Adsorption kinetics and isothermal adsorption model of crystal violet on modified red mud

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Abstract. The adsorption of crystal violet on red mud modified by sodium dodecylbenzene sulfonate (SDBS) was studied. The effect of the dosage of modified red mud on crystal violet adsorption was investigated. The results of kinetics and thermodynamics experiments showed that the adsorption of crystal violet by adsorbent fitted with the pseudo-second-order adsorption kinetic model better. The adsorption of crystal violet on modified red mud could be described by Langmuir and Freundlich models, and the adsorption was better in accordance with Freundlich isothermal adsorption model. According to the Langmuir adsorption model, the maximum adsorption capacity of adsorbent was 38.16mg/g at 303K.

1. Introduction
Red mud is a byproduct of alumina production, which is named for its red mud shape[1]. It is the largest waste produced in alumina production process and the largest pollution source of alumina production. About 120 million tons of red mud are produced in the world every year[2], and half of which is produced in China. The accumulated storage of red mud has been several hundred million tons, almost all of which are in the state of open-air storage[3]. A large amount of red mud not only occupied land and wastes resources, but also brought environmental pollution and security risks. The comprehensive utilization of red mud at home and abroad was mainly used for the production of cement, building materials, ceramics, etc.[4-5], while Bayer red mud with high iron and aluminum content was mainly used for the recovery of valuable metals[6-7]. Because of its fine particles and large specific surface area, red mud has high reactivity. Red mud could be used for waste gas treatment, absorption of non-metallic ions and soil treatment. Red mud in China has been mainly used as adsorbent or flocculant in water treatment to remove high concentration phosphate, fluorine, heavy metals, dyes, etc[8-9].

2. Materials and methods

2.1. Adsorbent and adsorbate
Red mud modified by sodium dodecylbenzene sulfonate (SDBS): 2.5 g red mud and 150mL of 0.5% sodium dodecylbenzene sulfonate solution was mixed in a 250mL conical flask and vibrated on an air bath oscillator at 25 ℃ for 24h. Then the adsorbent was washed with distilled water to neutral and dried in a drying oven at 105 ℃ for 24 hours.

Crystal violet (CV) was purchased from Tianjin Zhiyuan chemical reagent Co., Ltd. Crystal violet was weighed 1.0000g accurately to dissolve in distilled water, and transferred to a 1000mL volumetric
flask for constant volume and standby. In the experiment, a certain amount of distilled water was added to dilute the stock crystal violet solution to the required concentration before use.

2.2. Experiments of adsorption
A certain amount of SDBS modified red mud and 50ml of crystal violet solution with a certain initial concentration of 50mg/L was added into 150mL iodine volumetric flask. After shaking adsorption in an air bath shaking table for a certain period of time, the supernatant was centrifuged at 4000r/min for 15min to determine the residual crystal violet concentration. According to the fitting equation of the standard curve, the equilibrium concentration of crystal violet was calculated, and then the adsorption rate E (%) and adsorption amount q_e (mg/g) were calculated by equation (1) and (2), respectively.

\[ E(\%) = \left( \frac{C_0 - C_e}{C_0} \right) \times 100\% \]  
\[ q_e = \left( \frac{C_0 - C_e}{M} \right) \times V \]  

Where C_0 and C_e (mg/L) were the initial and equilibrium concentration of crystal violet solution, respectively; M (g) was the mass of SDBS modified red mud; V (L) was the volume of the solution.

3. Results and Discussion

3.1. Effect of the dosage of SDBS modified red mud on crystal violet adsorption

SDBS modified red mud of 1-8g/L was added to a conical flask containing 50mg/L crystal violet solution for mixing and shaking for 120min. It can be seen in Figure 1 that the adsorption rate of crystal violet gradually increased to a maximum and then decreased a little with the increase of the dosage of SDBS modified red mud. The adsorption capacity q_e decreased with the increase of the dosage of modified red mud. This was due to the increase of the amount of modified red mud, which made the contact area between red mud and crystal violet larger, the adsorption rate was also increased. Because the amount of crystal violet was fixed, increasing the amount of modified red mud would lead to the decrease of liquid-solid ratio, so the adsorption rate tended to balance in the later. The adsorption rate could get 94.2% at modified red mud dosage of 6g/L.
3.2. Adsorption kinetics

Adsorption kinetics was a theory to study the relationship between adsorption capacity and time in the adsorption process, that was, the problem of adsorption speed and adsorption dynamic balance. In this paper, the pseudo-first-order and pseudo-second-order kinetic models (equation (3) and (4)) were used to fit the adsorption kinetic curve and calculate the adsorption rate constant, respectively. The results were shown in Figure 2, Figure 3 and Table 1.

\[
\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)
\]

Where \(q_e\) and \(q_t\) were the amounts of crystal violet adsorbed at equilibrium and time \(t\), respectively; \(k_1\) and \(k_2\) was the rate constant of pseudo-first-order and the pseudo-second-order kinetic model, respectively.

![Figure 2 Plot of pseudo-first-order dynamic model of modified red mud on crystal violet adsorption](image)

Figure 2 Plot of pseudo-first-order dynamic model of modified red mud on crystal violet adsorption

![Figure 3 Plot of pseudo-second-order dynamic model of modified red mud on crystal violet adsorption](image)

Figure 3 Plot of pseudo-second-order dynamic model of modified red mud on crystal violet adsorption

It was found that the adsorption process of crystal violet by modified red mud could be well described by pseudo-first-order and pseudo-second-order kinetic model equation. The parameters were shown in Table 1, it could be seen that the pseudo-second-order kinetic model could better describe
the adsorption kinetics of modified red mud to crystal violet. The pseudo-second-order kinetic model included all the processes of adsorption, such as external liquid film diffusion, surface adsorption and particle internal diffusion, which could more truly reflect the adsorption mechanism of SDBS modified red mud on crystal violet. The value of $q_e$ calculated by the pseudo-second-order dynamic equation was closer to the actual value of $q_e$.

### Table 1 Parameters of pseudo-first-order and pseudo-second-order models of modified red mud on crystal violet adsorption

| CV concentration | Pseudo-first-order | Pseudo-second-order |
|------------------|--------------------|---------------------|
|                  | $q_e$(mg·g$^{-1}$) | $k_1$(min$^{-1}$)  | $R^2$   | $q_e$(mg·g$^{-1}$) | $k_2$(g·mg$^{-1}$·min$^{-1}$) | $R^2$   |
| 50mg/L           | 1.198              | 0.0181              | 0.8662 | 11.82              | 0.0682                       | 0.9999 |
| 80mg/L           | 1.239              | 0.0075              | 0.8494 | 16.08              | 0.0634                       | 0.9996 |

### 3.3. Isothermal adsorption model

Langmuir and Freundlich isotherm equations (equation (5)-(6)) were used to fit the adsorption data of crystal violet on SDBS modified red mud during 298K and 313K. The plots were shown in Figure 4, Figure 5, and the calculated parameters were in Table 2.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m}$$  \hspace{1cm} (5)

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e$$  \hspace{1cm} (6)

Where $q_e$ was the amount of crystal violet adsorbed per gram of modified red mud (mg/g); $C_e$ was the equilibrium concentration of crystal violet in a solution (mg/L); $b$ was the Langmuir constant, which was related to the affinity of binding sites; $q_m$ was the theoretical saturation capacity of the monolayer (mg/g), and $k$ and $n$ were the Freundlich constants, which corresponded to the adsorption capacity and the adsorption intensity of the adsorbent, respectively.

From 298K to 313K, the adsorption of crystal violet on SDBS modified red mud conformed to the adsorption isotherm of Langmuir and Freundlich, and fitted Freundlich isothermal better. The theoretical saturation capacity $q_m$ from 298K to 313K was 36.36, 38.16, 38.02 and 36.9mg/g, respectively. Higher affinity for adsorbate was related to higher value for $k$ and the values of the empirical parameter $1/n$ lied between 0 and 1, indicating favorable adsorption.

![Figure 4 Langmuir isotherms of crystal violet adsorption on SDBS modified red mud](image-url)
Figure 5 Freundlich isotherms of crystal violet adsorption on SDBS modified red mud

| Parameters of Langmuir and Freundlich isothermal adsorption model |
|---------------------------------------------------------------|
| Temperature (K) | \( q_m \) (mg/g) | b | \( R^2 \) | Temperature (K) | k | n | \( R^2 \) |
|-----------------|----------------|---|---------|----------------|---|---|---------|
| Langmuir        | 298            | 36.36 | 0.0605 | 0.9796        | 298 | 5.2273 | 0.4280 | 0.9922 |
|                 | 303            | 38.16 | 0.0467 | 0.9389        | 303 | 4.5869 | 0.4514 | 0.9831 |
|                 | 308            | 38.02 | 0.0421 | 0.9253        | 308 | 4.3492 | 0.4528 | 0.9745 |
|                 | 313            | 36.90 | 0.0385 | 0.9036        | 313 | 4.1732 | 0.4451 | 0.9558 |
| Freundlich      |                |      |         |               | 308 | 4.3492 | 0.4528 | 0.9745 |
|                 |                |      |         |               | 313 | 4.1732 | 0.4451 | 0.9558 |

4. Conclusion
SDBS modified red mud was used to treat crystal violet simulated dye wastewater in this paper. According to the experiment of the dosage of modified red mud, it showed that the adsorption rate of crystal violet could reach 94.2% at the dosage of modified red mud of 6g/L. The reaction kinetics of adsorption of crystal violet with different concentrations on modified red mud was in good agreement with the pseudo-second-order kinetic model. Crystal violet adsorbed on modified red mud fitted with Langmuir and Freundlich isothermal adsorption models at different temperatures by the isotherm adsorption model analysis. Both of them could describe the adsorption behavior of crystal violet on modified red mud, and Freundlich adsorption isotherm model was better in accordance with it. From the parameters of Langmuir adsorption isotherm, it could be concluded that the maximum saturated adsorption capacity was 38.16 at 303K. According to Freundlich's theory, 0<1/n<1 indicating that adsorption was a favourable adsorption process.

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