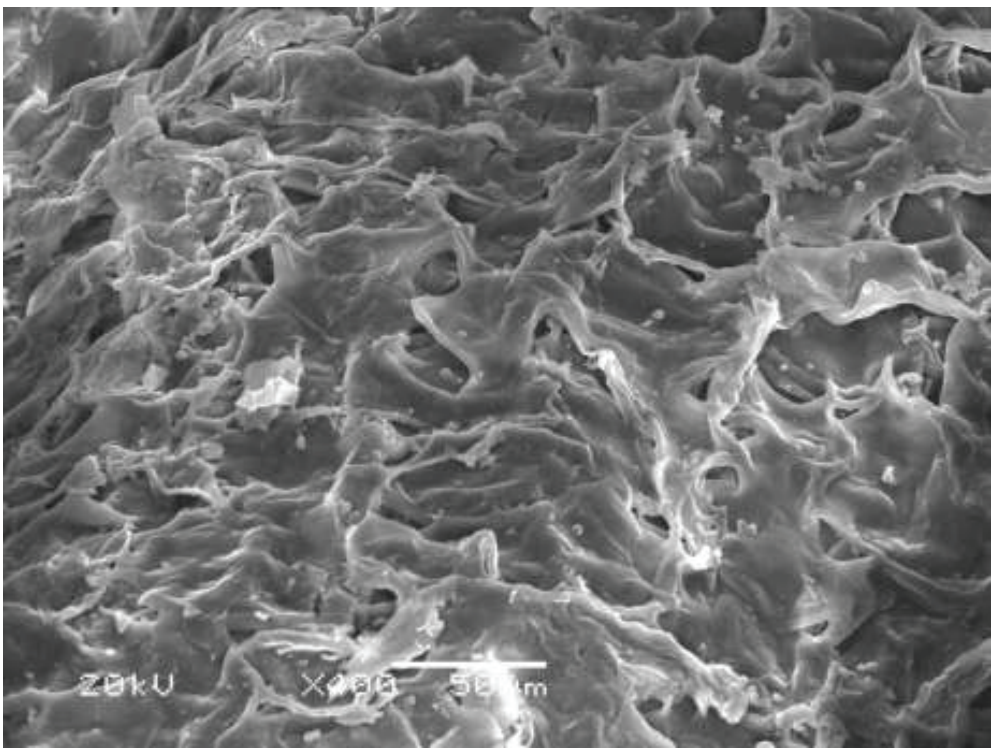


Fig. 1: SEM characterization of original rice wine lees.

results are shown in Fig. 1. It could be seen that the surface of the rice wine lees has many pores, larger pore size, rougher surface and larger specific surface area, which increased the contact area between the rice wine lees and the reactive brilliant red dye molecules. The increase in active sites provided further possibilities for the successful adsorption of reactive brilliant red by the rice wine lees.

Adsorption Experiment

0.500 g X-3B was accurately obtained and dissolved into the 500 mL bottle with deionized water to prepare the standard storage solution of 1 g/L, which was diluted to the corresponding concentrations according to the proportion used during the experiment. 1.25 g rice wine lees was added to a certain concentration of 500 mL containing X-3B solution, placed in a constant temperature shock water bath at 25°C, and stirred in an agitator with rotating speed of 400 r/min. The sample was filtered at a specific time, and the concentration of the remaining X-3B in the solution was measured by ultraviolet-visible spectrophotometry at a wavelength of 536 nm.

Experimental Data Analysis

A standard curve of the absorbance of X-3B concentration was plotted based on the measured absorbance of X-3B, and the equation obtained was y = 0.0178x-0.0028 with $R^2 = 0.9997$. Due to the high correlation coefficient ($R^2 = 0.9997$), it was seen that there was a good linear relationship between concentration and absorbance, which indicated that the equilibrium concentration of X-3B was more accurate. The adsorption could be calculated by equation 1.

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

Where, q_e is the equilibrium concentration of X-3B (mg/L), C_0 and C_e are the initial and equilibrium concentration of X-3B (mg/L), respectively. V is the volume of X-3B solution (L) and W is the weight of used rice wine lees (g).

RESULTS AND DISCUSSION

The FTIR Analysis of Rice Wine Lees

The FTIR spectra of the rice wine lees before and after the reaction are shown in Fig. 2. It can be seen from the figure that the FTIR spectrum of the rice wine lees ranged from 500 cm^{-1} - 4000 cm^{-1} and had a series of adsorption peaks, showing the complex characteristics of the rice wine lees. There was a distinct O-H vibration absorption peak near 3300 cm^{-1}, the characteristic region of the -COOH group near at 2500 ± 300cm^{-1}, C-H stretching vibration of saturated hydrocarbon at 1450 cm^{-1}, and C-O stretching vibration near 1720-1715 cm^{-1}, indicating that there were a lot of hydroxyl and carboxyl groups in the rice wine lees. The absorption peaks of the hydroxyl and carboxyl groups of rice wine lees after the reaction were significantly weakened.

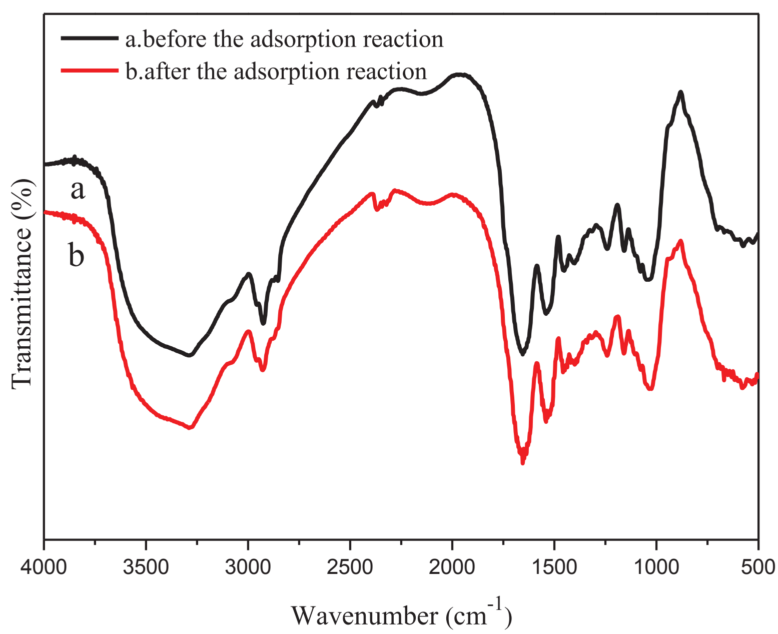


Fig. 2: The FTIR study of rice wine lees.

Effect of Initial pH on Adsorption of X-3B by Rice Wine Lees

The influence of initial pH on the removal efficiency of X-3B by rice wine lees was investigated and the results are shown in Fig. 3. It could be seen that the removal efficiency of X-3B decreased with the increase of pH value. When the pH values were 3.00, 5.00, 7.00 and 9.00, the removal rates of X-3B were 100%, 56.6%, 18.8% and 6.6%, respectively. It could be seen obviously that the pH value of the solution affected the removal efficiency of Reactive Brilliant Red X-3B by the rice wine lees, and the lower the pH value, the higher the removal efficiency of Reactive Brilliant Red X-3B. Since rice wine lees is a by-product of rice wine fermentation, it is rich in protein, amino acids and various amino groups ($-NH_2$, -NH, -N) on biological protein molecules, which are easily protonated under acidic conditions and existed as the forms of $-NH_3^+$, $-NH_2^+$ and $-NH^+$ (Won et al. 2004). These positively charged amino groups combined with negatively charged dye molecules, allowing the rice wine lees to adsorb X-3B successfully. The amount of protonated amine groups increased as the pH decreased, which provided more binding sites. This was consistent with the experimental results. A similar phenomenon was also reported by Wong et al. (2004), who considered that the removal of anionic dyes by Chitosan was mainly due to the combination with protonated amines.

Effect of Different Initial Concentrations on Adsorption of X-3B by Rice Wine Lees

Under the same pH value and the dosage of rice wine lees (5 g/L), the effects of different initial concentrations of dyes on dye removal efficiency by rice wine lees were investigated and the results are shown in Fig. 4. As the figure depicted, the removal efficiency of Reactive Brilliant Red X-3B gradually decreased as the initial concentration of X-3B increased. When the initial concentration of X-3B was 20 mg/L, the removal rate of X-3B was 96.9% after 24 h of reaction. And when the initial concentration of X-3B was increased to 40 mg/L and 60 mg/L, the degradation rate of X-3B was reduced to 92.5% and 90.3%. As the initial concentration of Reactive Brilliant Red X-3B continued to increase to 80 mg/L, the removal rate of Reactive Brilliant Red X-3B was only 73.6%. This may be due to the increasing number of anion sulfonate groups in reactive brilliant red molecules binding to a limited binding site, resulting in the saturation of binding sites and then leading to the degradation efficiency of X-3B.

Effect of Rice Wine Lees Dosage on X-3B Adsorption

Different dosages of rice wine lees were selected to explore the effect of dosage of adsorbent on the adsorption efficiency and the results are shown in Fig. 5. Obviously, in the condition of the same initial concentration of X-3B (10 mg/L) and pH, the removal efficiency of X-3B increased with the increase of rice wine lees dosage. When the dosage of rice wine lees was 5 g/L, the removal rate of X-3B was 29.9% after 120 min of reaction. And when it was 10 g/L, the removal rate of X-3B was 42.7% after 60 minutes of reaction. After 90 minutes of reaction, the removal rates of rice wine lees were 60.4% and 67.7%, respectively, as the dosage were 14

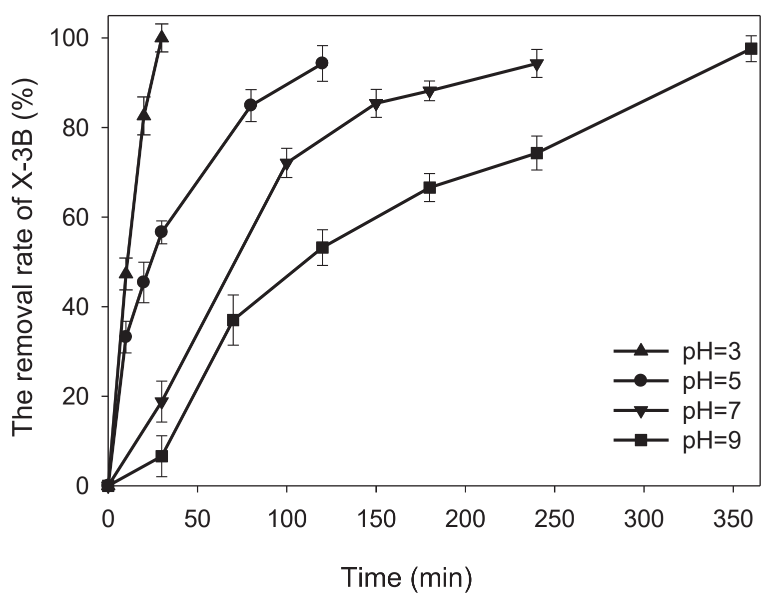


Fig. 3: Effect of different initial pH on the removal of X-3B.

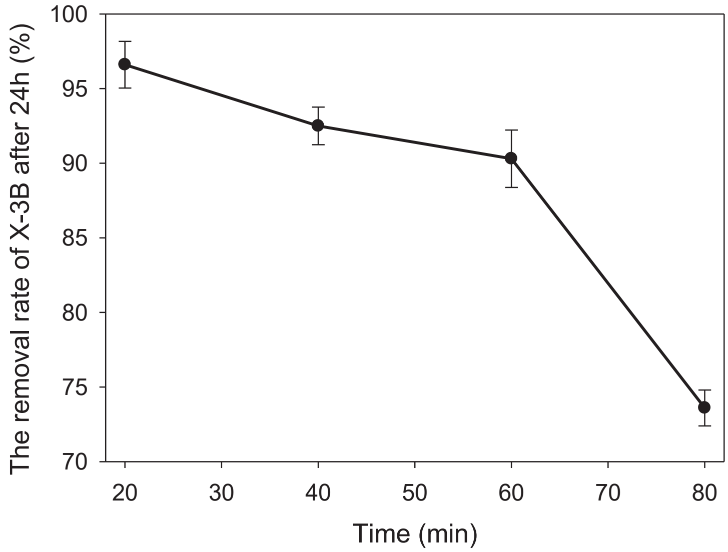


Fig. 4: Removal rate of X-3B at different initial concentrations after 24 hours.

g/L and 18 g/L. It could be seen that increasing the dosage of rice wine lees could increase the removal efficiency of X-3B, and the greater the dosage of rice wine lees, the higher the removal rate of Reactive Brilliant Red X-3B. This was due to the increase of adsorption dose, which led to the increase of adsorption surface area, the increase of functional groups and the increase of the number of qualitative amino groups, thus improving the adsorption efficiency.

Adsorption Isotherms

The adsorption isotherm results of the rice wine lees on reactive brilliant red X-3B are shown in Fig. 6. When the pH was 5, the adsorbent dosage was 5 g/L, and the dye concentration was 10 mg/L. The adsorption isothermal data were linearly fitted by the Langmuir equation, the Freundlich equation and the Temkin equation (equations 2-4), respectively, the fitting results are shown in Fig. 6 and Table 1.

$$\frac{q_e}{C_e} = \frac{C_e}{q_m} + \frac{1}{k_L q_m} \quad \ldots(2)$$

$$Lnq_e = LnK_F + \frac{1}{n} LnC_e \quad \ldots(3)$$

$$q_e = \frac{RT}{b_T} LnA_T + (\frac{RT}{b_T}) LnC_e \quad \ldots(4)$$

Where, q_e is the adsorption capacity of X-3B at equilibrium (mg/g), C_e is dye concentration at equilibrium (mg/L), q_m is saturated adsorption capacity (mg/g), and k_L is the equilibrium constant of Langmuir adsorption isotherm, K_F is Freundlich constant, and R, A, T and b are Temkin constants.

It can be seen from Table 1 that the Langmuir isothermal model has the highest correlation coefficient (R^2=0.9821) compared with the Freundlich and Temkin isotherm models, indicating that the adsorption of reactive brilliant red X-3B by the rice wine lees was more suitable for description by the Langmuir isotherm model. It was further illustrated that the adsorption was mainly the adsorption of the monolayer. The Langmuir equation obtained by fitting was y = 0.1095x+0.0838 (R^2=0.9821) and the maximum adsorption capacity of the residue was 12.38 mg/g. It could be seen that the adsorption performance of the rice wine lees was high.

Adsorption Kinetics

Under the condition of pH 5, the dosage of 5 g/L, the temperature of 298 k and initial dye concentration of 10 mg/L,

Table 1: Adsorption results of X-3B by rice wine lees.

Langmuir isotherm equation			Freundlich isotherm equation			Temkin isotherm equation		
R^2	q_m	k	R^2	k	n	R^2	A	B
0.9821	12.38	0.716	0.9414	4.951	3.026	0.9570	9.2627	2.3628

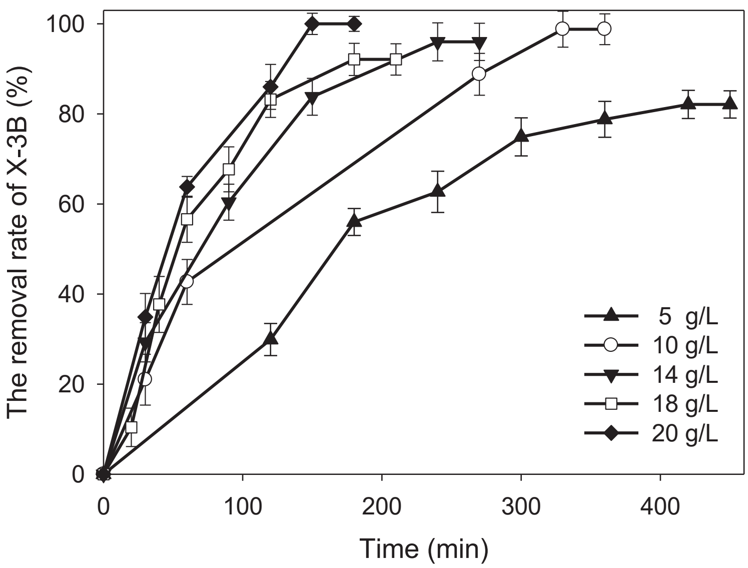


Fig. 5: Effect of different dosage of rice wine lees on the removal of X-3B.

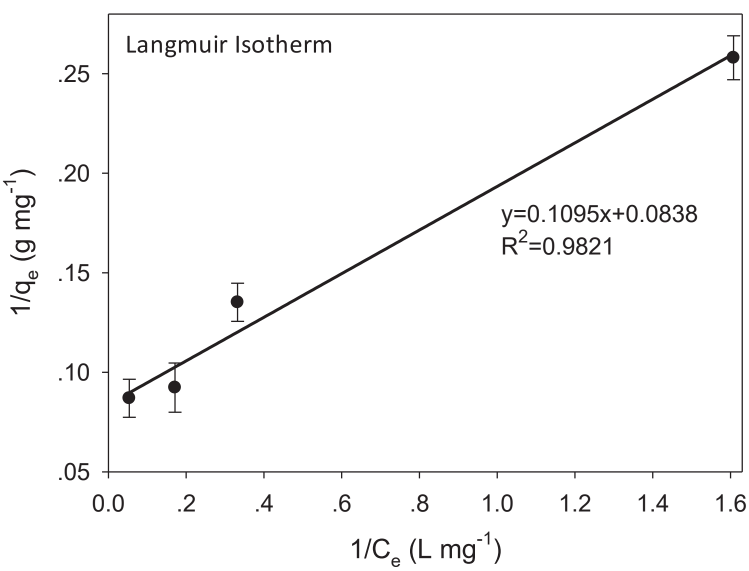
the adsorption kinetics of rice wine lees adsorbed X-3B was investigated. The pseudo-first-order kinetic equation, the pseudo-second-order kinetic equation and the intraparticle diffusion models were used to fit the adsorption data, which are represented by equations 5, 6 and 7, respectively.

$$Ln(q_e - q_t) = Lnq_e - k_1 t \quad \text{...(5)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\;2}} + \frac{t}{q_e} \quad \text{...(6)}$$

$$q_t = k_{id} t^{1/2} + C \quad \text{...(7)}$$

Where q_e and q_t (mg/g) are the amounts of X-3B at equilibrium and at any time t and k_1 and k_2 are the rate constants of pseudo-first-order and pseudo-second-order adsorption. k_{id} is the rate constant of the intraparticle diffusion model and C is truncation. The specific fitting results are shown in Fig. 7 and Table 2. It could be seen from Table 2 that the correlation coefficients (R^2) of the intraparticle diffusion model were



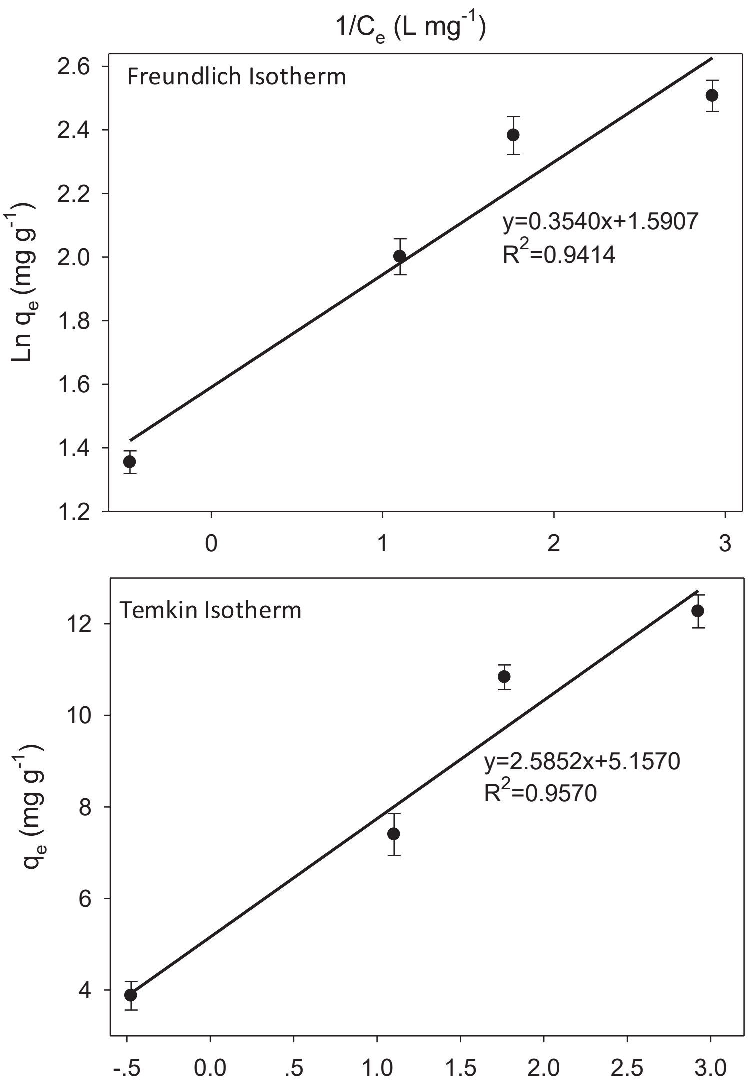


Fig. 6: Three adsorption isotherms for adsorption of X-3B by rice wine lees.

Table 2: Adsorption kinetics and intra-particle diffusion model constant and correlation of X-3B by rice wine lees

Rice wine lees (g/L)	q_e	pseudo-first-order kinetic model		pseudo-second-order kinetic model		intraparticle diffusion model	
		R^2	K_1	R^2	K_2	R^2	K_{id}
5	1.876	0.9975	-0.0023	0.9409	0.5687	0.9998	0.0832
10	1	0.9471	-0.0052	0.9716	0.9022	0.9930	0.0567
14	0.714	0.9775	-0.0058	0.9529	1.0163	0.9985	0.0504
18	0.556	0.9882	-0.0064	0.9098	1.5193	0.9997	0.0467
20	0.5	0.9785	-0.0073	0.9423	1.8127	0.9992	0.0382

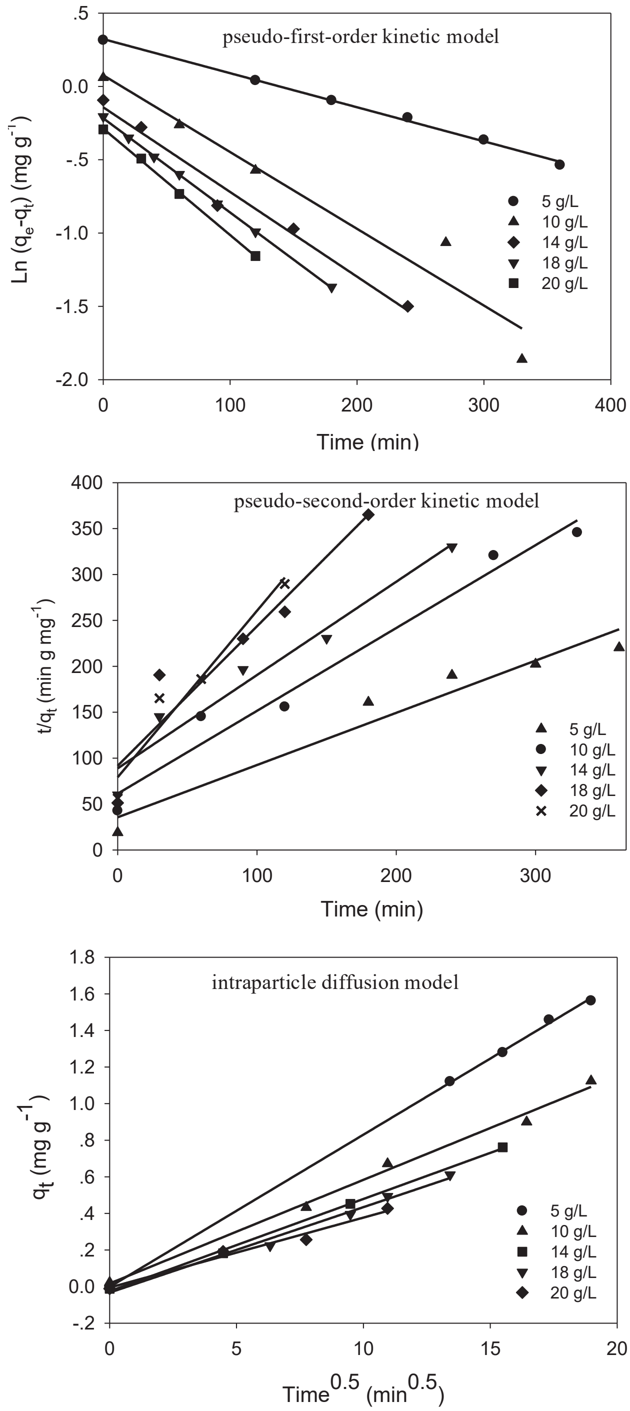


Fig. 7: Pseudo-first-order, pseudo-second-order plots and intraparticle diffusion model plots for X-3B adsorption on rice wine lees.

significantly higher than the correlation coefficient between the pseudo-first-order kinetics and the pseudo-second-order kinetics, which indicated that the intraparticle diffusion model was more suitable for describing the adsorption of X-3B by rice wine lees. Otherwise, we could see from Fig. 7 that the correlation line between q_t and $t^{1/2}$ did not pass through the origin.

CONCLUSION

In this paper, the effect of initial pH, initial concentration of X-3B and the different dosage of rice wine lees on the adsorption of X-3B by rice wine lees were investigated. The results showed that the effect of solution pH on adsorption performance was significant. As the pH value decreased, the adsorption performance enhanced, indicating that the removal rate of Reactive Brilliant Red X-3B became higher. At the same time, the removal rate of X-3B increased with the increase of the amount of rice wine lees and decreased with the increase of the initial concentration. By fitting the adsorption data, it was found that the adsorption reaction of rice wine lees to X-3B was consistent with the Langmuir isotherm adsorption model. The adsorption process accorded with intraparticle diffusion model, and the maximum adsorption capacity was 12.38 mg/g.

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