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Adsorption of Dye C.I. Reactive Red 15 onto Montmorillonite: Kinetics and Adsorption Isotherms

Chengcai Huang*, Muqing Qiu*, Linfa Bao*† and Hao Zhang**
*College of Life Science, Shaoxing University, Shaoxing, 312000, P.R. China
**Key Laboratory of Agro-Ecological Processes in Subtropical Region, Institute of Subtropical Agriculture, Chinese Academy of Sciences, Changsha, 410125, P.R. China
†Corresponding author: Linfa Bao

ABSTRACT

The adsorption of dye C.I. Reactive Red 15 in aqueous solution onto montmorillonite was carried out in detail. The operation parameters influencing the adsorption process of dye C.I. Reactive Red 15 such as contact time and initial dye concentration were studied. Physicochemical characterizations including microscopy and Fourier transform infrared spectroscopy analyses of the surface of montmorillonite were carried out. The kinetic study was performed by the pseudo first order and the pseudo second order reactions. According to the experimental data, the pseudo second order model better described the adsorption of dye onto montmorillonite. It implies that the predominant process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent. The adsorption isotherms were studied by Langmuir model and Freundlich model. The results indicated that the adsorption followed the Langmuir model. The dye C.I. Reactive Red 15 adsorption onto montmorillonite was monolayer adsorption.

INTRODUCTION

Organic dyes constitute one of the larger groups of pollutants in wastewater released from textile and other industries. Among 7×10^5 t and approximately 10,000 different types of dyes and pigments produced worldwide annually, it is estimated that 1-15% of the dye is lost in the effluents during the dyeing process (Ahmad et al. 2014). Effluents of textile industries are highly coloured and disposal of these wastes into receiving waters cause drastic damage to the environment. Indeed, they may significantly affect the photosynthetic activity and also be toxic to some aquatic life due to the presence of metals, chlorides, etc. (Emna et al. 2012). Most of the dyes released during textile clothing, printing and dyeing processes are considered as hazardous and toxic to some organisms and may cause direct destruction of the aquatic creatures. This massive influx of untreated organic chemicals into the waterways not only introduces aesthetic concerns but far more importantly it promotes eutrophication and adversely affects the environmental health of the region. It also represents an increasing environmental danger due to their refractory carcinogenic nature (Dogan et al. 2009). From an environmental point of view, the removal of synthetic dyes is of great concern. Among several chemical and physical methods, adsorption process is one of the effective techniques that has been successfully employed for colour removal from wastewaters (Barka et al. 2006).

Treatment of those wastewaters will, therefore, be essential to remove these dyes which are harmful to the environment (Safae et al. 2017). Several techniques have been developed to remove dyes from wastewater such as coagulation/flocculation (Zhou et al. 2014), oxidation (Malik & Saha 2003), membrane separation (Tan et al. 2015), photodegradation (Ledakowicz et al. 2001) and biological process (Chen et al. 2013), but most of these conventional methods are beginning to prove insufficient for simple and effective treatment, and in addition they are also very expensive (Chen et al. 2013). It is necessary to think about effective and inexpensive techniques.

Various types of adsorbents were tested for dye removal and include mineral or organic materials of natural and anthropogenic origin (Noroozi & Sorial 2013, Ismal et al. 2014). Among them, clay minerals are an inorganic alternative adsorbent that provides several advantages, which include its low-cost, abundant availability, non-toxicity and high potential of pollutant adsorption. The adsorption capacity for cations and organic molecules is high because of their colloidal properties and negatively charged layers (Maas & Chaudhari 2005).

In this study, the adsorption of dye C.I. Reactive Red 15 in aqueous solution onto montmorillonite was carried out in detail. The operational parameters influencing the adsorption process of dye C.I. Reactive Red 15 were studied, such as contact time and initial dye concentration. The ad-

sorption isotherms and kinetic models thermodynamic study were performed to describe the mechanism involved in the adsorption process. Furthermore, Brunauer Emmett Teller (BET) surface area analysis, transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were used to characterize the structure of montmorillonite.

The objective of this work is to study all the parameters influencing in the removal of dye C.I. Reactive Red 15 in aqueous solution onto montmorillonite to valorize the studied material for use in wastewater treatment as an alternative, low-cost and eco-friendly adsorbent.

MATERIALS AND METHODS

Materials

The dye C.I. Reactive Red 15 was chosen as an object in this experiment. It was purchased from Shanghai Chemical Co. Ltd. in China. Its molecular formula is $C_{25}H_{14}ClN_7Na_4O_{13}S_4$. The chemical structure of the C.I. Reactive Red 15 is shown in Fig. 1.

The montmorillonite was also purchased from Shanghai Chemical Co. Ltd. and crushed to obtain clay with a diameter of less than 50μm.

All the chemicals in this study were of analytical grade and used without further purification.

Experimental Methods

Degradation experiments were conducted in a set of 250 mL Erlenmeyer flasks containing montmorillonite and 100 mL of dye C.I. Reactive Red 15 with initial concentrations in aqueous solution. The pH of the solution was adjusted by (1+1) HCl and 10% NaOH. The flasks were placed in a shaker at a constant temperature and 120 rpm. The samples were then filtered and the residual concentration of dye C.I. Reactive Red 15 was analysed using a UV-1600 spectrophotometer at a wavelength corresponding to the maximum absorbance for the dye.

Analytical Methods

The value of pH was measured by a pH probe according to standard method. The concentration of the dye C.I. Reactive Red 15 was measured with a UV-1600 spectrophotometer at 510 nm.

The removal rate of the dye was calculated as follows:

$$Q = \frac{C_0 - C_t}{C_0} \times 100\% \qquad ...(1)$$

Where, C_o and C_t (mg/L) are the initial and equilibrium concentrations of the dye C.I. Reactive Red 15 in solution respectively. Q is the degradation rate of the dye.

The surface morphology of montmorillonite was observed with SEM (JEOL 6500F, Japan). NOVA 4200e surface area and pore size analyser (Quantachrome, FL, USA) was used to analyse the changes in the surface area and pore size of montmorillonite at a relative pressure of 0.95. Fourier transformed infrared (FT-IR) spectra of the samples were recorded on a Nexus 670 FTIR spectrometer (Thermo Nicolet, Madison) in the wave number range of 400-4000 cm^{-1}.

Statistical Analyses of Data

All the experiments were repeated in duplicate and the data of results were the mean and the standard deviation (SD). All error estimates given in the text and error bars in figures are standard deviation of means (mean±SD). All statistical significance was noted at α=0.05 unless otherwise noted.

RESULTS AND DISCUSSION

Characterization of the Montmorillonite

The surface area, average pore size and total pore volume of the montmorillonite obtained from N_2 adsorption-desorption isotherms were 31.3 m^2/g, 93.3 Å, and 0.073 cm^3/g, respectively. Investigation of the pore size distribution using Barrett Joyner Halenda (BJH) analysis showed that the pore size distribution was in the mesopore range.
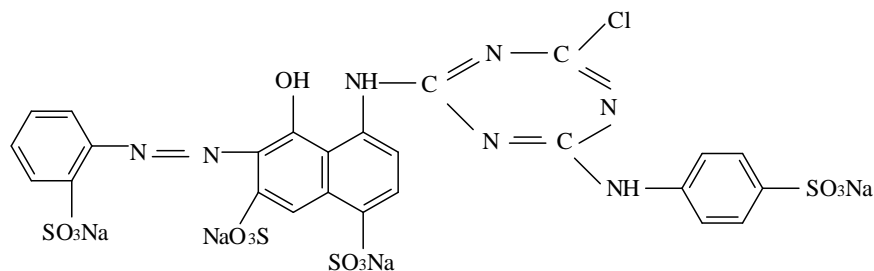

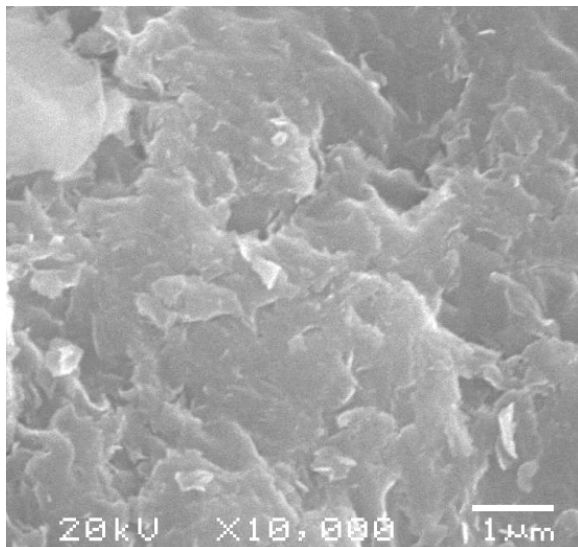Fig. 1: The chemical structure of the C.I. Reactive Red 15.

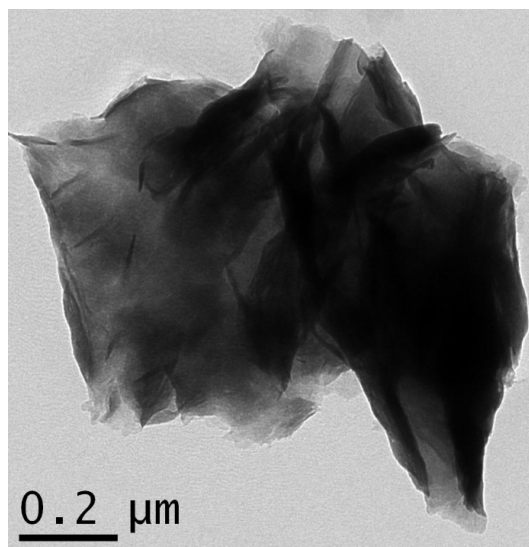Fig. 2: SEM micrographs image of montmorillonite.

Fig. 3: TEM micrographs image of montmorillonite.

Table 1: The kinetic parameters for the adsorption of dye C.I. Reactive Red 15 onto montmorillonite.

pseudo first order		pseudo second order	
k_1 (min^{-1})	R^2	k_2 (g·mg^{-1}·min^{-1})	R^2
0.032	0.906	0.015	0.986

Table 2: The adsorption parameters for dye C.I. Reactive Red 15 onto montmorillonite by Langmuir adsorption isotherm and Freundlich isotherm.

Langmuir parameters			Freundlich parameters		
q_{max} (mg/g)	K_L (L/mg)	R^2	n	K_F	R^2
16.14	0.13	0.9812	3.26	1.39	0.9527

SEM micrograph and TEM micrograph images of montmorillonite are shown in Fig. 2 and Fig. 3 respectively.

The surface of the montmorillonite is not very smooth and schistose in structure. There are many small particulates on the surface of the montmorillonite. It is clearly irregular and porous. This structural characteristic is suitable for improvement of adsorption capacity.

The SEM-EDS spectra of the montmorillonite are shown in Fig. 4. It can be confirmed that the montmorillonite contained the elements such as C, O, Al, Si, Mg, S, Cu, K, Ca and Fe. The strong peak of C, O and Si appeared. The C, O and Si contents of the composite materials were 51.9%, 21.1% and 16.8% respectively.

FTIR analysis was conducted to evaluate the roles of functional groups on the montmorillonite surface in the adsorption process. Fig. 5 shows the FTIR spectra of the montmorillonite.

As shown from FTIR, it is mostly related to the presence of -O-H functional group, -CO-O-CO-stretching of the anhydride groups and the -C=O stretching of the carboxyl group.

Adsorption Kinetics

In this study, the pseudo first order and pseudo second order models were used to describe the adsorption process.

The pseudo first order model is based on a linear relationship between the amounts of solute attached to the material surface over time (Dai et al. 2011, Toor & Jin 2012,
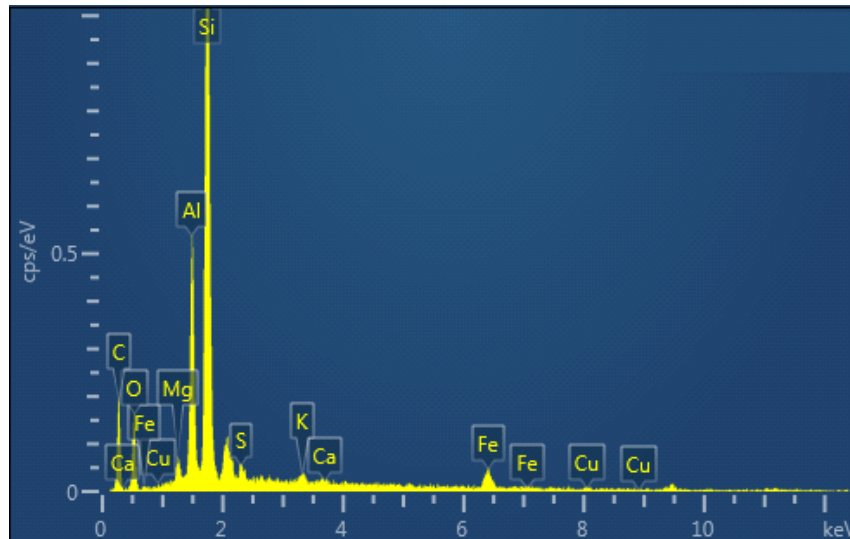
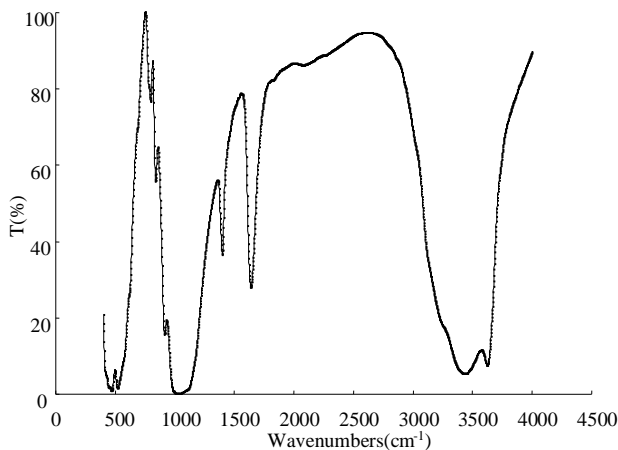Fig. 4: SEM–EDS spectra of the montmorillonite.

Fig. 5: FTIR spectra of the montmorillonite.

Safae et al. 2018). Several authors have used this irreversible kinetic model to describe the adsorption of organic and inorganic solutes on heterogeneous surfaces (Rudzinski & Plazinski 2009). It is represented by Eq. (2):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad \text{...(2)}$$

The pseudo second order kinetics model (Mckay & Ho 1999, Bentahar et al. 2015) has been developed to approximate the real reaction mechanism as much as possible. It is expressed by Eq. (3):

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \qquad \text{...(3)}$$

Where, q_e and q_t are the amounts of dye C.I. Reactive Red 15 molecules adsorbed (mg.g^{-1}) on the montmorillonite at equilibrium at time t, respectively and k_1(min^{-1}) and k$_2$ (g.mg^{-1}.min^{-1}) are the pseudo first and pseudo second order rate constants, respectively.

Effect of the contact time on the adsorption of the dye C.I. Reactive Red 15 onto montmorillonite has been studied by varying the contact time between 0 and 120 min with 0.5 g of montmorillonite, at an initial dye concentration of 100 mg/L, initial dye solution pH of 5.0 and at a constant temperature of 293 K. The experimental results are shown in Fig. 6.

According to the data of Fig. 6, the kinetic parameters can be calculated by the equation (2) and equation (3). The kinetic parameters are listed in Table 1.

The obtained results indicate that the pseudo second order kinetic model better described the adsorption of dye C.I. Reactive Red 15 onto montmorillonite with coefficients which are close to or equal to 1. It implies that the predominant process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent.

Adsorption Isotherms

In this experiment, the Langmuir model and Freundlich model were used to predict the validity of the experimental data.

Langmuir model assumes that the maximum adsorption corresponds to the monolayer coverage of the adsorbent
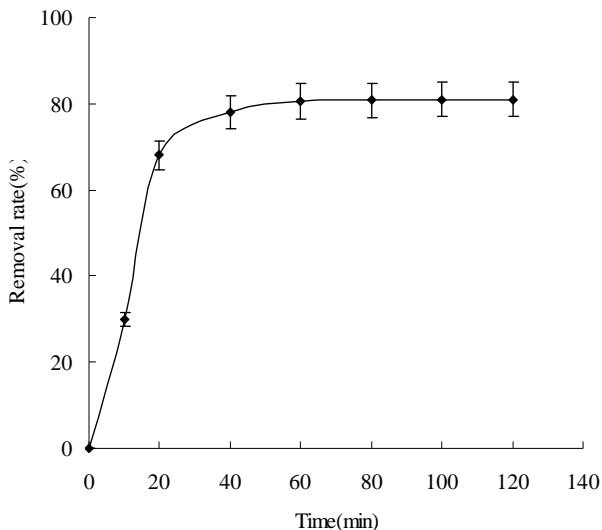
Fig.6: Effect of the contact time on the adsorption of dye C.I. Reactive Red 15 onto montmorillonite.
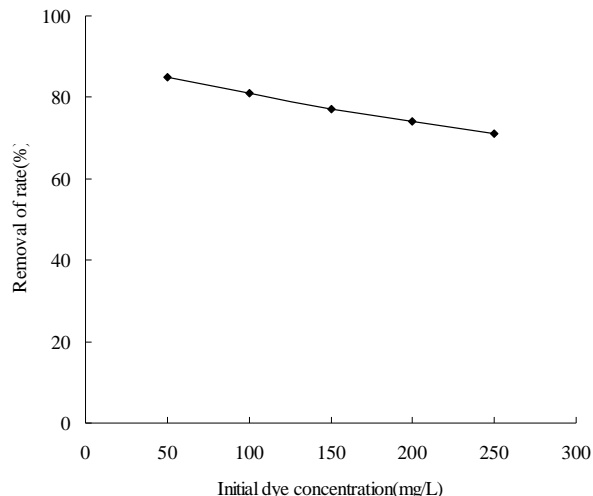

Fig. 7: Effect of initial dye concentration on the adsorption of dye C.I. Reactive Red 15 onto montmorillonite.

surface, that the adsorption sites are homogeneous and also the adsorbed molecules do not exhibit interactions between them (Özcan et al. 2009, Saeed et al. 2010).

The linear form of the Langmuir equation is given by the following Eq. (4):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \qquad ...(4)$$

Where, C_e (mg.L^{-1}), q_e (mg.g^{-1}), q_m (mg.g^{-1}) and K_L (L.mg^{-1}) are the equilibrium concentration of the dye, the amount of dye adsorbed at equilibrium, the maximum adsorption capacity, and the Langmuir constant.

Freundlich isotherm admits the existence of an interaction between adsorbed molecules and that the adsorption of adsorbate has taken place on a heterogeneous surface with a non-uniform distribution of the heat of adsorption. It is represented by the following Eq. (5):

$$\ln q_e = \ln K_F + \ln \frac{C_e}{n} \qquad ...(5)$$

Where C_e (mg.L^{-1}), q_e (mg.g^{-1}), K_F (mg.g^{-1}) (L.g^{-1})$^{1/n}$) and n represent the equilibrium concentration, the amount adsorbed, the Freundlich isotherm constant related to adsorption intensity, respectively (Wang et al. 2011). The n value indicated the favourability of the adsorption process, the adsorption is favourable if the values of $n>1$ and it is unfavourable if $n<1$.

Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.5 g of montmorillonite and 100 mL of C.I. Reactive Red 15 with initial concentra-

tions (50, 100, 150, 200, 250 mg/L) in aqueous solution and pH 5.0. The flasks were placed in a shaker at a constant temperature of 293 K. Effect of initial dye concentrations is shown in Fig. 7.

According to the data from Fig. 7, the adsorption parameters were obtained from the Langmuir adsorption isotherm and Freundlich adsorption isotherm. They are listed in Table 2.

It was shown that the Langmuir adsorption isotherm model was more suitable for dye C.I. Reactive Red 15 adsorption than the Freundlich adsorption isotherm model. It was also suggested that the adsorption process was homogeneous adsorption. The dye C.I. Reactive Red 15 adsorption onto montmorillonite was monolayer adsorption.

CONCLUSIONS

In this work, the adsorption of dye C.I. Reactive Red 15 in aqueous solution onto montmorillonite was carried out in detail. Brunauer Emmett Teller (BET) surface area analysis, transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were used to characterize the structure of montmorillonite. According to the experimental data, the pseudo second order model better described the adsorption of dye onto montmorillonite. The adsorption followed the Langmuir model.

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