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Adsorption of Azo Dye Malachite Green onto Rice Wine Lees: Kinetic and Adsorption Isotherms

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ABSTRACT

The adsorption of malachite green in aqueous solution onto rice wine lees was carried out in detail. The effects of different rice wine lees dosage, solution pH and initial concentration on the adsorption of malachite green by rice wine lees were studied. The experimental results showed that the removal rate of malachite green increases with the increasing dosage of rice wine lees. When the dosage of rice wine lees is 5 g/L, the removal rate within 30 min is 96.22%. At the same time, the removal rate increases as the pH of the solution increases, and the removal rate is higher in an alkaline environment. The kinetic study was performed by the pseudo-first-order and the pseudo-second-order reactions. According to the experimental data, the pseudo-second-order kinetic model better described the adsorption of dye onto rice wine lees, it implies that the predominant process is chemisorption. Besides, the adsorption isotherms were studied by Langmuir model, Freundlich and Temkin isotherm models. The results indicated that the adsorption followed the Langmuir model and the maximum adsorption capacity was 21.505 mg/g. The dye malachite green adsorption onto rice wine lees was monolayer adsorption.

INTRODUCTION

With the development of light industry, especially the rise of the textile industry, textile dyes have become the main source of polluted water, of which azo dyes are the most common (Lark & Lark 1979, Shindy 2012). And it is the most widely used synthetic dye in textile and garment printing and dyeing process. Malachite green (MG), as one of the azo dyes, is often used in the dyeing and printing of a variety of natural and synthetic fibres, as well as in the colouring of paints, plastics, rubber and so on (Culp et al. 1999). Not only that, but MG is also a good biocide widely used in aquaculture (Hoffman et al. 1974). However, it has been banned in several countries due to its harmful effects on the immune system, reproductive system, genotoxicity and carcinogenicity of mammals and other animals (Cha et al. 2001, Fernandes et al. 1991). Also, the potential harm of MG to the human body cannot be ignored. Stammati et al. (2005) found that malachite green plays a role as a tumour promoter in the human body. Expect these, the discharge of MG containing sewage would colour the running water and affect the beauty of the river environment. Therefore, dye sewage must be treated innocuously before discharge.

At present, the main treatment methods of printing and dyeing waste water are the electrochemical method, flocculation method, membrane separation method and adsorption method (Purohit et al. 2014). Among these methods, adsorption is considered to be a relatively effective method for removing dyes and controlling BOD. However, the high cost of industrial adsorbents makes the adsorption process more expensive. Therefore, it is of great significance to find cheap and effective adsorbents instead of industrial adsorbents (Tahir et al. 2017). Due to the characteristics of low cost, recyclable and easy to obtain of agricultural waste, some researchers used peanut shell (Liu et al. 2018), straw (Robinson et al. 2002), orange peel (do Nascimento et al. 2014), peanut (do Nascimento et al. 2014), garlic waste (Hameed & Ahmad 2010), rice husk (Forss et al. 2013) and other agricultural waste residues to adsorb waste water, and successfully achieve the purpose of adsorption. Otherwise, some researchers have used steel industry residue successfully removing the treat basic violet 3 dye from aqueous solutions (Amaral et al. 2016). However, the use of rice wine lees to treat dye waste water has rarely been reported at home and abroad.

As we all know, Shaoxing is not only a strong textile city but also the birthplace of rice wine. With the development of the textile industry and the rice wine manufacturing industry, a large amount of dye sewage and rice wine lees will be produced every year, which harms the environment. Baoe et al. (2009) successfully adsorbed two kinds of azo dyes, Reactive Black

31 and Reactive Blue 49, in certain conditions by using beer grains. Xiaolian et al. (2016) used distillers' grain to absorb Congo red and malachite green. The same as the by-product liqueur produced in the wine-making process, if the rice wine lees can be used for the adsorption of azo dyes, it will greatly promote the ecological environment and energy conservation of Shaoxing. In the previous experiments, we found that the main components of rice wine lees were similar to those of raw materials. After fermentation and saccharification, the starch content was significantly reduced, while the proportion of crude protein, crude fibre, crude fat and ash in the rice wine lees is higher. Besides, there was microbial flora in the rice wine grains, including yeast, mould, bacteria, etc. (Xie et al. 2013), which was also a kind of good adsorbent.

In order to further explore the decolourization effect of rice wine lees on azo dyes, malachite green was selected as the object of investigation. And the effects of the pH value of malachite green dye, initial malachite green concentration and the dosage of rice wine lees on the adsorption performance were investigated. The adsorption and removal mechanism of rice wine lees on the malachite green in sewage was discussed by fitting the isothermal adsorption equation and kinetic equation, which may provide a new idea for the treatment of azo dye sewage by rice wine lees.

MATERIALS AND METHODS

Pre-Treatments of the Adsorbents

The rice wine lees used in this experiment was the slag produced during the brewing process of rice wine. A certain amount of rice wine lees was taken in the container, firstly, rinsed with distilled water until the water flow was colourless, and then rinsed again with distilled water 3-4 times. Secondly, the rice wine lees was wrapped with gauze and squeezed to out the water. Then a clean tin foil was put on the tray and spread the previously treated lees. Thirdly, it was put in an oven for drying, during the period, and turned over every 5-6 hours to make it much drier. Finally, it was pulverized using a crusher.

Dye Solution Preparation

The dye solution (1 g/L) was prepared by adding 0.5 g malachite green to 500 mL ultra-pure water. The original solution was diluted to 3 mg/L, 5 mg/L, 7 mg/L and 10 mg/L respectively by dilution method as the experiment concentration.

Adsorption Experiment

The adsorption experiments were carried out in 500 mL jar at 25°C in a constant temperature shock water bath pot. The process variables, rice wine lees dosage (1~5 g/L), pH (5~10) and initial MG dye concentration (10~50 mg/L) were investigated. The pH of the medium was adjusted by 0.01 M NaOH/HCl. And to study the individual effect parameters, one variable was kept varying, while other parameters were kept constant. The residual concentration of MG dye was determined by the spectrophotometry at absorbance 618 nm.

Experimental Data Analysis

A standard curve of absorbance-MG concentration was plotted based on the measured absorbance of MG, and the equation was obtained as follows: $y = 0.1325x + 0.0275$, $R^2 = 0.9998$. Due to the high corresponding correlation coefficients (R^2) of 0.9998, there was a good linear relationship between absorbance and concentration, which indicated that the equilibrium concentration of MG was more accurate. And then the amount of adsorption could be calculated by equation 1.

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

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

RESULTS AND DISCUSSION

The Influence of Rice Wine Lees Dosage on Removal Efficiency of MG

The adsorption effect of rice wine lees dosage on the malachite green was investigated, and the results are given in Fig. 1. It can be seen that the adsorption capacity of MG increased with the increasing of rice wine lees dosage. When the adsorbent dosage was 1 g/L and 2 g/L, and reaction time was 20 min, the removal rates of malachite green were 44.24% and 57.94%, respectively, as the dosage increased to 3 g/L and 5 g/L, the removal rate increased to 68.67% and 81.36%. This attributed to the increase of adsorption surface area and adsorption functional groups. Based on previous research, in general, the adsorbate removal rate and adsorption capacity of adsorbents always increase with the increase of effective active sites (Fraga et al. 2018).

The Effect of Initial pH on Removal Efficiency of MG

The difference in adsorption of dyes in different pH ranges is related to the surface charge properties of the rice wine lees and the charge properties of the dye after dissociation. Therefore, the effect of initial pH on the removal efficiency of MG by rice wine lees was investigated, and the results are shown in Fig. 2. The removal efficiency of malachite green

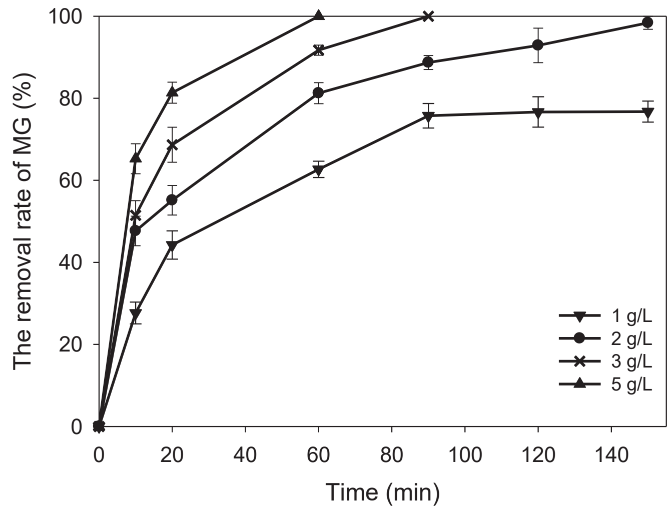

Fig. 1: Effect of different rice wine lees dosage on the removal of malachite green. (C_0=10 mg/L, pH=5.5, t=25)

increased when the pH increased from 5 to 10. When pH value was 5.00 and 7.00, after 20 min reaction, the removal rate of malachite green was 51.21% and 64.51%, respectively. As the pH reached 10, the removal rate of malachite green increased to 86.43%. This may be explained by the fact that MG is a kind of a cationic dye and in the acidic conditions, MG has the same charge as H^+, H_3O^+. The three compete with each other for the adsorption sites on the rice wine lees, resulting in a lower adsorption rate of MG. Contrary to acidic conditions, with the increase of pH, the competitive effect of H_3O^+ or H^+ is weakened, the negative charge functional groups are exposed, the electrostatic attraction between dye cations and adsorbents is produced (Shroff & Vaidya 2011). At this time, the surface of the rice wine lees has a negative charge, which is favourable for adsorbing the positive charge malachite green.

The Effect of Initial Concentration on Removal Efficiency of MG

The effect of initial concentration on the removal efficiency of malachite green by rice wine lees is shown in Fig. 3. The removal efficiency of the MG gradually decreased with the

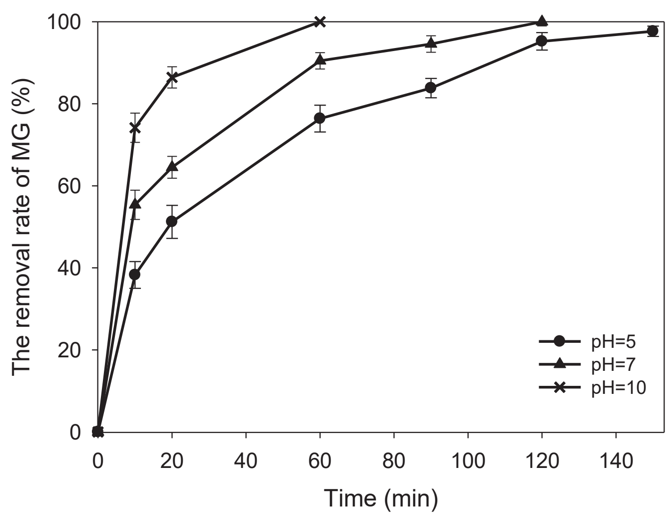

Fig. 2: Effect of different initial pH on the removal of malachite green.

(C_0=10 mg/L, dosage=1 g/L, t=25°C).

increase of the initial concentration of MG under the condition of the same pH value (pH=5) and the same dosage of the rice wine lees (5 g/L). When the initial concentration of MG was 20 mg/L, the removal rate was 93.13% after 24 hours of reaction, and the removal rate decreased to 89.87% and 84.07%, respectively as the initial concentration increased to 30 mg/L and 40 mg/L respectively. When the initial concentration of malachite green increased to 50 mg/L, the removal rate was only 76.42%. This is because when the amount of the adsorbent is constant, the adsorption sites are constant. There are sufficient adsorption sites to bind the MG when the initial concentration of the dye is low, so the adsorption efficiency is high. Therefore, it can be seen that the adsorption depends on the initial concentration, and the effective binding sites are saturated at a very high initial concentration. For the effective binding sites, the competition between ions will intensify and the adsorption will slow down (Manzoor et al. 2013).

Adsorption Isotherms

The adsorption isotherm is a curve, which refers to the relationship between the concentration of solute molecules in the two phases when the adsorption of solute molecules on the interface of the two phases reaches equilibrium at a certain temperature. At a certain temperature, the concentration relationship between the separated substances in the liquid phase and the solid phase can be expressed by the adsorption equation. Therefore, the relationship between adsorbates and adsorbents, the adsorption effect and maximum adsorption capacity of adsorbents can be understood by adsorption isotherms, which is helpful to understand the adsorption mechanism. The Langmuir adsorption model assumes that the surface of the adsorbents is uniform and the energy of each adsorption centre is the same, and in the certain conditions, the adsorption rate is equal to the desorption rate, then the adsorption equilibrium is reached (Nadeem et al. 2016, Ullah et al. 2013). The linear form of Langmuir adsorption isotherm is given in equation 1.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad \ldots(1)$$

Where, q_e is equilibrium adsorption capacity and q_m is limit adsorption capacity (mg/g), C_e is equilibrium concentration (mg/L) and K_L is Langmuir adsorption equilibrium constant.

The Freundlich isotherm model can be used to describe the adsorption on the non-uniform surface or to describe the multi-layer adsorption. The linear form of the Freundlich isotherm model is given in equation 2.

$$Lnq_e = LnK_F + \frac{1}{n} LnC_e \qquad \ldots(2)$$

Where, q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e represents the equilibrium concentration of dye in solution (mg/L), and K_F, n are Freundlich constant.

Temkin considered the effects of some indirect adsorbate/adsorbent interactions and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The linear

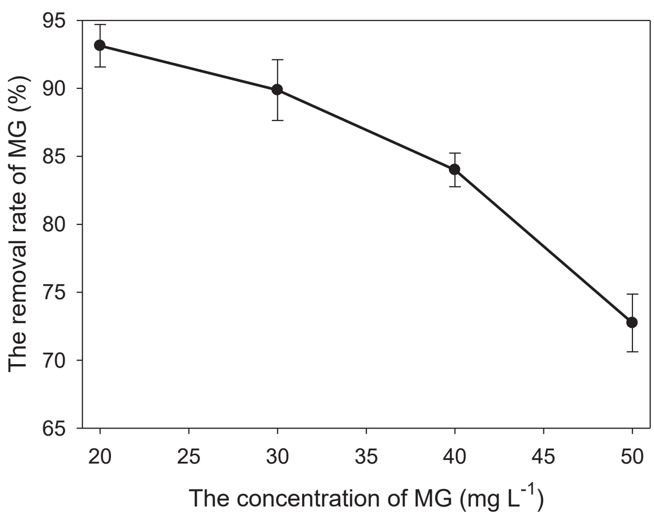

Fig. 3: Removal rate of malachite green at different initial concentrations for 24 hours. (pH=5, dosage=5 g/L, t=25°C).

equation of the Temkin isotherm model is given in equation 3.

$$q_e = \frac{RT}{b_T} LnA_T + (\frac{RT}{b_T}) LnC_e \quad \ldots(3)$$

Where, q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of GM (mg/L), R, A, T and b are the Temkin constants. The experimental data were simulated by these adsorption models, and the results are shown in Table 1 and Fig. 4. Compared with the R^2 of Langmuir, Freundlich and Tempkin isotherm model, the R^2 of Langmuir is the largest, so the Langmuir monolayer adsorption model can better explain the equilibrium adsorption data of MG dye. The fitted linear equation is y =0.0792x+0.0465. And the maximum adsorption capacity was 21.505 mg/g.

Adsorption Kinetics

The adsorption data of different rice wine lees dosage were subjected to pseudo-first-order and pseudo-second-order kinetic models and the intraparticle diffusion model. The linear form of pseudo-first-order kinetics is given in equation 4.

$$Ln(q_e - q_t) = Lnq_e - k_f t \quad \ldots(4)$$

Where, q_e is the adsorption efficiency (at equilibrium) (mg/g), q_t is the adsorption at time t (mg/g), and k_f is the rate constant of pseudo-first-order.

The linear form of pseudo-second-order kinetic model is given in equation 5.

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \quad \ldots(5)$$

Where, q_e represents the equilibrium adsorption capacity (mg/g), q_t represents the adsorption capacity when the time is t (mg/g), and k_s represents the second order adsorption rate constant.

The specific results are given in Table 2 and Fig. 5. According to Table 2, it was obvious that there was a good relationship between t/q_t and t with high R^2 of 0.9923, 0.998, 0.9997. Therefore, the pseudo-second-order kinetic model is more suitable for describing the adsorption of MG by rice wine lees. And the reaction is mainly chemical adsorption.

The linear form of the intraparticle diffusion model is given in Equation 6.

$$q_t = k_{id} t^{1/2} + C \quad \ldots(6)$$

Where, C is the constant of the boundary layer and the thickness. K_{id} is the internal diffusivity constant. If the line between q_t and $t^{1/2}$ through the origin, the internal diffusion is controlled by a single factor (otherwise, the adsorption process may involve multiple mechanisms) (Debrassi et al. 2012).

The fitting results are shown in Fig. 5. The adsorption data of the three kinds of rice wine lees dosages showed that q_t and $t^{1/2}$ had a good linear relationship with high R^2 and the line did not pass through the origin, which indicated that multiple mechanisms may be involved in the adsorption of MG by rice wine lees, and the adsorption was mainly based on chemisorption.

CONCLUSIONS

In this study, the adsorption properties of MG by rice wine lees were studied. The experimental results showed that MG can be adsorbed by rice wine lees, as the dosage is increased, the adsorption rate is faster. And it decreases with the increase in dye concentration. At the same time, the adsorption capacity is the largest when the pH reaches to 10. Kinetic

Table 1: Adsorption results of malachite green 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
0.9946	21.505	0.5871	0.9786	2.58597	3.0294	0.9168	2.225	10.415

Table 2: Adsorption kinetics and intra-particle diffusion model constant and correlation of malachite green 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}
1	7.4117	0.9287	0.0237	0.9923	0.1142	0.9435	0.6204
2	4.747	0.9194	0.0125	0.998	0.193	0.9156	0.3326
3	2.9131	0.9857	0.027	0.9997	0.2885	0.9515	0.3832

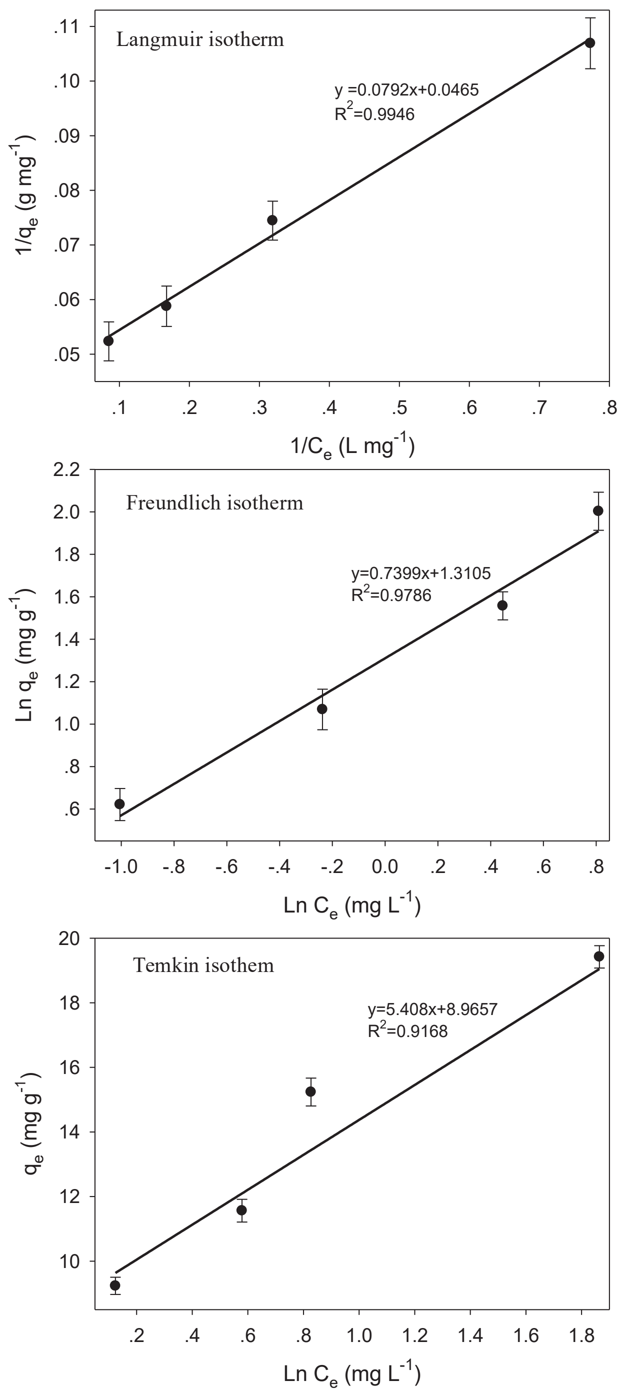

Fig. 4: Three adsorption isotherms for adsorption of malachite green by rice wine lees.

studies showed that the adsorption process of rice wine lees on malachite green accords with the pseudo-second-order kinetic equation. The experimental data were fitted using three theoretical adsorption models, Langmuir, Freundlich and Temkin. The results showed that the Langmuir adsorption equation can better describe the adsorption of dyes by rice wine lees. The saturated adsorption capacity of malachite green was 21.505 mg/g which was calculated by the

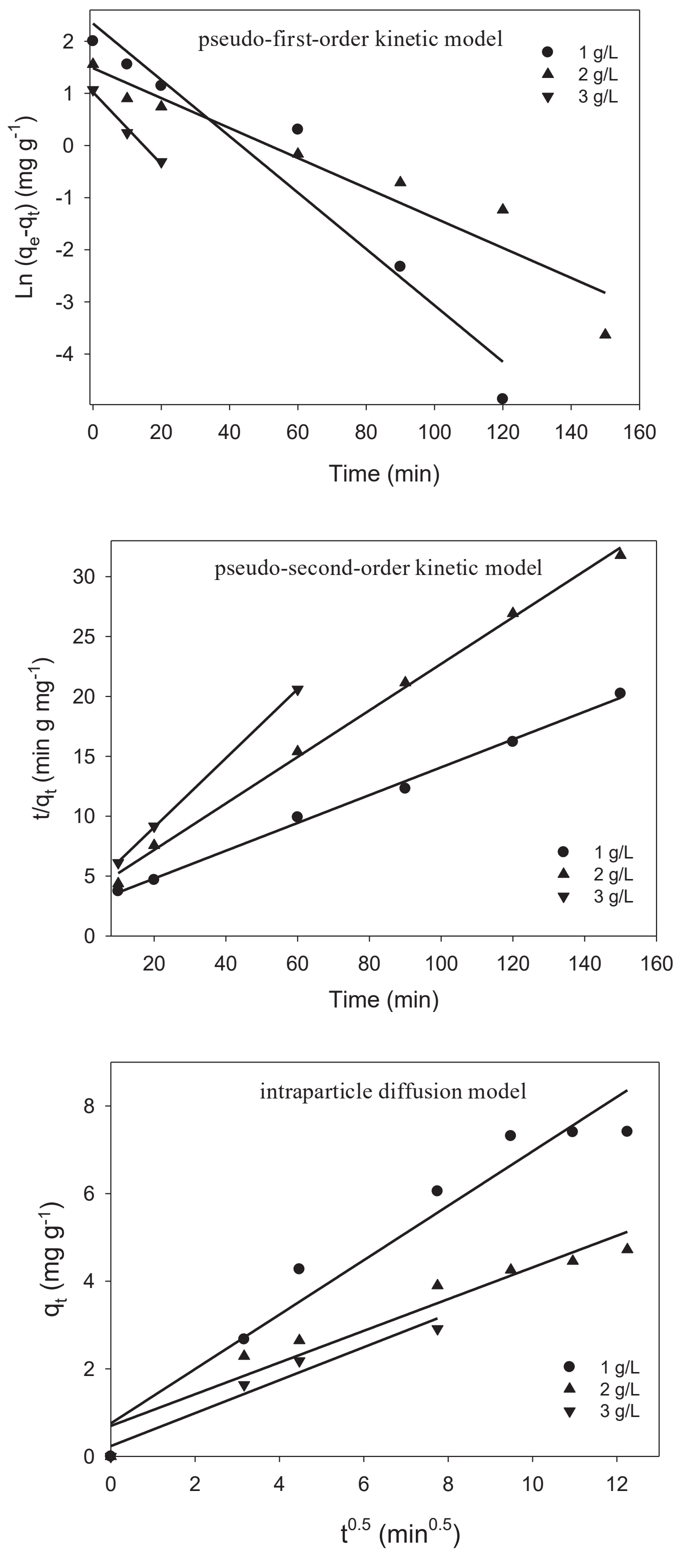

Fig. 5: Pseudo-first-order, pseudo-second-order plots and intraparticle diffusion model plots for MG adsorption on rice wine lees.

Langmuir equation. As a kind of brewing material, rice wine lees is a kind of “waste” for enterprises, if it can be used as a new type of adsorbent, it can provide a new way to treat dye-containing waste water and save energy.

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