Adsorption of Rhodamine B wastewater by sulphur acid modified fly ash

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Abstract. In this study, fly ash was modified using sulphur to remove Rhodamine B (RB) from aqueous solution. This paper discussed the influence of adsorption time, modified fly ash dosage, pH value, initial concentration on the removal efficiencies. The results showed that 50.0 mL RB wastewater whose concentration was 10.0 mg/L, the adsorbent dosage was 0.3000 g, the pH was 2.0, adsorption time was 60.0 min, the removal efficiencies (RE) and elimination capacity (EC) were 84.68% and 1.41 mg/L, respectively. The modified fly ash adsorption of RB obeyed the Freundlich isotherm equation, belong to the multilayer adsorption. The adsorption process was accorded with second kinetics reaction of Lagergren. The results implied that fly ash can be effective used as adsorbent to RB wastewater.

1.Introduction
Rhodamine B (RB) is well known color effluents and found problematic because of their chemical biochemical oxygen demand, amount of suspended solids, toxic components and color constituent. RB ingestion in human causes irritation, gastrointestinal disorders, carcinogenicity and reproductve damage, etc[1]. Fly ash usually refers to the pulverized coal powder in coal-fired power plants after combustion in the boiler from the flue, collected by dust collector. Each year about 50 billion tons of fly ash was produced around the world[2]. Fly ash with porous structure, larger specific surface area, adsorption performance to a certain extent, and even can be instead of activated carbon, silica gel as adsorbent for special purpose, such as fly ash main composition is SiO$_2$ and Al$_2$O$_3$. There are a lot of A1, Si and other active point, combined by chemical bonds and adsorbate[3]. In recent years, the potential of fly ash materials as enviromental pollutant absorbent were demonstrated[4].

In this paper, sulphuric acid modified fly ash was used as a adsorption for the removal of RB wastewater. The removal efficiencies (RE) and elimination capacity (EC) were investigated under different experimental conditions, including dosage, adsorption time, initial concentration of RB wastewater and pH. The Freundlich isotherm equation and kinetic models were used to analyse RB adsorption experimental data.

2.Materials and methods

2.1 Experimental material
Fly ash were obtained from Yanji power plant, and crushed through 0.5 mm sieve. Modification process of fly ash expressed as follows: 50.0 g fly ash were put in 1000 mL beaker, added 500 mL H$_2$SO$_4$ (1 moL/L) solution, soaked for 24 h, washed with deionized water to neutral pH, dried in oven at 103°C for 3 h.
2.2 Analytical methods
The concentration of RB in aqueous solution was analyzed via a 723 spectrophotometer at the maximum wavelength of 550.0 nm.

2.3 Experimental designs
Using the single factor variable method, the effects of adsorption time, modified fly ash dosage, pH value, initial concentration on the RB removal were investigated. The Experimental steps were: 50.0 mL of certain concentration of RB wastewater was transferred into a 100 mL flask, a certain weight of modified fly ash was added, then shaked at 180 r/min and 25°C for a certain time on the shaker. The filtrate was filtered, the concentration of RB was measured by 723 spectrophotometer at 550.0 nm. The removal efficiencies(RE) of RB was calculated: \( RE = \frac{(C_0 - C_e)}{C_0} \times 100\% \) and elimination capacity(EC) was calculated: \( EC = \frac{(C_0 - C_e) \times V}{W} \), \( C_0 \) was the initial concentration of RB wastewater (mg/L); \( C_e \) was the concentration of RB wastewater (mg/L) after adsorption, \( V \) was the volume (mL) of RB wastewater, \( W \) was the dosage (g).

3. Results and analysis
3.1 The effect of dosage
The influence of the dosage on the removal of RB was shown in Figure 1. The results of RE and EC are explained as follows. The RE gradually increased with the dosage increased, when the dosage was between 0.3000 and 0.5000 g, the RE changed little, from 91.07% to 96.61%. The reason is that the adsorption site and more available surface increased with the dosage increased. The EC was gradually decreased with the dosage increased. Increasing the dosage means that the adsorption sites are excessive, result in lower EC[5]. Therefore, when the adsorbent was added from 0.3000 to 0.5000 g, it was saturated and reached equilibrium. In summary, the next experiments were conducted with a dosage concentration of 0.3000 g. The corresponding RE and EC were 91.07% and 0.91 mg/g, respectively.

3.2 Effect of adsorption time
As shown in Figure 2, the effect of adsorption time on the RE and EC were studied. The RE and EC increased with the increase of adsorption time. Modified fly ash tended to remove RB within 60.0 min. The adsorption equilibrium time was 60.0 min-100.0 min, and the RE and EC changed little, were 92.15%-98.53% and 0.92 mg/L-0.98 mg/L, respectively. The adsorption mainly includes three processes[6]: firstly, the adsorbate diffused to the adsorbent surface through the liquid film or external diffusion; nextly, the adsorbate entered into porous structure of the adsorbent; at last, the adsorbate was adsorbed and desorbed by mass motion. Therefore, prolonging the adsorption time leded to desorption, 60.0 min was selected as the optimal adsorption time.

![Removal efficiencies and Elimination capacity](image_url)
3.3 Effect of initial RB concentration

Figure 3 showed the effect of initial concentration of RB wastewater on the RE and EC. When the initial concentration of RB wastewater increased from 4.0 to 16.0 mg/L, the RE decreased from 97.46% to 70.84%, while the EC increased from 0.65 mg/L to 1.89 mg/L. Ion mass transfer resistance is reduced by concentration gradient driving force, thus increasing the EC[7]. The initial concentration of RB wastewater was 10.0 mg/L, the RE and EC were 85.51% and 1.43 mg/L, respectively. The next experiments were conducted with initial RB concentration of 10.0 mg/L.

3.4 Influence of pH

The pH of RB wastewater can promote or inhibit adsorption efficiency, for the surface charge of adsorbent and adsorbate were affected. Figure 4 showed the effect of pH on the adsorption of RB by fly ash. The RE and EC decrease with pH increased from 2.0 to 12.0. It was mainly related to the RB pKa was 3, when the pH of the aqueous solution was greater than 3.0, the carboxyl group of RB was ionized to amphoteric RB ions, then formed dimer of RB in aqueous solution. The dimer has larger molecules, and difficulty entered into the micropores of fly ash, decreased adsorption efficiency[8]. Therefore, the RE and EC achieved the highest of 84.68% and 1.41 mg/g when pH was 2.0, respectively.
3.5 Adsorption isotherm curve

The Langmuir and Freundlich adsorption isotherms are frequently used to describe the adsorption behavior of solid-liquid systems[9]. The Langmuir adsorption isotherm model can be represented by $q_e = q_m K_a C_e / (1 + K_a C_e)$, which is based on a monolayer adsorption. Freundlich adsorption isotherm model can be represented by $q_e = K_f C_e^{1/n}$, which suggests the multilayer adsorption. The experimentally determined data of Figure 3 was fitted, and the results were shown in Table 1. It shown that coefficient of determination ($R^2$) of the Freundlich equation was 1, which indicated that sulphuric acid modified fly ash better fitted with Freundlich isotherm model gives linear relationship.

| Model equation | $q_m$ (mg/g) | $K_a$ | $R^2$ | Model equation | $K_f$ | $1/n$ | $R^2$ |
|----------------|--------------|-------|-------|----------------|-------|-------|-------|
| $C_e/q_e = 1.2914 C_e - 0.7838$ | 0.50 | -0.64 | 0.9671 | $\log q_e = \log C_e$ | 1 | 1 | 1.000 |

3.6 Adsorption kinetics

The pseudo-second-order kinetic mode was given by Lagergren and this model applicable during the initial stage of the adsorption process[10]. The linear form of the model expressed as follows $t/q_e = 1/k_2 q_e^2 + 1/q_e$, where $t$(min) is the adsorption time, where $q_e$(mg/g) and $q_t$(mg/g) are the EC at equilibrium and initial time, respectively, $k_2$ is the secondary adsorption rate constant(g/mg·min). The experimental data of Figure 2 was fitted using the Lagergren second-order kinetic adsorption equation. The results were shown in Table 2. It can be seen that $R^2$ was greater than 0.99, and there is a good linear relationship, indicated that the adsorption process of modified fly ash to RB is applicable to Lagergren second-order kinetic model.

| Lagergren second-order kinetic equation | $q_e$(mg/g) | $K_2$(g/(mg min)) | $R^2$ |
|----------------------------------------|--------------|-------------------|-------|
| $y = 0.9764x + 6.0056$ | 1.0242 | 0.1753 | 0.9948 |

4. Conclusion

The results of single factor experiment showed that the dosage of sulphur acid modified fly ash, reaction time, initial concentration of RB wastewater and pH of RB wastewater had a certain effect on adsorption efficiency. The results showed that 50.0 mL RB wastewater whose concentration was 10.0 mg/L, the adsorbent dosage was 0.3000 g, the pH was 2.0, adsorption time was 60.0 min, the RE and EC were 84.68% and 1.41 mg/L, respectively. The Freundlich adsorption equation and the Lagergren second-order kinetic model were more suitable for describing the adsorption of RB by sulfuric acid.
modified fly ash. The Freundlich isotherm model better described the adsorption equilibrium data, adsorption kinetic analysis data shown that pseudo-second-order kinetic model better fitted the RB adsorption.

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