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Evaluation of Adsorption Efficiency of *Ferronia elefuntum* Fruit Shell for Methylene Blue from Aqueous Solution

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Methylene blue adsorption from an aqueous solution on to *Ferronia elefuntum* fruit shell (FEFS) has been studied experimentally using the batch adsorption method. The operating variables studied are pH, initial dye concentration contact time. Adsorption isotherm (Langmuir and Freundlich) and kinetics model were studied. The adsorption capacity of FEFS was found to increasing with increase in temperature, thermodynamics parameters such as ΔG, ΔH and ΔS for adsorption were evaluated. Adsorption of methylene blue on FEFS found to be endothermic process. The aim of present work is to study the effectiveness of the adsorbent to remove dyes from their aqueous solution and the removal of colour from textile and various industrial wastewater.

Key Words: Adsorption, *Ferronia elefuntum* fruit shell, Methylene blue, Adsorption kinetics, Thermodynamics adsorption isotherm.

INTRODUCTION

The retrieval of colour from industrial effluent is a major problem as restriction become more stringent. Effluents from textile pulp and paper industries are highly coloured due to residual dyes and thus lower the aesthetic value structure and are toxic and harmful for aquatic and human life[1-3]. The presence of colour in water inhibits the growth of aquatic fauna and flora by reducing light penetration. Various techniques, such as chemical, coagulation, bio-sorption, oxidation using ozone and adsorption have been generally employed for retrival of colour. Adsorption is one of the most effective physical process and has a great potential for the removal of dyes from wastewater[4,5]. The aim of this study is to prepare activated carbon from *Ferronia elefuntum* fruit shell and adsorption isotherm was developed for methylene blue dye, which can be readily used to designing purposes in pollution amendment and control.

EXPERIMENTAL

Absorbent preparation: The adsorbent *Ferronia elefuntum* fruit shell (FEFS) was colleted from the Pandhari forest situated in between Warud and Padhurna. The *Ferronia elefuntum* fruit shell was first dried at 160 ºC for 6 h. After grinding, it was soaked overnight in 0.1 N NaOH solution to remove the lignin content, excess alkalinity was then neutralized with 0.1 N HCl solution. It was washed with distilled water several time till the wash water become colourless. Then it was kept in muffle furnace at 130 ºC for 6 h. It was sieved to obtain average particle size of 200 mesh. Finally it was dried again in an over at 50 ºC for 6 h. The adsorbent was then stored in desiccators for final studies.

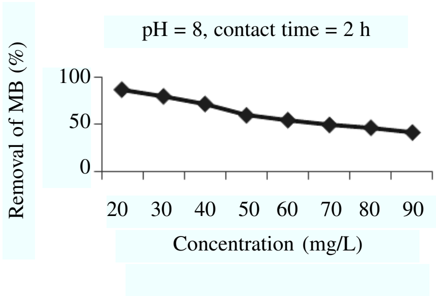

Fig. 1. Effect of initial concentrations

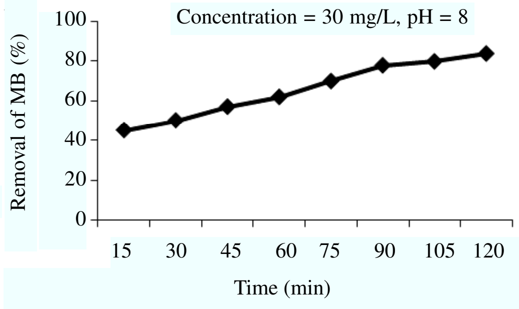

Fig. 2. Effect of contact time

Adsorbate preparation and batch study: Stock solution (1000 mg/L) of methylene blue was prepared by dissolving 1 g of dye in 1000 mL of double distilled water. The stock solution were diluted with double distilled water to obtain required standard solution. The dried amount of 0.2 g of *Ferronia elefuntum* fruit shell was take in 250 mL reagent bottle and standard solution (100 mL) containing various concentration of methylene blue dye was added and system is equilibrated by shaking the contents of the flask at room temperature. The adsorbent and adsorbate were separated by filtration and filtrate was determined by spectrophotometer at 665 nm a against a reagent blank. The spectrophotometer systrornic (model 104) was used to measure the concentration of methylene blue.

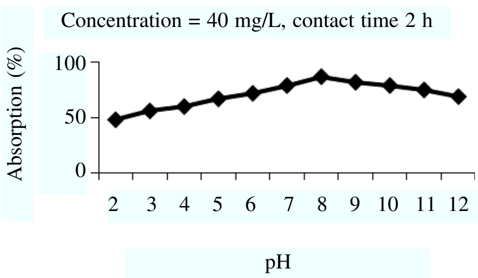

Fig. 3. Effect of pH

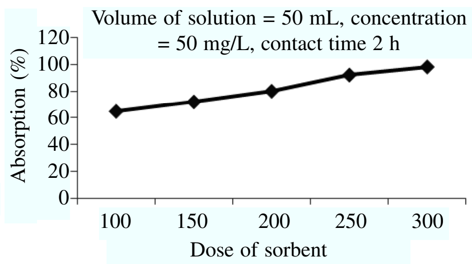

Fig. 4. Effect of sorbent dose

Effect of pH on the scavenging the dye was studied using 100 mL dye solution having 40 mg/L initial concentration. Effect of initial concentration, agitating time and adsorbent dose was also studied (Figs. 1-4).

Adsorption dynamics: To investigate the mechanism of sorption, three kinetic models were tested including Lagergren, pseudo second order and Elovich model[6-9].

Lagergren model: The rate of sorption of methylene blue dye on *Ferronia elefuntum* fruit shell was studied by using first order lagergren kinetic equation[10].

$$\log (q_e - q_t) = \log q_e - (kt/2.303)t$$

where q_e = amount of dye adsorbed at equilibrium (mg/g), q_t = amount of dye adsorbed at time (mg/g) and k_L = rate constant for first order adsorption (min).

The plot of log $(q_e - q_t)$ *versus* t is shown in Fig. 5.

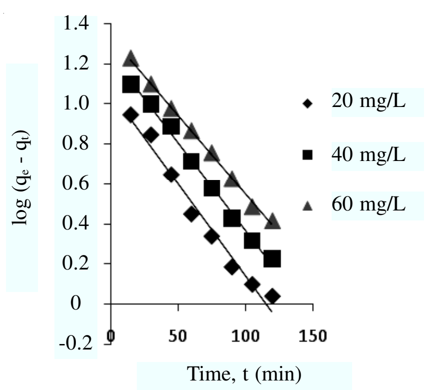

Fig. 5. Lagergren plot

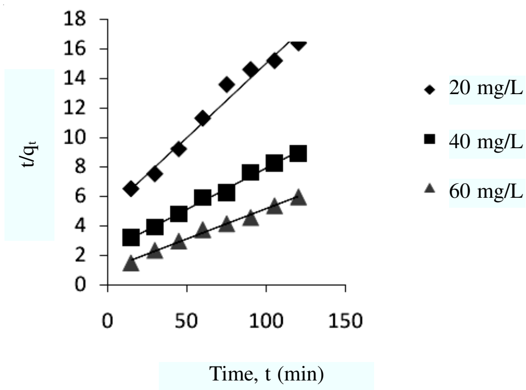

Fig. 6. Pseudo second order model

Pseudo second order model: To study dye sorption, modified pseudo second order equation is expressed as follows.

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2$$

where q_e = amount of dye adsorbed at equilibrium, q_t = amount of dye adsorbed at time t (mg/g) and K_2 = rate constant for pseudo second order adsorption (g/mg/ min).

Integrated form of equation is as follows.

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t$$

Linear form of equation can be expressed as

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} \times t$$

Thus, a plot of t/q_t *versus* t of above equation should give a linear relation (Fig. 6) with a slope of $1/q_e$ and an intercept of $= 1/K_2 \times q_e^2$.

Elovich model: Elovich or Roginsky zeldovich equation is generally expressed as follows[11]

$$\frac{dq_{(t)}}{dt} = \propto e^{-Bq}$$

integrated form of this equation is $q_t = 1/\beta \ln (\propto\beta) + 1/\beta \ln (t + to)$ if to << t, then this equation become $q_t = 1/\beta \ln (\propto\beta) + 1/\beta \ln t$.

A plot of q_t *versus* ln t gives a straight line, from which $\propto$ and β were calculated (Fig. 7).

Isotherm models: The adsorption capacity of *Ferronia elefuntum* fruit shell for methylene blue dye was determined by measuring equilibrium isotherm of this dye. Methylene blue is cataonic in nature. Equilibrium adsorption isotherm plot for C_e *versus* q_e plotted for *Ferronia elefuntum* fruit shell and methylene blue.

From plot the adsorption capacity in mg/L was calculated. Then the equation.

$$Q_e = (C_o - C_e)\ V/M$$

where, C_o = initial concentration of methylene blue, C_e = concentration of methylene blue at equilibrium in mg/L, V = volume of solution in liter and M = mass of adsorbent in grams.

Equilibrim isotherms was studied for both Langmuir and Freundlich isotherms. The result are shown in Figs. 8 and 9 which, illustrate the plot of Langmuir and Freundlich isotherm of methyle blue on *Ferronia elefuntum* fruit shell. The saturated monolayer can be represented by:

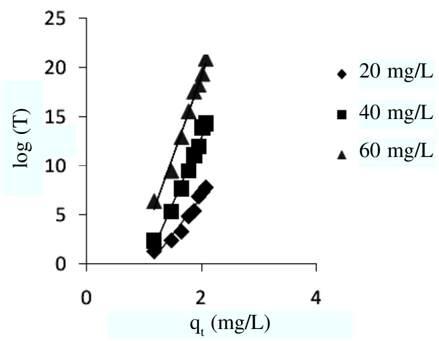

Fig. 7. Elovich plot-initial ion concentrations variations

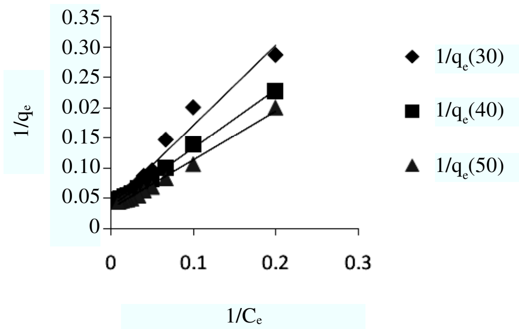

Fig. 8. Langmuir isotherm

$$q_e = \frac{Q^0 \cdot b \cdot C_e}{1 + bC_e}$$

The linearized form of the Langmuir isotherms is

$$\frac{1}{q_e} = \frac{1}{Q^0 b} \times \frac{1}{C_e} + \frac{1}{Q^0}$$

where Q^0 and b are Langmuir constants. The plot of $1/C_e$ *versus* $1/q_e$ was found to be linear indicating the applicability of Langmuir model. The parameter Q^0 and b have been calculated and presented in Table-1. Langmuir constant Q^0 is a measure of adsorption capacity and b is the measure of energy of adsorption. In order to observe whether the adsorption is favourable or not, a dimensionless parameter 'R' obtained from Langmuir isotherm is.

$$R = (1 + b \times C_m)^{-1}$$

TABLE-1
KINETIC MODEL VALUE FOR ADSORPTION OF METHYLENE BLUE ON FEFS

Concentration (mg/L)	1st order			Pseudo second order			Elovich		
	K_L	q_e	r^2	q_e	k_2	r^2	$\propto$	β	r^2
20	0.02070	8.60	0.978	10.0210	0.0018	0.9900	0.5948	0.1306	0.9897
40	0.01840	15.40	0.994	18.1820	0.0013	0.9921	1.2060	0.0732	0.9850
60	0.01612	22.10	0.998	24.390	0.0015	0.9923	2.446	0.0605	0.9860

where b is Langmuir constant and C_m is maximum concentration used in the Langmuir isotherm. The adsorption of methylene blue on FEFS favourable process as "R" values lies between zero to one. Coefficients of co-relation (r) are also shown in Table-2. The applicability of Freundlich isotherm was also tried using the following general equation.

TABLE-2
ISOTHERMAL CONSTANTS

Temperature (ºC)	Langmuir constants				Freundlich constants		
	b (L/mg)	Q^0 (mg/g)	R_L	r^2	1/n	k_f	r^2
30	0.0372	26.89	0.7710	0.969	0.579	1.549	0.933
40	0.0373	27.77	0.6346	0.997	0.495	2.455	0.982
50	0.0394	31.25	0.5341	0.991	0.452	3.273	0.979

$$q_e = k \cdot C_e B$$

linearised form of this equation is

$$\log q_e = B \cdot \log C_e + \log k$$

where B and k are Freundlich constants. These constants represent the adsorption capacity and the adsorption intensity, repectively.

Plot of log q_e *versus* log C_e was also found to be linear. The values of B and k are presented in Table-2. Since the values of B are less than 1, it indicates favourable adsorption.

RESULTS AND DISCUSSION

Effect of initial dye concentration and contact time: The initial concentration of methylene blue solution was varied from 20, 30, 40 and 60 mg/L and batch experiments were carried out by taking 200 mL of this solution with dried 200 mg of the adsorbent and the system is equilibrated by shaking the contents of the flask at room temperature, equilibrium reached in 2 h. Final concentration of methylene blue was determined by spectrophotometer at 665 nm. The percentage removal of methylene blue was observed to be 87 %. To establish equilibrium time for maximum uptake and to know the kinetics of adsorption process, the adsorption of methylene blue on adsorbent was studied as a function of contact time. Percentage removal of dye is found to decrease with increase in dye concentration. From contact time data it may be seen that dye removal is rapid during initial period of contact and the maximum are reached within the first 0.5 h removal.

Effect of pH: The adsorption capacity of methylene blue as a function of pH is plotted in Fig. 3. It was observed that percentage removal of methylene blue is maximum at pH = 8 and then decrease with increase of pH.

Effect of sorbent dosage: Batch sorption studies were performed to determine the effect of sorbent dosage on methylene blue removal (Fig. 4). The per cent removal increase rapidly and reaches about 95 %. For 100 % removal of the methylene blue, the dosage required is 300 mg/50 mL for the initial concentration of 50 mg/L at pH = 8.0.

Sorption kinetics: The rate of adsorption of methylene blue on *Ferronia elefuntum* fruit shell was studied by using the first order kinetic model, pseudo second order kinetic and Elovich models are used to test the experimental data.

First order kinetics: The rate of adsorption of methyle blue on FEFS was studied by using the first order rate equation proposed by Lagergren (Fig. 5). It is found that as initial dye concentration increases, Lagergren rate constant decrease. This indicate that adsorption does not follow the 1st order kinetics.

Pseudo second order models: Fig. 6 shows pseudo second order model and it is found that, rate constant K_2 is almost constant at different initial concentration which is shown in Table-1. This indicate that adsorption of methylene blue on *Ferronia elefuntum* fruit shell obey the 2nd order kinetics. Also the concentration of methylene blue increasing from 20-60 mg/L, equilibrium sorption capacity q_e increase.

Elovich model: Adsorption of methylene blue an *Ferronia elefuntum* fruit shell are shown in Fig. 7. A linear relationship is obtained betn the amount of methylene blue adsorbed, q_t and lnt. From the Table-1, show that value of $\propto$ and β varied as a function of methylene blue concentration. As the concentration of methylene blue increases from 20-60 mg/L value of $\propto$ increase and β decreases. This favoured the adsorption phenomenon.

Isotherm modeling

Langmuir adsorption isotherm: The Langmuir sorption isotherm is shown in Fig 8 and given in Table-2. Q_o values found to be comparable with commercial activated carbon. Value of R_L lies between 0 and 1 indicate the favourable adsorption. It indicates the applicability of Langmuir adsorption isotherm. The calculated value r^2 confirm the applicability of Langmuir adsorption isotherm.

Freundlich adsorption isotherm: Freundlich plot for the adsorption of methylene blue on *Ferromia elefuntum* fruit shell is given in Fig. 9 and the result of Freundlich plot are given in Table-2. It show that the values of adsorption intensity $1/n < 1$, reveal the applicability of Freundlich adsorption.

Thermodynamics parameters: The influence of temperature upon the adsorption rate was investigated at 30, 40 and 50 ºC. It is observed that mass of the methylene blue adsorbed per unit mass of adsorbent increase with increasing temperature. The heat of adsorption was calculated by plotting a graph of ln K_L, *versus* reciprocal of temperature as show in Fig. 10. The negative value of free energy change ΔG indicates the feasibility and spontaneous nature of adsorption of methylene blue. ΔH value suggests endothermic nature of methylene blue on *Ferronia elefuntum* fruit shell. Positive value of ΔS is due to increase randomness during adsorption of methylene blue.

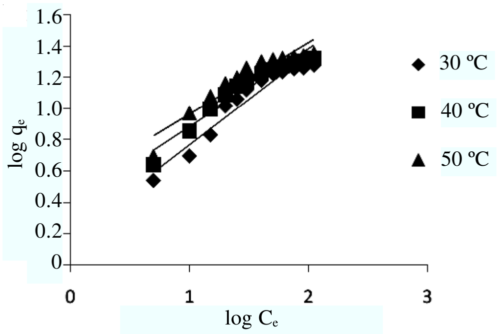

Fig. 9. Fruendlich isotherm

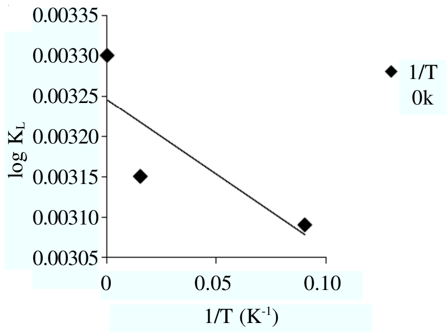

Fig. 10. Vant Hoff's plot

TABLE-3
THERMODYNAMICS PARAMETERS

Temperature (ºC)	ΔH	ΔS	ΔG
30			-0.75420
40	0.1914	0.05744	-91.54880
50			-560.36000

Conclusion

Ferronia elefuntum fruit shell was studied as good adsorbent for removal of methylene blue. The removal is found rapid in initial stage followed by slow adsorption up to saturation level. It also depend an initial concentration of adsorbate and agitating time. The present work on adsorption process is in good agreement with Langmuir and Freundlich isotherm indicating monolayer adsorption process. The result of adsorption process reveals that at pH = 8, methylene blue uptake capacity is better. The adsorption of methylene blue an FEFS followed the pseudo second order model and Elovich model.

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