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Adsorption Behavior of Reactive Blue 29 Dye on Modified Nanoclay

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ABSTRACT

The present study was conducted to evaluate the feasibility of modified nanoclay for reactive blue 29 dye removal from saqueous solution. The nature and morphology of the sorbent were characterized by Fourier Infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM) analysis. Batch adsorption studies were performed as a function of contact time, adsorbent dosage, temperature and pH. Montmorillonite (MMT) was modified by a facile and one-step procedure with diethylenetriamine (DETA). The equilibrium adsorption data were analyzed by Langmuir and Freundlich isotherms. The DETA-MMT showed a high uptake capacity in room temperature and 84% dye removal was observed with 6 g L^{-1} of adsorbent, in only 2 min. The results revealed that freundlich isotherm fit the experimental results well. Standard free energy ($\Delta G°$), standard enthalpy ($\Delta H°$) and standard enthropy ($\Delta S°$) were calculated by the data obtained from langmuir equation at different temperatures. All $\Delta G°$ and $\Delta H°$ values were negative indicating that the reactive blue adsorption was feasible and exothermic process.

Key words: Montmorillonite, modification, reactive blue 29, equilibrium isotherms

INTRODUCTION

Textile industry effluents shows large amounts of dye chemicals which are known as severe water pollution. Thus, it is important to reduce the dye concentration in the wastewater before its discharge into the environment. Discharging large amounts of dyes into water bodies, accompanied by organics can affect the physical and chemical characteristic of fresh water (Erdem *et al*., 2004). Dyes in wastewater can obstruct light penetration. Dyes are also stable to light irradiation and heat and are known toxic to microorganisms. The removal of dyes is stringent due to their complex structure and synthetic origins (Hu *et al*., 2006). Reactive blue 29 is an anthraquionone dye and due to the complex aromatic structure its considered stable in the environment and toxic to aquatic life (Crini, 2006). One of the effective treatment processes for the removal of dyes from water at low cost is adsorption. The successful removal of dyes have been demonstrated on lowering dye by using different adsorbents such as activated carbon, peat, chitin, clay and others (Tahir and Rauf, 2005). Adsorption techniques have gained attention in recent years due to their proven efficiency in the removal of pollutants from effluents. Besides the high quality product obtained, the processes have proved economically feasible (Jumasiah *et al*., 2005).

Montmorillonite is a very soft phyllosilicate mineral that typically forms in microscopic crystals, forming clay. The particles made this mineral are plate-shaped with an average diameter of approximately 1 micrometre. The particle thickness is extremely small (~1 nm). It is the main constituent of the volcanic ash weathering product, bentonite. Montmorillonite's water content is variable and it increases greatly in volume when it absorbs water. Chemically it is hydrated sodium calcium aluminium magnesium silicate hydroxide (Na, Ca)x(Al, Mg)2$(Si_4O_{10})(OH)_2 \cdot nH_2O$. Potassium, iron and other cations are common substitutes, the exact ratio of cations varies with source (Jaafar, 2006). Like other clays, montmorillonite swells with the addition of water. Montmorillonite is widely used in various science fields because of the large cation exchange capacity, high specific surface area, good swelling capacity and high platelet aspect ratio. Moreover, its surface can be modified easily (Ahmad *et al.*, 2009). Presence of inorganic cations such as Na^+ and Ca^{+2} on the basal planar surface of montmorillite layers makes it hydrophilic in nature and hence, shows the clay ineffective for absorption of aliphatic and relatively anionic compounds. Thus, the modification of the surface is of great importance.The properties of MMTcan be changed greatly by replacing the natural inorganic cations with other cation such as metal ions (Low *et al.*, 2000) and quaternary amines.

In this study, MMT modified with diethylentriamine (DETA) and evaluated as the possible sorbent for the removal of a reactive anthraquionone dye. The aim of this study is to investigate the effects of adsorbent dosage, temperature, contact time and pH on the adsorption process. Thermodynamic parameters, such as ΔG°, ΔH° and ΔS° were also calculated.

MATERIALS AND METHODS

Materials: Montmorillonite (sodium form) was purchased from F.C.C. (China). Reactive blue dye stock solution was prepared by dissolving RB29 in deionized (DI) water. Standards samples at a required concentration range were prepared by appropriate dilution of the stock solution with DI water. The formula, molecular weight and maximum wavelength of light absorbed by RB29 were $C_{31} H_{19} O_9 N_5 S_2 Cl_2 Na_2$, 788 g mol^{-1} and 589 nm, respectively. All reagents used were of analytical reagent grade. The method of detecting RB29 in aqueous solution had been described before (Nadafi *et al.*, 2011).

Preparation of adsorbent: The montmorillonite (5 g) was dissolved in 500 mL of deionized water. Then, the solution was stirred using nonmagnetic stirrer for 24 h at room temperature. The 5 mL diethylentriamine (DETA) was added to the obtained material and the pH value of the mixture was adjusted 3.5 by addition of hydrochloric acid (0.1 M). The suspension was stirred for 2 h in 50°C. The white precipitation was filtered, washed several times with distilled water and dried in a vacuum oven at 50°C.

General procedure: Adsorption of RB29 onto DETA-MMT was studied by batch experiments. A stock RB29 solution (1000 mg L^{-1}) was used in adsorption experiments. The required concentration of the dye solution was prepared by serial dilution of stock solution. A fixed amount of the adsorbent was added to dye solution. All batch adsorption experiments were carried out in 50 mL sealed plastic tubes with the working volume of 25 mL. The solutions were stirred continuously at room temperature (25±1°C) to achieve equilibrium. After equilibrium, the solid was separated by centrifugation (3000 rpm) and analyzed spectrophotometerically. The percentages of RB29 removal is calculated based on the following Eq:

$$\text{Removal (\%)} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \quad (1)$$

In this equation, C_0 is the initial dye concentration and C_e is the equilibrium concentration. The amount of nitrate adsorbed (q_e in mg g^{-1}) was calculated as follows:

$$q_B = \frac{(C_0 - C_B)\,V}{m} \quad (2)$$

where, C_0 and C_e are the initial and equilibrium concentrations of nitrate in solution (mg L^{-1}), V is the volume of solution (L) and m is mass of the adsorbent (g).

pH studies: In order to investigate the effect of pH on RB29 adsorption, the pH of the solutions were adjusted from 3-12. The initial pH of the solution was adjusted by using 0.1 M HCl or 0.1 M NaOH and DETA-MMT was added to 25 mL solution. The mixture was shaken using a temperature-controlled shaker. After adsorption, the final pH of all solutions were measured and the value providing the maximum nitrate removal was determined.

RESULTS AND DISCUSSION

Adsorbent characterization: The surface morphologies of the MMT and DETA-MMT were studied using scanning electron microscopy. Micrographs of the surface of each material are shown in Fig. 1(a-b). Figure 1(a) corresponds to the raw MMT. It is clearly shown that MMT consists of small particles and has a nonporous surface (Fig. 1a); however, it was not compact. After DETA-MMT composite fabrication, the sharp sheet is not observable anymore, due to the DETA coating onto the surface (Fig. 1b). This figure revealed the round surface texture and heterogeneous porosity. The chemically modified nanoclay developed more pores than that of the unmodified one. Figure 2 shows the FT-IR spectra of MMT and DETA-MMT. The FT-IR spectrum exhibited the characteristic bands of clay lattice -OH stretching vibrations (3630 cm^{-1}) while those at 3448 and 1639 cm^{-1} are attributed to the adsorbed H_2O deformation. The band at 1639 (Fig. 2a) was shifted to 1632 (Fig. 2b). Spectra of modifeid MMT showed all the characteristic bands of the MMTgroups with additional peaks at 3033 cm^{-1} which is due to the stretching vibration of N-H. These results confirmed that the MMT was modified by DETA adsorption isotherms.

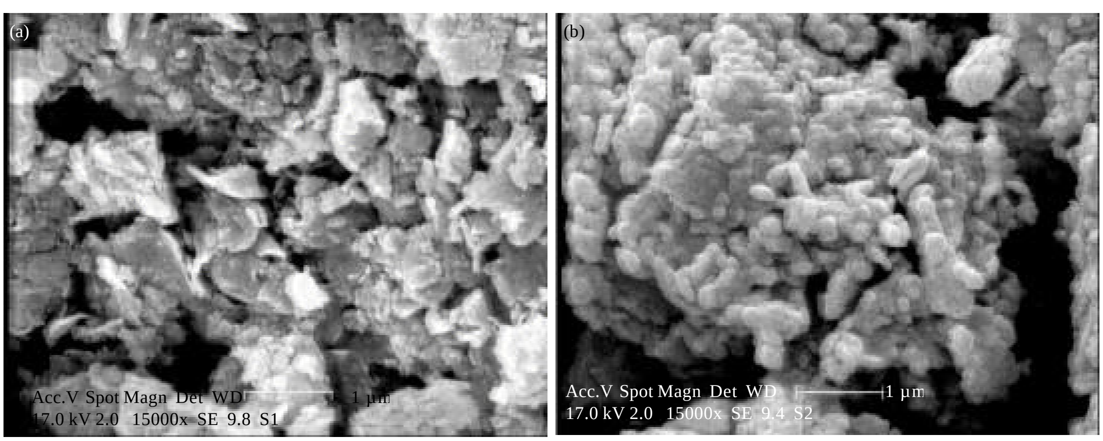

Fig. 1(a-b): SEM images of (a) MMT and (b) DETA-MMT

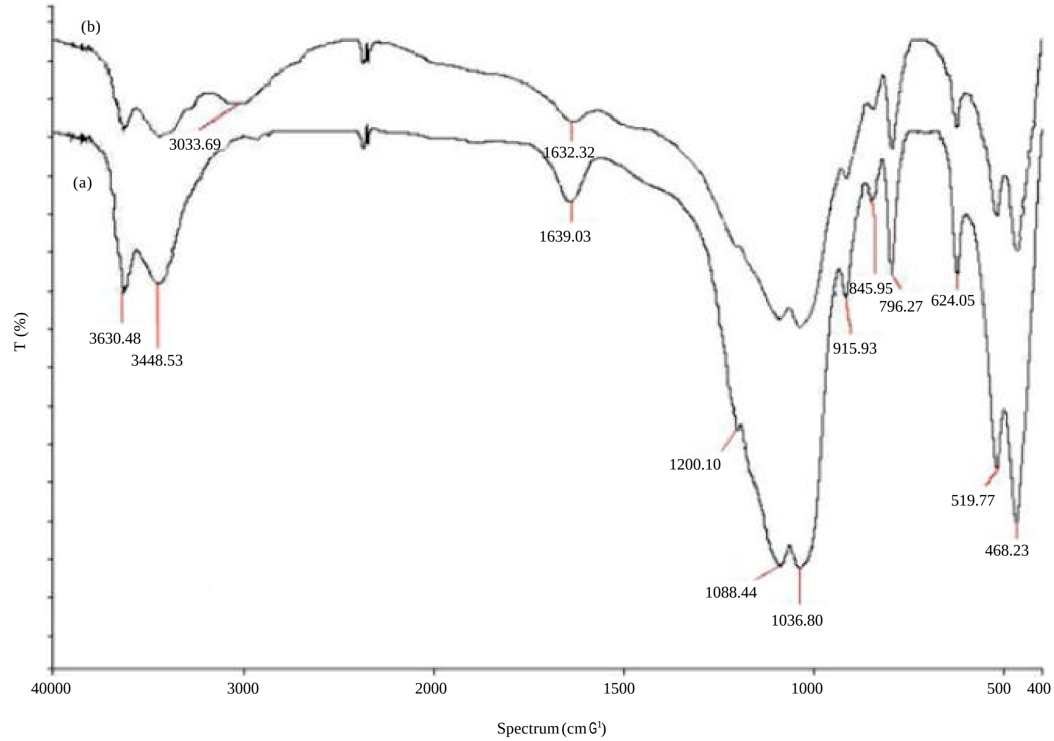

Fig. 2(a-b): FT-IR spectrum of (a) MMT and (b) DETA-MMT

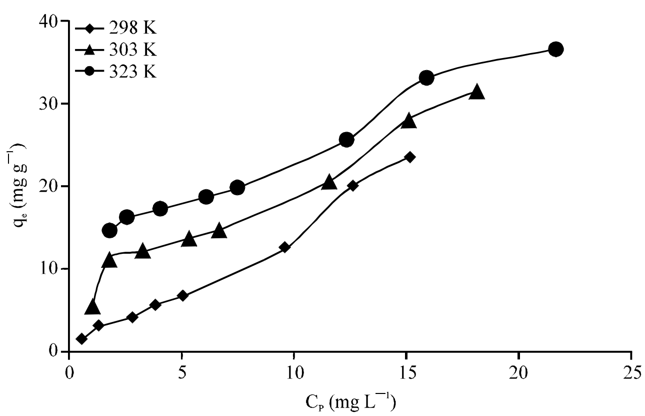

Fig. 3: Adsorption isotherm of RB29 onto DETA-MMT

The adsorption isotherm is of great importance for describing how the adsorbate molecules distribute between the liquid and the solid phases. The adsorption isotherm of RB29 on DETA-MMT is shown in Fig. 3. As shown in this figure, RB29 uptake increased with the increasing of dye concentrations which is due to the increase in the driving force from the concentration gradiant. From Fig. 3, the experimental adsorption capacity of RB29 on DETA-MMT was 23.44 (mg g^{-1}) at 293 K (25°C).

Table 1: Isotherm parameters for removal of RB29 by DETA-MMT

Isotherms	Estimated values at 298 K
Langmuir	
q_m (mg g^{-1})	14.280
b (L mg^{-1})	0.240
R^2	0.975
SD (%)	10.450
Freundlich	
K_f ((mg g^{-1}) (L mg^{-1})$^{1/n}$)	2.330
η	1.298
R^2	0.982
SD (%)	9.730

In this study, Langmuir and Freundlich isotherms were employed for the study of the adsorption of RB29 dye onto modified montmorillonite. Langmuir model is represented mathematically as follows (Adamson *et al.*, 1960):

$$\frac{1}{q_B} = \frac{1}{q_m} + \frac{1}{q_m bC_B} \tag{3}$$

Another important parameter, R_L, the separation factor or equilibrium parameter is determined from the relation:

$$R_L = \frac{1}{1+bC_o} \tag{4}$$

where, b is the Langmuir Constant and C_o (mg L^{-1}) is the highest nitrate concentration. The value of R_L shows this type of isotherm to be either favourable ($0<R_L<1$) or unfavourable ($R_L>1$), linear ($R_L = 1$) or irreversible ($R_L = 0$) (Zheng *et al.*, 2008). R_L values for the present study was less than 1 and greater than zero indicationg favourable adsorption (Table 1).

The freundlich isotherm model is an empirical relationship which assumes different sites with distinct adsorption energies are involved and its linear form is (Freundlich, 1906):

$$\text{Ln}q_B = \text{Ln}K_f + \frac{1}{n}\text{Ln}\,C_B \tag{5}$$

where, C_e (mg L^{-1}) is the equilibrium concentration, q_e (mg g^{-1}) is the amount of adsorbate adsorbed per unit mass of adsorbate and q_m and b are the Langmuir constants related to adsorption capacity and rate of adsorption, respectively. K_f and n are Freundlich constants.

The freundlich model assumes a heterogeneous adsorption surface with sites that have different adsorption energies which are not equally available. This isotherm is achieved through Eq. 5. In this equation, K_f and n are the empirical constants and their values were obtained from the intercept (Ln K_f) and slopes (1/n) of linear plots of Ln q_e versus Ln C_e. The K_f and n values in Freundlich equation were found to be 2.33 and 1.29, respectively (Table 1). It has been reported that values of n in the 2-10 range represent good, 1-2 moderately difficult and <1 poor adsorption characteristics. In the present research, the n obtained was 1.98, indicating that the adsorption is moderately difficult. The validity of models was determined by calculating the standard deviation as follows:

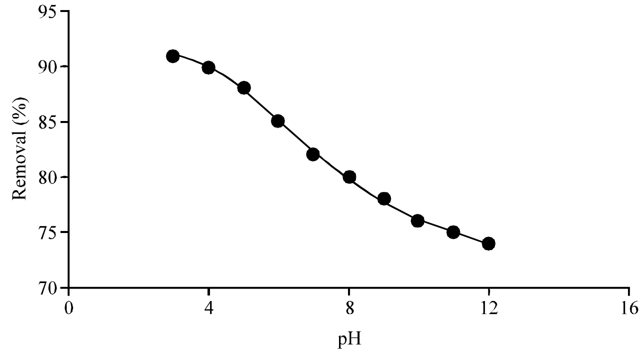

Fig. 4: Effect of pH on RB29 dye removal

Table 2: Reported adsorption capacities of some adsorbents for reactive blue

Adsorbent	q_e (mg g^{-1})	References
Activated carbon	120-140	Martins *et al.* (2013)
Carbon nanotubes	502-567	Machado *et al.* (2012)
Ferrite nanoparticles	24	Koseoglu *et al.* (2013)
Deacetylation degree chitosan	55	Li and Ding (2011)
Modified nanoclay	23.4	This study

$$SD = \sqrt{\frac{\Sigma(qexp - qcal)/qexp}{n-1}} \quad (6)$$

where, the exp and cal are the experimental and calculated data and n is the number of data points. As seen in Table 1, SD values are smaller than 12% for both models indicating that both isotherms fitted the experimental results obtained. On comparing the freundlich and langmuir isothermal models, it is evident that Freundlich isotherm is more favorable from the R^2 values presented. By comparing the results obtained from the present study with other reported works on adsorption capacities of other adsorbents for reactive blue dye removal it can be stated that our findings are acceptable due to the the natural character of montmorillonite and its low cost. (Table 2).

Effect of various parameters effect of pH: The adsorption of RB29 onto the composite as a function of pH was investigated at the initial dye concentration of 100 mg L^{-1} and the contact time of 24 h. The effect of pH on the adsorption of RB29 onto composite is shown in Fig. 4. The removal of dye was maximum in the pH of 3. In the acidic solution, the adsorption process of the RB29 by DETA-MMT is an electrostatic interaction, where the amine groups of DETA-MMT interact with the anionic groups of the dye. While at high pH, more OH^- ions present and compete with the anionic groups of RB29 for the adsorption sites of adsorbent, thus the available adsorption sites decrease.

Effect of adsorbent dosage: The influence of adsorbent dose on RB29 removal was studied by varying the adsorbent dosage from 1.0 to 7.0 g L^{-1} at an initial RB29 concentration of 100 mg L^{-1}. Increased adsorbent dosage implied a greater surface area and a greater number of binding sites available for the constant amount of RB29. The results showed (Fig. 5) that 2 g L^{-1} of DETA-MMT is required for 80% removal of RB29 for initial concentrations of 100 mg L^{-1}.

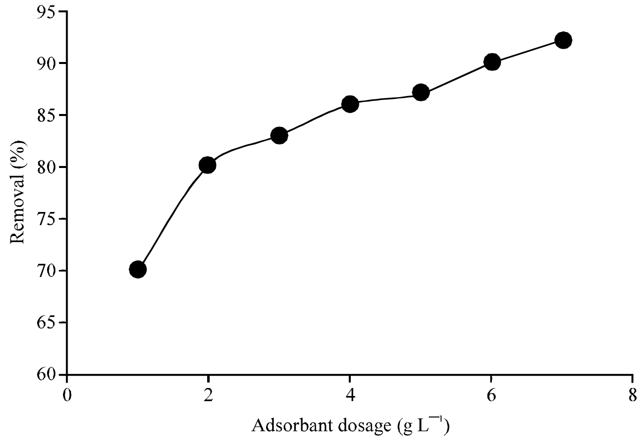

Fig. 5: Effect of adsorbent dosage on RB29 dye removal

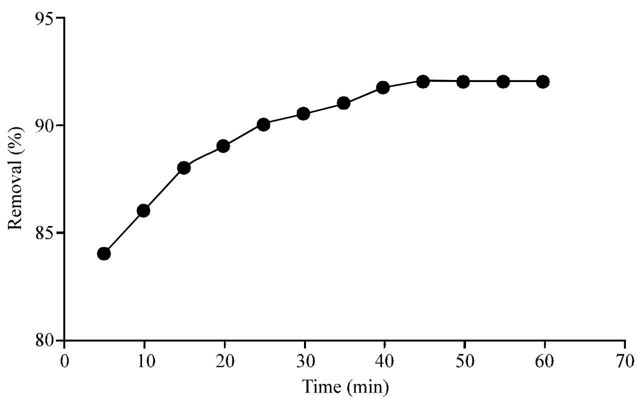

Fig. 6: Effect of contact time on adsorption of RB29 dye

Effect of contact time and agitation rate: The adsorption of RB29 on DETA-MMT was investigated as a function of contact time (2-60 min) at initial dye concentrations (100 mg L^{-1}) with an initial solution pH of 3.5. It was noticed that dye removal increased with time (Fig. 6). The trend of the plot in Fig. 6 exhibit that dye uptake was rapid in the beginning followed by a slower removal that gradually reached a plateau. Maximum removal of dye was achieved within the first 2 min of contact time and equilibrium was attained in 45 min. It was also found that about 84% removal of dye occurs within 2 min. The agitation speed ranging between 80 and 120 rpm was maintained (Figures not shown). For all speeds, the removal was not varied significantly. An agitation speed of 110 rpm was chosen as an optimum value. The small effect of agitation showed that external mass transfer was not the only rate limiting step.

Thermodynamic parameters: In adsorption processes the temperature plays an important role in determining thermodynamic dependency. The nature and thermodynamic feasibility of the sorption process were analyzed by standard free energy ($\Delta G°$), satndard enthalpy ($\Delta H°$) and standard enthropy ($\Delta S°$) using the following equations (Liu *et al*., 2009):

$$\Delta G^\circ = -RTLn(b) \tag{7}$$

$$Ln(b) = \frac{\Delta s^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{8}$$

where, b is the Langmuir constant (L mol^{-1}), R is the gas constant and T is the temperature (K).

On the basis of Eq. 7, the values of Gibb's free energy were calculated as -11.14, -11.43 and -15.3 at temperatures of 298, 303 and 323 K, respectively. The decrease in the negative value of ΔG° with an increase with temperature shows that the adsorption is favorable at higher temperature. The values of ΔH° and ΔS° were -46.37 kJ mol^{-1} and -0.11 J mol^{-1} suggesting that the adsorption is exothermic. The negative value of ΔS° suggest the probability of favorable adsorption.

CONCLUSION

The present investigation evaluated the effect of the chemically modified montmorillonite for the adsorption of RB29 dye. The adsorption of RB29 was found to be pH dependent with maximum removal was obtained at pH 3. The maximum sorption capacity of DETA-MMT was found to be 23.4 mg g^{-1} at 25°C. The equilibrium data were analyzed using the Langmuir and Freundlich isotherm models. Freundlich isotherm fitted the data well. The thermodynamic calculations indicate that the adsorption of RB29 is a feasible process which undergoes an exothermic process.

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