

Removal of Remazol Brilliant Blue Dye from Dye-Contaminated Water by Adsorption Using Red Mud: Equilibrium, Kinetic, and Thermodynamic Studies

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Abstract Utilization of industrial solid wastes for the treatment of wastewater from another industry could help environmental pollution abatement, in solving both solid waste disposal as well as liquid waste problems. Red mud (RM) is a waste product in the production of alumina and it poses serious pollution hazard. The present paper focuses on the possibility of utilization of RM as an adsorbent for removal of Remazol Brilliant Blue dye (RBB), a reactive dye from dye-contaminated water. Adsorption of RBB, from dye-contaminated water was studied by adsorption on powdered sulfuric acid-treated RM. The effect of initial dye concentration, contact time, initial pH, and adsorbent dosage were studied. Langmuir isotherm model has been found to represent the equilibrium data for RBB–RM adsorption system better than Freundlich model. The adsorption capacity of RM was

found to be 27.8 mg dye/g of adsorbent at 40 °C. Thermodynamic analysis showed that adsorption of RBB on acid-treated RM is an endothermic reaction with ΔH^0 of 28.38 kJ/mol. The adsorption kinetics is represented by second-order kinetic model and the kinetic constant was estimated to be 0.0105 ± 0.005 g/mgmin. Validity of intra-particle diffusion kinetic model suggested that among the mass transfer processes during the dye adsorption process, pore diffusion is the controlling step and not the film diffusion. The process can serve dual purposes of utilization of an industrial solid waste and the treatment of liquid waste.

Keywords Adsorption · Isotherm · Kinetics · Red mud · Remazol Brilliant Blue

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1 Introduction

Large amounts of colored wastewater are discharged from different industries, which use many kinds of dyes. There are more than 10,000 dyes available commercially and are used for coloring in different industries (Gong et al. 2005). Dyes are used in many industries such as food, paper, rubber, plastics, cosmetics, and textiles (Robinson et al. 2002) to color the products. The presence of these dyes in water, even at very low concentration is highly visible and undesirable (Jain and Sikarwar 2006). Dyes can be classified as (Mishra and Tripathy 1993)—anionic (direct, acid,

and reactive dyes), cationic (basic dyes), and non-ionic (dispersive dyes). Reactive dyes are typically azo-based chromophores combined with different types of reactive groups. These are presently used for coloring cotton fibers. They differ from all other classes of dyes in that they bind to the textile fibers such as cotton to form covalent bonds (Aksu and Tezer 2000). Some of the reactive dyes are toxic and carcinogenic (Brown and De Vito 1993). Hence, the wastewater containing reactive dyes must be treated prior to its discharge. At present, colored wastewater is treated by physical, chemical, and biological methods. Adsorption is one of the processes, which being the widely used physicochemical method for dye removal has wide applicability in wastewater treatment. Some of the adsorbents which are generally used for dye wastewater treatment are alumina, silica gel, zeolite, and activated carbon (AC). Studies have shown that these adsorbents are good and more efficient adsorbents for the removal of different types of dyes in general but their use is sometimes restricted in view of their higher cost (Walker and Weatherley 1999). This has resulted in attempts by various researchers to find low-cost adsorbents which may replace the above adsorbents. Recently, a number of non-conventional adsorbents such as sawdust (Khatti and Singh 1999), clay minerals (Lopezgalindo et al. 2007), chitosan (Wong et al. 2004), hardwood saw dust (Asfour et al. 1985), cellulose-based waste (Annadurai et al. 2002), apple pomace, wheat straw (Robinson et al. 2001), wood materials (McKay and Poots 1980), AC-bagasse (Juang et al. 2002), AC rice husk (Mohamed 2004), wood sawdust raw (Ho and McKay 1998), and Rice husk (McKay et al. 1999) have been extensively used as adsorbents.

Utilization of industrial solid wastes for the treatment of wastewater from another industry can help in solving environmental pollution problems or both solid waste and liquid waste disposals. By-product wastes of steel plants such as blast furnace sludge, blast furnace dust, and blast furnace slag were investigated for the removal of acid and basic dyes (Jain et al. 2003a, b, c). Slag has also been used as an adsorbent for removal of various other dyes (Gupta et al. 2003; Li et al. 2003).

Red mud is a by-product of the Bayer process in production of alumina. For every ton of alumina produced, between 1 and 2 tonnes (dry weight) of red mud residues are produced. It is composed primarily

of fine particles of silica, aluminum, iron, calcium, and titanium oxides and hydroxides. Due to its high calcium and sodium hydroxide content, red mud is relatively toxic and can pose a serious pollution hazard. In recent years, researchers have worked on the utilization of red mud for wastewater treatment, such as removal of toxic heavy metals such as cobalt (Hayrunnisa and Ekrem 2012), arsenic (Soner and Altundogan 2000), chromate ions (Danis et al. 1998), copper (II), lead (II), and cadmium (II) ions (Guclu and Apak 2000), as well as for the removal of phosphate (Liu et al. 2007). A few studies have also been reported on the use of activated red mud for adsorbing dyes such as Acid Blue 92 (Norouzi et al. 2010), Congo red (Tor and Cengeloglu 2006), Rhodamine B, fast green, and Methylene Blue (Gupta et al. 2004), and Acid Violet (Namasivayam et al. 2001), pesticides like organochlorine pesticides (Ozcan et al. 2011). However, the studies on utilization of activated red mud for removal of reactive dyes from aqueous solution are very scarce. The present paper focuses on the possibility of utilization of the sulfuric acid-treated red mud as an adsorbent for removal of Remazol Brilliant Blue, a reactive dye from dye-contaminated water.

2 Materials and Methods

2.1 Red Mud and Dye

Red mud (composition: Fe_2O_3 —42 %, Al_2O_3 —20 %, TiO_2 —9 %, SiO_2 —10–12 %, Na_2O —4–5 %) was obtained from Hindalco Aluminium Industry, Belgaum, India. Remazol Brilliant Blue dye was obtained from Campbell Knitwear Ltd, Belgaum, India. Dye contains NH and SO_3 functional groups as shown in Fig. 1. The dye concentration was measured at 608 nm using a UV–Vis bio-spectrophotometer (Elico BL-198).

2.2 Pretreatment, Activation, and Characterization of Red Mud

Red mud was washed thoroughly with distilled water, filtered, and dried at 110 °C for 24 h. Ten grams of this red mud was soaked in 200 ml of 1 N H_2SO_4 for 24 h, washed with water several times and dried at 110 °C overnight. The activated red mud sample thus prepared was sieved and the sample of average size 120 μm was used for the studies. The X-ray diffractograms of the raw

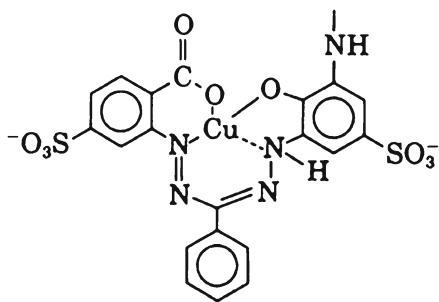


Fig. 1 Structure of Remazol Brilliant Blue dye

and acid-treated red mud samples were obtained using JEOL X-ray diffractometer; using CuK-alpha radiation ($\lambda=1.5425 \text{ \AA}$, $V=40 \text{ KV}$, $I=20 \text{ mA}$).

2.3 Batch Adsorption Experiments

The aqueous dye solutions of desired concentrations were prepared from 1,000 mg/l stock solutions. Batch adsorption experiments were carried out in 100-ml conical flask containing the aqueous dye solution of the desired concentration and the known amount of activated red mud. Initial pH was adjusted to the desired level with 1 N NaOH or 1 N HCl solutions. The solution was agitated at constant speed of 145 rpm and at 30 °C temperature till the equilibrium condition was reached. The dye solution was then separated from the adsorbent by centrifugation and the dye concentration in the supernatant was determined using UV spectrophotometer. Batch experiments were performed at different adsorbent dosages in the range of 0.6 to 4.2 g/l, initial dye concentration in the range of 10 to 70 mg/l and pH varying from 2 to 12.

3 Results and Discussion

3.1 Red Mud Characterization by XRD

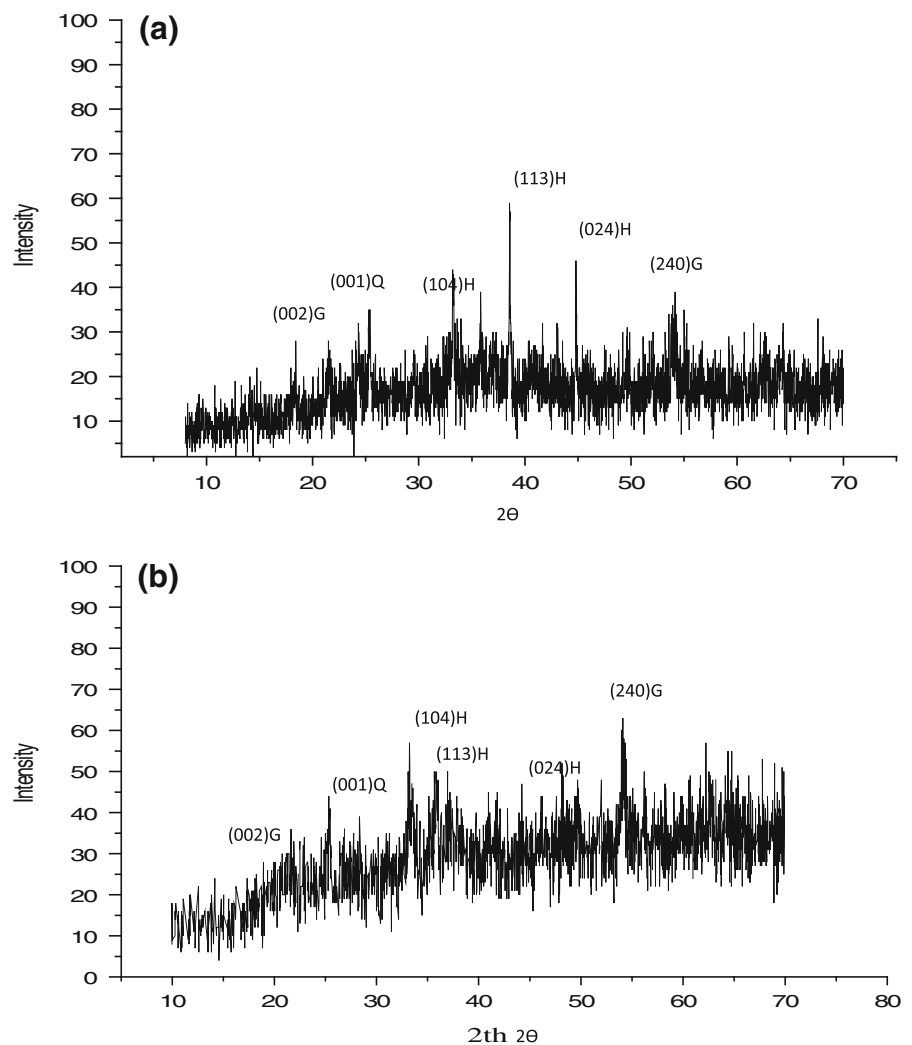
The X-ray diffractograms of raw red mud and acid-treated red mud are shown in Fig. 2. Red mud is found to be a complex mixture of phases mainly comprising of hematite (Fe_2O_3), goethite $\text{FeO}(\text{OH})$, and quartz (SiO_2). After the acid treatment the intensity for hematite (104) and goethite (240) were increased and the peaks for hematite (024) and goethite (002) have almost disappeared suggesting that phase transformation has occurred on red mud. Similar trend was observed

by Wang et al. (2005). The surface areas of original red mud and acid-treated red mud were determined by BET analysis using ASAP 2020 V3.04 H (Micromeritics, USA) surface area analyzer. The raw red mud and acid-treated red mud have specific surface area of 20.2 and 27.3 m^2/g respectively. The pore sizes of raw red mud and acid-treated red mud were 20.983, and 20.09 nm, respectively. The total pore volume of raw red mud was 0.093 cm^3/g and of acid-treated red mud was 0.1 cm^3/g . The surface area and pore volume of acid-treated red mud is higher than the raw red mud. The acid treatment leads to removal of sodium ions and compounds (Shing 1997; Pratt and Christoverson 1982; Snigdha et al. 2012), further it causes dispersion of dissolved metal oxides as hydroxides which leads to formation of pores thereby increasing the surface area. The surface activity of clay minerals for adsorption process is due to the micropores present in them. More micropores are retained, the higher is the activity and the larger is the surface. In acid treating, the adsorbed salts and exchangeable cations are dissolved first, and then the most aluminum ions and other metallic ions are removed from the lattice of structure so that many micropores are introduced (Shing 1997), hence leading to increase in pore volume and surface area.

3.2 Effect of pH

The initial pH values of dye solutions affect the chemistry of both the dye and an adsorbent. It is known that ionic dyes upon dissolution release colored dye anions/cations into solution. The adsorption of these charged dye groups onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent which is in turn influenced by the solution pH (Eren and Acar 2006). Hence, the batch adsorption experiments were conducted at different initial pH conditions ranging from 2 to 12. Figure 3 shows the effect of pH on percentage adsorption at equilibrium, with initial dye concentration of 30 mg/l and adsorbent dosage of 1.2 g/l. The percentage removal of dye by adsorption has decreased with the increase in pH from 2 to 8. Marginal decrease in percentage adsorption has been observed with the increase in pH from 2 to 6. At a pH above 6, a considerable decrease in adsorption takes place. The decrease in adsorption with increase in pH may be explained on the basis of acid–base dissociation at solid/liquid interface (Namasivayam et al. 2001). In the acid medium, positive charges are

Fig. 2 X-ray diffractograms of red mud **a** raw red mud, **b** red mud treated with acid. (G =FeO(OH), Q =SiO₂, H =Fe₂O₃)



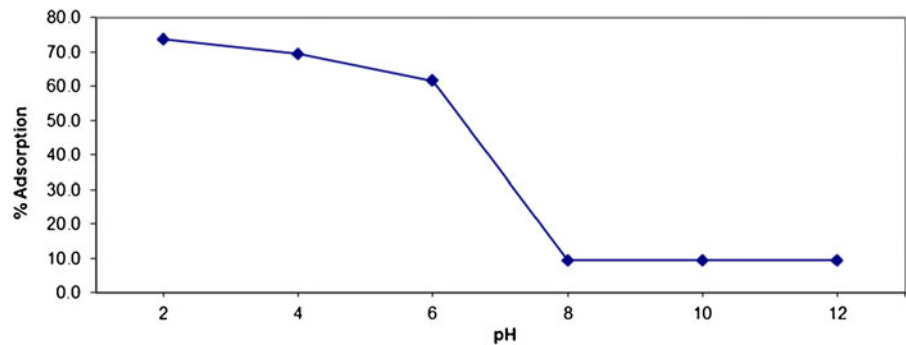
developed on the surface of metal oxides of adsorbent. The outer surface of positively charged interface of the adsorbent will be associated with Cl^- ions, as the solution is acidified by hydrochloric acid. The chloride ions are exchanged with dye anions. With an increase in pH, the positive charge on the oxide/solution interface decreases. At pH values above the pH_{ZPC} (zeta potential charge) of red mud, i.e., 8–10, the adsorbent surface becomes negatively charged and will be associated with the positively charged ions of the solution (Walker and Weatherley 1999). Thus there are no exchangeable anions on the outer surface of the adsorbent at higher pH values and consequently adsorption is very low. A similar trends were observed by earlier researchers in the adsorption of Acid Violet (Namasivayam et al. 2001) and Procion Orange (Namasivayam et al. 2002) by red

mud where the adsorption of dye decreased with increase in pH. It can be found from Fig. 3 that alkaline pH does not favor adsorption.

3.3 Effect of Contact Time

The time course variation for percentage removal of Remazol Brilliant Blue dye (RBB) during batch adsorption with various initial RBB concentrations is shown in Fig. 4. It can be observed that the adsorption is rapid within around 20 min of initial time, but the adsorption progressed at a lower rate for the remaining time. Earlier researchers have reported similar results in adsorption of Congo Red (Namasivayam and Arasi 1997; Tor and Cengeloglu 2006), Acid Violet (Namasivayam et al. 2001), Rhodamine B, and Methylene Blue (Gupta et

Fig. 3 Effect of initial pH on percentage adsorption of dye. Initial dye concentration 30 mg/l and red mud dosage 1.2 g/l



al. 2004) by red mud, where removal of dye was rapid in initial stages of contact time and gradually decreased with lapse of time. As at the initial times, the bulk solution concentrations are higher, the driving forces are the maximum, leading to maximum rates. But as the adsorption proceeds, the bulk concentration reduce approaching the equilibrium values and the rate decreases. At initial times, more number of active adsorption sites will be available and hence the number of successful collisions (collision of dye molecules on to the surface of red mud, leading to adsorption on to the active sites) onto the surface is higher, which lead to higher adsorption rate. But as the time proceeds, most of the active sites get bound with dye molecules and the number of free active sites decreases. It may decrease the number of successful collisions and hence decrease the rate of adsorption.

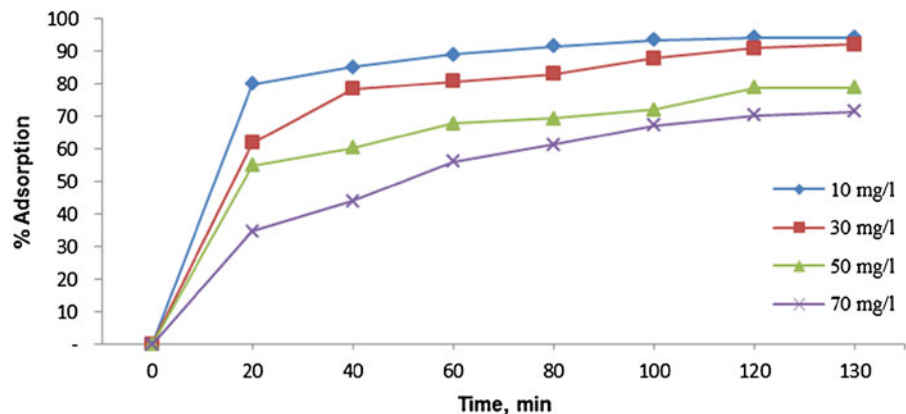
It can be observed from Fig. 4 that with a fixed amount of activated red mud the percentage RBB adsorption has increased with time and then attained a constant value at around 130 min. The time to reach equilibrium conditions appears to be independent of initial RBB concentrations. This can be shown as an

evidence of time for attainment of equilibrium being governed by the rate of mass transfer. Rate of mass transfer is a function of stirring conditions, interfacial surface area for mass transfer, and the driving force. Stirring conditions (shaker speed) and interfacial area for mass transfer (governed by adsorbent dosage) being the same for all the experiments, the rate of mass transfer is only a function of the driving force (difference between the bulk concentration and the equilibrium concentration). The variations in driving force with change in initial dye concentrations appear to be not very predominant in the range of concentrations studied, as evidenced by equal time(130 min) taken to reach equilibrium at all the initial concentrations.

3.4 Effect of Initial Concentration

The effect of initial dye concentration on percentage adsorption of the dye is presented in Fig. 4. The adsorption of the dye at equilibrium has decreased from 94 to 71 % with increase in dye concentration from 10 to 70 mg/l for a fixed red mud dosage of 3.2 g/l. Similar observations were made in adsorption of Congo Red (Namasivayam and

Fig. 4 Effect of contact time on percentage adsorption at different initial dye concentration with pH2 and red mud dosage 3.2 g/l



Arasi 1997), Acid Violet (Namasivayam et al. 2001), Rhodamine B, and Methylene Blue (Gupta et al. 2004) by red mud, where removal of dye decreased with increase in initial dye concentration. This may be attributed to surplus dye molecules being present in the solution, with respect to the available active adsorption sites owing to fixed surface area of mud. Insufficient active sites available for the adsorption of all the dye molecules, lead to higher residual concentration in solution with increasing initial dye concentrations.

3.5 Effect of Adsorbent Dosage

The variation of adsorption of the dye with varying amount of red mud was studied for different initial dye concentrations and the results of this study are shown in Fig. 5. The uptake increases with increasing adsorbent dosage. The percentage adsorption of the dye increased by 10 % when the quantity of adsorbent used was doubled, i.e., from 0.6 to 1.2 g/l. As the amount of red mud was increased further to 2.4 g/l, the adsorption has increased by only 2 %. As such, 3.2 g/l of adsorbent was considered to be quite appropriate. Further increase in dosage did not show much increase in uptake of dye. Similar trends were reported earlier, in adsorption of Acid Violet (Namasivayam et al. 2001), Rhodamine B, and Methylene Blue (Gupta et al. 2004) by red mud, where removal of dye was increased with increase in red mud dosage and reached a maximum value and remained constant with increase in dosage. The increase in dye removal with adsorbent dosage is due to greater availability of adsorbent surface area (Namasivayam et al. 2001) and more active sites. When the red mud

concentration is high, concentration of surface hydroxyl groups is higher through surface site density (Tor and Cengeloglu 2006; Sujana et al. 1998). Increased surface hydroxyl groups favor adsorption of the dye molecules.

3.6 Adsorption Isotherm Analysis

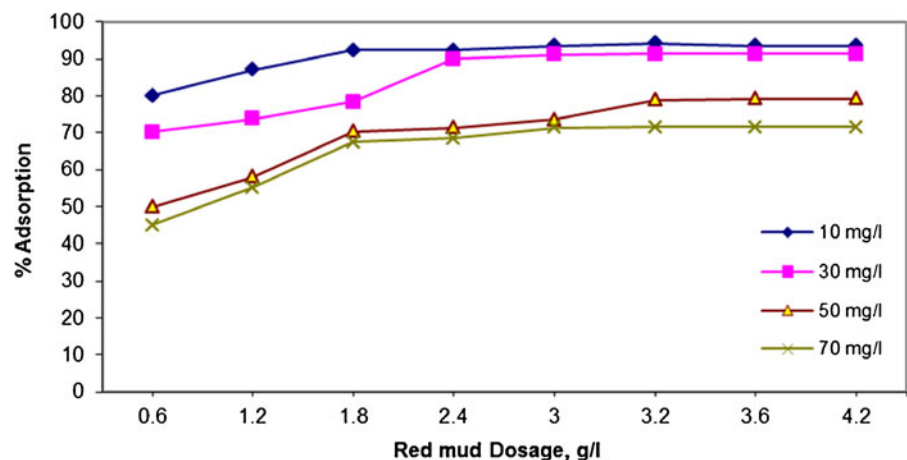
The relationship between the amount of RBB adsorbed and the equilibrium RBB concentration remaining in solution is described by an adsorption isotherm. The equilibrium isotherm is of fundamental importance for the design and optimization of adsorption system used for removal of the dye from aqueous solution. The two most common isotherm types for describing adsorption system are the Langmuir and the Freundlich isotherms.

The most important model of monolayer adsorption is the Langmuir isotherm given in Eq. (1):

$$q_e = \frac{Q_0 b C_e}{1 + b C_e}, \quad (1)$$

where C_e is the bulk solution concentration of RBB (milligram per liter) at equilibrium, q_e is the amount of adsorbed dye per unit mass of adsorbent (milligram per gram), Q_0 the monolayer capacity of the adsorbent (milligram per gram), and b is the Langmuir adsorption constant indicating the adsorption energy (liter per milligram). The Langmuir model (Agyei et al. 2000; Ho and McKay 1999) is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane.

Fig. 5 Effect of red mud dosage on percentage adsorption at pH=2 and temperature=30 °C with different initial dye concentrations



Langmuir equation can be linearized as shown in Eq. (2).

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{C_e Q_0} \quad (2)$$

The Freundlich isotherm is derived to model the multi layer adsorption and for the adsorption on heterogeneous surfaces. The Freundlich model is formulated as shown in Eq. (3):

$$q_e = k C_e^{\frac{1}{n}} \quad (3)$$

Where, k is the sorption capacity (milligram per gram) and n is an empirical parameter which is an indicator of adsorption intensity (Senthilkumar and Kirthika 2009) or the bonding energy between the adsorbent and the dye molecule. It is also considered as heterogeneity factor of the adsorbent and surface heterogeneity is due to the existence of crystal edges, types of cations, surface charges, surface modification groups, and degree of crystallinity of the surface. n indicates the relative distribution of energy sites and depends on the nature and strength of the adsorption process. The Freundlich isotherm model assumes that different sites with several adsorption energies are involved (Agyei, et al. 2000; Baup et al. 2000). The linear form of Freundlich isotherm can be given by Eq. (4):

$$\ln q_e = \ln k + \frac{\ln C_e}{n} \quad (4)$$

The equilibrium data obtained from the experiments were fitted into these two types of isotherms to test the validity of these for RBB-red mud adsorption system. The values of the constants for isotherms were obtained from the slope and intercept of the plots of linear form of

each of the isotherm equations. The sample plots of Freundlich and Langmuir isotherms at 30 °C are shown in Figs. 6 and 7, respectively. The values of parameters of the isotherms at three different temperatures of 20, 30, and 40 °C, along with the corresponding R^2 values representing the goodness of fit are presented in Table 1. The R^2 values indicate that the equilibrium for RBB-red mud adsorption system can be represented by both Langmuir and Freundlich isotherms under the conditions of the study, but Langmuir model has been found to fit better owing to higher R^2 values. With Freundlich isotherm, the values of n obtained are greater than one. It indicates that adsorption is much more favorable (Rozada et al. 2002). However, the smaller the value of n ($1 < n < 10$), the higher the adsorption intensity (Rozada et al. 2002; Weber 1973). The greater the k values, the higher the adsorption capacity of the adsorbent for the adsorbate. Increase in k and n with increasing temperature, suggest that adsorption capacity is higher at higher temperatures and adsorption is more favorable as the temperature is increased. From the results of Langmuir isotherm parameters, it is clear that the values of monolayer capacity Q_0 and adsorption energy b of the red mud increase with the increase in temperature.

The essential characteristics of the Langmuir isotherm can be expressed by a separation or equilibrium parameter (R_L), a dimensionless constant, which is defined by Eq. (5):

$$R_L = \frac{1}{(1 + bC_0)} \quad (5)$$

Where C_0 is the initial concentration of dye (milligram per liter) and b is the Langmuir constant (liter per milligram). R_L indicates the nature

Fig. 6 Linearized plot for Freundlich isotherm evaluation for adsorption of RBB on red mud at 30 °C

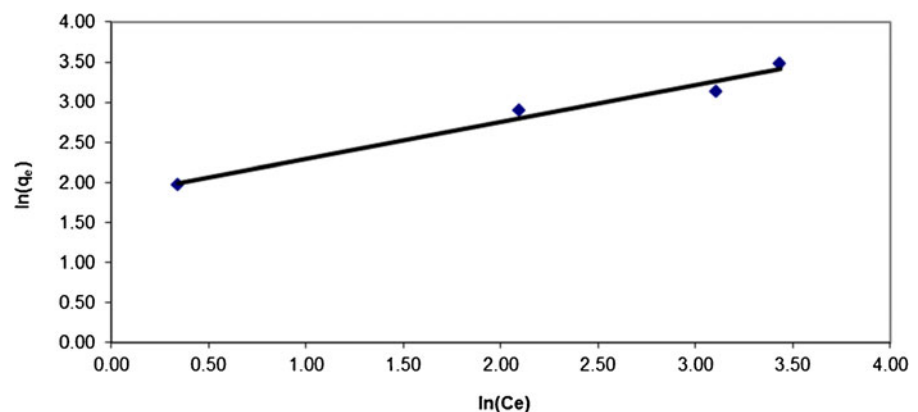
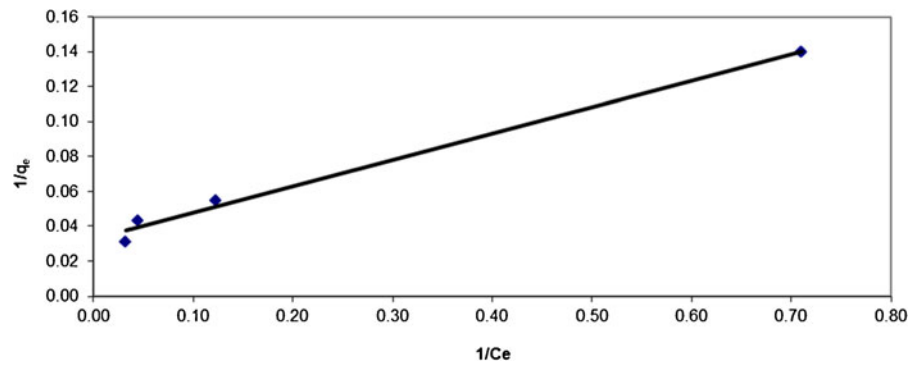


Fig 7 Linearized plot for Langmuir isotherm evaluation for adsorption of RBB on red mud at 30 °C



of the adsorption process as given below (Aksu and Dönmez 2003):

$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The values of R_L for the present system were found to be in the range of 0–1 at all the temperatures studied indicating that the process of adsorption of RBB on sulfuric acid activated red mud is favorable. R_L values at a temperature of 20 °C are presented in Table 2.

3.7 Thermodynamic Analysis

Increasing the temperature will increase the rate of diffusion of the adsorbate molecules in the internal pores of the adsorbent particle. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate. Effect of temperature on dye removal was studied by varying the temperature (20 to 40 °C) at which adsorption occurs. Results of these experiments are shown in Fig. 8. The percentage of dye

Table 1 Adsorption isotherm parameters at different temperature

Temperature, °C	Langmuir model	Freundlich model
20	$Q_0=25.64$ mg/g $b=0.30$ l/mg $R^2=0.99$	$n=1.934$ $k=3.19$ mg/g $R^2=0.91$
30	$Q_0=26.17$ mg/g $b=0.44$ l/mg $R^2=0.98$	$n=2.17$ $k=6.29$ mg/g $R^2=0.97$
40	$Q_0=27.8$ mg/g $b=0.63$ l/mg $R^2=0.99$	$n=3.18$ $k=7.20$ mg/g $R^2=0.97$

adsorption increases with increase in temperature for all the initial concentrations. The isotherm parameters of adsorption at different temperatures are presented in Table 2. From the table, it can be seen that the adsorption capacity increases with temperature. Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, ΔG^0 , is an indication of spontaneity of a process and therefore is an important criterion for spontaneity. Both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. A process occurs spontaneously at a given temperature if ΔG^0 is a negative quantity. Thermodynamic parameters, i.e., free energy change ΔG^0 , enthalpy change ΔH^0 , and entropy change ΔS^0 are related as in Van't Hoff's given by Eq. (6)

$$\ln b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)$$

Where b is the Langmuir adsorption equilibrium constant; ΔH^0 and ΔS^0 are the standard enthalpy and entropy changes of adsorption respectively and the values ΔH^0 and ΔS^0 were calculated from the slopes and intercepts of the linear plot of $\ln b$ vs $1/T$. The free energy ΔG^0 of specific adsorption calculated using Eq. (7).

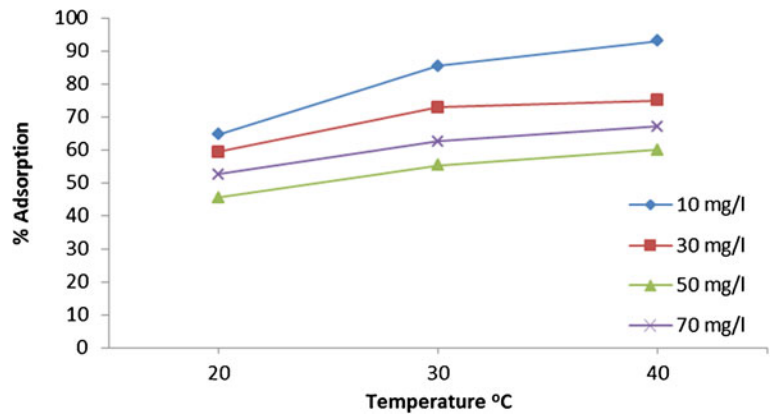
$$\Delta G^0 = -RT \ln b \quad (7)$$

The thermodynamic parameters calculated are presented in Table 3. The negative values of ΔG^0 indicate

Table 2 R_L values at different initial concentrations at 20 °C

C_0 , mg/l	R_L
10	0.25
30	0.10
50	0.06
70	0.04

Fig. 8 Effect of temperature on percentage of adsorption at different initial concentrations. pH=2 and red mud dosage=1.2 g/l



the feasibility and spontaneous nature of Remazol Brilliant Blue dye adsorption on red mud. The change in enthalpy ΔH^0 for RBB-red mud adsorption process was found to be positive. The positive values confirm the endothermic nature of adsorption. The increase in dye adsorption with increasing temperature might also be due to the enhanced rate of intra-particle diffusion of the adsorbate, as diffusion is an endothermic process (Mohan et al. 2000).

3.8 Adsorption Kinetics

The kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of adsorption. For kinetic studies, the adsorption experiments were carried out with different initial adsorbate concentrations at fixed temperatures. In order to evaluate the kinetics of adsorption process of RBB on the adsorbent, pseudo-first-order and pseudo-second-order kinetic models were tested with the experimental data.

3.8.1 Pseudo-First-Order Model

The experimental data were analyzed using the pseudo-first-order adsorption kinetic model and the

Table 3 Thermodynamic parameters for the adsorption of RBB on red mud

ΔG^0 , kJ/mol			ΔH^0 , kJ/mol	ΔS^0 , kJ/mol
20 °C	30 °C	40 °C		
-2.94	-2.07	-13.973	28.38	0.09

kinetic constants were calculated. The first-order rate expression based on solid capacity is generally expressed (Eren and Acar 2006) by Eq. (8).

$$\frac{dq}{dt} = K_1(q_e - q) \tag{8}$$

Where q is the amount of adsorbate adsorbed at time t (milligram per gram), q_e is the adsorption capacity at equilibrium (milligram per gram), K_1 is the pseudo-first-order rate constant. Integration of Eq. (8) gives Eq. (9):

$$\log(q_e - q) = \log(q_e) - \left(\frac{K_1}{2.303}\right)t \tag{9}$$

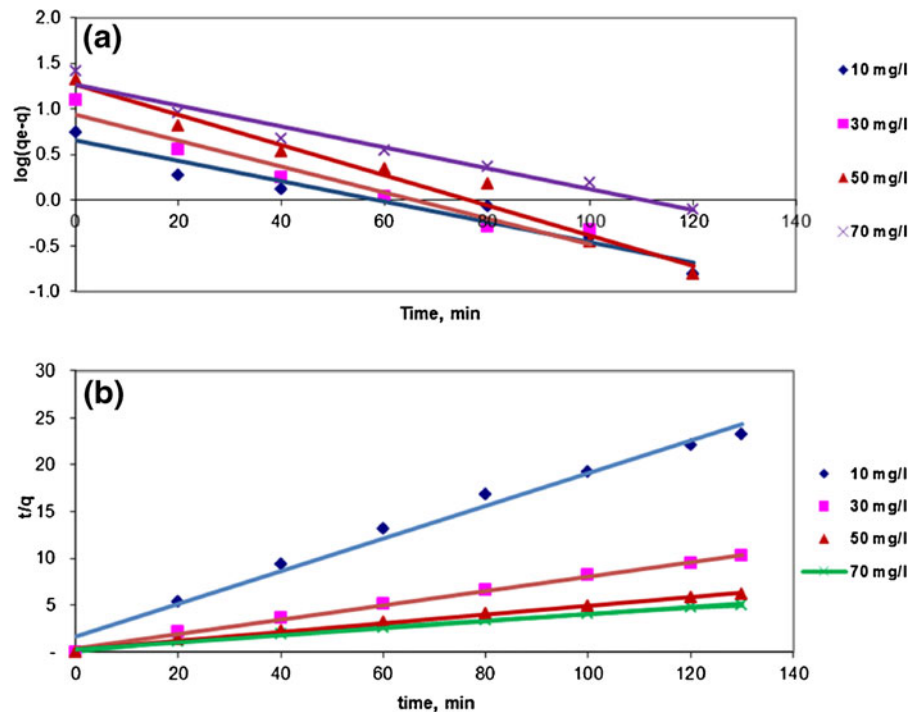
The plots of $\log(q_e - q)$ vs t are straight line as shown in Fig. 9, suggesting the applicability of this kinetic model. The constants were obtained from the slope and intercept. Table 4 shows the first-order rate constants obtained by the kinetic analysis based on experiments with different initial dye concentrations and the corresponding correlation coefficients (R^2 value). The first-order rate constant for the RBB-acid-treated red mud adsorption process is found to be 0.0285 ± 0.022 per min.

3.8.2 Pseudo-Second-Order Model

The pseudo-second-order equation is also based on the adsorption capacity of the solid phase. The pseudo-second-order model rate equation is expressed as following Eq. (10):

$$\frac{dq}{dt} = K_2(q_e - q)^2 \tag{10}$$

Fig. 9 **a** Pseudo-first-order model for different initial concentration of dye. **b** Pseudo-second-order model for different initial concentrations of dye



Where K_2 is the rate constant of second-order adsorption (g/mg.min). For the boundary conditions $t=0$ to $t=t$ and $q=0$ to $q=q$, the above equation can be integrated to give Eq. (11).

$$\frac{t}{q} = \frac{1}{q_e^2 K_2} + \frac{t}{q_e} \quad (11)$$

The plots of $\frac{t}{q}$ vs t are straight lines as shown in Fig. 9, suggesting the applicability of the second-order kinetic model. The constants were obtained from the slope and intercept. The values of second-order rate constants obtained by the kinetic analysis performed on experiments with different initial dye concentrations and the corresponding correlation coefficient (R^2 value) indicating the goodness of fit are given in Table 4. The second-order rate constant for the RBB–acid-treated red mud adsorption process is found to be 0.0105 ± 0.002 g/mgmin

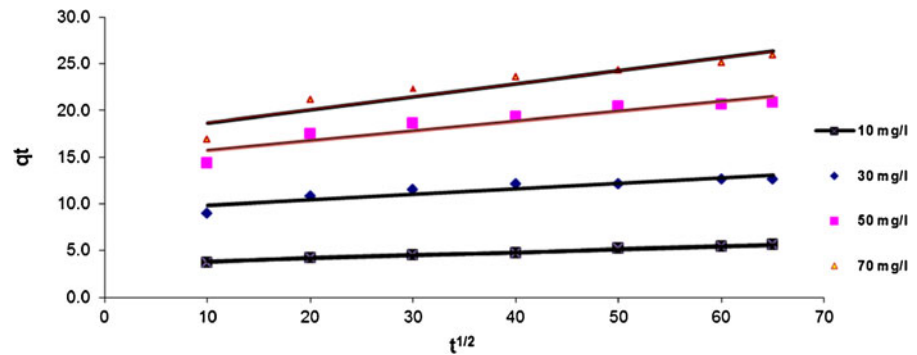
3.8.3 Intra-Particle Diffusion

The sorption rate is shown to be controlled by several factors (Igwe and Abia 2007), including the processes like (a) diffusion of the solute from the solution to the film surrounding the particle,

(b) diffusion from the film to the particle surface (external diffusion), and (c) diffusion from the surface to the internal sites (surface or pore diffusion). The first one is bulk diffusion, the second is external mass transfer resistance and the third is intra-particle mass transfer resistance. When the intra-particle mass transfer resistance is the rate limiting step, then the sorption process is described as being particle diffusion controlled. In

Table 4 Comparison of first- and second-order-kinetic models rate constants and calculated and experimental q_e values obtained at different initial Remazol Brilliant Blue concentrations

First order			
Co, mg/l	q_e , mg/g	K_1 , l/min	R^2
10	7.16	0.026	0.94
30	18.23	0.024	0.94
50	23.06	0.038	0.97
70	32.51	0.026	0.96
Second order			
Co, mg/l	q_e , mg/g	K_2 , g/mgmin	R^2
10	7.16	0.018	0.98
30	18.23	0.013	0.99
50	23.06	0.006	0.99
70	32.51	0.005	0.99

Fig. 10 Intra-particle diffusion plot of RBB on red mud

the batch mode adsorption process, initial adsorption occurs on the surface of the adsorbent. In addition, there is a possibility of dye molecules being diffused into the interior pores of the adsorbent (Parimaladevi and Venkateswaran 2001). The kinetic model to investigate the intra-particle diffusion being the rate limiting step is given by (Weber and Morris 1963)

$$q_t = K_{id}t^{\frac{1}{2}} + C \quad (12)$$

Where, K_{id} is the intra-particle diffusion rate constant and was calculated for different initial concentrations of dye by plotting q_t vs $t^{\frac{1}{2}}$ (Fig. 10). q_t is the diffusion rate of dye on red mud. The plots exhibit linearity at different initial dye concentrations for a wide range of contact time between adsorbent and adsorbate. The values of particle diffusion rate constant at 30 °C are presented in Table 5. The deviation from the origin or near saturation may be due to the variation of mass transfer in the initial and final stages of adsorption. Similar trend was observed in the adsorption of triphenylmethane dyes on to fruit waste by Parimaladevi and Venkateswaran (2001). Such a deviation from the origin indicates that pore

diffusion is the only controlling step and not the film diffusion. The initial pore diffusion due to external mass transfer is followed by the intra-particle diffusion.

4 Conclusion

Experimental investigations were carried out to evaluate the efficacy of sulfuric acid-treated red mud as an adsorbent for the removal of Remazol Brilliant Blue dye from aqueous solution. Sulfuric acid treatment was found to increase the surface area of red mud. Acidic pH values of 2 to 6 were found to favor the adsorption process. Adsorption rate was found to be faster initially, but decreased with the increase in contact time during the batch process. Red mud dosage of 3.2 g/l has been found to be adequate for dye solutions with initial dye concentrations ranging from 10 to 70 mg/l. Around 94 % removal of 10 mg/l dye and 71 % removal for 70 mg/l of RBB could be attained with the red mud dosage of 3.2 g/l. Langmuir isotherm model has been found to represent the equilibrium data for RBB-red mud adsorption system better than Freundlich model. Thermodynamic analysis confirmed that RBB-red mud adsorption is an endothermic process. Adsorption kinetics may be represented by second-order kinetic models for the sorption of RBB onto red mud and the kinetic constant was estimate to be 0.0105 ± 0.002 g/mg.min. Validity of intra-particle diffusion kinetic model suggested that among the mass transfer processes during the dye adsorption process, pore diffusion is the controlling step and not the film diffusion. The RBB-red mud adsorption process shows its potential to

Table 5 Intra-particle diffusion rate constants at 30 °C

Initial concentration, mg/l	K_{id} , mggmin ^{-1/2}
10	0.139
30	0.106
50	0.057
70	0.032

serve dual purposes of utilization of an industrial solid waste and the treatment of dye-contaminated wastewater from industries.

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