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Sorptive Removal of Methyl Green from Aqueous Solutions using Activated Bentonite

A. Maghni[a], M. Ghelamallah[b,*] and A. Benghalem[a]

[a]Laboratoire de Matériaux et Catalyse, Faculté des Sciences Exactes, Université Djillali Liabes, BP 89, Hai Larbi Ben M'Hidi, Sidi Bel-Abbes, Algeria

[b]Laboratoire de Matériaux, Applications et Environnement, Faculté des Sciences Exactes, Université Mustapha Stambouli, BP 305, Route de Mamounia, Mascara 29000, Algeria

Bentonite clay from Maghnia (North West Algeria) has been acid-activated. The activated bentonite was employed as adsorbent for the removal of methyl green from aqueous solutions using adsorption method. The influence of several parameters (kinetics, contact time, sorbent amount, adsorbate concentration and pH) on the adsorption capacity was evaluated and discussed. The Langmuir adsorption model was applied to experimental equilibrium data and the isotherm constant was calculated. The results indicated that the adsorption was favourable at neutral pH. This model provided the best fit to the experimental data with high correlation coefficient ($R^2 = 0.996$). The monolayer adsorption capacity of activated bentonite found to be 353.33 mg/g. It was seen that pseudo-first order equation describes the adsorption kinetics. The results indicated that this bentonite-type clay is potential to be used as an economical adsorbent for the removal of methyl green dye.

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PACS/topics: methyl green, activated bentonite, adsorption, Langmuir model, kinetics

1. Introduction

The wastewater of textile industries are laden with many organic micro-pollutants, including certain dyes [1, 2]. Some of the dyes are toxic, carcinogenic, reported to have connections with different respiratory disorders worldwide and induces pollution to the environment [3, 4]. Various techniques have been developed in investigation of processes of pollutant removal [5]. The research proved to treatment using natural materials such as clays for removing dye pollutants from wastewater has been gaining more attention because of the low-cost of the materials involved and their high specific area, and a variety of surface and structural properties [6, 7]. Adsorption is a method of treatment, although adapted to remove a variety of toxic compounds in our environment [8, 9]. In the present study, adsorption properties for removal of methyl green (MG) by activated bentonite (AB) clay, from an aqueous solution under varied experimental conditions were investigated.

2. Experimental

The sample of bentonite clay was obtained from deposit of Maghnia (North West Algeria), and underwent an acid-activation. Methyl green dye ($C_{26}H_{33}Cl_2N_3Cl_2Zn$) stock solution, 200 mg/l, is diluted in distilled water. Successive dilutions were prepared in the range of initial concentrations 1.8–57.7 mg/l. The absorbance value is measured at 628 nm with Sedico (VIS-7220G) UV/Visible Spectrophotometer. The adsorption of MG on AB was studied from different parameters, including adsorbent dose (0.1–0.4 g/l), solutions pH (2–11) and initial MG concentration (10–40 mg/l). In each adsorption experiment, 100 ml of dye solution of known concentration was added to 0.01–0.04 g of the clay and the initial pH of the MG solutions was adjusted by adding HCl or NaOH solutions. The adsorption percentage (R) and adsorption capacity values at equilibrium and t time (Q_e and Q_t mg/g) were calculated using the following equations:

$$R\% = \frac{C_0 - C_e}{C_0} \times 100\%, \tag{1}$$

$$Q_e = \left(C_0 - \frac{C_e}{m}\right) V, \tag{2}$$

$$Q_t = \left(C_0 - \frac{C_t}{m}\right) V, \tag{3}$$

where C_0, C_e and C_t (mg/l) are the MG dye concentrations at initial, equilibrium and t time, respectively. V [l] is the solution volume and m [g] is the mass of adsorbent used.

3. Results and discussion

The experiments were conducted at MG initial concentration of 20 ppm (0.020 g/l) and 0.1 g/l of AB. pH of solutions was changed in the range of 2–11 (see Fig. 1). In this study, the maximum dye removal (70.73%) with an adsorption capacity of 353.33 mg/g was observed in the pH of 7. This phenomenon is explained probably by electrostatic attraction between anionic dye (MG) and the positive surface charge of AB due to the protonation of functional groups on adsorbent [10].

In order to find the optimum amount of adsorbent for maximizing the interactions between MG molecules

*corresponding author; e-mail: m.ghelamallah@univ-mascara.dz

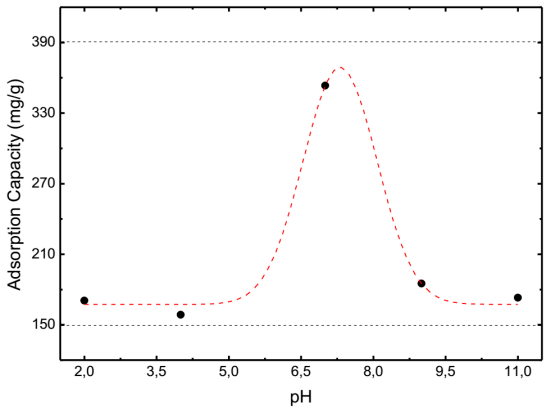

Fig. 1. Effect of pH on the removal of methyl green ($C_0 = 20$ ppm, $m_{AB} = 0.1$ g/l and room temperature).

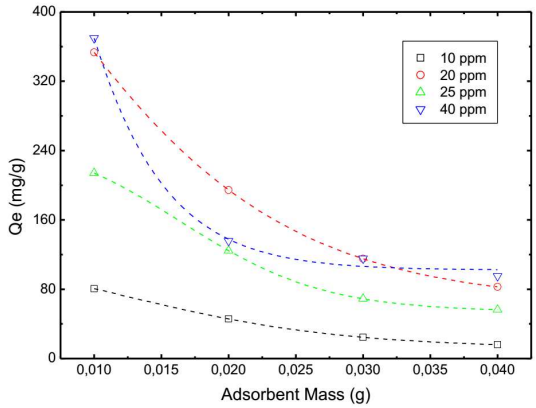

Fig. 2. Effect of adsorbent (AB) dosage on the removal of MG (C_0(MG) = 10–40 ppm; contact time = 180 min).

and adsorption sites of adsorbent in the solution, various amounts of AB (0.01–0.04 g/l) were added to 100 ml of dye solutions (10–40 ppm) and shaked for 180 min. It is demonstrated in Fig. 2 that the removal efficiency is high, mainly at low amount of adsorbent. The efficiency clearly elevated to 98% for AB dosage of 0.2 g/l for the initial concentration of MG of 25 ppm (results not shown). Also it can be seen that the amount of dye adsorbed increased with initial dye concentration and remained constant after equilibrium time (180 min) [11]. This can be explained by the presence of a large number of molecules that will diffuse to the site of the surface of the adsorbent and hence the partial adsorption depends on the initial concentration. When the initial dye concentration increased from 10 to 20 mg/l, the actual amount of dye adsorbed per unit mass of AB increased from 80.79 to 353.33 mg/g.

Adsorption of MG by AB has been modeled using isotherm of Langmuir with concentration of MG (20 ppm) and an adsorbent concentration 0.1 g/l (see Fig. 3). The experiments were carried out during a contact time of 180 min. The linear form of the Langmuir isotherm model can be represented by the following relation [12]:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max} b}. \tag{4}$$

The Langmuir equation model described the isotherm sorption with high correlation coefficient $R^2 = 0.9969$.

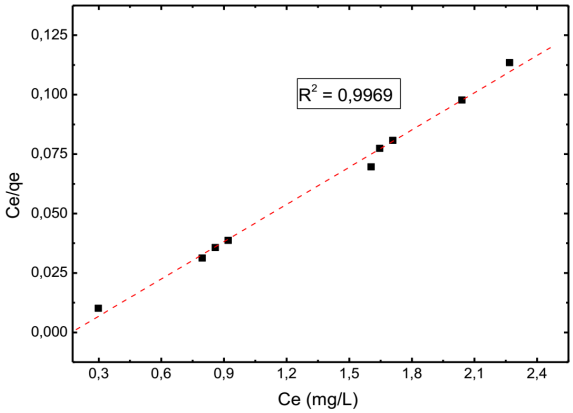

Fig. 3. Langmuir plot for adsorption of MG onto AB ($C_0 = 20$ ppm, $m_{AB} = 0.1$ g/l).

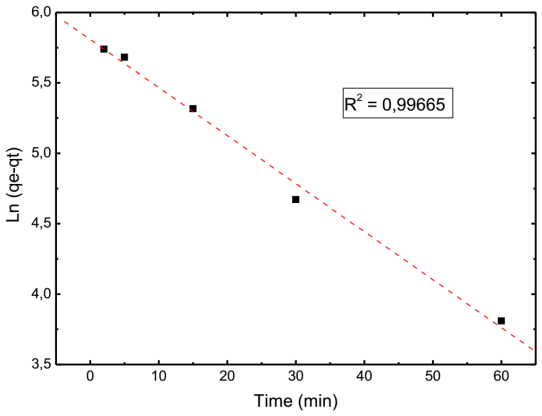

Fig. 4. The linear plot of pseudo-first-order model for adsorption of MG onto AB ($AB_{amount} = 0.1$ g/l).

In order to determine the kinetic parameters of MG adsorption on the AB, the pseudo-first-order, pseudo-second-order models were applied to fit the experimental data. The linear form of the pseudo-first order rate equation is given as [13, 14]:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t, \tag{5}$$

where K_1 is pseudo-first order rate constant and its value was calculated from the slope of the linear plot of ln $(Q_e - Q_t)$ versus time. The experimental data were also tested by the pseudo-second order kinetic model whose linear form is shown as Eq. (6) [15]:

$$t/Q_t = Q_e^2/K_2 + t/Q_e, \tag{6}$$

where K_2 [g/(mg min)] is the second-order rate constant. The select model is based on the regression correlation coefficient values (R^2). As exemplified in Fig. 4, the coefficient for pseudo-first-order kinetic model R_1 is slightly higher than 0.99, but for the second-order kinetics model R_2 value is less than 0.99 (results not shown). Thus indi-

cated that adsorption of MG dye could be described by the pseudo-first-order kinetics model.

4. Conclusion

In this work, the Maghnia bentonite clay was prepared by acidic activation and a comprehensive study was conducted on its adsorption capacity for the removal of dye pollutant (methyl green) from aqueous solution. MG adsorption onto the AB was found to be optimal in the pH of 7 and the adsorbent amount of 0.1 g/l. At 180 min, adsorption capacity of 353.33 mg/g was required. The adsorption kinetics of MG on the AB can be described by the pseudo-first-order model. Moreover, the equilibrium data were analyzed by the Langmuir model, which provided the best fit to the experimental data with high correlation coefficient ($R^2 = 0.996$).

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