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Thermodynamic and Isothermal Studies of Congo RedAdsorption onto Modified Bentonite

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Abstract – Adsorption of Congo Red (CR) from dye-containing effluents using modified bentonite (MB) has been investigated here. Isothermal studies were conducted to ascertain maximum adsorption capacity of the adsorbent. MB exhibited superior adsorption capacity compared to other low-cost adsorbents. Experimental data fitted the Langmuir isotherm better, indicating monolayer coverage of CR on MB. The feasibility of the process was measured in terms of separation factor R_L. The values of Gibbs free energy, entropy and enthalpy were calculated from the thermodynamics of the process. Adsorption was feasible and spontaneous, being endothermic. Analytical techniques including SEM, EDS, FTIR and XRD were applied to characterize MB and also to provide conclusive proof of the accumulation of CR on to MB.

Key words: Congo red, Bentonite, Isotherms, Thermodynamics, XRD, SEM, FTIR

1. Introduction

As earth's population continues to grow, pollution by human activities is becoming a major global concern. Pollution from toxic chemicals, especially those of anthropogenic origin, threatens life on this planet. The textile industry is one of the most prolific polluters in the world. Around 20% of global water pollution comes from textile dyeing with an exit of 72 toxic chemicals [1]. Dyes are particularly resistant to treatment, defying bio- as well as photo-degradation and persisting in the environment.

Congo red (CR) is one such carcinogen with a complex chemical structure ($C_{32}H_{22}N_6Na_2O_6S_2$) and high molecular weight (696.66). This diazo dye is water-soluble, forming a red colloid, but has higher affinity for organic solvents.Apart from its usage as a dye, CR is also a pH indicator and cell staining agent. However, its application as a dye is reducing due to its highly toxic and recalcitrant nature [2]. Hence, removal of CR from waste water is a challenge often faced by environmental chemists and engineers, requiring advanced treatment [3].

Adsorption is the commonest among all dye removal methods due to high efficiency and lower cost compared to other methods like reverse osmosis and ultrafiltration. Selection of the adsorbent plays a vital role in the cost of removal. Apart from being economical, it must be efficient and abundantly available for regular industrial application [4].

Currently, a number of studies have reported on the use of many natural materials such as zeolites [5, 6], clays [7-9], coal [10,11] and plant biomass [12-16] for decolorization of dye-containing effluents. These have been classified as low-cost sorbents since their initial cost is very low and they are locally available materials [17]. Among these, clay minerals have found widespread application as adsorbents. Clay minerals composed of tetrahedral and octahedral cationplanes occur naturally at the earth's near surface environments [18]. They have been known to mankind for thousands of years. Clay minerals have played a key role in the cultural and industrial development of mankind. Around 5000 B.C., they were used for the cleaning of animal skins and hides [19]. For thousands of years, clays have been used for making pottery, brick, and other building materials. Man's use of expanding clays such as bentonite began later. Today, there are hundreds of uses for clay minerals in a variety of products ranging from pet litter to pharmaceuticals [20].

Some clay minerals like kaoline, bentonite, and clinoptilolite possess unique properties that make them suitable for a broad range of scientific, industrial and consumer applications. Their applications are as diverse as the industries that utilize them [21].

Though all clay minerals have similar compositions, bentonite is superior with its unique cation chemistry andsurface area. It is mainly composed of montmorillonite with a chemical composition of SiO_2, Al_2O_3, CaO, MgO, Fe_2O_3, Na_2O, K_2O. It is a 2:1 type aluminosilicate, the unitlayer structure of which consists of one $A1^{3+}$ octahedral sheet between two Si^{4+} tetrahedral sheets [22]. It exhibits volumetric expansion and strong colloidal properties in aqueous phase. These unique properties make it suitable for many applications [23].

The desirable properties of bentonite can be further improved by activation. In an earlier study, bentonite was modified with $CaCl_2$, and used to remove CR from the textile industry effluent [24]. Several other studies have reported the successful removal of CR through adsorption onneem (*Azadirachtaindica*) leaf powder [25], chitosan hydrobeads [26], waste orange peel [27], and coal-based activated carbons [28]. This indicates that use of modified bentonite for the

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removal of CR needs to be explored from research as well as application points of view. The present study was, thus, undertaken to address this gap in our collective knowledge.

A detailed literature review was conducted to find various pollutants that had been successfully removed by bentonite in its raw or modified forms. Similarly, various adsorbents used to remove CR from effluents were also listed. Isothermal and thermodynamic studies ascertained the nature and gained an insight into the mass transfer process. Characterization was done to support the observation with evidence and help identify the functional groups responsible for the binding process.

2. Materials and Methods

2-1. Congo red

Congo red (CR) was supplied by M/S. Merck Chemicals, India (CI=22120); chemical formula: $C_{32}H_{22}N_6Na_2O_6S_2$; nature: anionic direct diazo; Molecular weight: 696.66.

2-2. Modified bentonite

Concentrated $H_2SO_4$was added to bentonite powder in 1:1 w/v ratio and kept in hot air oven at 110 °C for 12 hours. It was taken out, washed and then soaked in 2% $NaHCO_3$ solution for the same period to expel the residual acid. pH of the material was brought to neutral by washing with distilled water several times. It was again dried for a day and then stored in an air-tight container.

2-3. Instruments used

Analytical Balance: SHIMADZU - AX200
pH meter: ELICO-L1 612
Temperature-controlled Orbital Shaker: REMI - CIS 24 BL
Centrifuge: REMI C 24
UV-Visible Spectrophotometer: SYSTRONICS - 117

2-3-1. Characterization

The surface morphology examination and elemental analysis of MB was conducted by scanning electron microscopy (SEM, Carl Zeiss, EVO-18) equipped with Energy Dispersive X-ray Spectroscopy (EDS) analyzer. IR spectra of Modified Bentonite (MB) was obtained with a SHIMADZU, FTIR 8400S Fourier transform infrared spectrometer (FTIR). X-ray diffraction patterns were recorded by SHIMADZU XRD 7000 using Cu Kα radiation.

The adsorbent performance was measured in terms of uptake (qt) and percent removal (%R),which were calculated using the following equations:

$$qt = \frac{(C_0 - C_t)}{m}V \tag{1}$$

$$\%R = \frac{(C_0 - C_t)}{C_0}100 \tag{2}$$

where C_0 is the initial CR concentration (mg/1), C_t is the concentration of CR at time t, (mg/L), V is the volume of dye solution (L) and m is the mass (g) of the adsorbent.

3. Theory

3-1. Adsorption Isotherms

Isotherms are used to estimate the maximum adsorption capacity of a material in removing pollutant from the effluent. The characteristics and the interaction between two phases can be inferred from the shape of the equilibrium isotherm. Usually, it is derived from equilibrium data collected at different influent concentrations [29,30].

Solid/liquid interphase behavior can be described by various isotherm models. In general, the Langmuir and Freundlich isotherm equations are broadly used for interpretation of adsorption data obtained.

3-1-1. Langmuir isotherm equation

This is the simplest and the most widely used expression based on the assumption of homogeneous adsorption sites, with each site accommodating one molecule or one atom of zero interaction with each other; adsorption is through monolayer coverage. The Langmuir isotherm is represented by equation [31].

$$q_e = \frac{q_{max} bC_e}{1 + bC_e} \tag{3}$$

Its linear expresson is

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{bq_{max}C_e} \tag{4}$$

where q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium dye concentration (mg/L), q_{max} and b are the Langmuir constants representing the monolayer adsorption capacity (mg/g) and the energy of adsorption (L/mg), respectively. q_{max} and b are calculated from the slopes and intercepts of the straight lines of the plot of $1/q_e$ versus $1/C_e$.

3-2. Freundlich isotherm model

The Freundlich model is not restricted to the formation of a monolayer and is based on sorption on a heterogeneous surface. The well-known expression for the Freundlich model is [32].

$$q_e = K_f C_e^{1/n} \tag{5}$$

where K_f and n are the Freundlich constants that indicate adsorption capacity and adsorption intensity, respectively. The linearized form of the Freundlich isotherm can be written as,

$$\ln q_e = \ln K_f + 1/n \ \ln C_e \tag{6}$$

The values of K_f and n can be calculated by plotting $\ln q_e$versus $\ln C_e$. K_f(unit:mg/g) can be used as an alternative measure of adsorptive capacity, while 1/n (1/mg) determines the adsorption intensity.

It is also possible to predict the possibility of separation by adsorption by calculating the separation factor 'R_L', which can be determined from the following equation [33]:

$$R_L = \frac{1}{1+K_L C_o} \tag{7}$$

where K_L is the Langmuir constant and C_o is the highest initial dye concentration. This isotherm is (i) unfavorable when $R_L>1$, (ii) linear when $R_L = 1$, (iii) favorable when $R_L<1$, and (iv) irreversible when $R_L = 0$.

3-3. Adsorption thermodynamics

Thethermodynamic feasibility of aprocess depends on the values of standard free energy (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0), which can be determined by using the following equations [34]:

$$K_c = \frac{C_A}{C_s} \tag{8}$$

$$\Delta G^o = -RT\ln K_c \tag{9}$$

$$\ln K_c = -\frac{\Delta G^o}{RT} = \frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{10}$$

where K_c is the equilibrium constant, and C_A and C_s are equilibrium concentrations (mg/g) of the dye in solid andliquid phases, respectively, T is the temperature in Kelvin and R is the gas constant [35].

4. Results and Discussion

4-1. Adsorption isotherms

Experiments were conducted by taking 50 ml of effluent atdifferent concentrations (10~1000 mg/L) and a dosage of 0.1 g of bentonite was added to each. The mixture wasagitated at 303 K, up to the equilibrium condition. The data obtained was fitted to linear forms (Eq. 4 and 6) of both Langmuirand Freundlich isotherms, the plots were prepared (Fig. 1 and 2, respectively) and the parameters calculated (Table 1). Both of the expressions fit well for the data, with high correlation coefficients (greater than 0.97), but Langmuir exhibited a better fit with the R^2 value of 0.992. Maximum adsorption capacity that was calculated from the Langmuir isotherm was333.33 mg/L, proving the efficiency of MB inremoving CR from aqueous solutions.

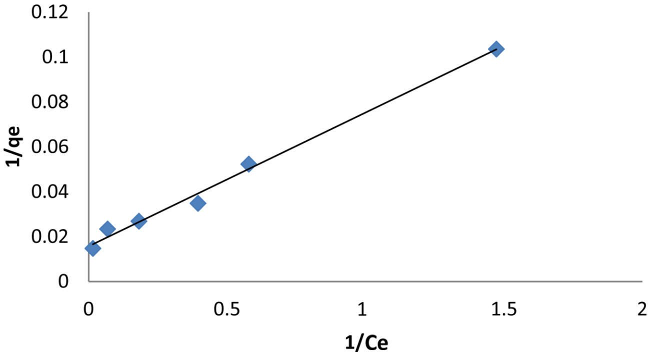

Fig. 1. Langmuir Isotherm for Adsorption of CR using MB at 303.15 K, pH 6.0, adsorbent dose 0.1 g and contact time 180 min.

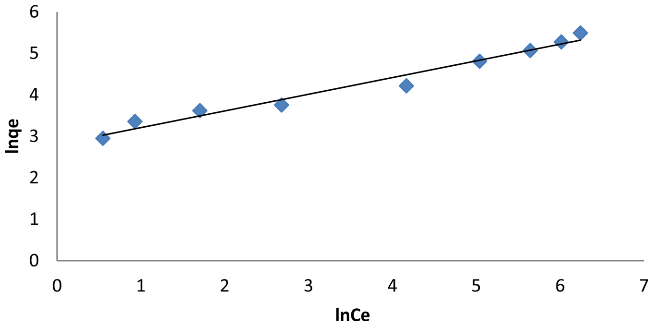

Fig. 2. Freundlich Isotherm for adsorption of CR using MB at 303.15 K, pH 6.0, adsorbent dose 0.1 g and contact time 180 min.

The values of R_L calculated from the experimental data and Langmuir constant (Equation 7) are in the range of 0.03~0.55, indicating that adsorption is favorable.

4-1-1. Adsorption thermodynamics

Experiments were conducted at five different temperatures 293.15, 303.15, 313.15, 323.15 and 333.15 K with two different effluent concentrations (20 and 60 mg/L)and0.1 g MB. Equilibrium constant was calculated from equilibrium concentrations of both phases at each temperature. From these values,a plot of $\ln K_c$ as a function of 1/T was generated. Fig. 3 represents this plot. From the slope andintercept of lines presented in Fig. 3, thermodynamic parameters ΔG^0, ΔH^0 and ΔS^0 were calculated using Equations 8, 9 and 10, values of which are presented in Table 2.

The increase in Gibbs free energy values with temperature indi-

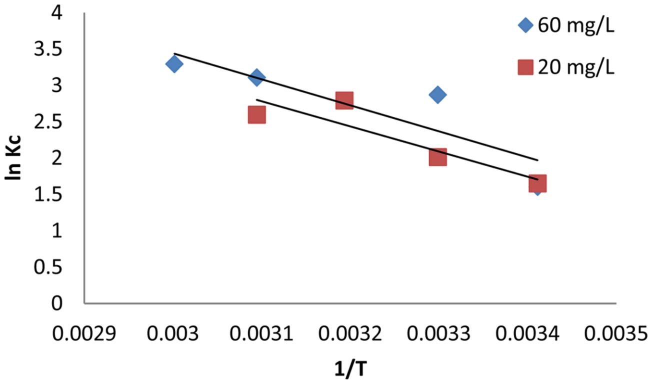

Fig. 3. $\ln K_c$ vs. 1/T for estimation of thermodynamic parameters at pH 6.0, adsorbent dose 0.1 g and contact time 180 min.

Table 1. Adsorption Isotherm Constants for CR Removal using MB

Isotherm	Langmuir isotherm				Freundlich isotherm		
Parameters	q_{max} (mg/g)	B L/mg	R^2	R_L	K_f	n	R^2_f
	333.33	0.003995	0.992	0.03-0.55	16.58336	2.485	0.974

Table 2. Thermodynamic Parameters for the Adsorption of CR on MB

Temp, ^oK	ΔG^o, kJ/mol		ΔH^o, kJ/mol		ΔS^o, kJ/mol	
Concentration	60 mg/L	20 mg/L	60 mg/L	20 mg/L	60 mg/L	20 mg/L
293.15	-4.788	-4.13762	29.74749	28.71656	0.1178	0.112073
303.15	-5.966	-5.25835				
313.15	-7.144	-6.37908				
323.15	-8.322	-7.4998				
333.15	-9.5	-8.62053				

cates an increase in the feasibility of absorption at higher temperatures. It may be due to swelling of pores at high temperature, leading to a high rate of diffusion. The negative ΔG^o values indicate the spontaneous nature of the process, which increased with temperature.

The magnitude of the enthalpy change (ΔH^o) provides information about the type of sorption. If change in enthalpy is in the range of 2.1~20.9 kJ/mol, adsorption is considered to be physical, while if it falls in the range of 80~200 kJ/mol, the process is assumed to be chemisorption. ΔH^o values obtained for 20 and 60 mg/L samples were 28.71656 and 29.74749 kJ/mol, respectively. These positive values of enthalpy indicate that the process is endothermic in nature. These values are close to the range of physisorption, indicating the involvement of weak physical forces in the binding process. The ΔS^o values were 0.1120 and 0.1178 kJ/mol for 20 and 60 mg/L samples, respectively. The positive values of entropy indicate an increase in randomness at the interface.

We did a detailed literature review to find various pollutants that were successfully removed by bentonite in its raw or modified forms, results of which are presented in Table 3. Similarly, various adsorbents used to remove CR from water effluents are presented in Table 4. MB with a maximum uptake of 333.3 mg/g proved to be the most efficient among all the other materials.

Table 4. Adsorption Capacities of Congo RedDye on Various Adsorbents

Adsorbent	Capacity (mg.g^{-1})	Reference
$CaCl_2$ modified bentonite	227.27	[24]
Coir Pitch	6.72	[43]
Red mud	4.05	[44]
Azadirachtaindica Leaf powder	41.2-28.3	[25]
Fly ash	4.13	[45]
Chitosan hydrobeads	93.40	[26]
Waste orange peel	22.44	[27]
Coal-based activated carbons	52-189	[28]

4-2. Characterization

Scanning electron microscopy (SEM) was used to study the surface morphology. SEM image (Fig. 4) for MB shows particles of irregu-

Table 3. Adsorption Capacities of Bentonite used in the Removal of Different Pollutants

Adsorbent	Solute	Capacity, mg/g	Ref.
$CaCl_2$ modified bentonite	Congo red	227.27	[3]
Naturalbentonite	Hydroxyl quinoline	120	[36]
Na-bentonite	Reactive Yellow 2	67	[37]
CTS-CTAB-Bentonite	weak acid scarlet	175	[38]
Chitosan/bentonitecomposite matrix	Thorium (IV)	126	[39]
AMP-bentonite composite	Humic acid	121	[40]
Chitosan immobilized on bentonite	Copper, lead, and nickel	28,20,12	[41]
Yellowbentonite	2-NP, 4-NP, and 2,4-DNP	3.34, 6.2, 4.31	[42]

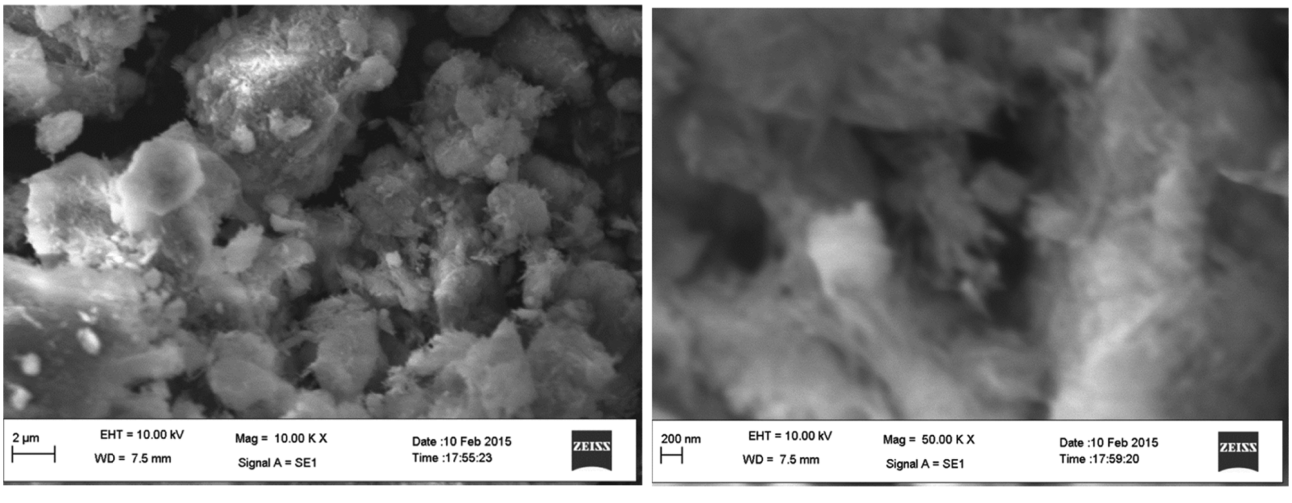

Fig. 4. SEM Image for MB at magnification of 10 K and 50 K.

Table 5. Elemental analysis for MB

Element	Before Adsorption		After Adsorption	
	Weight %	Atomic %	Weight %	Atomic %
O	57.28	69.8399	39.31	34.73
Mg	5.138	4.1218	2.66	1.5493
Al	5.1499	3.7242	0.0518	0.0202
Si	31.3978	21.8014	0.145	0.0708
K	1.029	0.5126	1.5123	0.5468
C			39.734	46.7645
N			15.765	15.9088
Na			0.2072	0.1316
S			0.631	0.2734

lar agglomerates, with a porous network and extended textural surface. The particle size is uneven and relatively small.

The chemical composition of MB and CR-loaded MB was obtained by EDS analysis, results of which are in Table 5. MB is composed of silica and alumina as major constituents along with traces of magnesium and potassium, due to which it was expected to play a key role in dye uptake. The presence of carbon, sodium, nitrogen and sulfur in the CR-loaded sample confirmed the transfer of CR from aqueous phase on to MB, as these elements were absent in the MB sample.

FTIR spectra for both samples (before and after adsorption) were taken to understand the surface changes during the sorption process. A dry sample of powder (about 0.1 g) was mixed with KBr and pressed into tablet form. The recorded FT-IR spectrum has been depicted in Figures 5(A) and 5(B). Broad peaks were observed at 3545, 3404, 1116 and 1093 cm^{-1}, while medium peaks were seen at 2360, 1622, 505 and 482 cm^{-1}. These indicate OH stretching and vibration in Al-Al-OH, Si-O stretching, Si-O-Al stretches and Si-O-Si bending. These are indications of the key role of aluminium and silicon oxides in the sorption process. The peak intensity of MB and CR loaded MB is compared in Table 6. Percent transmittance (% T) for CR loaded MB was lower than that of MB alone, by a difference ranging from 25-30% T. This is acceptable evidence for adsorption of CR on MB.

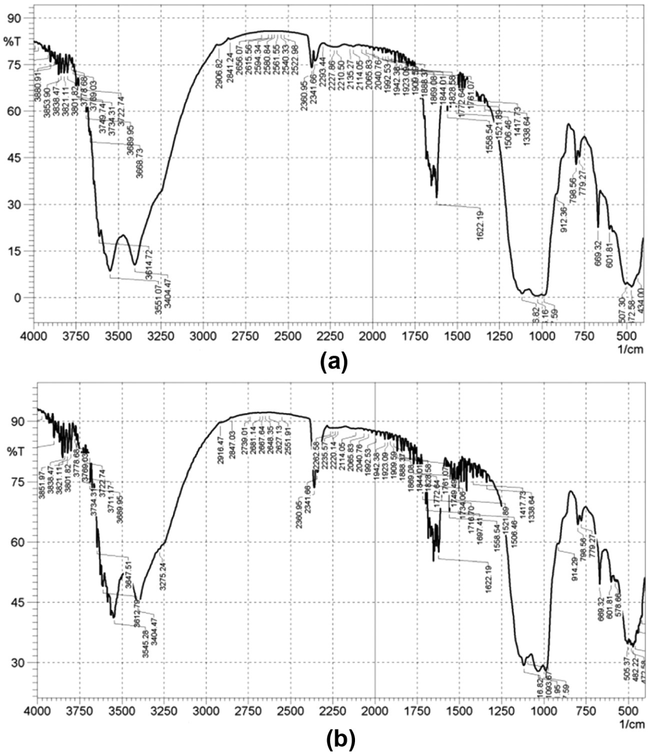

Fig. 5. (a) FTIR Spectrum before adsorption of CR on MB, (b) FTIR Spectrum after adsorption of CR on MB.

Table 6. Comparison of peak intensities of MB and CR loaded MB from FT-IR Spectra

Peak location wave length, cm^{-1}	Peak intensity, % Transmittance		
	MB	CR loaded MB	Difference
482	35.031	3.448	31.583
505	34.763	4.249	30.514
1622	57.44	32.151	25.289
1093	31.372	0.415	31.957
1116	29.3	1.179	28.121
3404	44.48	10.444	34.036
3545	41.355	8.526	32.829

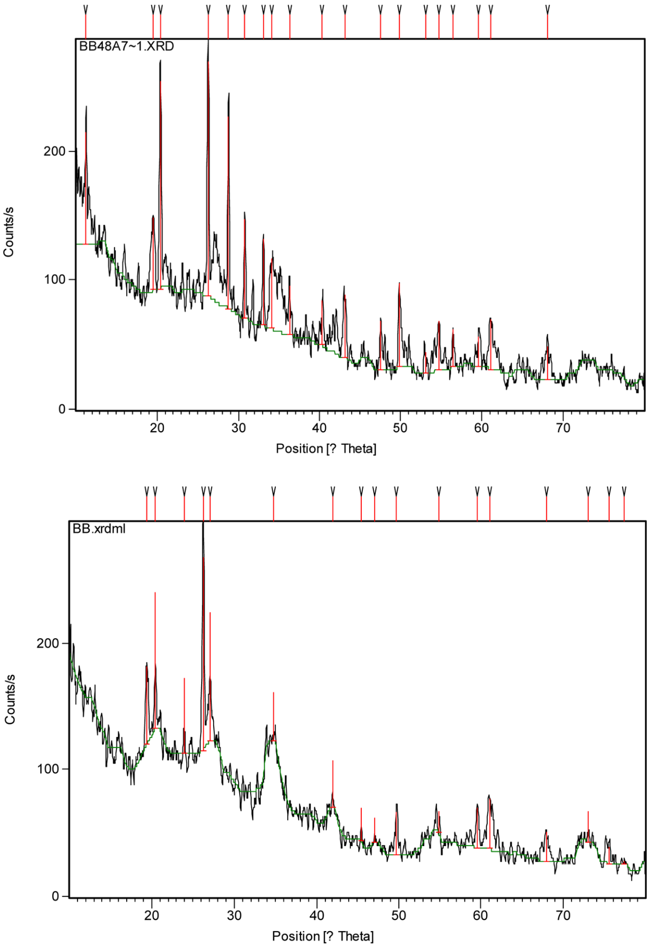

Fig. 6. (A) XRD spectrum for MB before CR loading, (B) XRD spectrum for MB after CR loading.

XRD analysis was used to confirm CR adsorption on MB. XRD patterns of MB before and after adsorption are displayed in Fig. 6.

An increase in the basal spacing of MB was observed after adsorption of CR, which indicates intercalation of CR into the clay galleries. The changes in peak positions are due to ionic bondage with CR molecules at MB surface. These indicate the adsorption of the dye on MB.

5. Conclusions

Modified bentonite proved to be a promising alternative to commercial activated carbon with an adsorption capacity of is 333.33 mg/g, which is much higher than that of other low cost adsorbents such as leaf powder, coir pith, fly ash, and even coal-based activated carbons. Experimental data fitted the Langmuir isotherm better, indicating monolayer coverage of CR on MB. Adsorption was thermodynamically favorable with R_L values less than 1. The process was endothermic with positive values of enthalpy. Randomness increased at the interface and the process was found to be spontaneous. SEM-EDS displayed MB as agglomerated particles with Al_2O_3 and SiO_2 as the major components. Decrease in energy level in FTIR and shift of XRD peaks confirmed the accumulation of CR on to MB.

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