

Removal Of Methylene Blue From Aqueous Solution Using Expanded Perlite

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Abstract. The adsorbent of expanded perlite (EP) was investigated to determine the removal effect on methylene blue (MB) from wastewater through static adsorption. The factors, such as adsorbent dosage, shaking time, temperature, and pH, were investigated. The optimum dosage, shaking time, temperature, and pH was 0.80 g, 100 min, 20 °C, and 5.67, respectively. Isotherm analysis showed that the patterns of MB adsorption onto expanded perlite was not in line with two adsorption isotherm models, namely, Langmuir and Freundlich. The kinetic characteristics of adsorption were also evaluated. The adsorption process of the MB onto EP was in accordance with the pseudo second-order rate equation. Under ideal experimental parameters, the MB removal efficiency was 94.12% for EP, which indicated that EP is a potential adsorbent for the treatment of MB wastewater.

Keywords: Expanded perlite; Adsorption; Methylene blue; Wastewater

INTRODUCTION

China is the world's largest dye producer. Consequently, environmental pollution in China has become severe. Owing to the advent of increasingly complex dye structures and the development of the dye industry, dyes demonstrate stable performance, which makes dye wastewater treatment highly complicated. Dye as a contaminant is toxic to human beings and aquatic life; for example, if dyes enter the eyes, burns and even permanent damage could occur [1]. Dyes in aqueous environments provide undesirable color to water and reduce the penetration of sunlight. The breakdown products of dyes in water can also be toxic [2], carcinogenic, or mutagenic to life forms [3, 4]. MB, a common cationic dye, is widely used to dye cotton, leather [5, 6]. Consequently, removing MB from aqueous solutions is a difficult requirement faced by leather and dye manufacturing. The use of different sewage treatment technologies to deal with different types of dye wastewater to meet wastewater discharge or recycling standards is an urgent problem.

Adsorption is a commonly used method for the treatment of dye wastewater. It can selectively adsorb dye molecules, and the effect is evident. Developing an efficient adsorbent and studying its adsorption mechanism are important research directions. Currently, a portion of perlite tailing is neglected because of limitations in perlite processing [7]. Such neglect results in resource wastage and environmental pollution [8]. To expand its application, perlite tailing is processed into expanded perlite (EP), which is an abundant and economical material [9], and used as an adsorbent. This action can facilitate EP change from single building materials to green environmental materials. With these

considerations, EP were selected as a adsorbent and its adsorption performance for MB was examined in this study.

EXPERIMENTAL

Materials

Commercially available EP (0.25-0.5mm) was chosen as a raw material. Screening EP to remove the fine sand from EP, and then the sample was washed 3-5 times with distilled water, followed by drying at 120°C until constant weight.

Methods

All batch experiments were performed at desired dosage, contact time, temperature, and pH value using the necessary EP in 250mL conical flasks containing 50.00 mL of MB solution (20 mg/L, pH 5.67) under 140 rpm. The effect of dosage on the adsorption capacity of EP and removal rate of MB were performed with 0.1, 0.2, 0.3, 0.5, 0.8 and 1.0g EP for 80 min at 20 °C. The samples was collected at 20, 40, 60, 80,100 and 120 min to investigate the effect of shaking time on the adsorption. The temperature was adjusted to 20, 30, 40, 50, 60, 70 and 80 °C to determine the effect of temperature. During the determination of the effect of pH on the adsorption capacity of the adsorbents and MB removal rate, the pH of MB solution was adjusted to 3, 5, 7, 9 and 10 with 0.10 mol/L of NaOH or HCl solution by using a pH solution meter.

For the adsorption isotherm study, batch experiments were conducted by oscillating 50.00 mL of various concentrations of MB solutions (pH 5.67) with EP, the dosage of which was the best, until adsorption equilibrium was reached at 20 °C. For the kinetic study, 20 mg/L of MB solutions (50.00 mL, pH 5.67) were oscillated with the adsorbent, the dosage of which was the best, at 20 °C for a predetermined time. Additionally, the pore structure of EP was examined by field emission scanning electron microscope (FESEM).

The removal rate and adsorption capacity of EP were calculated with Equations (1) and (2) [8], respectively.

$$R_e = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

where $R_e(\%)$ is the removal rate of MB, C_0 (mg/L) is the initial concentration of MB, and C_e (mg/L) is the equilibrium concentration of MB in the solution.

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (2)$$

where q_e (mg/L) is the amount of MB adsorbed on the adsorbent, C_0 (mg/L) is the initial concentration of MB, C_e (mg/L) is the equilibrium concentration of MB in the solution, V (L) is the volume of the solution used, and M (g) is the mass of the adsorbents used.

RESULTS AND DISCUSSION

Effect Of Dosage On Adsorption

Figure 1 shows that with the increase in the dosage of EP, the removal rate of MB gradually increased. However, the increment rate gradually decreased. When the dosage of EP reached a certain

level, the removal rate of MB stabilized probably because a small amount of EP could not provide sufficient adsorption sites. When the amount of EP was sufficient, MB was basically removed; the removal rate did not change and was stable. With the increase in EP dosage, the adsorption capacity of the three adsorbents decreased. The increase in EP dosage possibly increased the adsorption sites and reduced the amount of MB adsorbed per unit area. As a result, the MB adsorption amount per unit mass of the adsorbent declined. When the dosages of EP was 0.8, the highest MB removal rate was achieved at 93.74% . Therefore, the ideal dosages of EP was 0.8 g. A good removal effect can be obtained at EP, and the amount of EP can be reduced.

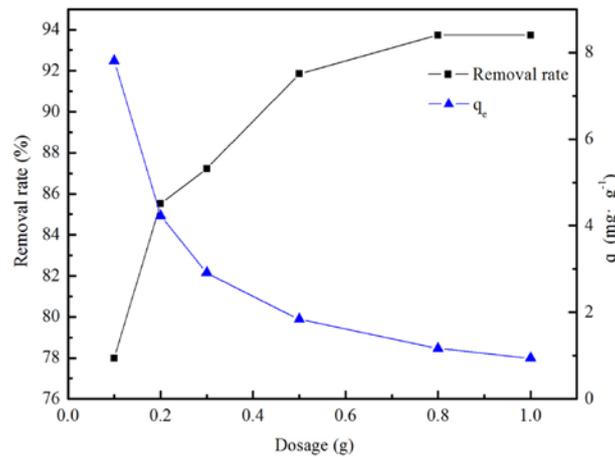


FIGURE 1. Effect of dosage of EP on the removal of MB

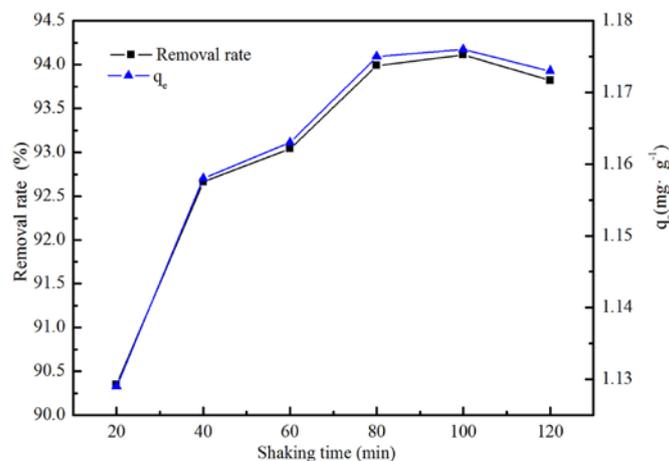


FIGURE 2. Effect of shaking time on the removal of MB

Effect Of Shaking Time On Adsorption

The effect of time on MB adsorption is shown in Figure 2. When the dosage of EP and other adsorption conditions were unchanged, the removal rate of MB and adsorption capacity increased with the increase in time and eventually stabilized. In the beginning of the adsorption reaction, the removal rate of MB was high for two main reasons. First, the concentration of MB in the solution was high, so the adsorption impetus was large [10]. Second, many unoccupied high-energy adsorption sites existed on the surface of adsorbents [11], such that the possibility of MB coming into contact with EP increased. Consequently, the adsorption reaction was implemented quickly. Afterward, with MB being constantly adsorbed, the concentration of the MB solution and adsorption impetus declined. With the

increase in MB on the adsorbents' surface, the available adsorption sites gradually decreased. Figure 2 shows that when the contact time was 100 min, the removal rate of MB and the adsorption capacity of expanded perlite reached the maximum, which were 94.12% and 1.18 mg/g, respectively. Thus, 100 min were selected as ideal adsorption time for EP.

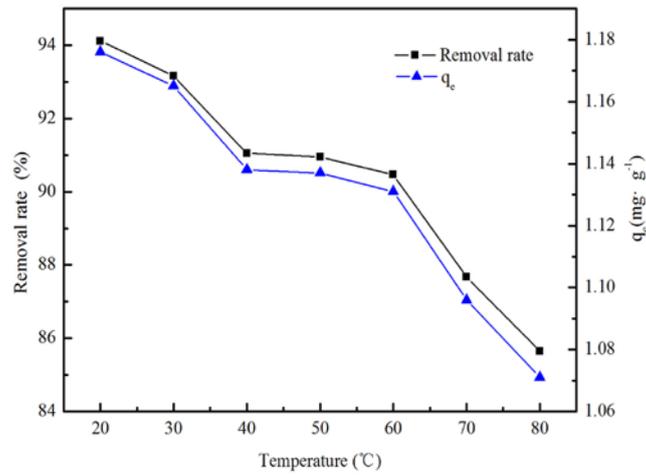


FIGURE 3. Effect of temperature on the removal of MB

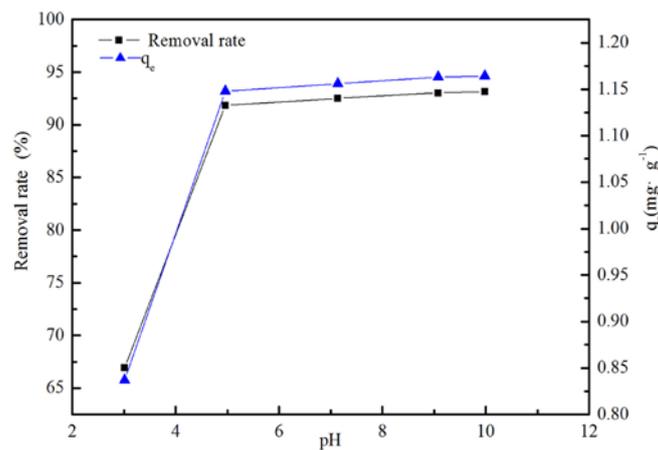


FIGURE 4. Effect of pH on the removal of MB

Effect Of Temperature On Adsorption

The effect of temperature on adsorption is presented in Figure 3. The Figure 3 indicates that the removal rate of MB and the adsorption capacity of EP gradually decreased with the increase in temperature, suggesting that the adsorption process was an exothermic reaction [6, 12, 13]. Thus, the increase in temperature decreased adsorption efficiency. Additionally, with the increase in temperature, the average kinetic energy of the MB molecules increased. The increase in the kinetic energy of adsorbed MB molecules provided them adequate energy to overcome the attraction force between MB and the adsorbent and to desorb to the aqueous solution [13]. That is, the increase in temperature was beneficial to desorption rather than adsorption. When the temperature was high, MB was difficult to adsorb on the surface of EP. Therefore, a low temperature is more favorable for MB removal than a high one. At a temperature of 20 °C, the removal rate of MB and the adsorption capacity of EP reached the maximum, which was 94.12% and 1.18 mg/g, respectively. Therefore, 20 °C was selected as the optimal temperature in the subsequent experiments.

Effect Of PH On Adsorption

The effect of pH on adsorption is shown in Figure 4. For EP, MB removal rate and the adsorption capacity of EP significantly increased as the pH of the solution increased. EP had a low adsorption rate at a low pH (pH<5). As pH decreased, H⁺ on the surface of EP increased, and negative electricity decreased. Competitive adsorption and electrostatic repulsion occurred between H⁺ and the cation of MB. Therefore, MB removal was low. At a high pH (pH>5), OH⁻ on the surface of expanded perlite increased, such that the negative electricity of EP also increased [14, 15]. Therefore, with the increase in the pH of the solution, the removal rate of MB and the adsorption capacity of EP increased.

Adsorption Isotherm

The adsorption isotherm is important in the design of adsorption systems. Two isotherm equations, Langmuir and Freundlich, were investigated in this study [16]. The Langmuir isotherm is suitable for monomolecular layer adsorption [17]. The Langmuir and Freundlich equations are represented as Eqs. (3) and (4), respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{3}$$

where q_e (mg/g) is equilibrium MB dye adsorption quantity on the adsorbent, q_m (mg/g) is the monolayer capacity of the adsorbent, K_L (L/mg) is the adsorption constant, and C_e (mg/L) is the equilibrium concentration of MB in the solution [13]. According to Eq. (3), the plot of C_e/q_e versus C_e should be a straight line with a slope of 1/q_m and intercept of 1/(q_m K_L), when adsorption follows the Langmuir equation.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

where K_F and n are Freundlich adsorption isotherm constants that indicate the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively. q_e (mg/g) is equilibrium dye concentration on the adsorbent, and C_e (mg/L) is equilibrium dye concentration in the solution.

The adsorption isotherm data of EP are shown in Table 1. The R² of the Langmuir adsorption isotherm was 0.9802. A significant difference was observed between fitting q_m with 4.83 mg/g and experimental q_m with 3.89 mg/g. The R² of the Freundlich adsorption isotherm was 0.9782. Thus, adsorption process of EP was incompatible with neither the Langmuir model nor the Freundlich model.

Adsorption Kinetics

In this paper, pseudo first-order and pseudo second-order kinetic models [2, 11, 16, 18] were used to investigate the adsorption process of MB. The pseudo first-order and pseudo second-order kinetic model equations both assume that adsorption amount is related only to adsorption time. The parameters of the two model equations were estimated with the experimental data. The two model equations are expressed as Eqs. (5) and (6), respectively.

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{5}$$

where q_e (mg/g) is equilibrium MB adsorption quantity on the adsorbent, q_t (mg/g) is adsorption quantity at a particular time, K_1 (min⁻¹) is the adsorption constant, and t (min) is the adsorption reaction time.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right)t \tag{6}$$

where K_2 is the adsorption constant of the pseudo second-order kinetics model equation (g/mg • min).

The adsorption kinetics data of the three adsorbents are shown in Table 2. The R^2 of the pseudo second-order kinetic model equation was 0.9999, and the q_e experimental value of 1.18 mg/g and the calculated value of 1.19 mg/g were close. Compared with the pseudo first-order kinetic model, the pseudo second-order kinetic model could better describe the process of MB absorption onto the surface of EP.

TABLE 1. Fitting Results of Langmuir Equation and Freundlich Equation

		Langmuir Equation			Freundlich Equation		
		y=0.20723x+2.05792			y=0.35096x+0.07892		
Expanded		q_m	K_L	R^2	K_F	n	R^2
Perlite		4.83mg/g	0.08	0.9802	1.08	3.23	0.9782

TABLE 2. Fitting results adsorption kinetics of MB onto EP

	Kinetic parameter	kinetics equation	R^2	experiment value of q_e	calculated value of q_e
Expanded	pseudo-first-order	y=-0.03072x-2.83541	0.6343	1.18mg/g	0.06mg/g
Perlite	pseudo-second-order	y=0.84422x+0.77926	0.9999	1.18mg/g	1.19mg/g

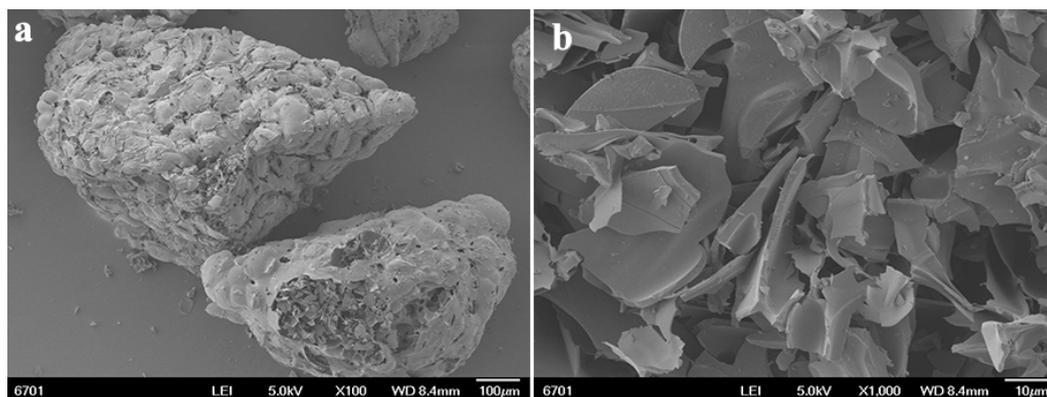


FIGURE 5. FESEM images of EP at different magnifications (a: x100; b: x1000)

Characterization Of Three Adsorbents

The adsorbing materials of EP were investigated further by FESEM. The FESEM images are shown in Figure 5. The surface of EP is loose and porous (Figure 5a). And the internal of EP presented a loose

fragments structure(Figure 5b). The arrangement of fragments is irregular. The size of pores and the gap between fragments were about 2-10 μm . The structure of EP was macropore ($>50\text{ nm}$) [19], which played a positive role in removing MB from aqueous solution that allowing MB molecules to quickly enter internal holes [20]. Thus, EP showed a good absorption properties, consistent with the experimental results.

CONCLUSION

Experiment data on MB absorption by EP showed that the optimal dosage of EP, adsorption time, temperature and pH was 0.80 g, 100 min, 20 °C and 5.67, respectively. Under ideal experimental parameters, the MB removal efficiency was 94.12%. The adsorption process was inconsistent with the Langmuir and Freundlich models. The fitting result of the kinetic model equation suggested that the pseudo second-order kinetic model can describe this process well. The experimental results indicated that EP is a potential adsorbent for the treatment of MB wastewater.

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