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REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTIONS USING A NOVEL GRANULAR RED MUD MIXED WITH CEMENT

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Abstract

A novel adsorbent was prepared from granular red mud (GRM) mixed with cement and its potential to be a suitable adsorbent for removal of methylene blue (MB) from aqueous solutions was evaluated. By investigating duration of oscillation, dosage of MB, pH and temperature on the adsorption effect, the best experimental condition was obtained: the methylene blue with the dosage of 150 mg/L and a constant pH of 11, after 240 minute oscillation at 303K, the removal of MB and the state balance of absorption capacity up to 86.89 % and 2.6040 mg/g. The equilibrium adsorption was found to increase with increase in temperature of the adsorption process. It was observed that the adsorption isotherms are well represented by both the Langmuir and Freundlich isotherm models. But because the Freundlich isotherm model had a better fitting, the adsorption was attributed to successive multilayer adsorption. Meanwhile, thermodynamic parameters depict the endothermic nature of adsorption and the process is spontaneous. The pseudo-second-order kinetic model was used to correlate the kinetic experimental data and the kinetic parameters were evaluated.

Introduction

Automation and industrialization has resulted in rapid deterioration of water quality. The effluents released from different industries such as textile, leather, paint and so on comprise of hazardous and toxic compounds, which are known to be potential carcinogens [1-3]. And dyes and their effluent produced by the textile industry have become the most polluting among all industrial sectors, which is featured by complicated organic matter composition, high density and toxicity, and is difficult to be degraded bio-chemically [4-8]. Physical or biochemical processes have been usually used to treat them, however these processes are costly and cannot be used effectively to treat the wide range of dye wastewater [9-13]. Of the conventional chemical methods for removing color from wastewater, such as chemical coagulation, flotation, chemical oxidation and adsorption, adsorption is the most common technique because of its effectiveness [14-15].

At present, activated carbon adoption has been one of the most effective methods for the treatment of dye wastewater and has been widely used around the world [16-21]. Nevertheless, it has merely a limited application because of its high cost, which have aroused scholars and professionals' great interest in researching and developing a new absorbent material of low cost. Red mud has proved to be a good alternative for wastewater treatment with the consideration of efficiency and cost, and to date, the current research mainly adopted powdered red mud as adsorbent [22-26]. Powdered red mud, though endowed with a high specific adsorption area, it is not suitable for industrial application as it requires filtration for removal of the adsorbent.

The present work attempts to prepare a novel granular red mud adsorbent (GRM), and assess the GRM's ability to remove methylene blue (MB) from aqueous solution using batch tests. By investigating duration of oscillation, dosage of MB, pH and temperature on the adsorption effect, we have obtained the optimum adsorption process. In addition, the study also intends to research adsorption mechanism by establishing the adsorption isotherm.

1 Experimental

1.1 Preparation of adsorbent

Fresh red mud filter cake, containing 28.24 % water with initial pH of about 13.3, supplied by the Kaiman Aluminum Co. Ltd. in China, is utilized as the principal raw materials for granulation. The high quality Portland cement was supplied by a cement plant of the Kunming city. The preparation procedures are described below. Firstly, we mix the wet red mud directly without dealkalization with cement in a certain proportions and produce GRM using granulating machine. Then the Fresh Granular Red mud (-2 mm) will need the maintenance at wet environment for more than 4days. Finally, Aged Granular Red mud (-2mm) will be gained through the screening.

The study adopts the GRM prepared in fresh red mud mixed up with 2 percent of cement according to the mass percentage, which presents excellent performances in the textural characteristics and the physical strength. When the particle size is smaller than 2 mm, the 2 % addition of cement GRM has both a efflorescence ratio of 4.83 % and a specific surface area of 17.42 m2/g, and it is stable in aqueous media.

1.2 Chemicals and reagents

Methylene blue (basic blue 9, C.I. 52015; chemical formula $C_{16}H_{18}N_3SCl{\cdot}3H_2O$; MW, 373.90 g/mol) was purchased as analytical- laboratory grade and used without any further treatment. The dye stock solution was prepared by dissolving a fixed amount of methylene blue into 1 L of deionized water. To prevent the decolorization by direct sunlight, the dye stock solution was stored in dark bottle and kept in dark place before used.

1.3 Adsorption studies

The adsorption process was conducted by adding a known amount of GRM into a series of 250 mL conical flasks containing 100 mL

of methylene blue solution with an initial concentration ranging from 50 mg/L to 150 mg/L. The conical flasks were then covered with aluminum foil, placed in thermostat shaker and shaken in thermostat shaker at 100 rpm until equilibrium state was achieved. After equilibrium time reached, the methylene blue solution was centrifuged at 4000 rpm for 5 min to remove solid particles. The supernatant was then carefully taken and measured its residual methylene blue concentration by UV/VIS spectrometer at maximum wavelength (664.1 nm). The pH of methylene blue solution was also measured at the start of each experiment using digital pH-meter. Isotherm experiments were conducted at various pH (3, 5, 9 and 11) and temperatures (20℃, 30℃ and 40℃). To adjust the pH, an appropriate amount of 2 mol/L NaOH or 1 mol/L HNO_3 solutions were added to the system. The amount of methylene blue adsorbed at equilibrium and a certain time t were determined by the following equations:

$$q_e = \frac{C_0 - C_e}{m} V \quad (1)$$

$$q_t = \frac{C_0 - C_t}{m} V \quad (2)$$

Where q_e and q_t (mg/g) are the amount of methylene blue adsorbed at equilibrium and at a certain time t, C_0 and C_e (mg/L) are the initial and equilibrium methylene blue concentration in liquid phase, respectively, m (g) is the miss of GRM used and V (L) is the volume of methylene blue solution.

2 Result and discussion

2.1 Effect of contact time

Figure 1 shows the effect of contact time on adsorption of methylene blue with initial concentration of 150 mg/L, at an adsorbent dosage of 5g, at 30±1℃.

As can be seen from the figure the rate of adsorption is very high initially, while the rate reduces with increase in the adsorption time, eventually reaching a steady state. The steady state concentration estimated at 320 minutes serve as the equilibrium data. The high rate of adsorption initially is due to the high concentration driving force available for mass transfer from the liquid to the adsorbent active sites. When the contact time was 120 minutes, the removal of methylene blue was over 99.9 %.

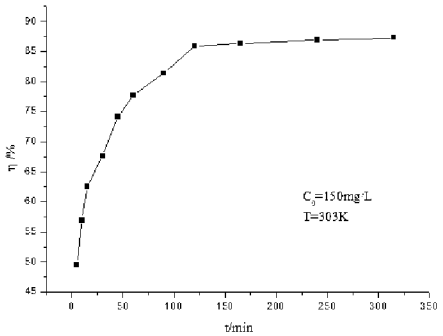

Figure 1. Effect of contact time on methylene blue uptake

2.2 Effect of the dosage of GRM

The influence of adsorbent dosage on the efficiency of MB removal can be viewed in Figure 2. After 240 minutes, the MB removal rate increased from 10.57 % to 86.89 % as the dosage of GRM increased from 5 g/L to 50 g/L. This is due to the increase in surface area resulting from the increase in adsorbent mass, thus increasing the number of active adsorption sites. The amount of MB adsorbed per unit mass of adsorbent decreased with increasing adsorbent mass, due to the reduction in effective surface area. This may be also attributed to overlapping or aggregation of adsorption sites resulting in a decrease in total adsorbent surface area available to MB and an increase in diffusion path length. Based on the results presented in Figure 2, the remaining experiments were conducted for an adsorbent dosage of 50 g/L.

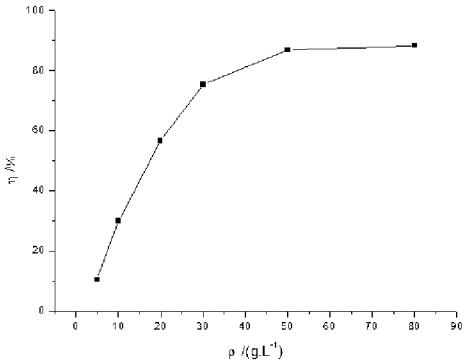

Figure 2. Effect of the dosage of GRM on the MB removal rate

2.3 Effect of initial methylene blue concentration

The initial solute concentration provides a necessary driving force to overcome mass transfer resistance between the liquid and the solid phase. The variation in initial solute concentration influences the amount of methylene blue adsorbed and its removal efficiency. Figure 3 shows the effect of initial concentration of methylene blue on the amount uptake by GRM. The increase of initial MB concentration caused an increase on the amount of MB adsorbed onto the GRM surface.

By increasing the initial concentration, the mass transfer resistance (kx) in the liquid phase becomes smaller because the mass transfer driving force (concentration gradient) in the solution becomes greater, thereby providing faster adsorption rate of methylene blue (MB) onto the GRM pore structure.

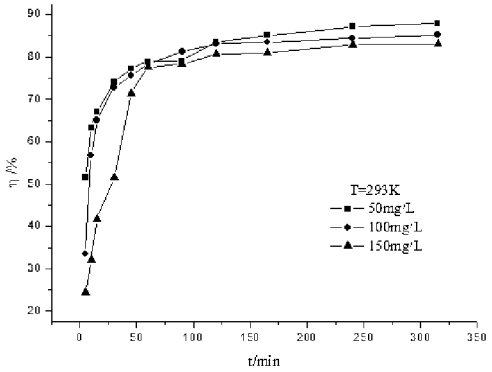

Figure 3. Effect of initial concentration of methylene blue on the amount uptake

2.4 Effect of initial solution pH

The pH of initial solution from which adsorption occurs is expected to influence the extent of adsorption. pH affects adsorption in that it governs the degree of ionization of the acidic and basic compounds [27]. In general, initial pH value may enhance or depress the uptake. This is attributed to the change of the charge of the adsorbent surface with the change in pH value. The effect of pH can be described on the basis of the influence of pH on the zero point of charge, which is the point at which the net charge of the adsorbent is zero.

The effect of pH (3, 5, 9 and 11) on the methylene blue adsorption at various contact times is given in Figure 4. It can be seen from the figure that as the initial solution pH increases, the removal rate of MB (150 mg/L) has increased from 59.61 % to 86.89 % as the pH increased from 3 to 11. This implies that adsorption of MB could be enhanced at higher pH. Such results confirm that the GRM surface became predominantly negatively charged, enhancing the electrostatic attraction between the surface and MB cations.

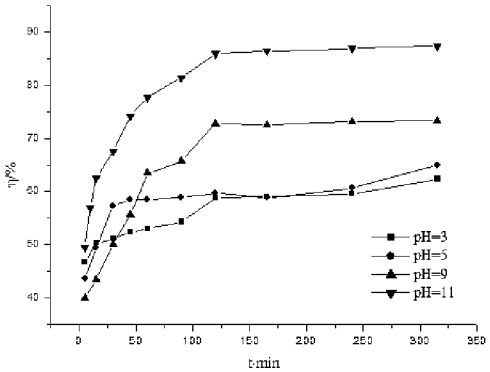

Figure 4. Effect of initial solution pH of methylene blue on the removal rate

2.5 Effect of reaction temperature

Temperature is one of the most important factors in adsorption process. The effect of temperature (20, 30, and 40℃) on the methylene blue adsorption at various initial concentrations (50, 100, 150, 300, 500, 800 mg/L) is given in Figure 5. Generally, temperature has two major effects on the adsorption process. Increasing the temperature induces an increase in the diffusion rate of adsorbate molecules onto adsorbent surface, thereby diminishing mass transfer resistance in liquid phase as a result of the reduced viscosity of bulk solution.

Figure 5 shows that increasing in temperature enhances the equilibrium adsorption capacity for the particular adsorbate. And an increase in the adsorption capacity with increase in temperature indicates a significant adsorption being endothermic reaction. Because a physical adsorption is generally understood to be exothermic and the equilibrium adsorption would decrease with increase in the temperature of adsorption process, we can conclude that chemisorption is the control mechanism in the process and increasing the temperature will reduce the activation energy, enhance the rate of adsorption.

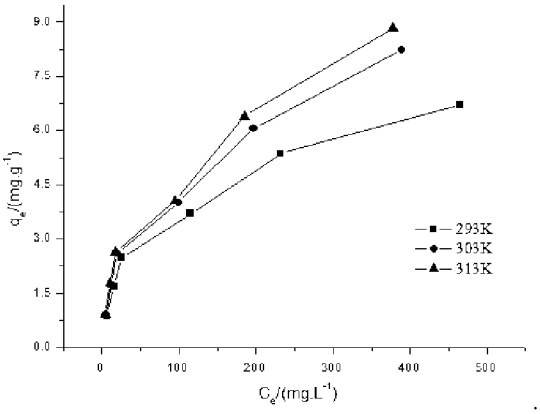

Figure 5. Effect of temperature in methylene blue uptake at various initial concentrations

2.6 Adsorption Isotherms

The equilibrium adsorption of MB was tested with the popular adsorption isotherms, Langmuir and Freundlich models. Both these models are well detailed in literature [28] and hence only the representative model equations are provided. The Langmuir equation is expressed as follows,

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

The linearized form of Equ.(3) is provided as follows,

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L C_e}{K_L} \tag{4}$$

Where q_e is the equilibrium adsorption capacity of the adsorbent, Ce is liquid phase concentration at equilibrium , K_L(L·g^{-1})and a_L(L·mg^{-1})are Langmuir constants.

The model constants, K_L and a_L along with the coefficient of determination (R^2) are calculated and listed in Tab 1.

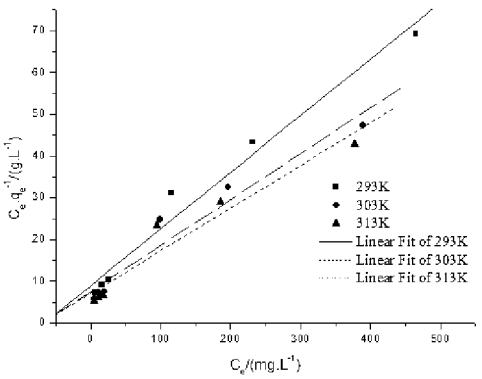

Figure 6. Langmuir adsorption isotherm

Based on experiments, Freundlich isotherm is the semiempirical equation, with the assumption of multilayer absorption. The equation is expressed as follows:

$$q_e = a_f C_e^{b_f} \quad (5)$$

Transfer equation 6 into linear form, as follows,

$$\ln q_e = \ln a_f + b_f \ln C_e \quad (6)$$

where a_f (mg·g^{-1})is the constant of Freundlich equation, to a certain extent reflecting the strength of the adsorption ability; b_f is the component factor, which indicates the intensity of adsorption increasing with increase in the concentration and can also indicate the adsorption difficulty. The model parameters af and bf along with the R^2 value are also provided in Table 1.

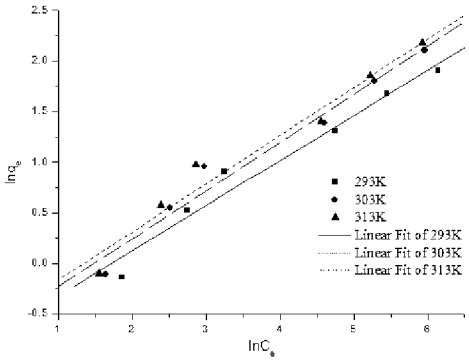

Figure 7. Freundlich adsorption isotherm

Table 1. Langmuir and Freundlich parameters of GRM adsorbent at different temperatures

T (K)	Langmuir constants			Freundlich constants		
	Q_{max} (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	1/n	R^2
293	7.3670	0.0151	0.9762	0.4618	0.4474	0.9645
303	9.0975	0.0144	0.9496	0.4946	0.4750	0.9680
313	9.9771	0.0144	0.9370	0.5260	0.4768	0.9645

The R^2 value shown in Table 1 clearly indicates better fit of the Langmuir model as compared to Freundlich model. The value of q_{max} indicates the monolayer adsorption capacity of the GRM, which increases with increase in the temperature of the adsorption process. The increase of monolayer adsorption capacity with increase in temperature also indicates the process to be chemisorptions.

2.7 Adsorption Kinetics

The adsorption kinetics is generally modeled using pseudo first order and pseudo and second order models and generally a second order model fits the experimental data better as compared to the first order model, as demonstrated [29]. Hence the second order model is tested with the kinetic data generated for the adsorption of methylene blue using GRM. The suitability of the pseudo second order model to match the experimental data was based on the R^2 value. Figure 8 shows the closeness of the model equation with the experimental data. The R^2 value is presented in Table 3 along with the model kinetic parameters. The quasi second order kinetic model is as given below,

$$\frac{dq}{dt} = k_2 (q_e - q)^2 \quad (7)$$

which can be linearized to the following form,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

$$h = k_2 q_e^2 \quad (9)$$

Where h (mg·g·min^{-1}) is initial adsorption rate, k_2(g·mg-1·min) is the quasi second order model of rate constant, q_t is the amount adsorbed at any given time, while q_e is the equilibrium adsorption capacity.

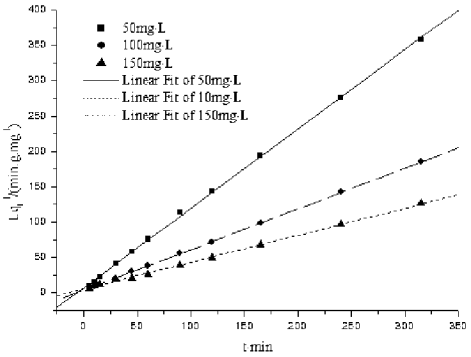

Figure8. Fit of pseudo-second-order kinetic model with the experimental data

Table 2. Pseudo second order model parameters at different concentrations

C_0 (mg.L^{-1})	$q_{e,exp}$ (mg.g^{-1})	Pseudo-second-order		
		k_2 (g.mg^{-1}.min^{-1})	q_e (mg.g^{-1})	R^2
50	0.8716	0.1760	0.8906	0.9995
100	1.6870	0.0939	1.7348	0.9999
150	2.4839	0.0281	2.6226	0.9985

Table 2 showed that the pseudo-second order model can have a good description of the granular red mud adsorption process.

3 Conclusions

This study showed that the granular red mud (GRM) mixed with cement can be used for the removal of organic compounds from aqueous solution under a wide range of conditions. The best experimental condition was obtained: the methylene blue with the

dosage of 150 mg/L and a constant pH of 11, after 240 minute oscillation at 303K, the removal of MB and the state balance of absorption capacity up to 86.89 % and 2.6040 mg/g. The adsorption isotherms are well represented by both the Langmuir and Freundlich isotherm models. But because the Freundlich isotherm model had a better fitting, the adsorption was attributed to successive multilayer adsorption. Meanwhile, thermodynamic parameters depict the endothermic nature of adsorption and the process is spontaneous. The adsorption process of methylene blue could be described by the pseudo-second order kinetics model.

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