LOESS CLAY BASED COPOLYMER FOR REMOVING METHYLENE BLUE

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Abstract
The loess clay based copolymer (LC/PAAHM) was prepared by in-situ copolymerization and used for the removal of methylene blue (MB) from aqueous solution. The removal rate of MB got to 98 % at room temperature and the adsorption capacity got to 348 mg/g. Langmuir and Freundlich isotherms are applied in order to determine the efficiency of LC/PAAHM used as an adsorbent. The pseudo-second-order kinetic models were applied to test the experimental data. The results indicated that LC/PAAHM was an effective adsorbent and can be used to treat MB wastewater.

1 Introduction

Over the past several decades, a large amount of wastes containing dyes and pigments have been discharged into the receiving aquatic environment due to the rapid development of the modern industries, such as dyestuffs, textile, paper and plastics. It is recognized that public perception of water quality is greatly influenced by the color [1]. The color is the first contaminant to be recognized in wastewater. The presence of even very small amounts of dyes in water was highly visible and undesirable [2]. Cationic dyes used for paper, polyacrylonitrile, modified nylons, modified polyesters, cation dyeable polyethylene terephthalate and to some extent in medicine too [3]. Methylene blue (MB) is one of cationic dyes that can cause eye burns, which may be responsible for permanent injury to the eyes of human and animals [4]. On inhalation, it can lead to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [5]. As such it is important to treat coloured effluents for the removal of dyes. However, wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat and oxidizing agents [6].

Various physicochemical and biological treatment technologies have been applied to remove dyes from aqueous solutions, such as coagulation [7], filtration [8], oxidation [9], integrated chemical-biological degradation [10], and adsorption [11,12]. However, most of above treatments suffer from one or another limitation, and they are unsatisfactory in terms of efficiency and economy [13]. The adsorption method is the use of adsorption to remove contaminants in wastewater [14]. Furthermore, this method had been found to be superior to

other methods for treatment of the water on the grounds of first cost, flexibility, practicality and simplicity of operation.

Natural materials, which cost less and can be used as such or after some minor treatment as adsorbents are generally called low-cost adsorbents. Some of the reported low-cost adsorbents are activated carbon [15], fly ash [16], biosorbent [17] and lignin [18]. Especially, natural and modified clay materials have received wide attention due to their low cost, high specific surface areas, and variety of surfaces and structural properties, such as kaolinite [19], montmorillonite [20], bentonite [21]. In China, the Loess clay covers almost all the northwestern region, and parts of others. As being rich in raw material and cheap, loess can be used to remove the dyes from aqueous solution [22]. However, its adsorption capacity was not higher in comparison with other adsorbents. In another side, the adsorption capacity of loess clay towards dye compounds remains unknown. In the present study, the loess based poly(acrylic acid - 2 - hydroxyethyl methacrylate) complex (LC/PAAHM) was applied to remove MB. The effects of adsorbent dosage, initial concentration, pH and contact time on the removal of MB from its aqueous solutions were investigated. The kinetic models of adsorption was also discussed.

2 Materials and testing methods

2.1 Materials and Reagents

Loess clay (LC) used as the starting material, was obtained for free from the local hill near Lanzhou of China. Acrylic acid (AA) was distilled under reduced pressure before use. 2-hydroxyethyl methacrylate (HEMA), glycidyl methacrylate (GMA) and ammonium persulfate were all analytical reagent and commercially available. Stock solution was prepared by dissolving 1.0 g of methylene blue (MB) supplied by Beijing Chemical Plant, China in 1 L distilled water. The test solutions were prepared by diluting stock solution to the desired concentrations. The maximum wavelength of this dye is 664 nm.

2.2 Adsorbent

The LC/PAAHM was prepared in-situ copolymerization as followings: The LC and acrylic acid (AA) (5.0 g/7.2 g) was dispersed in 30 mL of H_2O for 1 hr. It was neutralized (70% neutralization degree) by NaOH solution . 0.72 g of HEMA was added and stirred 30 min. Then,0.72 g of ,GMA used as the cross-linking agent and ammonium persulfate, was added with stirring. The mixture copolymerized under continuous stirring 30 min at 50 °C. The loess based copolymer (LC/PAAHM) was obtained until the mixture reacted for 40 min at 85°C. Finally, the product was washed with water for several times and dried at 80°C in hot air oven until the weight of the product was constant, then was sieved with a 100 Mesh.

2.3 Adsorption Studies

The adsorption experiments were carried out to determine the optimum pH for MB adsorption, the best adsorbent dosage. Tests were performed by shaking the amount of the adsorbent (0.01-0.12 g) with 50 mL of aqueous MB solution of the desired concentration at various pH (2-11) and at room temperature (20 °C) in several 250 mL stoppered conical flask for 60 min using a thermostatted water bath shaker. The dye solutions were filtered and then measured by a double beam UV – vis spectrophotometer. The results were then used to calculate the loading of dye onto LC/PAAHM in the following equations:

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

$$\text{Re}\,moval\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where, V is the total volume of the solution used (L), W is the mass of PAA/HB used (g). C_0 and C_e (mg/L) are the initial and equilibrium concentrations of dye in the solution.

3 Results and discussion

3.1 The adsorption performance of various adsorbents to methylene blue

The characters of adsorbability of loess clay (LC), the loess based poly(acrylic acid) complex (LC/PAA), the loess based poly(2-hydroxyethyl methacrylate) complex (LC/PHEMA), and the loess based poly(acrylic acid-2-hydroxyethyl methacrylate) complex (LC/PAAHM) to MB were researched by contacting 50 mL of MB solution of initial concentration of 20 mg/L with 0.02 g of adsorbents into 250 mL conical flasks at temperature of 20℃, respectively. The conical flasks were put in a thermostatic oscillator and agitation was provided at 150 rpm for 60min. As shown in Table 1, the adsorption capacity of LC/PAAHM was higher than other adsorbents.

Adsorbents	**Removal%**	**qe（mg/g）**
LC	83.7	42.87
LC/PAA	97.7	48.87
LC/PHEMA	88.6	44.29
LC/PAAHM	97.9	48.96

Table 1 Effect of different adsorbents on the adsorption of MB

3.2 Effect of adsorbent dose on dye adsorption

The dose of adsorbent had been varied in the range of 0.01-0.12 g, using 100 mg/g of MB, *at* 20 °C, and stirring speed 150 rpm. The influence of adsorbent dosage in percent adsorption of MB is shown in Figure 1. At equilibrium time, the percent removal reaching a plateau value in the 0.05 g of LC/PAAHM. The percent removal of MB increased was due to the increase of the number of active sites and available surface area.

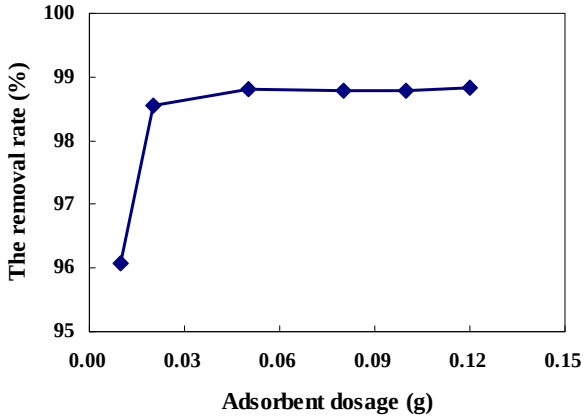

Figure 1 Effect of adsorbent dosage on the adsorption of MB on LC/PAAHM

3.3 Effect of dye solution pH

The effect of pH on the adsorption of MB by LC/PAAHM is presented in Figure 2. The dye removal efficiency was minimum at pH 2 (85%), this increased up to 3 and remained almost constant (98%) at pH 3-10. This result caused due to the presence of excess hydrogen ions

competing with the cationic dye for adsorption sites in strong acid environment. However, MB reacted with strong alkali to form quaternary sulphur alkali in strong alkali environment.

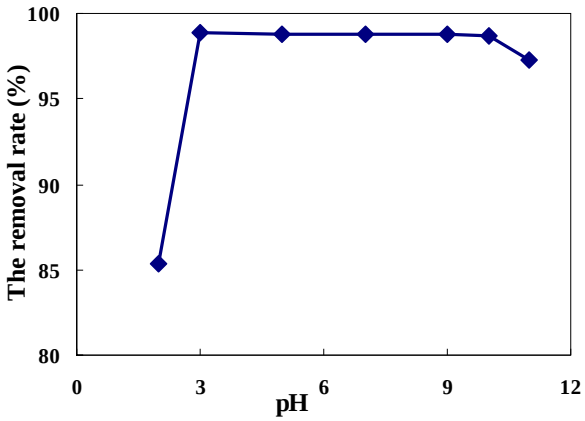

Figure 2 Effect of solution pH on the adsorption of MB ([MB]initial = 100 mg/L, agitation speed = 150 rpm, Temp: 20°C, contact time = 60 min and adsorbent dosage = 0.0 5g/50 mL)

3.4 Effect of initial dye concentration and contact time on adsorption

Figure 3 shows the effect of initial concentration on the adsorption of MB. It was found that the adsorption rate of LC/PAAHM was faster in the first 5 minutes, and then the adsorption rate was slowing down with the increase of contact time and finally achieved the equilibrium adsorption. The rapid adsorption rate during the initial stage may be ascribed to the availability of sufficient active sites. The adsorption capacity increases from 49 to 348 mg/g as the MB concentration increases from 50 to 350 mg/L. This could be due to the mass transfer resistances of the MB between the aqueous and solid phases are overcome by the main driving force provided by the initial concentration. The increase of the initial concentration of dye will help to promote the adsorption process.

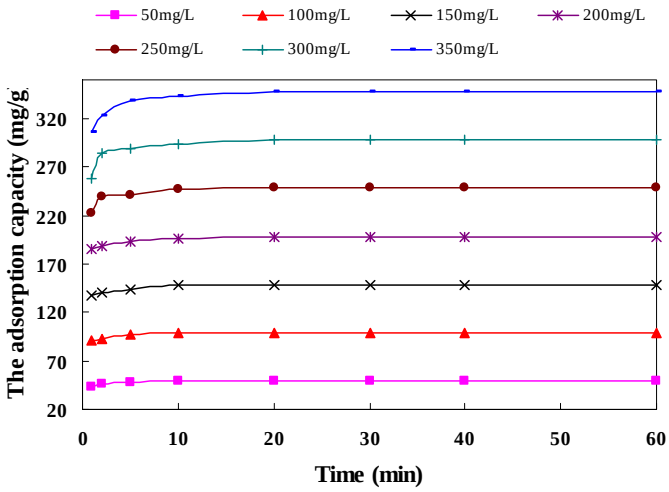

Figure 3 Effect of contact time and initial concentration on the adsorption of MB (adsorbent dosage: 0.05g/50 mL, agitation speed: 150 rpm, Temp: 20°C).

3.5 Effect of Temperature

For adsorption of MB onto LA/PAAHE, adsorption experiments were investigated at 10, 20, 30 and 40 °C at optimum conditions obtained the above experiments. As Figure 4 shows, the

adsorption capacity increased with the increase of temperature in the first 20 min. The reason of this result is that the temperature can decrease liquid viscosity and to increase diffusion processes. When the adsorption capacity reached the maximum, the temperature hardly has effects on the adsorption of MB.

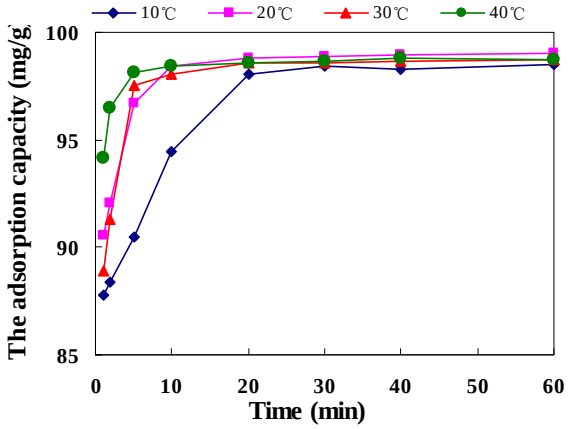

Figure 4 Effect of temperature on the removal rate of dye

3.6 Adsorption Isotherms

In this study, two adsorption isotherms (Langmuir and Freundlich isotherms) were used to interpret the obtained experimental data.

The Langmuir isotherm which assumes monolayer coverage of the adsorbent on the surface and is expressed as follows [23]:

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

where C_e is the equilibrium concentration of MB in the aqueous phase (mol/L), K_a is the Langmuir adsorption constant (L/mol), q_m is the maximum adsorption capacity of the adsorbent (mol/g), and q_e is the amount of MB adsorbed per mass of adsorbent at equilibrium (mol/g). q_m and K_a were determined from the slopes and intercepts of the straight-line plot between Ce/qe versus Ce. The result showed that the slope is negative, indicating that the adsorption of MB onto LC/PAAHM can not be described by the Langmuir isotherm model.

The Freundlich model is an empirical equation that is used to describe heterogeneous systems. The equation is given as follows [24]:

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

The K_F gives an indication of the capacity of the adsorbent and n gives an indication of favorability. Linear plots of log q_e versus log C_e show that adsorption follows Freundlich isotherm well for LC/PAAHM. The calculated isotherm constants from the slope and intercept of the Freundlich models are listed in Table 2. The correlation coefficients is 0.9733, indicating that the Freundlich isotherm is suitable to describe the adsorption processes of MB onto LC/PAAHE.

Freundlich	**Parameters**
K_F ((mg/g)(L/g)$^{1/n}$	78.29

n	0.48
R^2	0.9733

Table 2 Parameters of Freundlich Isotherms

3.7 Kinetics Studies

To investigate the adsorption process of MB on LC/PAAHM, the pseudofirst-order, pseudosecond-order were used. The Lagergren pseudo-first-order model[25] is given by the following equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{5}$$

where q_e is the amount of MB adsorbed per unit mass of adsorbent at equilibrium (mg/g), q_t is the amount of MB adsorbed at time t (mg/g), and k_1 is pseudo-first-order rate constant (min^{-1}). By plotting $\log(q_e - q_t)$ as a function of the contact time t (Figure 5), the values of the calculated q_e ($q_{e,cal}$) and the rate constant k_1 can be obtained from the intercept and the slope of the plot, respectively. The data obtained for sorption of MB on LC/PAAHM based on the pseudofirst-order kinetic model showed that the adsorption kinetics were not in a good agreement with the pseudofirst-order model.

Pseudo-second-order model[26] can be expressed as follows:

$$\frac{t}{qt} = \frac{1}{k_2 q_e^{\ 2}} + \frac{t}{q_e} \tag{6}$$

where k_2 is the pseudosecond-order rate constant (g $mg^{-1}min^{-1}$). Plotting t/q_t against t (Figure 5), gives a straight line where k_2 can be calculated. The adsorption kinetic parameters are listed in Table 3. The calculated $q_{e,cal}$ are close to the experimental values ($q_{e,exp}$(mg/g)), and the R^2 were found to be all 0.999. It indicated that the pseudo-second-order model is appropriate for the adsorption phenomena.

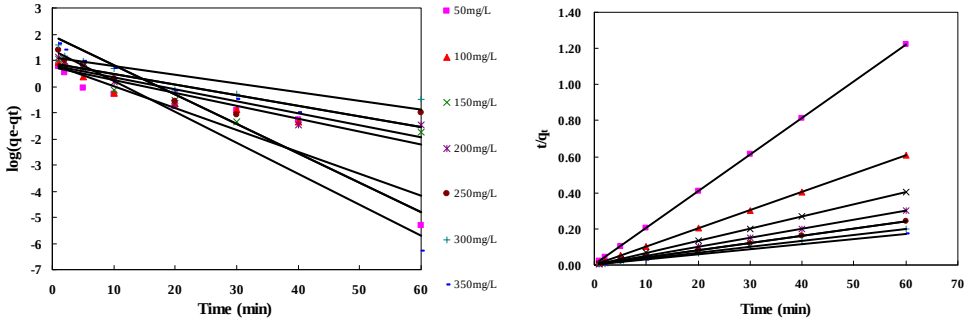

Figure 5 Kinetic models for MB adsorption

C_0(mg/L)	$q_{e,exp}$(mg/g)	pseudo-first-order			pseudo-second-order		
		$q_{e,cal}$(mg/g)	k_1(1/min)	R^2	$q_{e,cal}$(mg/g)	k_2[g/(mg·min)]	R^2
50	49.17	6.80	0.19	0.8545	49.26	0.41×10^{-3}	0.9999
100	98.99	25.66	0.27	0.8163	99.01	0.10×10^{-3}	0.9999
150	148.64	5.56	0.11	0.8535	149.25	0.04×10^{-3}	0.9998

200	198.27	6.63	0.11	0.8715	200.00	0.03×10^{-3}	0.9999
250	248.42	7.37	0.09	0.7216	250.00	0.02×10^{-3}	0.9998
300	297.93	12.71	0.06	0.7490	303.03	0.01×10^{-3}	0.9999
350	348.04	90.22	0.26	0.8708	344.83	0.01×10^{-3}	0.9999

Table 3 Kinetic Parameters

4 Conclusions

The acrylic acid and 2-hydroxyethyl methacrylate were used to modify the natural loess by in-situ copolymerization, which obtained loess based copolymer (LC/PAAHM). The low-cost adsorbents, LC/PAAHM, presented excelllent adsorption capacity for removing MB. The MB removal efficiency of 98 % was achieved under appropriate conditions. The adsorption follows Freundlich isotherm well for LC/PAAHM. Kinetic data tended to fit the second-order kinetic model well. studying summary, the LC/PAAHM was found to be a very effective adsorbent especially for removing MB.

Acknowledgement

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