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Research Paper

REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTION USING *GREWIA ORBICULATA ROTTL.*: EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES

K Siva Prasada Rao[1]*, M Venkateswara Rao[1] and P Bangaraiah[2]

Corresponding Author: **K Siva Prasada Rao, ✉ sivakrosuri@gmail.com*

Removal of methylene blue, a priority pollutant, is carried out by abundantly and freely available *Grewia Orbiculata Rottl.* leaf powder. The extent of removal depends on initial concentration of methylene blue in the solution, pH of the solution, temperature, etc. The percentage removal increases marginally from pH 1 to 4. A significant increase in percentage removal of methylene blue is observed as pH is increased from 4 to 7.28. As the initial concentration of methylene blue is increased from 5 to 100 mg/l. the percentage removal is decreased from 80% to 35%. Freundlisch and Langmuir isotherm models well describe the data indicating favourable biosorption. The biosorption is endemic, irreversible and follows second-order kinetics, and rate constant is 0.3158 (g/mg-min) for a dosage of 33.33 g/L. The equilibrium agitation time is 30 min.

Keywords: Biosorption, Methylene blue, *Grewia Orbiculata Rottl.,* Thermodynamics, Kinetics

INTRODUCTION

Over the last few decades, society has become increasingly sensitive towards the protection of the environment. Due to this problem, mankind nowadays has concern about the potential adverse effects to the chemical industry on the environment. Dyes and pigments are highly visible material. Thus even minor release into the environment may cause the appearance of color. Dyes can have acute and/or chronic effects on exposed organisms depending on the dye concentration and on the exposure time. In view of these problems, strict environmental regulations on the discharge of dyes are specified. These regulations make it necessary to develop efficient technologies for removal or concentration of dyes. Among the dyes that are present in industrial effluents methylene blue represents one of the major hazardous wastes in environment. Several methods such as fungal

[1] Department of Chemical Engineering, RVR&JC College of Engineering, Chowdavaram, Guntur, AP, India.
[2] Department of Chemical Engineering, Vignan University, Vadlamudi, Guntur, AP, India.

decolorization, microbial degradation, bioremediation, coagulation, electro kinetic coagulation, irradiation or electrochemical process, conventional oxidation methods, membrane processes such as nano filtration, reverse osmosis, ion exchange, electro dialysis, etc., are available for the removal of methylene blue dye from industrial effluents. The capital and operating costs for the removal of dyes using these methods are very high. Adsorption also plays an important role in the removal of dyes from the effluents. Again the effective adsorbents like activated carbon are prohibitively costly at least in developing countries. The treatment costs should be minimized while technical objectives are met. Recently, biosorption has been gaining importance due to its cost effectiveness, performance enhancement and abundant availability. The literature review indicates that *Grewia Orbiculata Rottl.*leaf powder has not been tested for removal of methylene blue from aqueous solution. This biomass can be freely and abundantly available and can be disposed off without regeneration. The present investigation deals with the effectiveness of *Grewia Orbiculata Rottl.* leaf powder to remove methylene blue from aqueous solutions.

MATERIALS AND METHODS

Preparation of Adsorbent

Mature *Grewia Orbiculata Rottl.* leaves are washed with distilled water to remove dust and soluble impurities and dried under sun light till leaves became crisp. The dried leaves are ground and powdered by using domestic mixer and the resulting powder is sieved to different sizes by using BSS standard sieves using rotap sieve shaker. The size fractions—82.5 µm, 97.5 µm, 115 µm, 137.7 µm, 165 µm and 215 µm are preserved in bottles for use as adsorbent.

Preparation of Methylene Blue Stock Solution (Aqueous Solution)

Analytical Reagent grade methylene blue ($C_{14}H_{18}N_3SCl$) dye powder is purchased from Kamphasol (Mumbai). 1 g of powder is dissolved in 1 L of distilled water to prepare 1000 mg/l of stock solution. Samples of different concentrations of methylene blue are prepared from this stock solution by appropriate dilutions— 10 mg/L, 20, 30, 40 50, 60, 80 and 100 mg/L etc.,

Studies on Equilibrium, Kinetics and Thermodynamics of Adsorption

A calibration graph is drawn with different concentrations of methylene blue against absorbance using UV spectrophotometer. Using this standard graph the final concentrations of the methylene blue after adsorption can be calculated.

30 ml of aqueous solution is taken in a 250 ml conical flask and 0.5 g of adsorbent having a size of 82.5 µm is added. This sample is shaken on an orbital shaker at 160 rpm at room temperature for 1 min. Similarly few more samples are prepared in conical flasks and adding 0.5 g of adsorbent and exposed to varying agitation times (2, 4, 8, 12, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60 min). These samples are filtered separately with Whatman filter papers and the filtrates are analyzed in UV spectrophotometer at 665 nm wavelength to obtain final concentrations of methylene blue. The same experimental procedure is repeated for 1 g of adsorbent for various agitation times.

The percentage removal of methylene blue is calculated as $(C_0 - C_t) \times 100 / C_0$. Graphs are plotted between the agitation time and % removal of methylene blue to identify the optimum agitation times for different dosages of the adsorbent.

At the optimum contact time and dosage, different sizes adsorbent is analyzed with similar procedure and found an optimum size of the adsorbent which gives the maximum removal of methylene blue. The amount of solute adsorbed is calculated from the relation $q = (C_0 - C_t)/m$. From these data the equilibrium agitation time, optimum adsorbent size and dosage are identified. The above experimental procedure is repeated at these optimum values b varying pH of the aqueous solution the initial concentrations of methylene blue in the aqueous solution and the volume of the aqueous solution (V) to assess the effects of these parameters on % removal. The order of biosorption is determined by conducting the experiments for agitation time 1 to 50 min. The thermodynamic data of adsorption are obtained by varying temperature of the aqueous solution for different C_0 values. The experimental conditions investigated are shown in Table 1.

RESULTS AND DISCUSSION

The equilibrium agitation time is determined by plotting the % removal of methylene blue against agitation time for different dosages (Figure 1). The % adsorption is found to increase up to 30 min and thereafter, negligible increase in % removal is noticed with agitation time. As the time increases, more amount of methylene blue gets adsorbed onto the surface of the adsorbent and surface area decreases. The adsorbate, normally, forms a thin one molecule thick layer over the surface. When this monomolecular layer covers the surface, the capacity of the adsorbent is exhausted.

Effect of Adsorbent Dosage and Size

The variations % removal of methylene blue from aqueous solution with various particle sizes (82.5 µm, 97.5 µm, 115 µm, 137.5 µm, 165 µm and 215 µm) are obtained at different dosages – 0.5 g and 1 g at the optimum agitation time. The results are shown in Figure 2 with % removal of methylene blue increased as the adsorbent particle size decreases from 215 µm to 82.5 µm. This phenomenon is expected, thereby the number of active sites on the adsorbent are better exposed to the adsorbate. These results are in consistent with the findings reported by some other researchers (Oualid hamdaoui *et al.,* etc.).

The percentage removal of methylene blue is drawn against adsorbent dosage for different adsorbent sizes (82.5 µm and 97.5 µm) in Figure 3. It is evident from the plots that the percentage removal of dye from the aqueous phase

Table 1: xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx	
Parameter	**Values Investigated**
Agitation time, t, min	1, 2, 4, 8, 12, 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60
Adsorbent dosage, w, gm	0.5, 1, 1.5, 2, 2.5 and 3
Adsorbent Size, d_p, µm	82.5, 97.5, 115, 137.5, 165 and 215
Initial methylene blue concentration,C_0,mg/l	5, 10, 15, 20, 30, 40, 50, 60, 80 and 100
Volume of the aqueous solution, V, ml	20, 30, 40, 50, 60, 80 and 100
pH of the aqueous solution	1.0, 2.2, 4, 5.4, 6.2, 7.28, 8.3, 9.6, 11.2, 12.4 and 14
Temperature, K	293, 303, 313, 323, 333 and 343

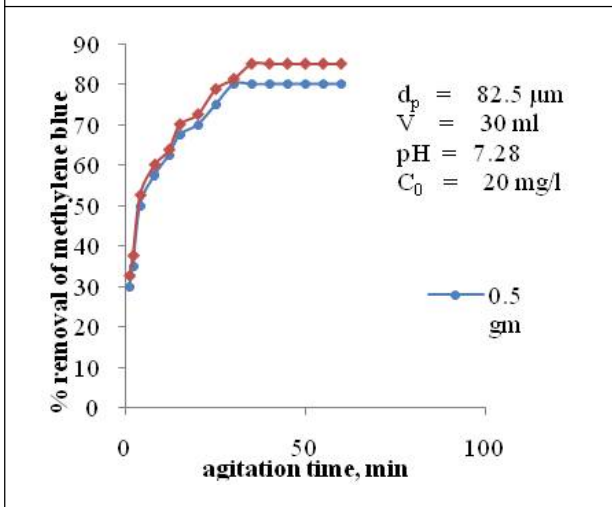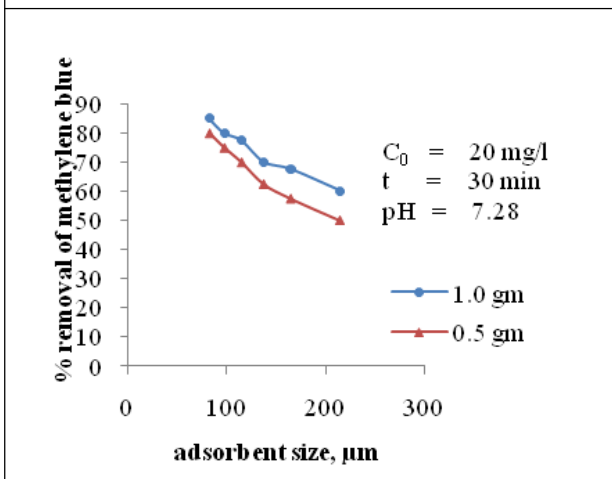**Figure 1: % Removal of Methylene Blue Vs. Agitation Time**

Figure 2: % Removal of Methylene Blue Vs. Adsorbent Size

increases with increase in the adsorbent dosage. % removal of methylene blue from the aqueous solution increases from 72.5% to 90% for the adsorbent size 82.5 µm, as dosage increased from 0.5 g to 3 g. Such behavior is obvious because the number of active sites available for dye removal would be more as amount of the adsorbent increases. The change in % removal of methylene blue is marginal when 'w' is increase from 1.0 g to 3 g. So all the other experiments are conducted at w = 1 g and 0.5 g. The results

Figure 3: % Removal of Methylene Blue Vs. Adsorbent Dosage
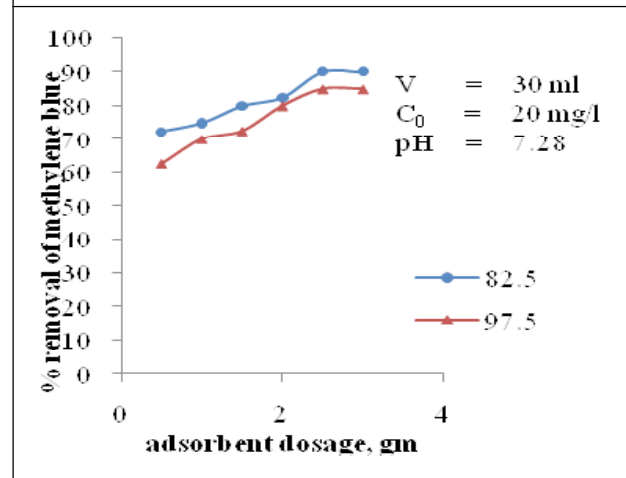
are in consistent with the findings reported by some other researchers (Sarigolu *et al.*, ZohreShahryari *et al.*, etc.).
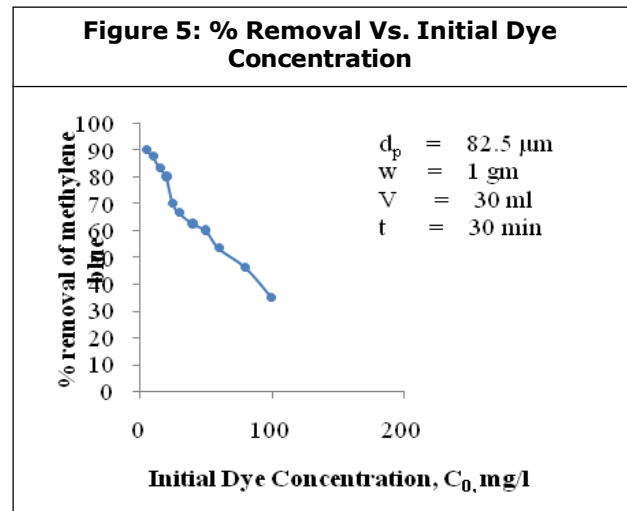
Effect of pH

pH influences the surface charge of the adsorbent, the degree of ionization and the species of adsorbate. So, pH is an important factor controlling the process of adsorption. In the present investigation, adsorption data are obtained in the pH range of 1 to 14 for methylene blue initial concentration of 20 mg/l and 1 gm of 82.5 µm size adsorbent. The effect of pH of the aqueous solution on % removal of methylene blue is drawn in Figure 4. The % removal methylene blue dye is increased from 65% to 95% as pH is increased from 1 to 7.28. The graph reveals that % removal increased significantly from 4 to 7.28 (72.5 to 90). Increase in the percentage adsorption is marginal for values 1 to 4. This is due to partial hydrolysis of ions resulting in the formation of $M(OH)+$ and $M(OH)_2$. $M(OH)_2$ would have been adsorbed on the non polar surface than on $M(OH)+$. The % removal is decreased for pH value above 7. In the present investigation, the maximum % removal of methylene blue is

Figure 4: % Removal of Methylene Blue Vs. pH

Figure 5: % Removal Vs. Initial Dye Concentration
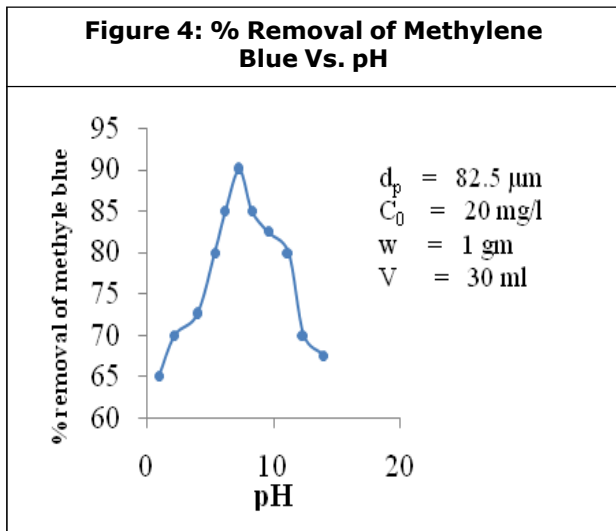
obtained for 1 g of 82.5 μm size adsorbent at optimum agitation time. The principal driving force for dye ion adsorption is the electrostatic interaction (i.e.) attraction between adsorbent and adsorbate. The greater the interaction, adsorption of dye will be more. With an increase in interaction, the dye ions replace H^+ ions bound to the adsorbent for forming part of the surface functional groups such as –OH, -COOH, etc. As the electro-negativity of *Grewia Orbiculata Rottl.* leaf powder is greater, more methylene blue ions are adsorbed. The results are in consistent with the findings reported some other researchers (Ansari *et al.*, Oualid hamdaoui *et al.*, etc.).

## Effect of Initial Concentration of Methylene Blue

The effect of initial concentration of methylene blue in the aqueous solution on the percentage removal of methylene blue is shown in Figure 5. The percentage removal of methylene blue is decreased from 90% to 35% by increasing the initial concentration of methylene blue in the aqueous solution from 5 mg/l to 100 mg/l. Such behavior can be attributed to the increase in the amount of adsorbate to the unchanging number of available active sites on the adsorbent (since

the amount of adsorbent is kept constant). The results are in consistent with the findings reported by other researchers (ZohreShahryari *et al*, Changwei Hu *et al*, Silmani *et al* etc.)

Effect of Volume of the Aqueous Solution

Change in % removal of methylene blue with variation in the volume of the aqueous solution from 20 ml to 100 ml is shown in Figure 6, for an adsorbent dosage of 1 g of 82.5 μm size for an optimum agitation time of 30 min. From these plots, it is clear that % removal of methylene blue is gradually decreased from 95% to 65%. As the volume of the aqueous solution increases, the amount of methylene blue present in the solution

**Figure 6: % Removal Vs. Initial Dye Concentration**
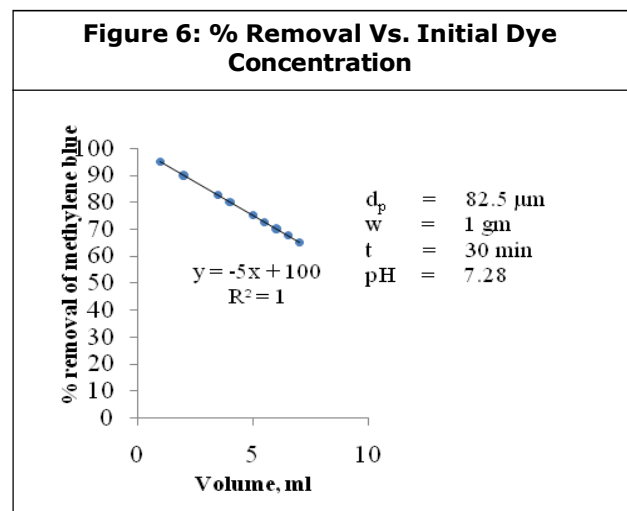
also increases. This implies that % removal by unaltered surface area of adsorbent decreases as the amount of methylene blue in the solution is increased.

Sorption Isotherms

The adsorption isotherm is an equilibrium relation between the concentration of dye in the fluid phase and its concentration on the adsorbent at a give temperature. The Freundlich relationship: $q_e = K_f C_e^n$ is an empirical equation. It does not indicate a finite uptake capacity of the adsorbent and can thus only be applied in case of low and intermediate concentration ranges. It can be anticipated as first pointed out by Langmuir that chemisorbed adsorbate layers may be only one molecule thick. The relationship $q_e / q_m = b C_e / (1+b C_e)$ can be rearranged as $(C_e / q_e) = 1/bq_m + C_e/q_m$. From the plots between (C_e/q_e) and C_e, the slope $(1/q_m)$ and the intercept $(1/bq_m)$ can be calculated. Further analysis of Langmuir equation is made on the basis of separation factor R_L and $0 < R_L < 1$, indicates favorable adsorption.

Freundlisch isotherm for the present data is drawn between log Ce and log qe (Figure 7). The data are well represented by log qe = 0.584 logCe – 0.966 and has a correlation coefficient of 0.993.

Figure 7: Freundlisch Isotherm
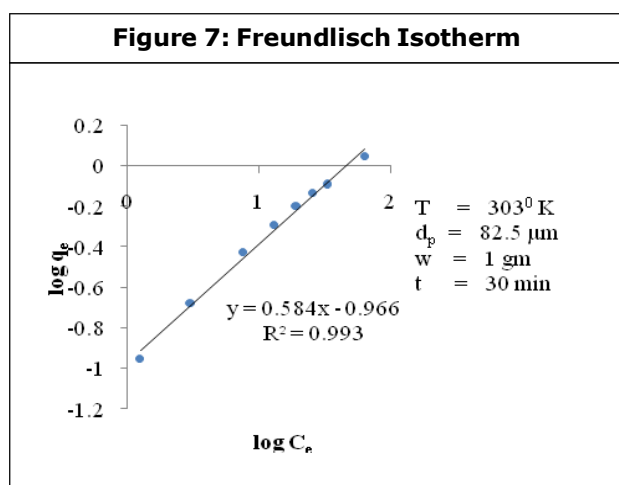
'n' and Kf values obtained in the present study are 0.584 and 0.108 L/g respectively at 303 K. The 'n' value satisfies condition 0<n<1 indicating the favorable adsorption. Langmuir isotherm is shown in Figure 8, and the data are represented by the equation Ce/ qe= 0.730 log C_e + 14.1. The linearity of 0.98 indicates the applicability of isotherm for biosorption of methylene blue. The q_m values 1.2897 mg/g at 303 K. The separation factor (R_L) value of 0.398 confirms favorable biosorption (0<R_L<1). Hence, the present data can well be explained by Freundlisch isotherm as well as by Langmuir isotherm. The q_m and R_L values are well consistent with the results of other biosorption authors.

Figure 8: Langmuir Isotherm
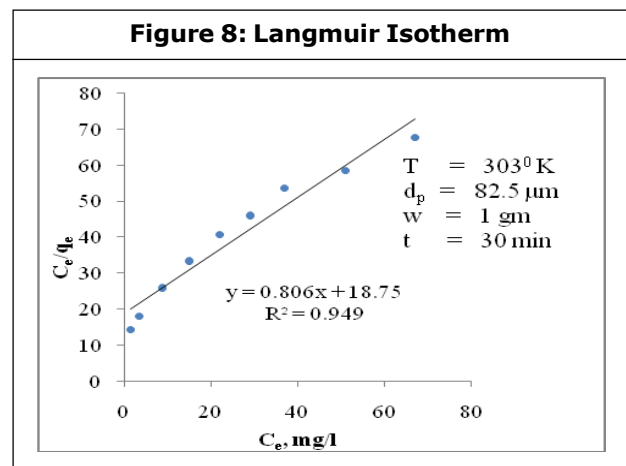
Kinetics

The order of adsorbate-adsorbent interaction has been described by using various kinetic models. Traditionally, the pseudo first order model derived by Lagergran[7] finds wide application. On the other hand, several authors have shown that pseudo second order kinetics also describe these interactions very well in certain specific cases. In the case of adsorption preceded by diffusion through a boundary, the kinetics in most cases follows the pseudo first order rate of equation of Lagergren: *(dq_t/dt) = K_{ad} (q_e − q_t)*.

This can be written as:

log (q$_e$ − q$_t$) = log q$_e$ = (K$_{ad}$/2.303) t.
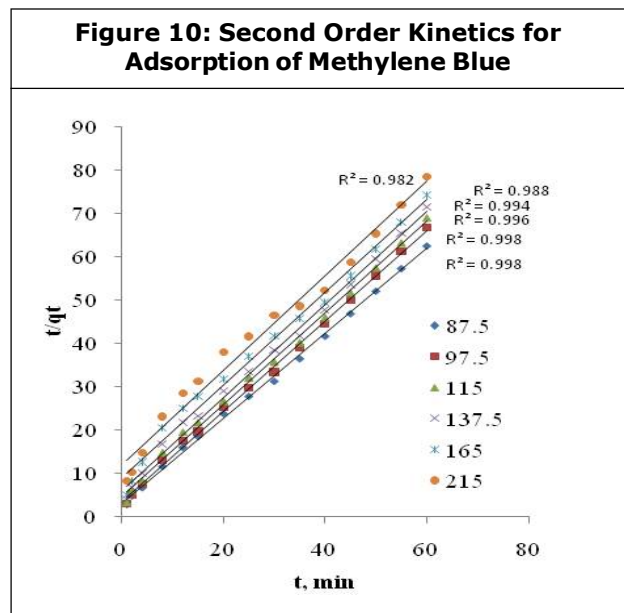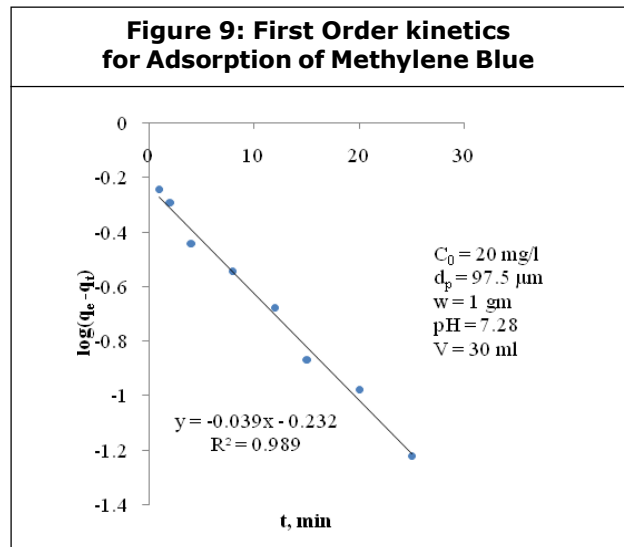
Plot of log (qe− qt) vs t gives a straight line for first order kinetics, which allows computation of the adsorption rate constant, K$_{ad}$. If the experimental results do not follow the above equations, they differ in two aspects. (i) K$_{ad}$ (q$_e$ − q$_t$) then does not represent the number of available adsorption sites; and (ii) log q$_e$ is not equal to the intercept of the plot of log (q$_e$ − q$_t$) against t. In such cases pseudo second order kinetics is given by

(dq$_t$/dt) = K (q$_e$ − q$_t$)^2

i.e. (dq$_t$ / (q$_e$ − q$_t$)^2) = K dt

Integrating the above equation and by rearranging we get (t/q$_t$) = 1/K q$_e$^{2} + 1 / q$_e$ t.

If the pseudo second order is applicable, the plot of (t/q$_t$) vs. t gives a linear relationship that allows computation of q$_e$ and K. In the present study the kinetics are investigated with 30 ml of aqueous solution containing initial concentration of methylene blue of 20 mg/l at different adsorbent dosages and at different adsorbent sizes. Lagergren plot of log (q$_e$ − q$_t$) versus agitation time t for adsorption of methylene blue by *Grewia Orbiculata Rottl.*leaf powder is drawn in Figure 9, but the plot is not linear in nature. Hence, pseudo first order kinetics cannot describe the adsorption mechanism of methylene blue – *Grewia Orbiculata Rottl.* leaf powder interactions. The pseudo second order model based on equation which considers the rate – limiting step as the formation of chemisorptions bond involving sharing or exchange of electrons between the adsorbate and adsorbent is therefore applied. The (t/q$_t$) vs. t for the present data is indicated in Figure 10. The linearity of the plots (R = 0.99) confirms

Figure 9: First Order kinetics for Adsorption of Methylene Blue

$C_0 = 20$ mg/l
$d_p = 97.5$ μm
w = 1 gm
pH = 7.28
V = 30 ml

y = -0.039x - 0.232
R^2 = 0.989

Figure 10: Second Order Kinetics for Adsorption of Methylene Blue

R^2 = 0.982
R^2 = 0.988
R^2 = 0.994
R^2 = 0.996
R^2 = 0.998
R^2 = 0.998

◆ 87.5
■ 97.5
▲ 115
✕ 137.5
✱ 165
● 215

Table 2: Kinetic Orders for Different Methylene Blue – Adsorbent Interactions

Adsorbent	Order	Reference
Acid Activated Algerian Bentonite	Second	[8]
Treated Sawdust	First	[9]
Activated carbon prepared from palm kernel shell	Second	[10]
Animal bone meal	First	[6]
Wheat Bran	Second	[1]

the suitability of pseudo second order rate equation.

The following second order rate equations are obtained from graphs:

For w = 1 g, d_p = 82.5, 97.5, 115, 137.5, 165 and 215 µm

(t/q_t)=0.981 t + 3.046q_e= 0.9598 R^2=0.998

(t/q_t)=1.042 t + 3.438q_e= 0.8998 R^2=0.998

(t/q_t)=1.059 t + 4.677q_e= 0.8698 R^2=0.996

(t/q_t)=1.077 t + 5.940q_e= 0.8398 R^2=0.994

(t/q_t)=1.091 t + 11.97q_e= 0.8098 R^2=0.982

(t/q_t)=1.091 t + 11.97q_e= 0.7648 R^2=0.982

THERMODYNAMICS OF ADSORPTION

During adsorption process, many changes occur and they can be explained by the three main important thermodynamic parameters enthalpy of adsorption (ΔH), entropy of adsorption (ΔS) and Gibbs free energy (ΔG) due to transfer of unit more of solute from solution to the solid – liquid interface.

The Vanthoff's equation is

$\log(q_e/C_e)$ = -(ΔH/2.303R)T + (ΔS/2.303R)

Figure 11: Thermodynamic studies
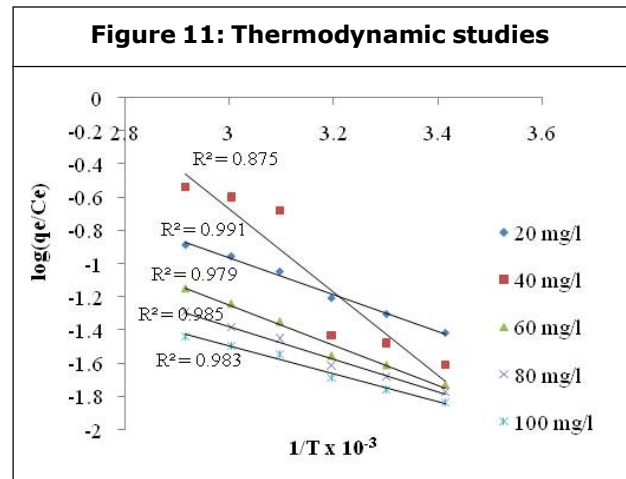
ΔH and ΔS values are calculated from the plots between $\log(q_e/C_e)$ and (1/T) as

Slope = ΔH/2.303R and

Intercept = ΔS/2.303R

Gibbs free energy (ΔG) is related to ΔH and ΔS as $\Delta G = \Delta H - \Delta S$

The adsorption data obtained for w = 1 g, d_p = 82.5 µm at different temperatures and initial concentrations of the methylene blue and shown in Figure 11.

In the present study, the positive value of enthalpy indicates that the adsorption process is endothermic in nature and the physical sorption play a role in adsorption of methylene blue and can easily be reversed by applying heat [equal to

S. No.	Initial Conc.C_0, mg/l	ΔS, J/mol-K	ΔH J/mol	ΔG at Different Temperatures kJ/mol					
				293 K	**303 K**	**313 K**	**323 K**	**333 K**	**343 K**
1	20	44.938	21.1384	13.145	13.595	14.044	14.493	14.943	15.392
2	40	131.656	48.155	38.53	39.84	41.16	42.48	43.79	45.11
3	60	45.8	23.245	13.4	13.85	14.31	14.77	15.23	15.69
4	80	30.39	18.92	8.88	9.19	9.49	9.8	10.1	10.4
5	100	19.28	15.95	5.63	5.82	6.02	6.21	6.4	6.6

Table 3: Thermodynamic Data at Various Temperatures

calculated (ΔH) value] to the adsorption system. The value of entropy above zero confirms the irreversibility of the adsorption process. The negative value of Gibbs free energy shows the reaction as spontaneous. The values of (ΔH), (ΔS) and (ΔG) obtained in the present investigation for different initial concentrations of methylene blue are shown Table 3.

CONCLUSION

The *Grewia Orbiculata Rottl.* leaf powder can be used as an effective adsorbent for the removal of Methylene Blue from its aqueous solutions. The equilibrium agitation time for the methylene blue adsorption onto *Grewia Orbiculata Rottl* .is 30 min. The percentage removal of methylene blue from the aqueous solution increases with a decrease in the particle size of the adsorbent. The percentage removal of methylene blue from aqueous solution is augmented with increase in weight of the adsorbent. Higher the concentration of methylene blue in the aqueous solution, the percentage removal of methylene blue from the aqueous solution is decreased. Percentage removal of methylene blue from aqueous solution is increased significantly with increase in pH value from 4 to 7.28. Increase in % removal is marginal between pH values 1 to 4. The % removal decreases for pH beyond 7.28. The data are well represented by Freundlich and Langmuir isotherms indicating favorable adsorption of methylene blue by the adsorbent. The kinetic studies show that the adsorption of methylene blue is better described by pseudo-second order kinetics. The thermodynamic data show that percentage adsorption increases with increase in temperature. The experimental data indicate that sorption process is endothermic. The adsorption process is found to be irreversible and spontaneous.

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APPENDIX

Nomenclature	
C_0	Initial concentration of methylene blue in aqueous solution, mg/l
C_t	Concentration of methylene blue in aqueous solution after t min, mg/l
C_e	Equilibrium adsorption concentration of methylene blue, mg/l
t	Agitation time, min
T	Absolute temperature, K
W	Adsorbent dosage, coagulant dosage, gm
B	Langmuir equilibrium constant
N	Freundlich constant for methylene blue in the aqueous solution
d_p	Adsorbent size, μm
V	Volume of aqueous solution, ml
M	Amount of adsorbent taken per 1 L of aqueous solution, mg/L
q_e	Mass of solute adsorbed per mass of adsorbent at equilibrium, mg/gm
q_t	Mass of solute adsorbed per mass of adsorbent at t min, mg/gm
q_m	Langmuir monolayer capacity, mg/g
K	Second order rate constant, g/mg. min
K_f	Freundlich coefficient for methylene blue in aqueous solution, 1/g
K_{ad}	First order rate constant, min^{-1}
ΔG	Change in Gibbs free energy, kJ/mol
ΔS	Entropy change, J/mol-K
ΔH	Heat of reaction, J/mol
R_L	Separation factor