POTENTIALS OF INDIGENOUS SILTY CLAY FOR ERADICATION OF METHYL BLUE FROM CONTAMINATED MEDIA: KINETIC MODELING

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Silty clay collected from Khojak mountain ranges near Chaman city, Pakistan, was used as adsorbent for the removal of toxic methyl blue from aqueous solutions. The silty clay was characterized by FTIR. The effect of various pysico-chemical factors such as adsorbent dose, pH of solution, time of contact and temperature for the removal of dye was investigated. The optimum conditions for the maximum removal of dye noted were 0.3g dose, 40 minutes contact time, pH 6, and temperature 30°C under the batch test conditions. Kinetic studies revealed that pseudo second order kinetics was followed showing that the dye adsorption on silty clay was controlled by the more than one-step. The data was well fitted to Langmuir Isotherm showing that the adsorption of dye on silty clay was monolayer. The value of thermodynamic parameters such as free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) revealed that the process was spontaneous, endothermic and feasible in nature.

1. Introduction

Excessive amount of effluents are being discharged to natural water sources by various industries. These wastewater contaminants includes biodegradable and volatile organic compound, dyes, toxic metals, plant nutrients, suspended solid particles, parasites and various pathogens [1]. Large number of industries, in their operation, release effluents containing different dyes. Among the industries, textile industries excessively make use of water and thus give rise to substantial amount of dye in their effluents [2]. There exists more than 100,000 commercial dyes, and some 7×10^5 tons are being produced per year, with an ample fraction of them discharged in aqueous effluent directly [3]. As dyes are clearly visible so their presence in river stream after discharge of wastewater in them, can easily be noticed. These dyes not only causes threat to aesthetic nature of ecosystem but are also extremely toxic to aquatic life [4]. The transparency of water is lost and the dyes result in modified absorption of solar radiation, and hence photosynthetic process is disturbed which has severe adverse effects on food web and thus on aquatic life[2].

Various physicochemical operations such as flocculation, coagulation, reverse osmosis, ozonation, and adsorption on silica gel, manganese oxide, activated carbon and clays etc. are being commonly applied for the removal of dyes [5-11].

Among them, adsorption finds excellent applications in removing dyes from water systems with activated carbon as adsorbent because of its high adsorption capacity [12-14].However, activated carbon has high cost and difficulty in its regeneration so there is a dire need for a cheap and effective adsorbent. Clay is an excellent adsorbent due to its low cost, environment friendly nature, abundance and accessibility. The clays can either be used in natural form or its modified form with certain chemical agent relying on target pollutants [15]. Clay has sound applications in the fields of oil drilling, agriculture, and building industry. Clay has high surface area, excellent cation exchange capacity, better lamellar structure and other interesting physicochemical characteristics. Owing to these salient features, clays have great capacity to remove pollutants such as colors, heavy metals and organic contaminants [16].

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In the present study, clay sample was collected from "Khojak mountain ranges near Purana Chaman Karaiz", Chaman city, Baluchistan. The said clay is called as silty clay, SC. This silty clay was used as adsorbent for the removal of Methylene blue from aqueous media. Different adsorption parameters such as Temperature, contact time, pH of solution, and dose were optimized. Isothermal study was performed at optimized conditions. Kinetic modeling and thermodynamic studies were made to understand the mechanism and nature of adsorption process.

2. Experimental

2.1. Preparation and characterization of adsorbent

The silty clay sample was collected around Purana Chaman Karaiz in Khojak mountain ranges near Chaman city, Baluchistan. The clay was first ground and then, was kept in oven for 1 hours at 100^0 C so that all water content was removed. The dried clay was then sieved through 125µm mash and was obtained in fine granular form. No further chemical or physical treatment of sample has been made. The clay sample was kept in a sealed jar for its further use as adsorbent. The clay was subjected to FTIR analysis to know the different functional groups present in the sample. Tensor 27, Burker Germany FT-IR spectrophotometer was used. For pH adjustment, 0.1M HCl and 0.1M NaOH were used stepwise to obtain the desired pH.

2.2 Methylene blue solutions

Methylene blue of PanreacQuimica SA Company was used for experimentation without any more purification. 1000 ppm stock solution of dye was prepared in double distilled water by dissolving 1g/L of solution. The required solutions of different concentration were prepared from the stock solution by making use of dilution formula. The absorbance of different concentration solutions was measured at λ= 665nm by using UV–Visible spectrophotometer (PG instrument T60, UK).

2.3. Adsorption studies

50 mL of MB solutions were taken in titration flask of 250ml capacity and to this known quantity of clay adsorbent were added. The mixtures were then gently shacked by mean of isothermal shaker at speed of 150 rpm to achieve equilibrium. Afterwards the solutions were allowed to rest for some time. The upper supernatant solution was carefully separated and collected from adsorbent residue. The absorbance (A_f) of the said solutions were measured by spectrometer. All the experimental procedure was performed in duplicate. From absorbance values, the adsorption capacity (q) and percentage removal (% R) were calculated by making use of following formulas.

$$q \quad = \frac{Co-Ce}{m} x V \tag{1}$$

$$\%R \quad = \frac{Co-Ce}{Co} x 100 \tag{2}$$

Where Co is dye initial concentration in mg/L, Ce is dye concentration in mg/L at equilibrium, V is volume of dye solution in liter and m is the mass of adsorbent in grams.
Kinetics of MB adsorption on clay was investigated for the determination of rate limiting step. This was accomplished by knowing rate of adsorption of dye on clay as a function of time. The amount of dye adsorbed (q_t) at time, t was calculated using the following equation.

$$qt \quad = \frac{Co-Ct}{m} x V \tag{3}$$

Where C_t is conc. of dye at any time in mg/L[17].

3. Result and discussion

3.1. FTIR Spectra of Clay

FTIR spectra was used to characterize the given silty clay as shown in Figure 1. Generally, clay includes various constituents such as tetrahedral silicate and aluminate anions, hydroxyl group, octahedral cations of metals, and different interlayer cations. In FTIR spectra, stretching 0H- modes are found in the region 3400-3750 cm^{-1}. Metal-O-H bending lie in the range 600-950 cm^{-1}. Al-O and Si-O stretching modes give peaks in region 700- 1400 cm^{-1} while their bending modes are in the range 150-600 cm^{-1}.

The FTIR spectra of SC recorded shows peaks for bending vibration of Al-O-H at 987cm^{-1} and Fe-Al-OH at 877 cm^{-1}. The peaks at around 3600 cm^{-1} and 3400 cm^{-1} are due to stretching vibrations of O-H groups. The peaks appearing at 1426 cm^{-1} are due to Si-O stretching and the peak at 779 cm^{-1} are due to bending vibrations of Al-O bond [18].
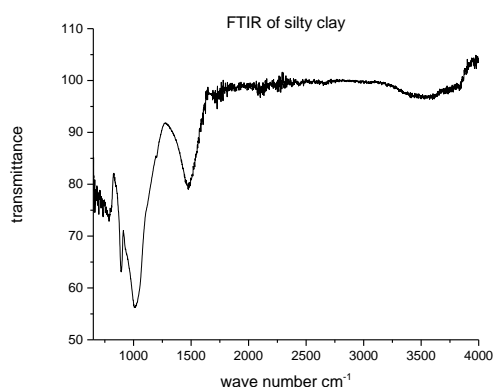

Figure 1: FTIR Spectra of silty clay

3.2. Optimization of parameters
3.2.1 Effect of adsorbent dose

The effect of clay adsorbent on the adsorption of MB was investigated by changing the adsorbent dose from 0.1g to 2.0g in 20ppm dye solution. The data revealed that adsorption was found to increase till 0.3g because as sorbent concentration rises, greater surface area is achieved and thus it enhances the removal capacity of MB. It was found that 0.3g of clay was the optimum dose where maximum adsorption of MB took place. As the dose was further increased, the percentage removal started decreasing which may be referred to no availability of more binding sites on the surface of adsorbents. The results are depicted in Figure 2 (a). Similar trend of removal has been reported for the adsorption of Congo red on activated red mud [19].
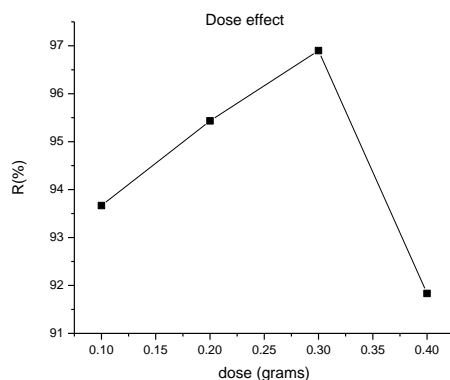

Figure 2(a). Effect dose on the %age removal of MB

3.2.2 Effect of temperature

Temperature has a remarkable effect on the process of adsorption because temperature influences dye molecules diffusion at interface of dye outer boundary layer, and as well affects inside adsorbent pores [17]. Temperature effect was investigated from 283K to 333K as is shown in Figure 2(b). The results suggested that the percentage removal was found to increase as temperature was increased from 283K to 303K, and then from 313K to 333K adsorption started decreasing again. The maximum removal of dye was noted at 303K which is the optimum temperature for the adsorption. The results revealed that initially adsorption is endothermic from 283K to 303K and then it changed into exothermic in temperature range 313K to 333K. Yang et al. had also reported same endothermic–exothermic trend for the adsorption of methylene blue (cationic) on starch (anionic) [20].
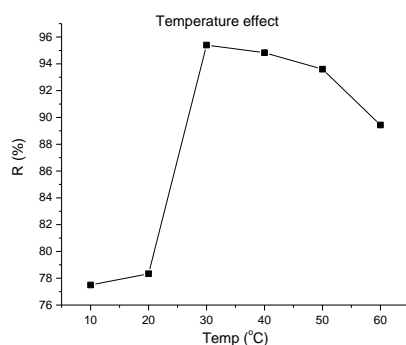

Figure 2(b): Effect of temperature on %age Removal of MB

3.2.3 Effect of the contact time

The contact time required to achieve equilibrium depends on initial concentration of dye. It has been seen that the adsorption generally increases with rise in concentration [21], and also the rate of adsorption on surface of adsorbent has been found proportional to driving force times an area [22].

Contact time studies relate dye quantity adsorbed on a given mass of adsorbent with the passage of time. Effect of contact time studies help to know the equilibrium time for the given adsorption process [23, 24]. The effect of contact time on the percentage removal of dye by SC is given in Figure 2(c). Percentage removal has a trend of sharp increase during first 40 min showing quick adsorption. After 40 min, there is a gradual increase of dye removal showing that there is slow adsorption and then onwards no improvement in adsorption. Thus, 40min time is required for the system to reach equilibrium where maximum removal of dye has taken place.

The rapid uptake of dye by clay in first 40 minutes is due to availability of higher bare surface area of adsorbent. Resultantly, initial sharp adsorption and enough contact time, make surface of adsorbent saturated which resist more adsorption of dye and thus the process of adsorption gets slower [25].
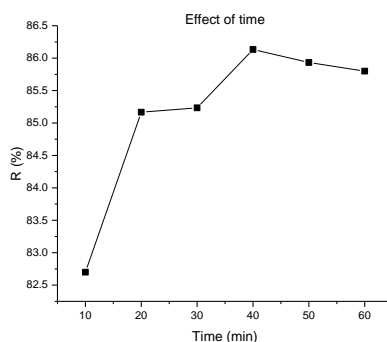

Figure 2(c): effect of time on the % age removal of MB

3.2.4 Effect of pH

As per much research, it has been noted that pH plays an important role in the process of adsorption[26]. In the present study, some experiments were carried out for 20ppm solutions of MB dye adsorption on clay adsorbent at 30^0C as a function of pH. The pH range was kept from 2 to 11. The data has been show in Figure 2(d). It is inferred that the process of adsorption is largely dependent on pH factor. The amount of MB adsorbed on clay is maximum at 6 pH. The adsorption of MB dye on the surface of clay is affected by the charge on the surface of the adsorbent [27]. Lower adsorption of dye at low pH depicts the presence of excess H^+ ions which compete with cations of dye for adsorption sites [28].
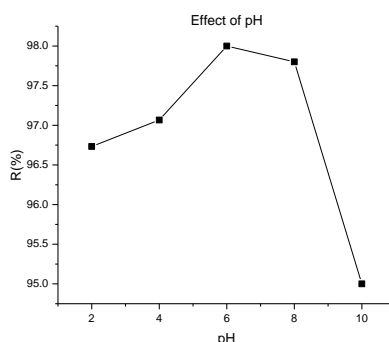

Figure 2(d): Effect of pH on the % age Removal of MB

3.3. Adsorption kinetics

In adsorption studies, it is quite necessary to predict the rate at which the contaminants are being removed from the media by the sorbent because the knowledge of rates help in designing the treatment plant for adsorption. As it can be seen that the sorption process is much rapid and much quantity of dye is removed in first 1 h. The rate of adsorption of MB on SC was studied using pseudo first-order, pseudo second-order, and intra particle diffusion model. The above models are being used to investigate the adsorption of dyes and heavy metals on various solid adsorbents [29-31]. Ho and McKay has shown that the use of a single model to predict the adsorption on a sorbent may remain questionable due to heterogeneity of adsorbent surface and various sorption phenomena such as surface reaction and transport etc. With the help of Non-linear curve fitting procedure, kinetic models were estimated.

The pseudo first-order model is quite appropriate for lower solute concentrations. The pseudo first order equation is;

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{4}$$

In the equation above, q_t is amount of adsorbate adsorbed at time t in mol/g, q_e represents adsorption capacity at equilibrium in mol/g, t is time in min and k_1 is rate constant in min^{-1}.[32] After integration, the equation gets the form,

$$\ln (q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

To test the model, plot of $\ln (q_e - q_t)$ against t was plotted as is shown in Figure 3(a). From the data, it was observed that R^2 has very small value and also the value of q was lower in comparison to experimental values. From the said values it could be inferred that the adsorption of MB on SC do not follow pseudo first order.
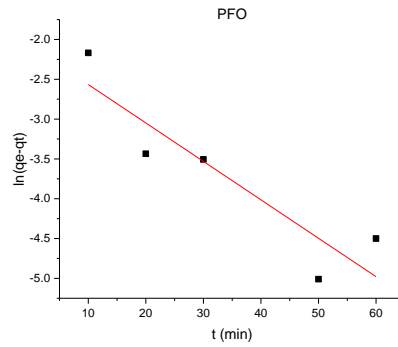
Figure 3(a): Pseudo-first-order (PFO) kinetic model for sorption of MB

The pseudo seconder kinetic model can be represented as,

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{6}$$

Where k_2 is rate constant for second order having unit mol^{-1}lit.min^{-1}.
After integration, the above equation assumes the form,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e \, 2} + \frac{t}{q_e} \tag{7}$$

For testing the above model, a plot of **t/q$_t$** against **t** was studied as is shown in Figure 3(b). The slope of graph gives the value of $1/q_e$ while the intercept of the plot is equal to $1/K_s.q_e^2$. The data revealed that R^2 value is unity and the calculated value of adsorption capacity, q_e, is much close to experimental value. These parameters are not so closer in other kinetic models. On the basis of the above results, it can be said that for the adsorption of MB on SC, the data can best be fitted with pseudo seconder order kinetic model.
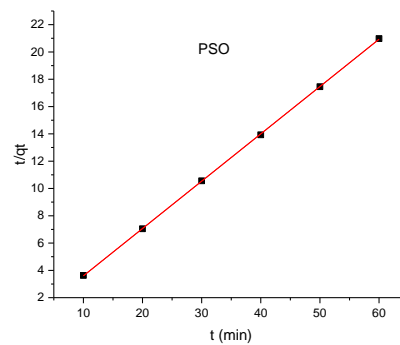

Figure 3(b): Pseudo-second-order (PSO) kinetic model for sorption of MB

Intra particle diffusion model was tested by plotting q_t (mg/g) against $t^{1/2}$ as is shown in figure 3(C). Controlling step can be ascertained if the straight line is passing through origin[33]. The deviation of R^2 value from unity shows that intra particle diffusion are not followed by MB adsorption on unity.
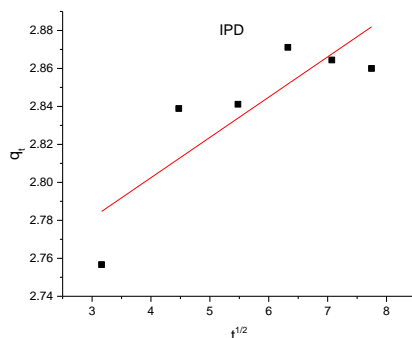
Fig. 3(c): Intra particle diffusion (IPD) kinetic model for sorption of MB

3.4. Adsorption isotherms

Adsorption isotherms find applications in describing the process of distribution of adsorbate between the liquid and solid phase at equilibrium. It is represented by correlating the quantity of adsorbate taken up per gram sorbent, q_e, in mg/g to the solution concentration at equilibrium Ce in mg/L at a given temperature.

For the isothermal study, optimum conditions were maintained to investigate various adsorption isotherms. Temperature 303K, pH 6, shaking seed of 150rpm, at contact time 40 min with adsorbent dose 0.3g were all kept maintained.

The data of adsorption of MB on SC didn't give appropriate results when Freundlich model was applied. The plot between ln q_e against $\ln C_e$ was plotted in figure 4(a).The results depict that the adsorption of MB on SC is not multilayer adsorption.
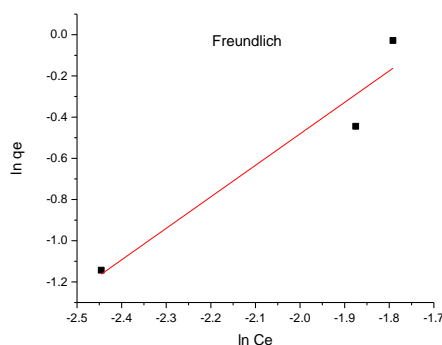

Fig. 4(a): Freundlich adsorption isotherm for sorption of MB

The said data was also tested by applying Langmuir model. The Langmuir isotherm has been applied successfully to large number of sorption processes[28, 34]. The main assumption of Langmuir isotherm is that adsorption process takes place on a homogeneous sorbent surface having identical sites. Each site has the capacity of binding same numbers of molecules and there exists no interaction between the molecules of adsorbate[35]. The Langmuir equation and its straight line form are written as,

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$$

(8)

$$\frac{1}{q_e} = \frac{1}{K_L.q_m.C_e} + \frac{1}{q_m}$$

(9)

Where q_e is quantity of MB sorbed per gram of sorbent in mg.g^{-1}. Ce is the concentration of MB in solution at equilibrium in mg.L^{-1}.K$_L$ is Langmuir constant in L.mg^{-1}.

A graph was plotted between Ce/qe against Ce as is shown in figure 4(b). The slope of plot is 1/qm and intercept is equal to 1/K$_L$.q$_m$.

The Langmuir isotherm for the adsorption of MB on SC is shown in the figure. The figure suggests that the data fits well to Langmuir model as the value of R^2 is close to unity. The adsorption capacity value calculated was from the isotherm is 1.394mg/g very close to experimental value. The model suggests that there is monolayer adsorption of MB on the SC and no interaction is there between adsorbate molecules.
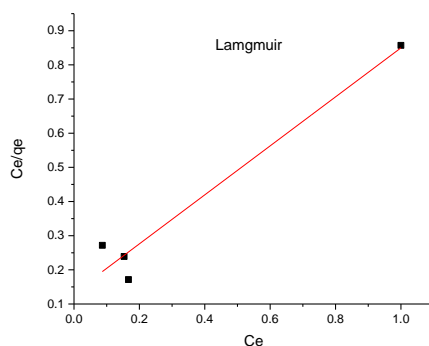

Fig. 4(b). Langmuir adsorption isotherm for sorption of MB

Temkin model is about the fact that heat of adsorption falls linearly for molecules present in same layer due to interaction of the molecules between adsorbate-adsorbent [36]. The isotherm is shown by equation as:

$$q_e = \beta lnKt + \beta \ln Ce \tag{10}$$

Where K$_t$ shows equilibrium binding constant (1/g) and β represents Heat of adsorption [37].
The values of K$_t$& β can be obtained from the plot between q$_e$ and ln Ce. The said graph was plotted as is shown in figure 4(c). The parameters obtained suggested that the data could not be fitted to the model.
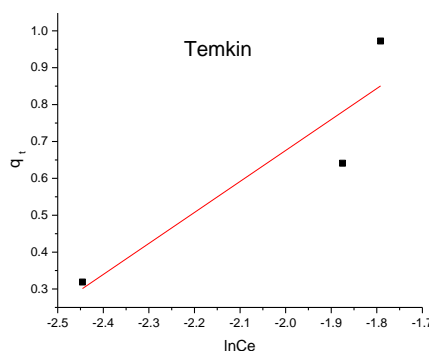

Fig. 4(c). Temkin adsorption isotherm for sorption of MB

To test the Dubinin-Radushkevich isotherm,lnq$_e$ was plotted against ε as is shown in figure 4(d). The D-R equation is,

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{11}$$

In the above equation,

$$\varepsilon = RT \ln(1 + \frac{1}{C_e})$$

D-R equation shows that biosorbent surface is heterogeneous [38].Neither the calculated value of q_m is equal to experimental value nor the value of R^2 near to unity. It is inferred that the data does not fit well to D-R model.
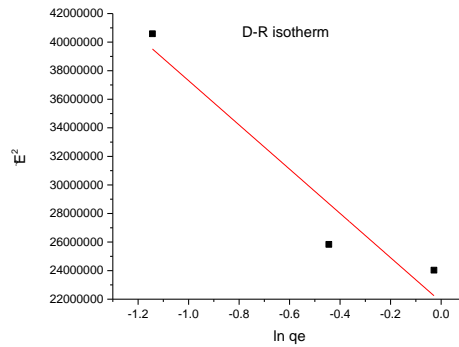

Fig. 4(d): D-R adsorption isotherm for sorption of MB

3.5. Thermodynamics of Adsorption

For the calculation of thermodynamic parameters, following important equations of thermodynamics were used.

$$\ln K_D = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{12}$$

$$K_D = \frac{C_{AS}}{C_e} \tag{13}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{14}$$

$$\Delta G° = -RT \ln K_D \tag{15}$$

Where $\Delta G°$ is change in Gibbs free energy, $\Delta S°$ is Entropy change, $\Delta H°$ shows change in Enthalpy, R is gas constant, K_D is distribution coefficient, C_{As} represents adsorbed quantity of adsorbate, C_e is the quantity of MB at equilibrium.

To calculate thermodynamic parameters, a graph was plotted between $\ln K_D$ and $1/T$ as is shown in figure 5. The values of $\Delta H°$ and $\Delta S°$ were calculated from the slope and intercept of the plot respectively. In the said case of adsorption of MB on SC, the $\Delta H°$ value calculated was positive which indicates that the process is endothermic in nature [39, 40]. The positive value of $\Delta S°$ calculated showed that the movement of MB on the surface of SC is random[41]. The negative value of $\Delta G°$ showed that adsorption of MB on SC is feasible and spontaneous process [42].
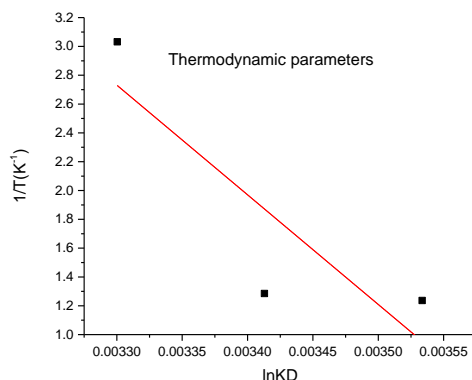
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Fig. 5. Thermodynamic parameters for sorption of MB

4. Conclusions

In the present study, the adsorption of MB on SC was investigated. Contact time of 40 min, pH 6, temperature 303K, and dose 0.3g/50mL were optimum conditions noted for the maximum removal of MB dye by SC. It was noted that maximum MB dye was removed by SC at optimized conditions. Kinetic studies revealed that psuedo second order rate law is followed. Langmuir adsorption isotherm best interpreted the experimental data showing monolayer adsorption process.The values of thermodynamic parameters such as enthalpy change, free energy change,and entropy change showed that the process of adsorption of MB on SC is an endothermic, feasible and spontaneous in nature.

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