

Physiochemical Modification and Characterization of Bentonite Clay and Its Application for the Removal of Reactive Dyes

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Abstract

The textile effluents have been considered as potential source of water contamination in the last few decades. Thus the effective methods were adopted for the removal of dyes and colorants from the textile effluents. In the present research, the removal of textile dye reactive red 223 (RR 223) was carried out by modified bentonite clay (MBC). The modification of bentonite clay was carried out by acid treatment method. The adsorption properties of MBC towards RR 223 were investigated using the batch method, at various temperatures 303-318 ±2 K under the optimized conditions. The adsorption equilibrium data were fitted in Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherm models and the values of the respective constants were evaluated by employing standard graphical method. From the correlation coefficient values (r^2), it was founded that Langmuir model is the best fitted isotherm. Feasibility of adsorption process (R_L) and sorption energy (E_s) was also determined. The pH_{PZC} of adsorbent was estimated by pH drift method. Thermodynamic parameters such as free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of the system were calculated. Kinetics of dye removal was investigated that it follows pseudo second order rate constant. The surface morphology of adsorbent was observed by the Scanning Electron Microscope (SEM). The interaction forces involved between the adsorbent and adsorbate was determined by Fourier Transform Infrared Spectroscopy (FTIR). In addition the recovery of dye and regeneration of adsorbent was carried out by desorption experiments. The sorption and desorption capacity of MBC was found to be 95.15% and 78%.

Keywords: adsorption, adsorption isotherms, modified adsorbent, thermodynamics, kinetics, desorption

1. Introduction

During the recent years, the rapid progress in industrial activities leads to excessive discharge of textile effluents which is associated with the incomplete exhaustion of dyes onto fiber during dyeing processes (Olukanni et al., 2006).

The textile finishing industries generates a large amount of wastewater which contains dyes and heavy metals which causes environmental pollution. It is estimated that approximately 100,000 units of textile dyes used and their annual production in the world wide are more than 7×10^5 metric tons (McMullan et al., 2001; Pearce et al., 2003).

Reactive dyes pose the great problems in terms of color, which is exacerbated by the dominance of cotton. The human eyes can detect about 0.005 mg/L of reactive dye in waste water, and therefore, presence of dyes exceeding this limit would not be permitted on aesthetic ground (Almedia et al., 2009).

Reactive dyes are widely used in industries including textiles, leather, printing, plastics and foods etc. Most of them present in the textile effluents which are responsible for the contamination of water and disturbing the ecosystem (Teng & Lin, 2006). They have highly visible colors; even their small portion released in the environment may cause the appearance of intense color. The critical attentions of public and local legislation are needed to remove the coloring materials from textile effluents before discharging into the environment (Pearce et al., 2003). The presences of chromophore in the reactive dyes have a greater capability for the direct reactions with a substrate of the fiber and make them more permanent. The colors of reactive dyes are not easy to remove by effluent treatment processes and in many cases it's not easily degradable (Robinson et al., 2003).

Although some existing technologies may have certain efficiency for the removal of reactive dyes but their

operational costs are so great. On the other hand, low cost technologies don't allow a wishful color removal or have certain disadvantages, required more complex treatment plan (Yeh et al., 1993).

Hence, researches have been directed to other non-conventional procedures for the color removal that will be effective with their low cost (Laszlo, 1994). Adsorption is one of the most effective physical processes for the removal of textile effluents (Allen & Koumanova, 2005, Hu et al., 2006; Alkan & Dogan, 2008). Many adsorbing materials have been tested to lower the dye concentration from aqueous solutions, such as activated carbon, rice husk, silica, chitin, fly ash, saw dust, bagasse pith, orange peel (Alkan & Dogan, 2000; Gupta & Ali, 2001; Sanghi & Bhattacharya, 2002; Voudrias et al., 2002; Malik, 2003; Arami et al., 2005; Ozacar & Sengil, 2006; Nevin, 2008; Gehlot & Daga, 2011). The application of natural adsorbents has received much attention for the adsorption of various pollutants from aqueous medium.

Recently, bentonite clay was successfully employed for the adsorption of metal ions and dyes (Naseem & Tahir, 2001; Rauf & Tahir, 2006; Tahir et al., 2010). It has been considered as a potential adsorbent for the removal of pollutants from water. The effective application of bentonite for the water treatment is limited due to its surface area and presence of net negative charge leading to its low adsorption capacity. As a result in the present research work modification of physical structure and chemical properties of bentonite results the maximization of its adsorption capacity. The modification was carried out with hydrochloric acid and creating the modified bentonite clay (MBC) which act as an effective adsorbent. During the acidification of clays, the octahedral ions can be leached out, and the specific surface area increases (Teng & Lin, 2006). It is a beneficial and low cost method for the minimization of pollutants.

2. Materials and Methods

2.1 Preparation of Adsorbent

Bentonite clay was used as an adsorbent and obtained by the province of Punjab (Pakistan). Before the adsorption process, the surface of clay was modified with 1 mol/dm³ Hydrochloric acid in a ratio of (1:1) and magnetically stirred for five to six hours at room temperature. It was then filtered by using Whatman 41 filter paper and dried at 70±1 °C in electric oven.

2.2 Preparation of Adsorbate

Reactive Red 223 was one of the textile dyes. It is also known as Reactive Red 3GF, Reactive Brilliant Red M-GE.

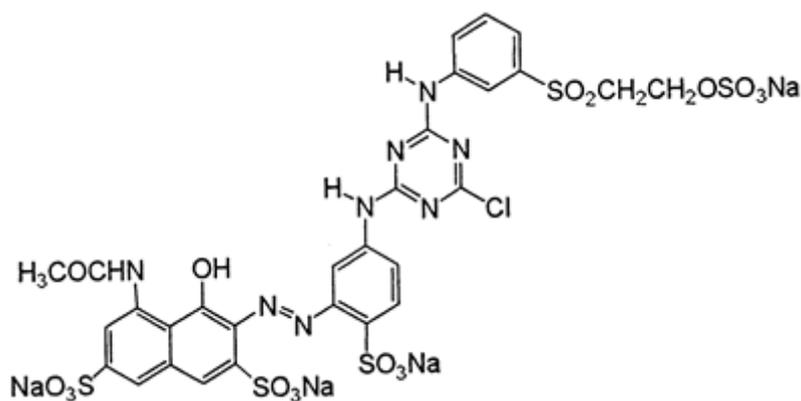


Figure 1. Chemical structure of Reactive Red 223

Its molecular formula is C₂₉H₂₁ClN₈Na₄O₁₇S₅, and molecular weight is 1041.26 g/mol as shown in Figure 1.

The stock solution of 9.60×10⁻⁵ mol/dm³ of RR 223 was prepared and λ_{max} was recorded by UV-visible spectrophotometer (T80 UV/VIS Spectrophotometer) it was found to be 510 nm.

3. Batch Adsorption Studies

3.1 Optimization of Amount of Adsorbent

In order to analyze the optimum amount of adsorbent at which maximum adsorption takes place, various amounts of adsorbents (0.2-1.5 g) were added in separate Erlenmeyer flasks having 50mL of dye solution and placed in electronic shaking incubator (JISICO Shaking Incubator) for 60 min. at 120 rpm and temperature was

maintained at 302 ± 2 K. After specific time period the content were filtered and absorbance was recorded by using UV-visible spectrophotometer (Boparai et al., 2011).

3.2 Optimization of Contact Time

The optimum contact time for the adsorption was determined by keeping the flasks in shaking incubator containing 50 mL of dye solution for 60 min at 120 rpm and temperature was maintained as 303 ± 2 K. The contents of the flasks were filtered after the interval of 10 minutes and the absorbance of filtrate was recorded by UV-visible spectrophotometer (Hu et al., 2006).

3.3 Dye Concentration and Temperature

The range of concentration of dye solution was maintained by following Lambert-Beer's Law. The dye solutions were prepared having concentrations 1.9×10^{-5} - 1.4×10^{-4} mol/dm³. 50 mL of each set was place in separate Erlenmeyer flasks by keeping optimized amount of adsorbent and contact time at temperatures ranges from 303 - 318 ± 2 K. The absorbance of filtrate was recorded by UV-visible spectrophotometer at 510 nm. By graphical method optimum concentrations of adsorbate was determined (Mylsamy et al., 2012).

3.4 Desorption Studies

Desorption experiments were conducted to investigate the possibility of repeated use of the adsorbent. The RR 223 loaded-MBC was washed with distilled water and dried at room temperature for 24 hrs. The dried adsorbent was added in 200 mL of 0.1 mol/dm³ NaOH solution in Erlenmeyer flask and shaken at 200 rpm for 9-14 h. The adsorbent was again collected by filtration and washed several times with distilled water for the removal of excess base and used for the next adsorption cycle. The absorbance of desorbed RR 223 was recorded by UV-visible spectrophotometer (Voudrias et al., 2002).

3.5 pH at the Point of Zero Charge (pH_{ZPC})

The point of zero charge (pH_{zpc}) is the pH at which the total number of positive and negative charges on its surface becomes zero (Jia et al., 2002). The pH at the point of zero charge (pH_{ZPC}) of MBC was measured by using the pH drift method. The pH of 0.005 mol/dm³ NaCl solution was adjusted between 2-12 by adding either HCl or NaOH. The optimum amount of adsorbent (0.9 g) was added in 20 mL of respective pH solution and left it at room temperature for 24 and 48 h. After the pH stabilized the final pH was recorded. The graphs of pHs were drawn and used for the determination of points at which the initial and final pH values were equal (Vijayakumar et al., 2012).

4. Results and Discussion

In the present work, the removal of RR 223 by MBC was examined. The adsorption, desorption, effect of point of zero charge, thermodynamic and kinetic studies were run by batch method under the optimized conditions of amount of adsorbent, contact time and temperatures.

4.1 Investigation of Adsorption Parameter

4.1.1 Effect of Amount of Adsorbent Dosage

The adsorption of RR 223 dye onto MBC was analyzed by changing the amount of adsorbent from 0.2-1.5 g. The values of % removal of RR 223 dye were increased with the increase in the amount of MBC and at 0.9 g of adsorbent it shows the optimum adsorption. This may be due to the increase in adsorbent surface area and availability of more adsorption sites. The amount of adsorption at time t, K_D (mol/g), was calculated as:

$$K_D = (C_i - C_f)V/W \quad (1)$$

Where C_f (mol/dm³) is the concentration of dye at time (t), C_i (mol/dm³) is the initial concentration of dye, V is the volume of the solution (mL) and W is the mass of the adsorbent (g).

The amount of equilibrium adsorption, X/m (mol/g), was calculated as:

$$X/m = (C_i - C_e)V/W \quad (2)$$

Where C_i and C_e (mol/dm³) are the initial and equilibrium concentrations of dye.

The percentage removal of dye can be calculated as:

$$\% \text{ Removal} = (C_i - C_e)/C_i \times 100 \quad (3)$$

4.1.2 Effect of Contact Time

The adsorption of dye was increased with the increase in contact time and reaches to an optimum value when the adsorption equilibrium was achieved. The maximum adsorption capacity of RR 223 on MBC 95.15 % was

obtained at 20 min. The comparative removal of dyes with reported literature is represented in Table 1, which shows that the present research work has the maximum level of decolorization of reactive dyes.

Table 1. Comparison of the adsorption capacity with respect to reactive dyes and the present study with those reported in the literature

Reactive Dye	% Removal	Adsorbent	References
Reactive Yellow K-RN(Y.3)	20.00	Bentonite Clay	Tilaki (2012)
Reactive Red 141	59.00	Chitin	Sukumal et al. (2011)
Reactive Yellow 15	82.00	Banana Peel	Khan et al. (2012)
Remazol Red F-3B	84.00	Coconut Coir activated carbon	Santhy & Selvapathy (2006)
Reactive Black 5	90.36	Loquat Seed	UCUN (2011)
Remazol Brilliant Blue R	93.47	Bagasse Fly Ash	Rachakornkij et al. (2004)
Reactive Orange 4	94.44	Activated Carbon	Baseri et al. (2012)
Reactive Red 180	95.00	Citrobacter sp. CK3	Hui et al. (2009)
Reactive Red 223	95.15	Modified Bentonite Clay	Present Study

4.1.3 Effect of Temperature

Adsorption isotherm is a graphical representation between the bulk activity of adsorbate and amount adsorbed at constant temperature. It characterizes the distribution of adsorbed solute between the adsorbate and solid phase at various equilibrium concentrations.

The effect of temperature for the removal of dye was studied at temperatures 303–318±2 K. The critical review of adsorption isotherm shows a decrease in the adsorption of dye with the rise in temperature. It shows that adsorption of dye on MBC is exothermic in nature and the results of the following isotherms are represented in Table 2.

Table 2. Isotherm constants and correlation coefficients for the adsorption of RR 223 on MBC at different temperatures

Isotherm	Temperature (K)	Parameters		r^2
		$K \times 10^{-4}$	$V_m \times 10^4$	
Langmuir	303	1.36	6.35	0.531
	308	8.43	4.56	0.909
	313	3.30	5.82	0.770
	318	3.10	6.85	0.853
Freundlich		$K \times 10^3$	N	r^2
	303	11.5	2.63	0.607
	308	2.24	6.16	0.090
	313	2.17	5.68	0.372
Dubinin Radushkevich		$X_m \times 10^3$	$Es \times 10^4$	r^2
	303	5.35	1.00	0.583
	308	0.95	2.24	0.111
	313	2.11	1.58	0.347
	318	3.65	1.29	0.534

4.1.3.1 Freundlich Adsorption Isotherm

Freundlich expressed an empirical equation for representing the isothermal variation of adsorption on the quantity of gas adsorbed by unit mass of solid adsorbent it is expressed as;

$$\text{Log } X/m = \text{Log } K + 1/n \text{ Log } C_e \quad (4)$$

Where X/m is the amount adsorbed per unit mass of the adsorbent (mol/g), C_e is the equilibrium concentration (mol/dm³) and the constant K relates to the degree of adsorption, while n provides the rough estimation of the intensity of the adsorption (Hema & Arivoli, 2008). Freundlich plot was obtained at various temperatures 303–318 K, as shown in Figure 2. The decreasing in the values of K with the rise in temperature indicates that adsorption affinity of dye on MBC is less favorable at higher temperatures.

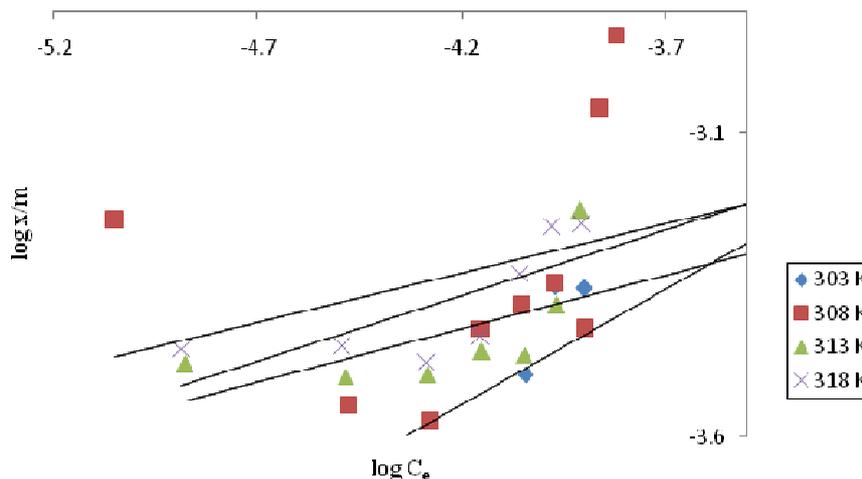


Figure 2. Freundlich isotherm plot of Modified Bentonite Clay(MBC)-Reactive Red 223 (RR 223) system

4.1.3.2 Langmuir Adsorption Isotherm

The Langmuir isotherm assumes monolayer adsorption on a homogeneous surface with a finite number of adsorption sites. The theory can be expressed by the following linear equation:

$$C_e/X/m = 1/kV_m + C_e/V_m \quad (5)$$

Where C_e is the equilibrium concentration (mol/dm³), X/m is the amount adsorbed at equilibrium (mol/g) and V_m (mol/g) and k (dm³/mol) are Langmuir constants related to monolayer capacity and adsorption coefficient respectively (Hameed & Daud, 2008). The linear plot of $C_e/X/m$ vs. C_e is shown in Figure 3.

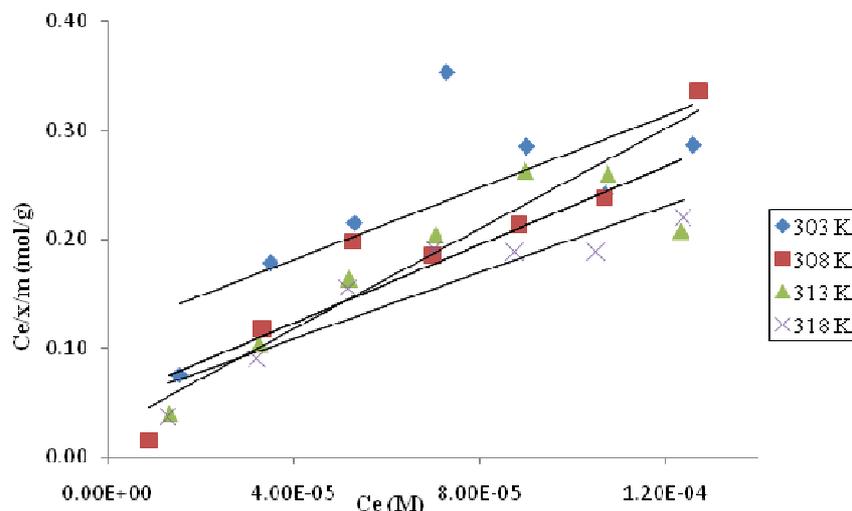


Figure 3. Langmuir isotherm plot of Modified Bentonite Clay(MBC)-Reactive Red 223(RR 223) system

The value of V_m and k were determined from intercept and slopes of the respective plot. The increase in the values of K at low temperatures predicts strong interaction between dye molecules with adsorbent, while in few cases; they decreased with the rise in temperature which indicates the weakening of adsorbate-adsorbent interactions at high temperatures. The adsorption systems follow Langmuir adsorption isotherm equation by correlation coefficient values (r^2). The values of the monolayer capacity (V_m), decreases with increase in temperature, indicating high affinity of dye at low temperatures.

The essential characteristic of the Langmuir isotherm is dimensionless constant which is referred as separation factor or equilibrium parameter R_L given by:

$$R_L = 1 / (1 + kC_i) \quad (6)$$

Where k represents the Langmuir constant and C_i is the highest initial dye concentration (mol/dm^3). The parameter R_L shows whether the adsorption system is favorable if ($0 < R_L < 1$), unfavorable ($R_L > 1$), irreversible ($R_L = 0$) or linear ($R_L = 1$) (Tahir et al., 2010).

Table 3. Equilibrium factor of RR 223 at different temperatures

Temperature (K)	R_L
303	0.299
308	0.065
313	0.150
318	0.158

Since R_L values were obtained at temperatures ranges from 303–323 K as shown in Table 3, indicating that the adsorption of RR 223 onto MBC is favorable.

4.1.3.3 D-R Adsorption Isotherm

Dubinin-Radushkevich (D-R) isotherm was also applied for the adsorption of RR 223 onto MBC. The D-R equation can be expressed as:

$$\ln X/m = \ln X_m - K\epsilon^2 \quad (7)$$

Where, X_m is the monolayer capacity of adsorbent, K is a constant related to adsorption energy; ϵ is the adsorption potential which can be obtained as follows:

$$E = RT \ln(1 + 1/C_e) \quad (8)$$

Where C_e is the equilibrium concentration of dye (mol/dm^3), R is a gas constant and T is the absolute temperature (Tahir et al., 2010).

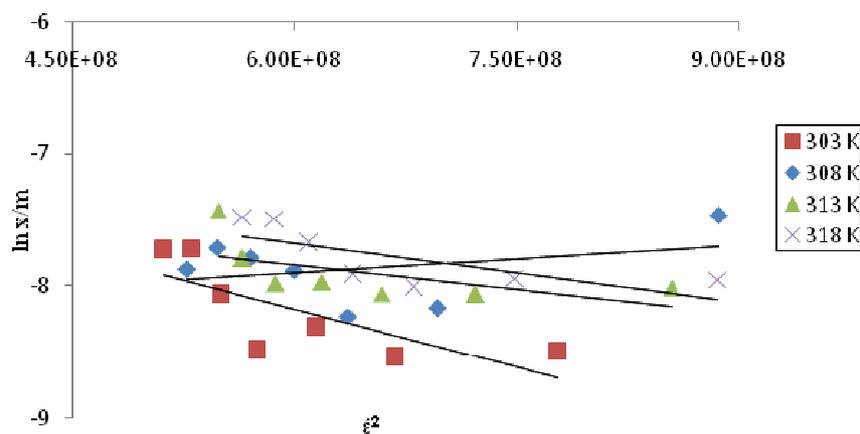


Figure 4. D-R Isotherm plot of Modified Bentonite Clay (MBC)-Reactive Red 223(RR) system

The D-R plot of $\ln X/m$ versus ϵ^2 was obtained at various temperatures as shown in Figure 4. The values of K and X_m were obtained from the slope intercept while the values of mean free energy of adsorption (E_s) were estimated by using the value of K expressed as:

$$E_s = (-2K)^{-1/2} \quad (9)$$

The value of E_s for RR 223-MBC system was increased with the increase in temperature, indicating the higher adsorption capacity at higher temperatures.

4.2 Investigation of Desorption Parameter

As presented in Table 4, the desorption experiments show that after 14 hours shaking of adsorbent in alkaline medium, the % desorption was significantly increases and reaches to a maximum level 78.11, which shows that RR 223 was recovered from MBC and adsorbent has the ability to reuse for the next adsorption cycle, where as for the neutral, acidic and oxidizing medium, there was no effect observed.

Table 4. Desorption of RR 223 on MBC

Solvents	% Desorption	
	After 9 hours	After 14 hours
H ₂ O	0	0
HNO ₃	0	0
H ₂ SO ₄	0	0
NaOH	26.50	78.11

4.3 Investigation of Point of Zero Charge (pH_{pzc})

By the investigation of point of zero charge of MBC, the values of the final and initial pHs were plotted as shown in Figure 5, at 24 and 48 hours time interval.

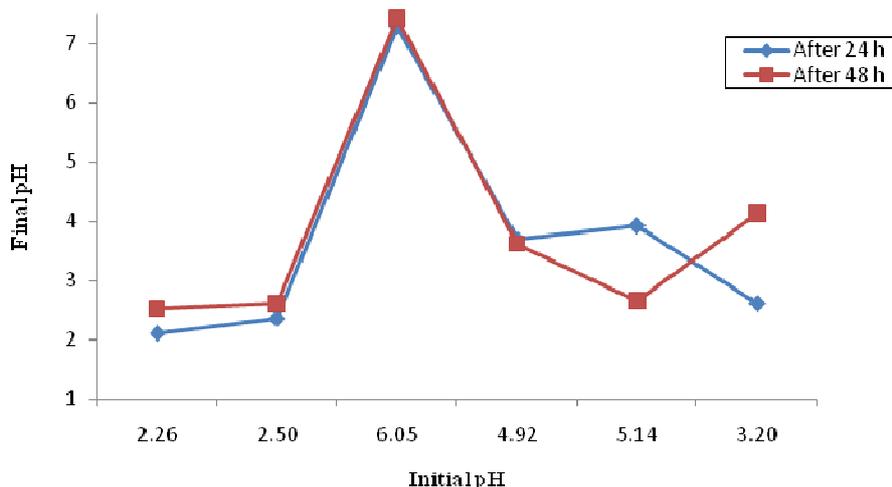


Figure 5. Effect of point of zero charge of MBC

From the graphical representation, the values of pH_{pzc} of MBC were determined from the point where the initial pH equals the final pH, which implies that the surface of MBC was acidic in nature since the pH_{pzc} values increases from acidic pH to neutral and then moves toward the acidic behavior again.

4.4 Investigation of Thermodynamic Parameters

The effect of temperature on the adsorption capacity was determined by calculating the thermodynamic parameters like change in enthalpy (ΔH^0), entropy (ΔS^0) and Gibbs free energy (ΔG^0) which were evaluated by using the following equations:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{10}$$

$$Lnk = \Delta S^0/R - \Delta H^0/RT \tag{11}$$

$$\Delta G^0 = -RTLnk \tag{12}$$

Where R is the gas constant, T is the absolute temperature, k is the equilibrium constant.

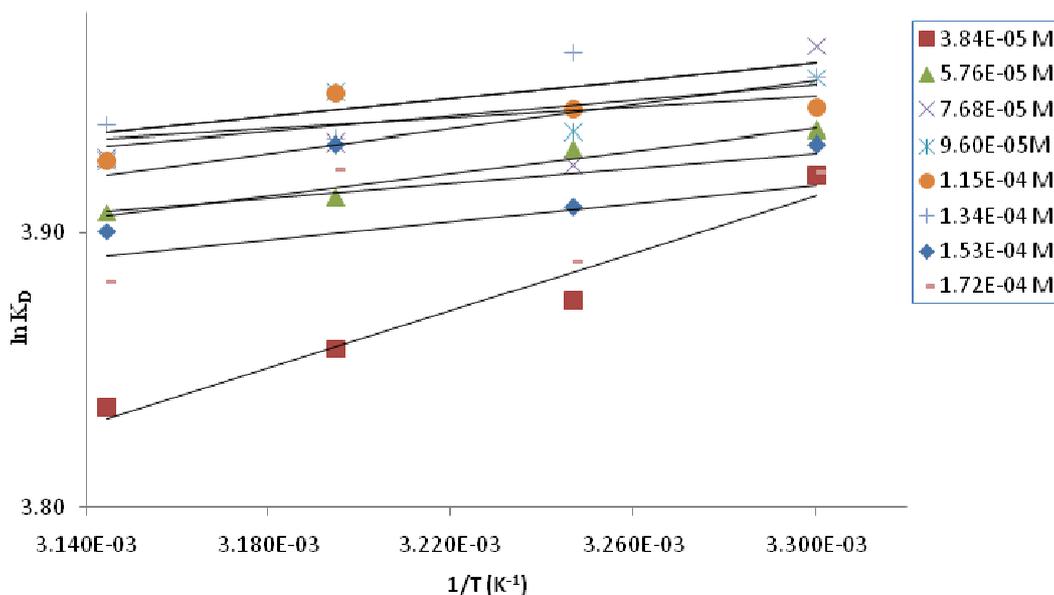


Figure 6. Plot of 1/T vs ln KD of Modified Bentonite Clay (MBC)-Reactive Red 223(RR 223) system

The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the Van't Hoff plot of $\ln K_D$ versus $1/T$ as shown in Figure 6 (Tahir et al., 2009; UCUN, 2011).

Table 6. Thermodynamic parameters for the adsorption of reactive red 223 onto Modified Bentonite Clay

Concentration (M)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol.K)	ΔG^0 (kJ/mol)			
			303 K	308 K	313 K	318K
3.84E-05	4.381	18.075	-1.10	-1.19	-1.28	-1.37
5.76E-05	1.707	27.104	-6.51	-6.64	-6.78	-6.91
7.68E-05	1.829	26.846	-6.31	-6.44	-6.57	-6.71
9.60E-05	1.202	28.899	-7.55	-7.70	-7.84	-7.99
1.15E-04	0.812	30.155	-8.32	-8.48	-8.63	-8.78
1.34E-04	1.348	28.484	-7.28	-7.43	-7.57	-7.71
1.53E-04	1.136	28.916	-7.63	-7.77	-7.92	-8.06
1.72E-04	1.383	28.002	-7.10	-7.24	-7.38	-7.52

As presented in Table 6, the values of ΔG^0 were negative at all temperatures indicating that the adsorption of RR 223 on MBC was spontaneous process and its magnitude is shifted to a higher negative values as the temperature is increased indicating that the adsorption was more spontaneously proceeded at higher temperatures. The positive values of ΔH^0 show the endothermic nature of adsorption and positive values of ΔS^0 reflects the increased randomness of the solid-solution interface and suggests some structural changes in adsorbate and adsorbent during adsorption process.

4.5 Investigation of Adsorption Kinetics

The time dependent behavior of adsorption was determined by varying the equilibrium time 1-60 min between adsorbate and adsorbent. The percentage removal of the RR 223 against contact time plotted in Figure 7 indicates that the equilibrium was established between RR 223 and MBC within 20 min.

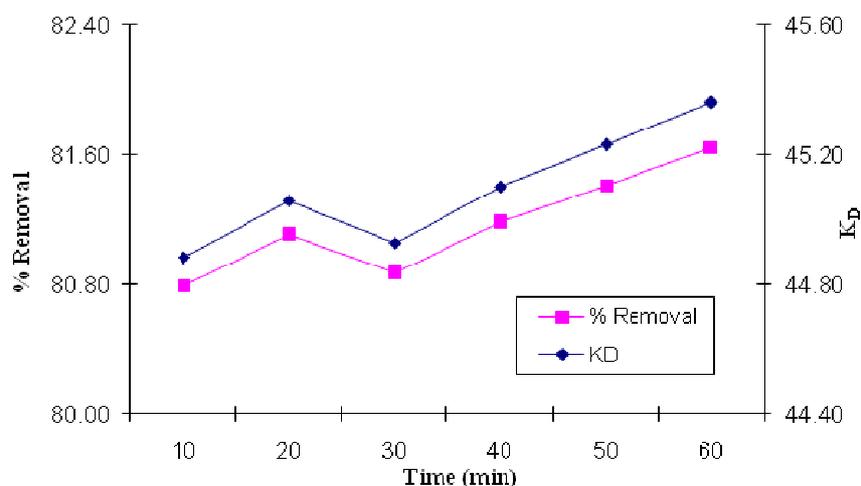


Figure 7. Effect of shaking time on the adsorption of RR 223 by MBC

For the investigation of possible mechanism of adsorption, pseudo first order model was adopted by the Lagergen (1898) and pseudo second order models were adopted by the Ho and McKay (1999). They are expressed as,

$$\text{Log} (q_e - q_t) = \log q_e - k_1 t/2.303 \quad (13)$$

$$t/q_t = 1/2k_2q_e^2 + 1 t/q_e \quad (14)$$

Where q_e and q_t are the amount of the dye adsorbed on the adsorbent (mol/g) at equilibrium and time t , k_1 is the adsorption of pseudo first order rate constant (min^{-1}) and k_2 is the adsorption of pseudo second order rate constant (mol/g min). The pseudo second-order adsorption kinetic plots are shown in Figure 8, which shows that it follows a pseudo-second order reaction.

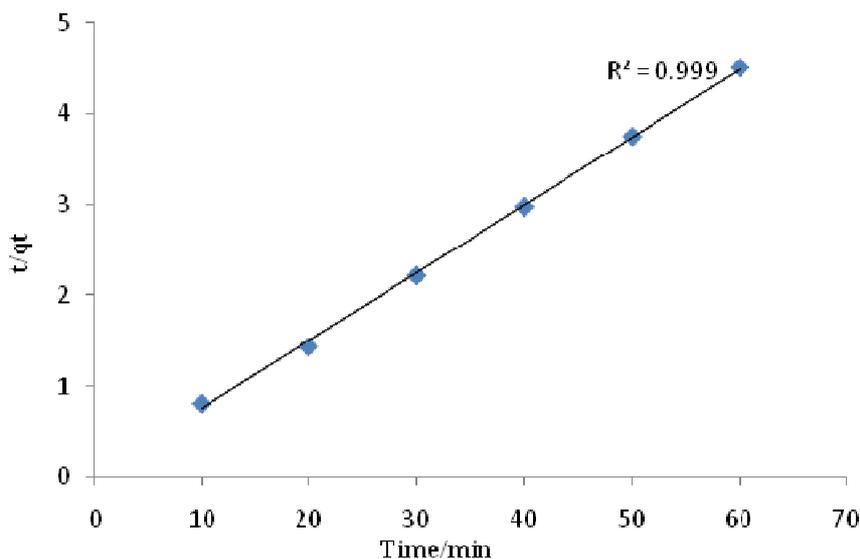


Figure 8. Pseudo-second order adsorption kinetics of RR 223 onto MBC

5. Characterization of Modified Bentonite Clay

The surface of adsorbent before and after adsorption was scan by FTIR and SEM techniques. For FTIR analysis IR Prestige-21 spectrometer was used, while SEM images were taken by Joel JSM-6380A Analytical Scanning Electron Microscope in which samples were initially coated by Ion sputtering device.

5.1 Interpretation of FTIR

FTIR spectra of MBC before and after adsorption of RR 223 are shown in Figures 9 and 10. The disc of MBC before and after adsorption was made by the binding agent potassium bromide (KBr) which is also IR active. Therefore, the peaks due to the KBr were appeared at 3452.58 , 2372.44 cm^{-1} and 1645.28 cm^{-1} and were slightly shifted in the both the spectrums due to the adsorption process of RR 223 dye. In the spectrum of MBC before adsorption of dye a broad transmittance band at 3415.93 cm^{-1} is due to the stretching frequency of hydroxyl group (-OH) (Moreira et al., 2001). The band at 1045.42 cm^{-1} shows the stretching of alkene bonds (Sathorn et al., 2008). The bands at about 524.64 show the stretching of alkyl halides and slightly shifted to 466.77 due to the adsorption of RR 223 Dye (Moreira et al., 2001). After adsorption of RR 223, the spectrum shows that the transmittance bands are considered at different frequencies range. The band of hydroxyl group is slightly shifted at 3431.36 cm^{-1} . The slight variation of halogen band frequency is also shifted at 1043.49 cm^{-1} .

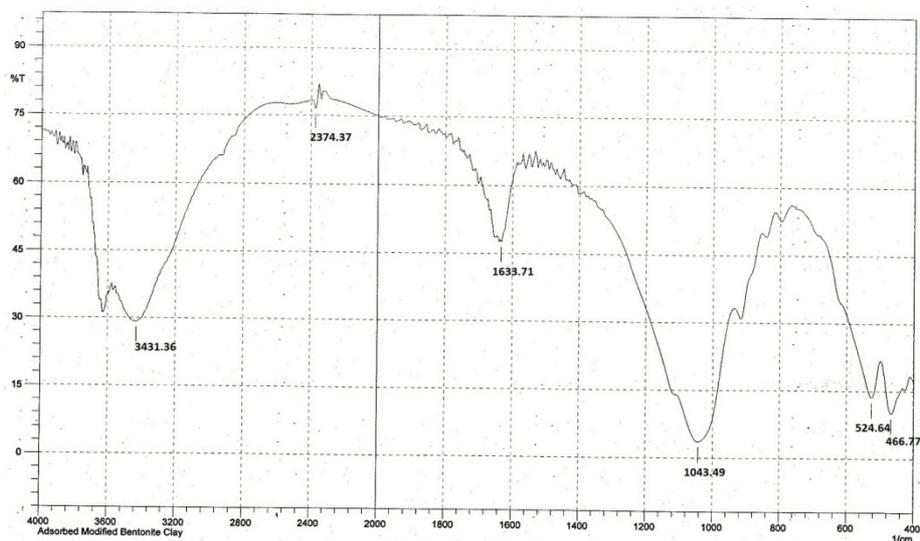


Figure 9. FTIR spectrum of MBC before adsorption of RR 223

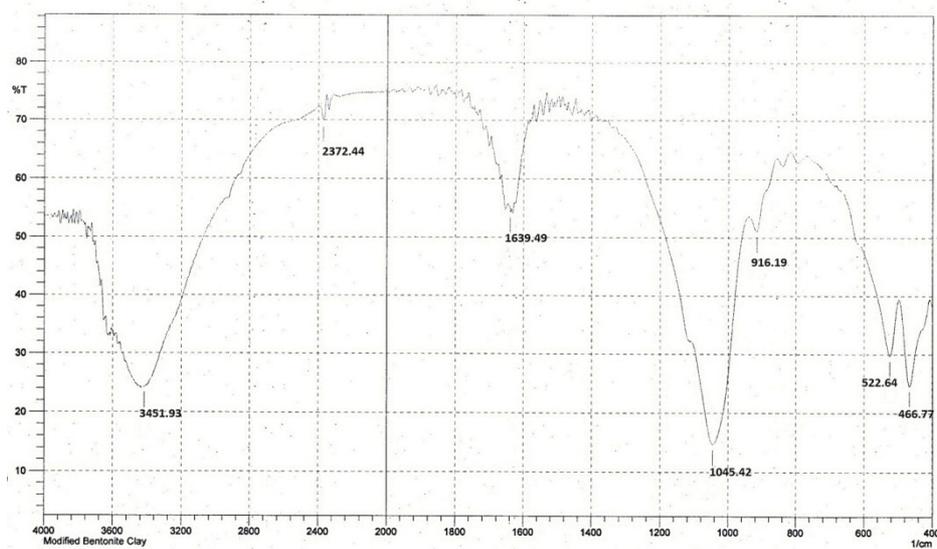


Figure 10. FTIR spectrum of MBC after adsorption of RR 223

5.2 Surface Morphological Studies

The images of Scanning Electron Microscope of MBC before and after adsorption of RR 223 are shown in Figure 11 at different magnifications. SEM image of MBC before adsorption of RR 223 indicates that the material is composed of irregular shapes which provide a large surface area for the adsorption. After the adsorption of RR 223, the structures become saturated.

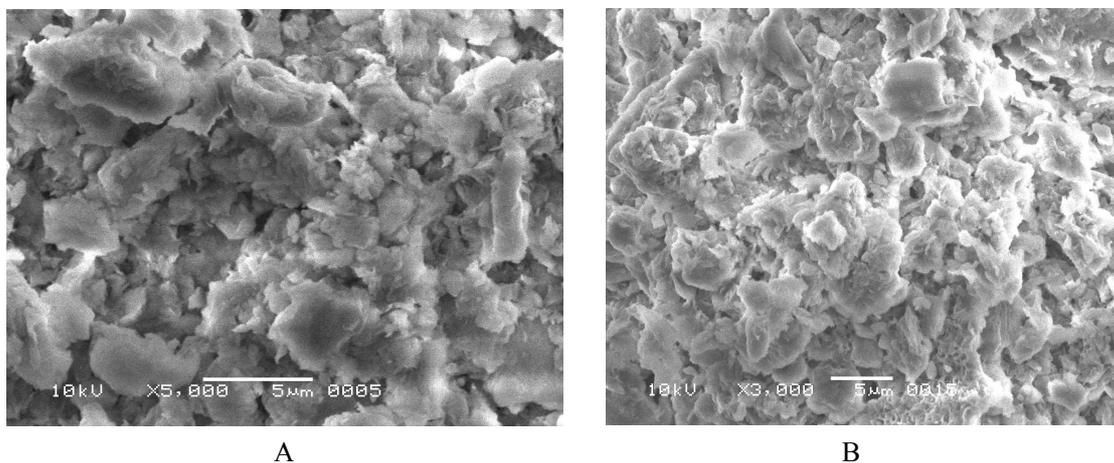


Figure 11(A & B). SEM image before and after adsorption of RR 223

6. Conclusion

In the present study, bentonite clay was used as a local and readily available adsorbent for the removal of reactive dye. The modified surface of bentonite was prepared by its acidification with hydrochloric acid which enhances the specific surface area. It results the significant changes in the adsorption capacity toward reactive dyes. Adsorption, desorption, point of zero charge pH_{pzc} , thermodynamic and kinetics studies were proceeded to determine the validity of process. The adsorption experiments were run under the optimized conditions of amount of adsorbent, stay time, initial concentration and at different temperatures. The adsorption models like: Freundlich, D-R and Langmuir adsorption isotherm models were applied for the mathematical description of the adsorption equilibrium data. From the values of r^2 it was suggested that Langmuir model is the best fitted model. Thermodynamic parameters, Gibbs free energy, enthalpy and entropy changes show that the adsorption of RR 223 onto MBC was spontaneous and endothermic process. The kinetic data showed that the adsorption of RR 223 onto MBC followed the pseudo second order kinetics.

The feasibility of adsorption and desorption process was estimated in the present study. It was estimated that inexpensive, locally available and effective materials can be utilized as adsorbents for the removal of dyes. Undoubtedly low-cost adsorbents offer a lot of promising benefits for commercial purposes with respect to utilization and minimization of waste.

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