Full Length Research Paper

Batch adsorption technique for the removal of malachite green and fast green dyes by using montmorillonite clay as adsorbent

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Due to the major environmental problems of colorants in the present study, the removal of malachite green and fast green dyes were studied on montmorillonite clay adsorbent under optimized conditions. The concentration of dyes, amount of adsorbent and agitation time was optimized. Spectrophotometric technique was adopted for the measurement of concentration of dyes before and after adsorption. The adsorption data were fitted on Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherm equations. The values of their corresponding constants were determined from the slope and intercepts of their respective plots. Thermodynamic parameters such as free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) of the system were also calculated by using Langmuir constant k. From the percentage (%) removal data, it was obtained that fast green-montmorillonite clay system and malachite green-montmorillonite clay system shows about 97 and 95% adsorption tendency. The scanning electron microscopy (SEM) technique was applied to study the surface morphology of the adsorbent.

Key words: Adsorption, dyes, montmorillonite clay, adsorption isotherms, thermodynamics of adsorption.

INTRODUCTION

The textile industries are confronted with serious environmental problems associated with its immense wastewater discharge, substantial pollution load, extremely high salinity, alkalinity and heavy colored effluents. Different types of dyes are used in industries like textile, paper, rubber, plastic, leather, cosmetics, pharmaceutical and food stuff (Reed et al., 1998). The effluents of these industries are composed of large amount of dye contents, which on mixing with water bodies causes severe problems such as increasing the chemical oxygen demand (COD) and reducing light penetration and visibility, thereby pose adverse effects on the marine life (Murray and Parsons, 2004). The presence of these dye stuffs in water bodies also makes water unfit for drinking due to toxic effects of different types of dyes on living cells. Dyes usually have a synthetic origin and complex aromatic molecular structure which makes them more stable and difficult to biodegrade. Degradation of dyes is typically a slow process. Various physical methods were applied for the purification of waste water like, coagulation, flocculation, oxidation, ozonation, membrane separation, ultra chemical filtration, chemical treatment etc (Parsons and Jeffersons, 2006; Brown and Hamburger, 1987; Shu et al., 1994; Shu and Huang, 1995; Gurses et al., 2006; Allègre et al., 2006; Pagga and Taeger, 1994; Santhy and Selvapathy, 2006; Robinson et al., 2002). The adsorption processes are more efficient methods for removing pollutants from wastewater. It also provides an alternative treatment method, especially if the adsorbent is inexpensive and readily available. Various types of adsorbent materials are available: Activated carbon, bagass, fly ash (Gupta and Ali, 2001), wool fiber (Perineu and Molinier, 1983), fertilizer waste (Shrivastava and Tyagi, 1995), shale oil ash (Al-Qodah, 2000), rice husk (Srinivasan et al., 1988), fruit stones (Gharaibeh et al., 1998), red mud (Gupta et al., 2001), used tea leaves (Tahir et al., 2009), montmorillonite clay powder (Tahir et al., 2008), algea (Tahir et al., 2008) which can be utilized to remove dyes and colorants from waste water.

Fast green FCF is a sea green triarylmethane food color dye, which is also known as food green with maxi-

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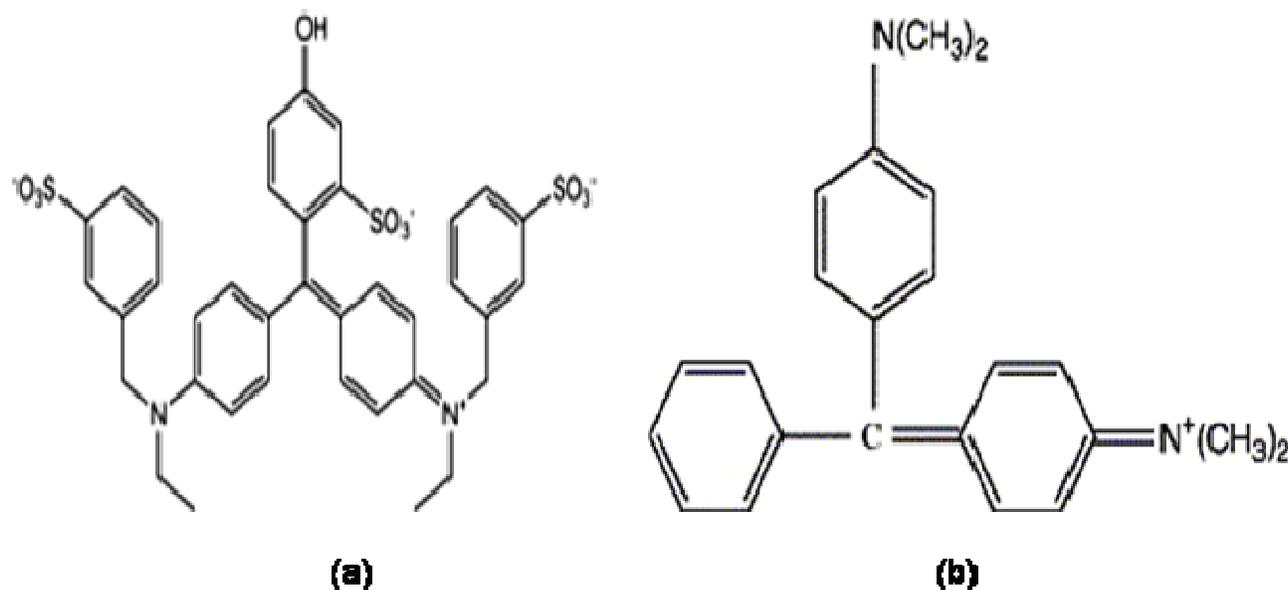
Figure 1. Structure of (a) Fast green and (b) Malachite green dyes.

mum absorption ranging from 622 to 626 nm. Fast green FCF possess a brilliant color, which is less likely to fade (Mittal et al., 2009). It is widely used as a staining agent like quantitative stain for histones at alkaline pH after acid extraction of DNA. Toxicological data reveal that fast green FCF is highly toxic (Ali, 2006). It is an allergen to humans and causes eyes and skin irritation and affects the upper respiratory tract. It also acts on a presynaptic locus by inhibiting the release of neurotransmitters in the human and animal nervous system (Van Hooft, 2002). It is carcinogenic and can produce sarcomas at the site of repeated subcutaneous injection. Still, FCF is used for coloring foodstuffs.

Malachite green is a tri phenyl methane dye, which is most widely used for coloring purposes (Gupta et al., 2006; Daneshvar et al., 2007). When Malachite green dye is discharged into receiving water bodies even at low concentrations, it will affect the aquatic life and causes detrimental effects on their liver, gills, kidneys, intestine and gonads (Srivastava et al., 2004). In humans, it may cause irritation to the gastrointestinal tract. There is a significant health risk to humans who eat fishes grown in contaminated water having Malachite green dyes and also causes irritation, redness and pain.

It is very important to establish a method to remove these substances from water and solutions (Kumar et al., 2005; Almeida et al., 2009; Monvisade and Siriphannon, 2009). The aim of the present study is to remove Malachite green and fast green dyes from aqueous solution using montmorillonite clay as an adsorbent material and check the efficiency of the removal of acidic and basic dyes from aqueous medium. The sorption capacity of montmorillonite clay at various temperatures was also studied by applying equilibrium studies.

MATERIALS AND METHODS

Adsorbent

The Montmorillonite clay was used as an adsorbent and was collected from the province of Baluchistan (Pakistan). The clay sample was dried and then sieved to particle size of 100 μm. Before starting adsorption process for the removal of cationic dye Malachite green, the montmorillonie clay was treated with 6 N hydrochloric acid (HCl) and stirred at 100 rpm for 72 h at 423 K. Then it was filtered and washed with deionized water and dried at 480 K, and then montmorillonie clay was active for the removal of cationic dye malachite green. For the removal of Fast green dye, the montmorillonie clay was used without any treatment because it has a natural affinity for anionic dyes.

Adsorbate

The commercial dyes, Malachite green and Fast green were used as adsorbate. The structures of dyes are shown in Figure 1. Stock solutions (1×10^{-2} mol/dm^3) of Fast green (mol.wt: 808.86 g) and Malachite green dyes (mol.wt: 927.02 g) were prepared in double distilled water and λ_{max} of dyes were recorded by using UV visible spectrophotmeter. The dye solutions of 1×10^{-5} mol/dm^3 were prepared for adsorption studies.

Adsorption studies

Determination of optimum amount of adsorbent

In order to find out the optimum amount of adsorbent at which maximum adsorption takes place, 30 ml dye solutions was taken in a series of flasks with different quantities of adsorbent montmorillonite clay: 0.1, 0.2, 0.3, 0.5, 0.8, 1.0 and 1.2 g. The solution of dye was kept on a shaking incubator for 30 min at 120 rpm. After that time period, content was filtered and absorbance was noted by using UV visible spectrophotometer.

Determination of optimum concentration of adsorbate

For the determination of optimum concentration of dyes, solutions of different concentrations of dye were prepared (1 x 10^{-3} to 1 x 10^{-6} mol/dm^3). Thirty mililitres of dye solution was placed in respective flasks with optimum amount of montmorillonite clay for 30 min. After that time period, content was filtered and absorbance was noted by using UV visible spectrophotometer.

Determination of optimum agitation time

For the determination of effect of agitation time for the adsorption of fast green dye on montmorillonie clay, the optimum amount of adsorbent was added in the respective flasks with 30 ml of optimum concentration of dye solution for different intervals of time. After that time period, content was filtered and absorbance was noted by using UV visible spectrophotometer.

Adsorption at different temperatures

The 30 ml of dye solution having different concentrations were put in flasks. Optimum amount of montmorillonite clay was added in each agitation flask and placed on the shaking incubator at desired temperature under the optimized conditions. After the specific agitation time period, the solutions were filtered and analyzed for the determination of concentration of dye remaining in the solution by spectroscopy. The experiments were repeated at various temperatures ranging 303 to 318 K. The data were also incorporated in Freundlich, Langmuir and Dubinin-Radushkevich (D-R) adsorption isotherm equations.

RESULTS AND DISCUSSION

Effect of amount of adsorbent

The effect of amount of adsorbent of montmorillonite clay on the adsorption of fast green and malachite green were studied. The amount of adsorbent varied from 0.1 to 1.2 g using concentration of dye 3 × 10^{-5} M. The 1.0 g adsorbent system show optimum adsorption.

Effect of concentration of dyes

The effect of dye concentration on its adsorption by montmorillonite clay was studied. The concentration ranges of dyes were 1 x 10^{-3} to 5 x 10^{-5} M. The concentrations at which Malachite green and fast green dyes show maximum adsorption were 3 x 10^{-4} and 6.3 x 10^{-4} M, respectively.

Effect of agitation time

Dye solutions were shaken in a shaking incubator for different intervals of time. When they came in contact with the surface of montmorillonite clay, the unsaturated part of the dyes molecules strike with the surface of the adsorbent for the process of adsorption. It was observed that the adsorptions of dyes were increased with increasing time and reaches to maximum removal and then attains a constant removal value when adsorption equilibrium is reached. For fast green-montmorillonite clay system and malachite green-montmorillonite clay system, maximum adsorption capacity were obtained at 10 and 30 min, respectively.

Adsorption isotherms

An adsorption isotherm is a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium. It maps the distribution of adsorbed solute between the adsorbate and solid phases at various equilibrium concentrations. The adsorption isotherm based on data is specific for each system. The inspection of adsorption isotherm shows a decrease in the amount of adsorption of dyes with increase in temperature. It shows that adsorption of dyes on montmorillonite adsorbent is exothermic in nature. Adsorption isotherms of both dyes are shown in Figures 2 and 3. The Freundlich isotherms have been expressed as:

$$\text{Log } X/m = \log K + 1/n \log C_s \tag{1}$$

Where, X/m is the amount adsorbed per unit mass of the adsorbent, C_s the equilibrium concentration and 1/n and K are constants. The Freundlich plots were obtained at various temperatures. The values of K and n computed from the respective slopes and intercepts of the plots are listed in Table.1. The constant K relates to the degree of adsorption, while n provides the rough estimate of the intensity of the adsorption. The decrease in the values of K with the rise in temperature reveals the adsorption affinities of dyes on montmorillonite clay system. The decreases in adsorption with rise in temperature show that adsorption is less favorable at higher temperatures. The simplest theoretical model that can be used to describe monolayer adsorption is the Langmuir equation and is most frequently used to determine the adsorption parameters.

$$C_s/X/m = 1/kvm + C_s/Vm \tag{2}$$

Where, k is the adsorption coefficient or langmuir constant, V_m is the monolayer capacity, X/m is the amount of dye required to form the monolayer over the surface of adsorbent and C_S is the equilibrium concentration. Straight lines were obtained by plotting C_S/X/m versus C_S at different temperatures ranging from 303 to 318K. The slope and intercept of these plots were representatives the values of respective constants V_m and K as shown in Figures 4, 5 and Table 2. The increase in the values of K for fast green-montmorillonite system at low temperatures
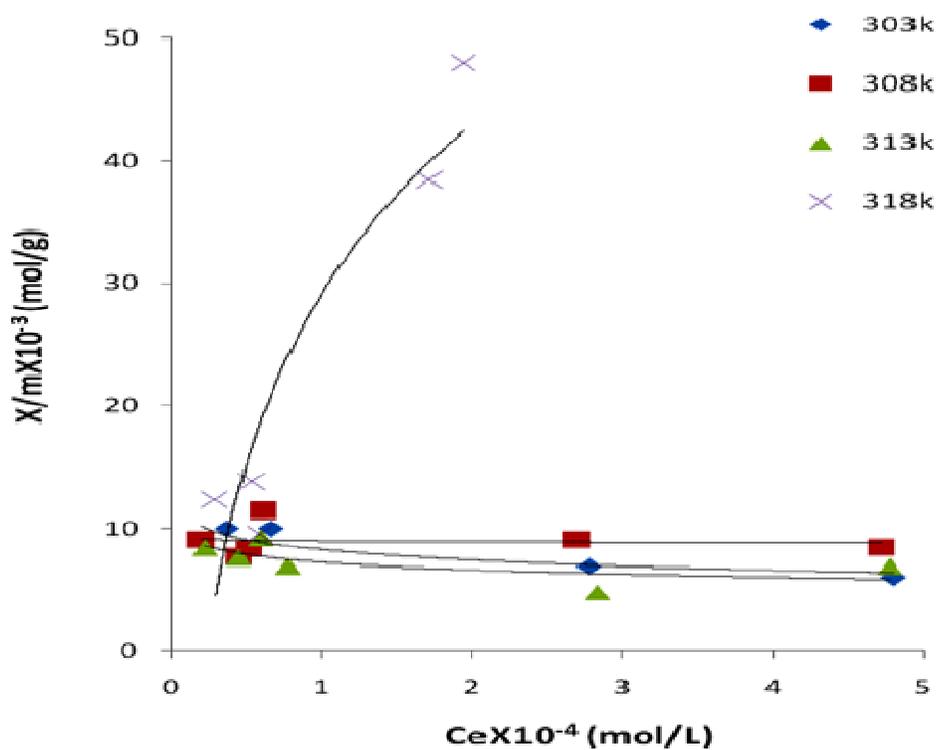
Figure 2. Adsorption isotherms of Malachite green on montmorillonite at different temperature.
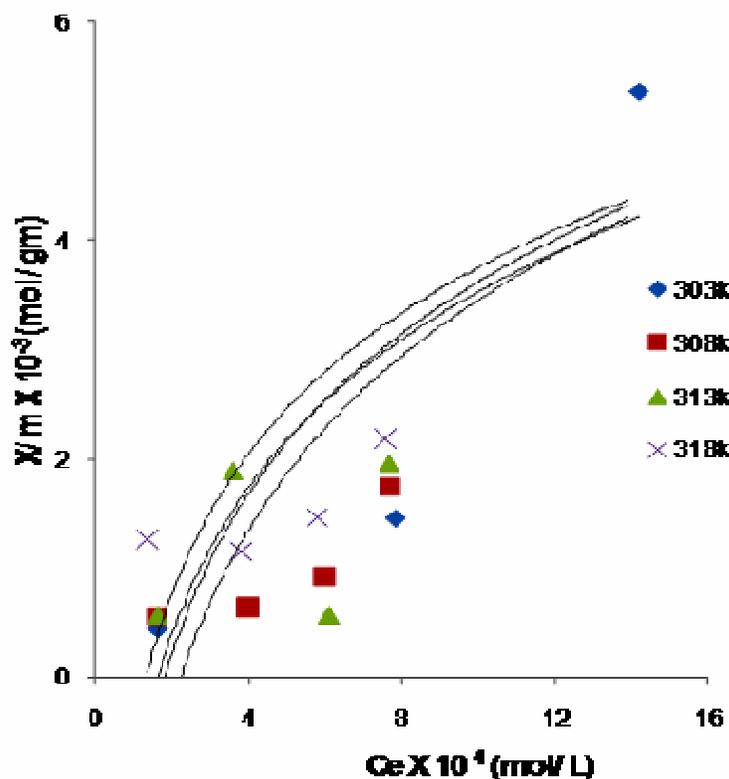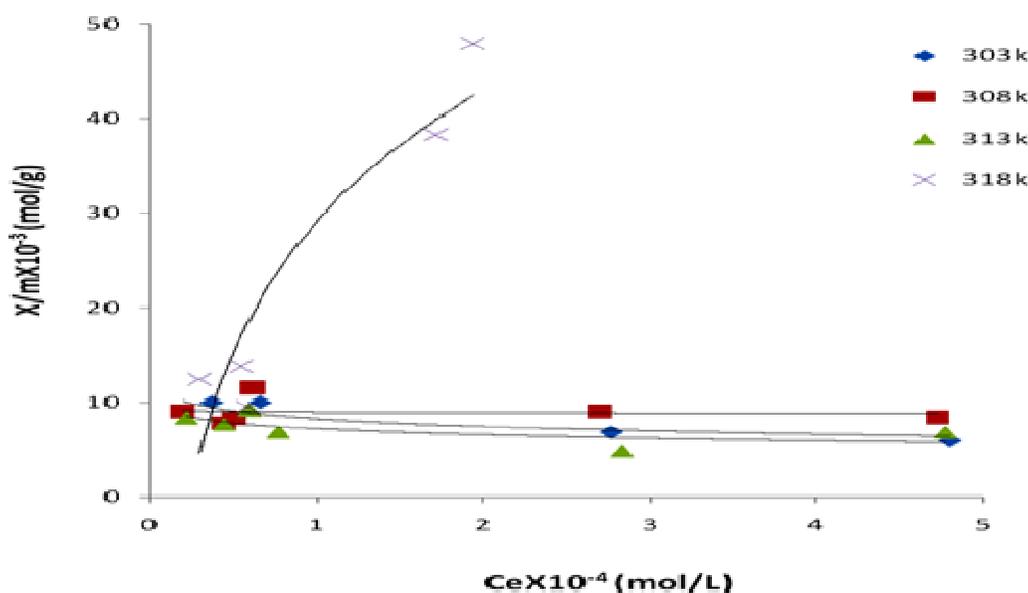

Figure 3. Adsorption isotherms of Fast green on montmorillonite at different temperature.

Table 1: The Freundlich parameters for the adsorption of malachite green and fast green dyes on montmorillonite clay.

Dyes	Temperature (K)	K	n
Malachite green	303	0.0620	-24.013
	308	0.0004	-136.90
	313	0.0066	-7.5470
	318	0.0049	0.9658
Fast green	303	4.5940	0.9300
	308	4.2740	0.9300
	313	1.3674	1.1090
	318	0.2600	1.5530

Figure 4. Langmuir adsorption isotherms for Malachite green on montmorillonite at different temperatures.

predicts strong interaction between dye molecules with adsorbent, while in few cases, they decreased with the rise in temperature for malachite green-montmorillonite system which indicates the weakening of adsorbate-adsorbent interactions at high temperatures. The adsorption systems follow Langmuir adsorption isotherm equation except at 313 K for malachite green-montmorillonite system. The monolayer capacity (V_m), for fast green-montmorillonite system decreases with increase in temperature, indicating high affinity of dye at low temperatures. In the case of malachite green-montmorillonite system, monolayer capacity (V_m) increases with the rise in temperature. The essential characteristics of Langmuir equation is the separation factor or equilibrium parameter, R_L, which is calculated as:

$$R_L = 1/ (1+bC_0) \qquad (3)$$

Where, R_L value is Nature of adsorption process; $R_L > 1$ is unfavorable; $R_L = 1$ is linear; $0 < R_L < 1$ is favorable; and $R_L = 0$ is Irreversible.

The values of R_L are shown in Table 2 and observed in the range of $0 - 0.1$, indicating that the adsorption process is favorable for both fast green-montmorillonite clay and malachite green-montmorillonite clay systems.

The adsorption data were also applied on Dubinin-Radushkevich (D-R) isotherm equation, which is represented as:

$$Ln\ X/m = ln\ X_m - K\ \acute{\epsilon}^2 \qquad (4)$$

$$\acute{\epsilon} = RTln\ (1+1/ C_S) \qquad (5)$$

Where, X_m is the monolayer capacity of adsorbent, K is a constant related to adsorption energy, $\acute{\epsilon}$ is adsorption
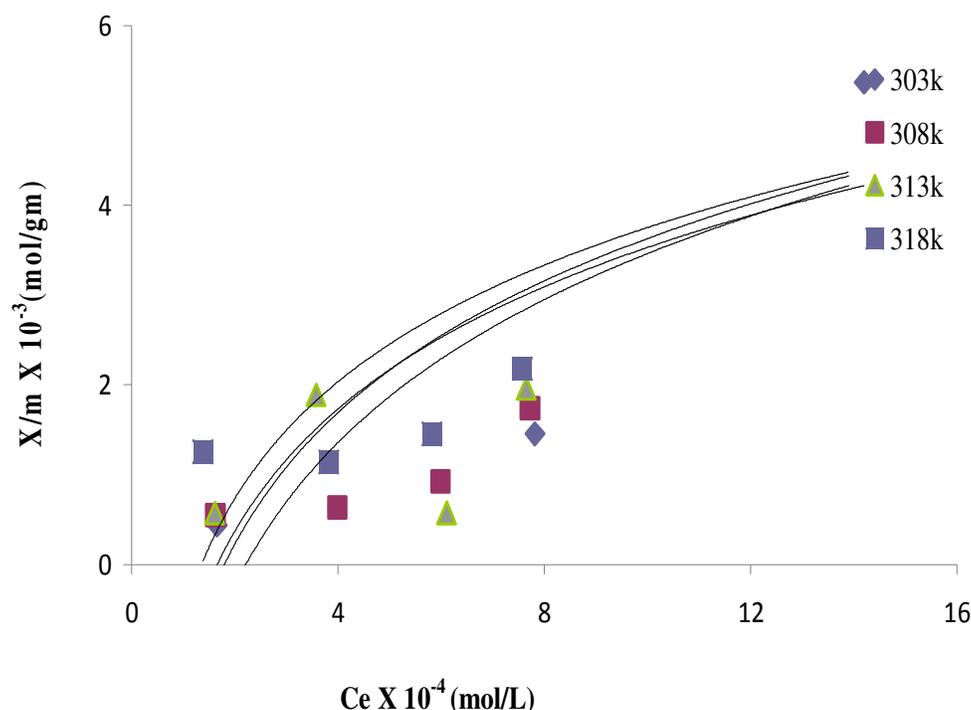
Figure 5: Langmuir adsorption isotherms for Fast green on montmorillonite at different temperatures.

Table 2: The Langmuir parameters for the adsorption of malachite green and fast green dyes on montmorillonite clay.

Dyes	Temperature (K)	(K)	(Vm)	R_L
Malachite green	303	3.6390	0.0835	0.0009
	308	0.4710	0.2591	0.0075
	313	6.3178	0.0628	0.0005
	318	0.1938	1.4168	0.0182
Fast green	303	0.1153	30.300	0.0124
	308	0.1470	23.809	0.0131
	313	0.3347	15.698	0.0058
	318	0.1755	33.448	0.0110

potential, R is a gas constant, T is absolute temperature, X/m and C_S have usual meaning as described in Equation (2). The D-R plots of ln (X/m) versus $\acute{\epsilon}^2$ were obtained at various temperatures are shown in Figures 6, 7 and in Table 3. Values of X_m and K were calculated from the intercept and slopes of their respective plots and the mean free energy of sorption (E_S) were calculated from K by using the equation:

$$E_S = (-2K)^{-1/2} \tag{6}$$

The values of E_S for fast green-montmorillonite clay

system increased with the rise in temperature, indicating an increase in the dye sorption with the rise in temperature. For malachite green-montmorillonite clay system, E_S values decreased with the increase in temperature, indicating less adsorption capacity at higher temperatures.

Thermodynamic parameters

The thermodynamic studies play an important role in understanding the nature of adsorption. The thermodynamics parameters related to the adsorption of dyes
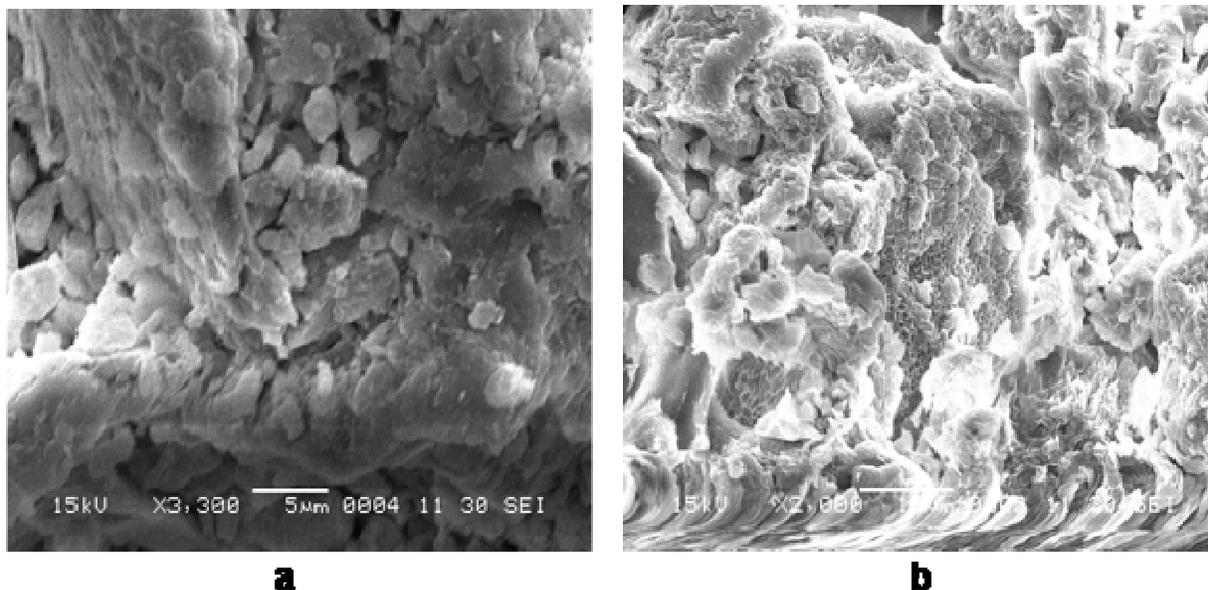
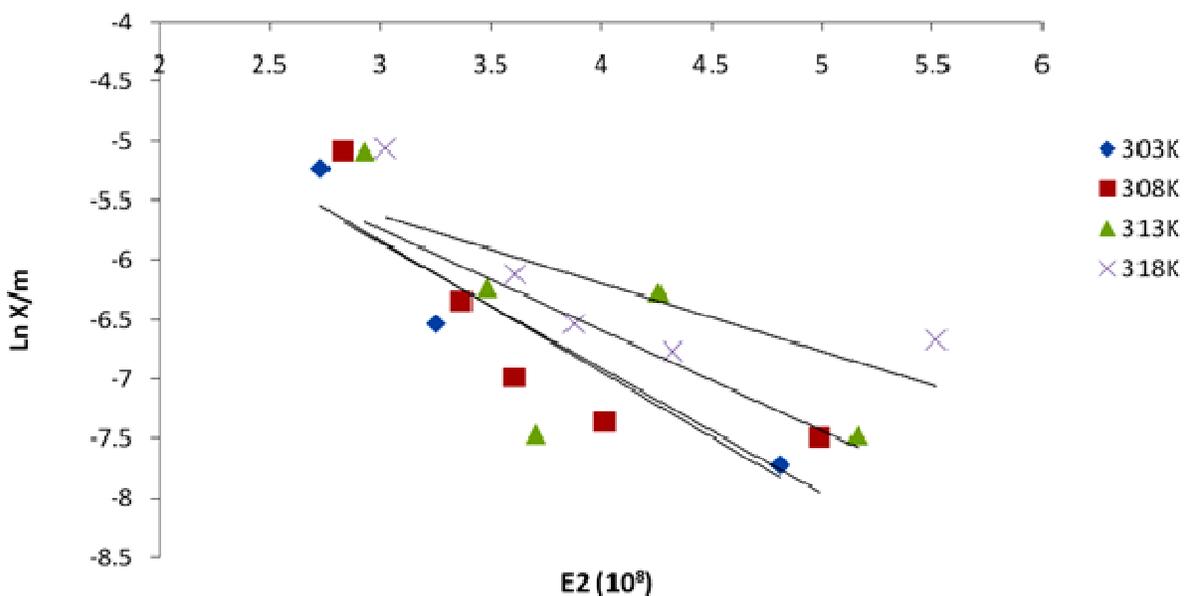**Figure 6. a**: SEM of montmorillonite clay before adsorption; **b**: SEM of montmorillonite clay after adsorption.

Figure 7. D-R plots for the adsorption of fast green on montmorillonite at different temperatures.

such as free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) were evaluated, and are tabulated in Table 4. The following expressions were used for calculating these parameters:

$$Ln\ k = \Delta S°/R - \Delta H°/RT \tag{7}$$

$$\Delta G° = \Delta H° - T\ \Delta S° \tag{8}$$

The values of $\Delta H°$ and $\Delta S°$ were calculated from the slope and intercept of the linear variation of Ln K with the reciprocal of temperature (1/T). The values of $\Delta G°$ for fast green-montmorillonite system and malachite green montmorillonite system are negative at different temperatures showing the spontaneous behavior of adsorption process. The values of $\Delta H°$ were positive for both dye systems which indicates that the adsorption of malachite green and fast green on montmorillonite is exothermic in nature. The values of $\Delta S°$ show random behavior.

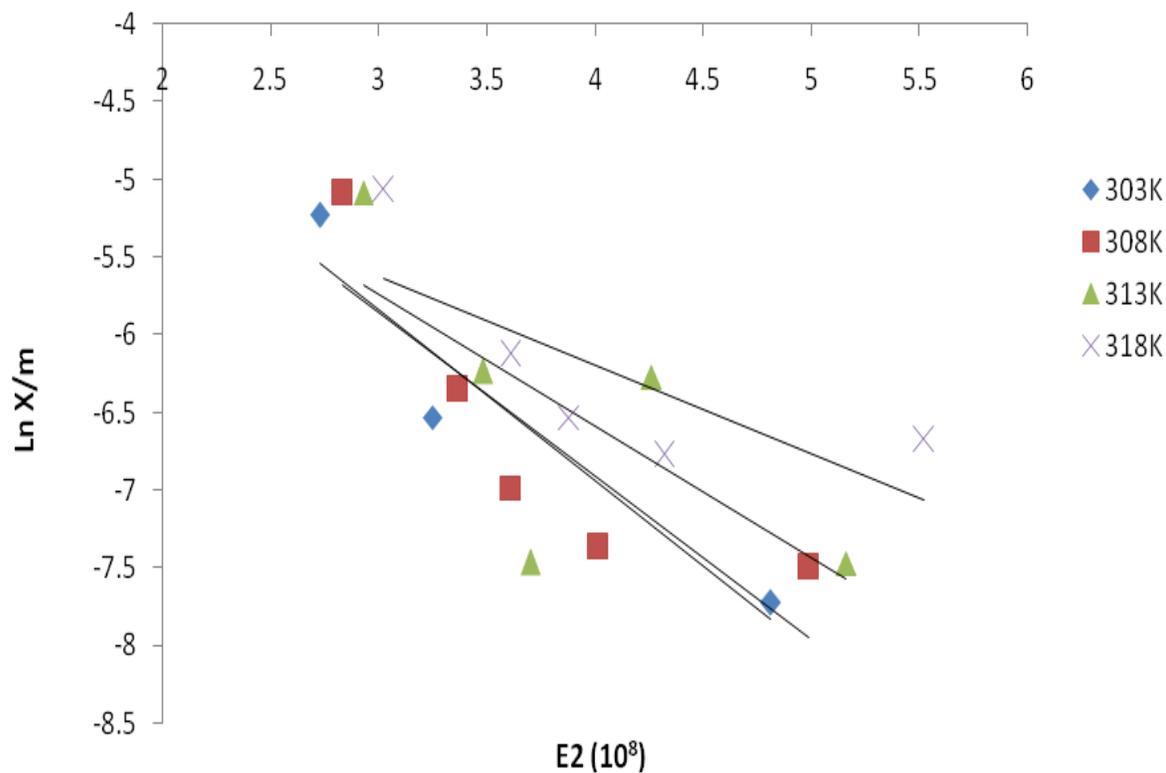The comparative removal studies were done at different

Figure 8: D-R Plots for the adsorption of Fast green on montmorillonite at different temperatures.

Table 3: D-R parameters for malachite green and fast green dyes adsorption on montmorillonite clay.

Dyes	Temperature (K)	X_m	Es KJ/mol
Malachite green	303	0.0057	-2.6315
	308	0.0167	2.3112
	313	0.0016	-1.5040
	318	3.2110	0.7972
Fast green	303	0.0786	0.6745
	308	0.0669	0.6898
	313	0.0409	0.7684
	318	0.0197	0.9383

Table 4. Thermodynamic parameters for the adsorption of malachite green and fast green dyes on montmorillonite clay.

Dye	Concentration mol.L^{-1}	ΔH° KJ mol^{-1}	ΔS° KJ deg^{-1}mol^{-1}	ΔG° KJmol^{-1}			
				303K	308K	313K	318K
Malachite green	0.7 x 10^{-4}	2.016	1.496	-451.27	-458.72	-466.23	-473.71
	9 x 10^{-4}	0.405	3.939	-1193.10	-1212.80	-1232.50	-1252.19
	1 x 10^{-4}	0.787	2.726	-825.19	--838.82	-852.41	-866.08
	3 x 10^{-4}	2.641	3.003	-907.26	--922.28	-937.29	-952.31
Fast green	4.2 x 10^{-4}	0.422	1.951	-590.73	-600.48	-610.24	-619.98
	6.3 x 10^{-4}	0.304	2.376	-719.62	-731.50	-743.38	-755.26
	8.3 x 10^{-4}	0.198	2.684	-813.05	-826.47	-839.84	-853.31
	1.6 x 10^{-3}	0.142	2.816	-853.10	-867.18	-881.26	-895.34

temperatures for both dye systems. The Malachite green-montmorillonite and Fast green-montmorillonite system shows about 97% at 313K.

Morphological studies

The surface studies of adsorbent were also done before and after adsorption by taking images through scanning electron microscope (SEM). Figure 6a and b show the surface of adsorbent which was unsaturated before adsorption and saturated after adsorption.

Conclusion

The montmorillonite clay can be efficiently utilized as an adsorbent for the removal of toxic dyes from aqueous solutions. By applying the adsorption models, the values of respective constants show the validity of adsorption phenomena under optimized conditions. By calculating the thermodynamic parameters like $\Delta G°$, $\Delta H°$ and $\Delta S°$, the variation of temperatures show the spontaneity of the system. The surface morphology studies reports that the excess amount of dye contents was adsorbed on the surface which show changes on the active sites of adsorbent. The values of percentage (%) removal at different temperatures for Fast green-montmorillonite clay system and Malachite green-montmorillonite clay system shows that about 97% removals were obtained.

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