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Removal of Methylene Blue Dye from Aqueous Solution by Using *Cestrum nocturnum* Leaves, as a Low Cost Adsorbent

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Abstract: In textile industries, Methylene blue (M.B.) dye is used for dyeing cotton and woolen silk fabrics. This dye is hazardous and responsible for severe water pollution. The present study focuses on effective removal of M.B. dye using *Cestrum nocturnum* leaves as an adsorbent by batch adsorption process. The effect of various parameters viz. pH, contact time, adsorbent dose, particle size, concentration and temperature on removal of dye have been studied. The adsorption efficiency of *Cestrum nocturnum* leaves was found to increase after chemical treatment of the leaves. The adsorption study, revealed that effective removal of the M.B. dye (4 ppm), was found to be 99.6% at pH 5, contact time 35 min., adsorbent dose 0.01gm and particle size 105µm. *Cestrum nocturnum* leaves were found to be potential novel adsorbent for the removal of M.B. from aqueous solution. Its adsorption followed pseudo second order kinetics. Adsorbed dyes can be effectively recovered using 0.1N HCl as an eluent. Thermodynamic analysis showed negative values of ΔG and Δ**S** indicating adsorption was favorable and spontaneous, Negative value of ΔH indicates sorption process was exothermic.

Keywords: Adsorption, Methylene Blue, *Cestrum nocturnum* leaves, Kinetics thermodynamics

1. INTRODUCTION

Rapid progress in industrial activities leads to discharge of large amount of unprocessed wastewater containing synthetic dyes which pollutes aquatic environment and consequently affect flora and fauna. Wastewater containing dyes are very difficult to treat. The dyes are organic molecules, resistant to photolysis and biological degradation[1,2]. There are various methods for the removal of effluents. Dyes can be removed by three different processes: biological, chemical and physical processes. Wastewater treatment using biological process is conventional and most economical as compared to other chemical and physical processes[3, 4]. Various types of physical methods are also successfully tested, such as membrane-filtration processes (nanofiltration, reverse osmosis, electrodyalysis) and adsorption processes[5,6]. Dye containing wastewater cannot be effectively treated by traditional methods, because of the high cost and disposal problems for treating dye containing wastewater at large scale industries[7-9.] Adsorption is the most effective technique and a well-known equilibrium separation process for dye removal from wastewater. Adsorption has been found to be superior to other techniques in terms of initial cost, simplicity of design and ease of operation[8]. Cost effective natural adsorbents were used for removal of hazardous dye such as MB, Crystal Violet[10, 11] and Reactive Red-120. MB is one of the most toxic industrial pollutants even at low concentrations. Therefore, it affects public health and causes many serious environmental problems. Hence, it is important to remove this dye effectively from the environment.

2. MATERIALS AND METHODS

The leaves of *Cestrum nocturnum* were collected from home garden. The MB dye used in this study was obtained from Fisher Scientific (Qualigens fine chemicals).

2.1. Preparation of adsorbent: The leaves of *Cestrum nocturnum* were washed under tap water to remove any dust or dirt adhered on the leaves. The leaves were soaked with 1:1 ortho-phosphoric acid for 24 hours and filtered through whatman filter paper 42. The treated leaves were boiled and washed with distilled water to remove organic component such as pigment. They were stored in air tight glass container.

2.2. Batch Adsorption process: Batch Adsorption process is used to study the removal of dye. The various parameters viz. pH, concentration, adsorbent dose, particle size and contact time were optimized to obtain maximum removal of dye. Thermodynamic and Kinetic studies were carried out at optimized conditions.

2.3. Characterization of adsorbent: *Cestrum nocturnum* adsorbent was characterized by various techniques. The IR spectrum of adsorbent before and after adsorption was studied using FTIR spectrophotometer (Shimadzu 8400) in the range of 4000-400 cm^{-1} using KBr disk for reference. Surface morphology of adsorbent, before and after adsorption was studied by Field Emission Scanning Electron Microscopy (FET Nova nanoSEM-450). The energy dispersive spectrum (Brouker SLASH-6130) X-ray detector measures number of emitted X-ray as a function of energy which helps determination of the elements present in the sample. It was evaluated from spectrum of the energy as function of relative counts of the detected X-rays.

2.4Adsorption of Dye: Adsorbent was dried at 333 K for one hour before use. 25 ml of desired conc. of MB was stirred for 30 minutes after addition of 0.01g adsorbent. A parameter to be optimized was varied while others were kept constant. Then solution was centrifuged for 10 minutes and filtered through whatman filter paper 42. Filtrate thus obtained was analyzed using UV-VIS spectrophotometer and percentage removal was calculated from equation given below:

$$\% Adsorption = \frac{C_0 - C_e}{C_o} \times 100 \qquad \ldots (1)$$

Where: C_0= Initial concentration of dye solution (mg L^{-1}) and

C_e=Concentration of dye solution (mg L^{-1}) after adsorption.

2.5. Recovery of Dye: Dye recovery was carried out at optimum conditions of adsorption by using 25 ml of water, 0.1N NaCl, 0.1 N NaOH and 0.1 N HCl solutions with contact time 35 min. Amount of dye desorbed was measured by using UV- Visible spectrophotometer.

% recovery of dye was calculated using the equation given below,

$$\% Recovery = \left(\frac{c_d}{c_a}\right) \times 100 \qquad \ldots (2)$$

Where: C_d is amount of dye desorbed (mg L^{-1}) and C_a is dye adsorbed (mg L^{-1}).

3. RESULTS AND DISCUSSION

Adsorption of MB on bio-adsorbent *Cestrum nocturnum* was studied by optimizing various parameters viz. pH, contact time, adsorbent dose, particle size, concentration and temperature.

3.1. Effect of pH: Variation of % removal as a function of pH is shown in **Fig.1**

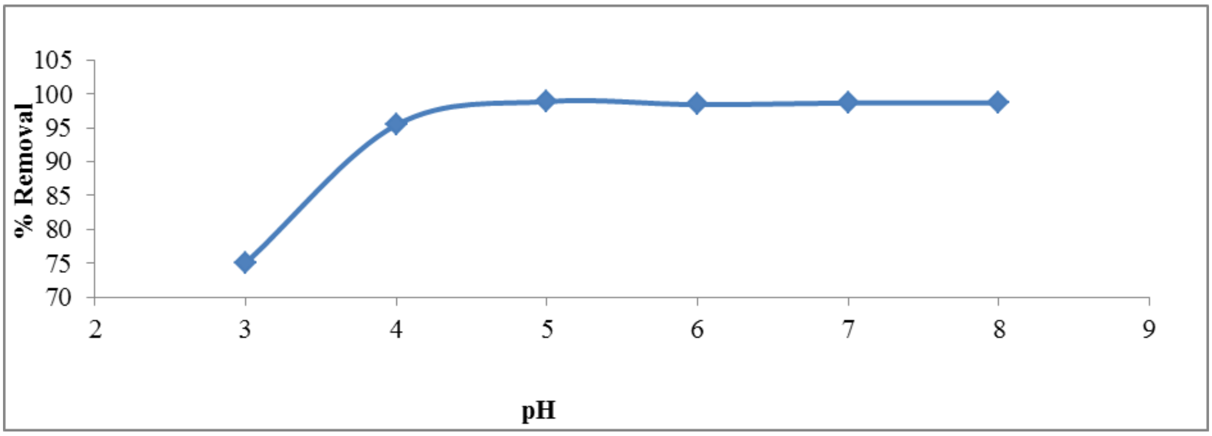

Fig.1: Effect of pH on removal of MB [concentration 5ppm, adsorbent dose 0.01 g, contact time 30 min, particle size 420µm],

It is seen from **Fig.1**, that the maximum removal of MB was obtained at pH 5, it is also observed that adsorbed amount decreased with increase in pH up to 5 then it remains constant up to pH 8 of the solution. Similar results are also reported by Uddin *et al.*[5]

3.2. Effect of contact time: The contact time between adsorbent and adsorbate was varied between 5 to 40 min. and is presented in **Fig.2**

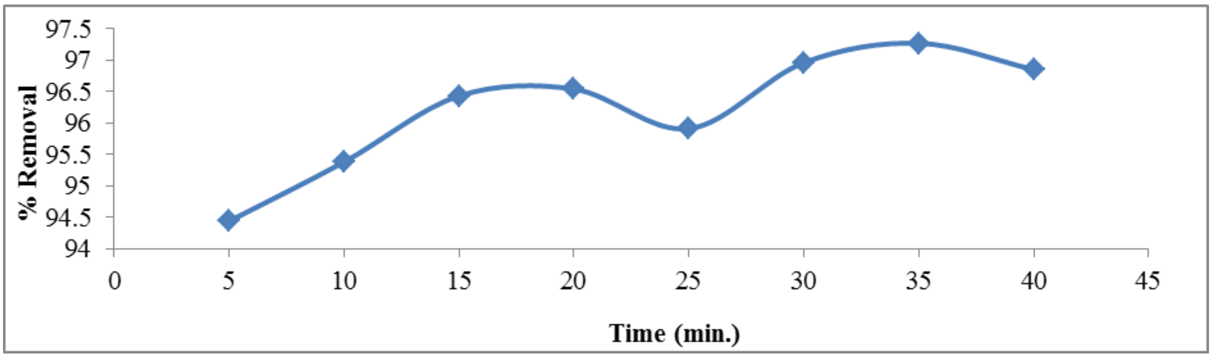

Fig.2: Effect of contact time on removal of MB [pH 5, adsorbent dose 0.1 g., particle size 420µm, Concentration 5 ppm]

An examination of **Fig.2** reveals that the efficiency of removal increases gradually with increase in time up to 35 minutes. Beyond this time % removal decreases. These results are matching with that reported by Rajurkar *et al.*[3] Around 97 % of MB was removed within 35 min, due to strong attractive forces between the dye molecules and adsorbent[12]. As contact time increases adsorption increases but at particular time interval, % removal decreases that might be due to dissolution of adsorbed dyes. At this point, adsorbed and desorbed dyes are in equilibrium with an adsorbent.

3.3. Effect of adsorbent dosage: Effect of adsorbent dose on % removal is displayed in **Fig.3** The rate of adsorption decreases with increase in the amount of adsorbent. 0.01g. is the optimum dose for the removal of initial dye concentration of MB solution.

Adsorbent dose plays vital role in adsorption process by affecting adsorption efficiency of the adsorbent. The amount of dye adsorbed per unit mass of adsorbent is equivalent to increase in adsorbent dose. The optimum value for loading of adsorbent dose was found to be 10 mg. after which equilibrium state was reached.

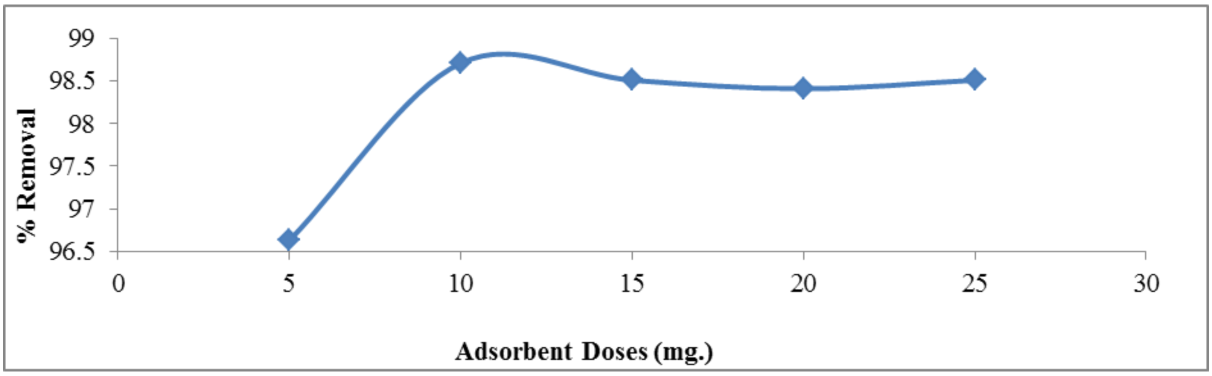

Fig.3: Effect of adsorbent doses on removal of MB [pH 5, contact time 35 minutes, particle size 420µm, concentration 5 ppm].

3.4. Effect of particle size on adsorbent: Effect of particle size of adsorbent on removal of MB is depicted in **Fig.4.**

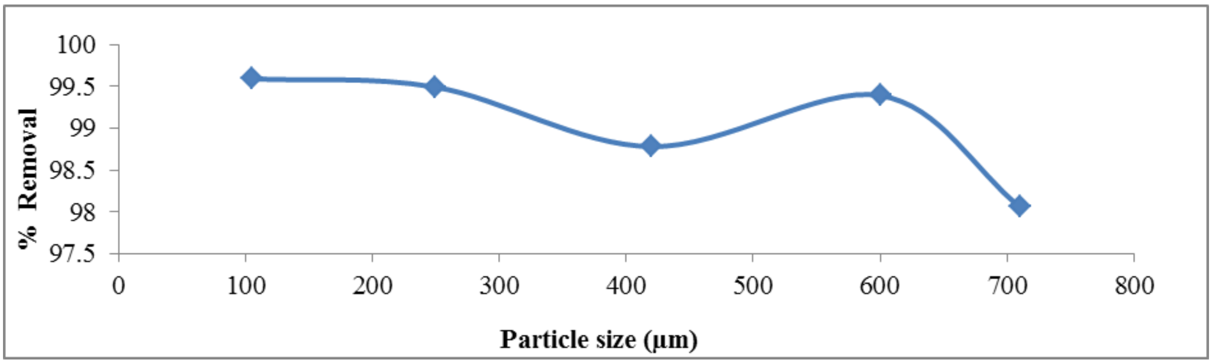

Fig.4: Effect of particle size of adsorbent on removal of MB [pH 5, contact time 35 minutes, adsorbent dose 0.01 g, concentration 5 ppm].

It was observed that, % of dye removal decreases with increase in particle size and maximum dye removal was achieved at 105µm particle size of adsorbent. As particle size of adsorbent decreases, percentage removal of dye increases, this is due to increase in surface area and more availability of adsorption sites[13].

3.5. Effect of concentration on adsorbent: Variation of % removal with concentration 1 to10 ppm is represented in **Fig.5.**

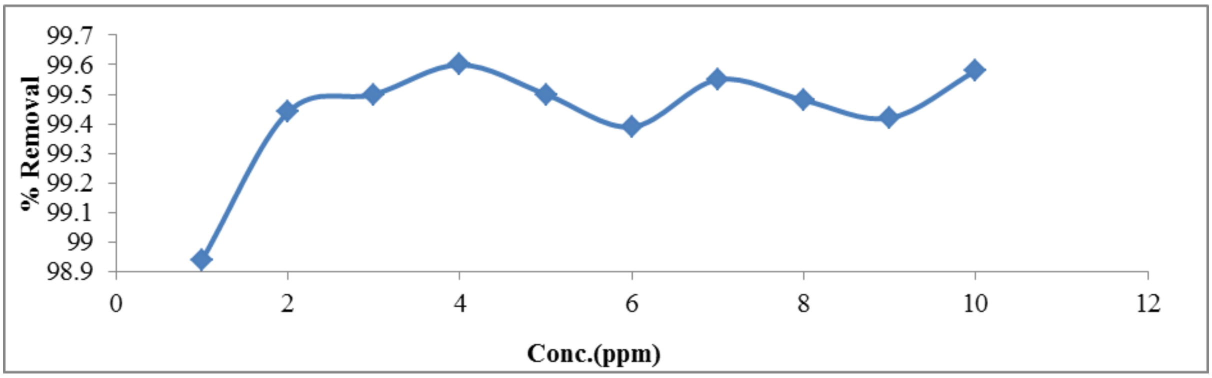

Fig.5: Effect of concentration, on removal of MB [pH 5, contact time 35 min, particle size 105µm, adsorbent dose 0.01 g].

An examination of **Fig.5** reveals that % removal increased from 98.94 % to 99.6%, as the concentration increased from 1 ppm to 10 ppm. Amount of dye adsorbed per unit mass of adsorbent increases with increases in the dye concentration from 1- 4 mg L^{-1} at the same period of time (35 min.) and thereafter, abruptly decreases. Adsorption is more predominant at 4ppm concentration of MB, due to strong driving forces of concentration gradient[14].

3.6. Effect of Temperature on adsorbent: Effect of temperature on % removal is shown in **Fig.6.** From **Fig.6**, it was observed that the amount of dye adsorbed decreases with increase in temperature that was due to increased solubility of adsorbed MB with increase in temperature.

It is concluded that 298 K is most favorable temperature for adsorption of MB on adsorbent. At this temperature 97.49% removal was observed.

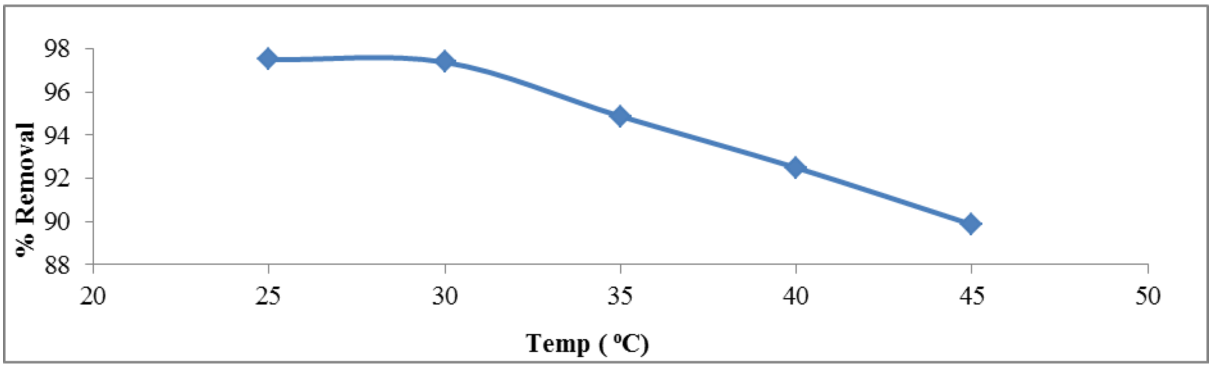

Fig.6: Effect of temperature on % removal of MB [concentration 4 ppm, pH 5, contact time 35 min, particle size 105µm, adsorbent dose 0.01 g].

4. ADSORPTION ISOTHERMS STUDIES

4.1 Freundlich isotherm:

Optimized conditions of the system are used to study the adsorption isotherms. Following equation 3 was used for the adsorption of MB onto the adsorbent,

$$\log q_e = \log K_f + 1/n \log Ce \qquad \ldots(3)$$

Where:

q_e = Amount of MB adsorbed at equilibrium,

Ce = equilibrium concentration of MB in solution,

K_f & n = Constant incorporating factor affecting the adsorption capacity and intensity of adsorption respectively.

Good linearity is observed for a graph of logq_e verses log Ce (R^2=0.896) **(Fig.7)** which indicate that the adsorption of MB obeys freundlich adsorption isotherm with freundlich Constant (K_f=1.56) and (n=2.73). The adsorption intention ‘n’ was found to be 2.73 i.e. in the range $1<n<10$ and value of K_f indicate the amount of MB per unit weight of adsorbent is favorable adsorption process[7]. Freundlich adsorption process is better than langmuir isotherm, which indicates that adsorption process is heterogenous in nature[15].

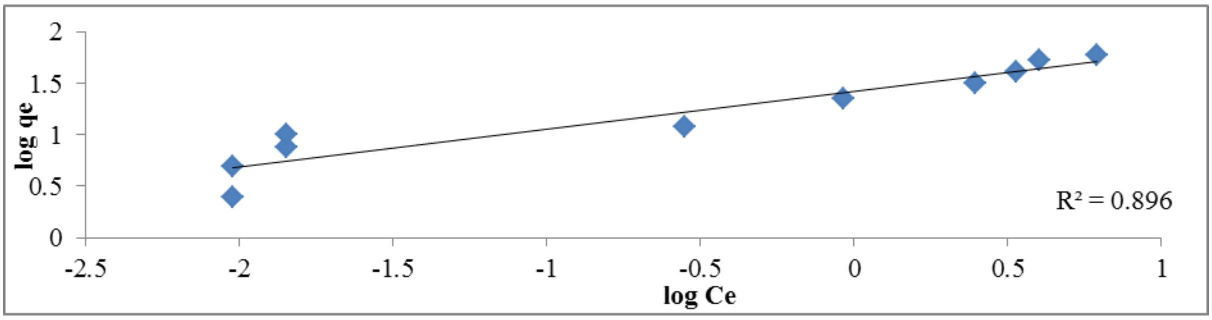

Fig.7: Freundlich isotherm plot for adsorption of MB on *Cestrum nocturnum* under optimized condition.

4.2 Langmuir isotherm: Following equation was used for the adsorption of MB onto the adsorbent.

$$1/q_e = 1/ab \times 1/Ce + 1/b \qquad \ldots (4)$$

Where: q_e = Amount of MB adsorbed at equilibrium, Ce = Equilibrium concentration of MB in solution,

a = Langmuir constant (K_L) related to adsorption efficiency (L/mg),

b =The maximum adsorption capacity (q_m) related to complete monolayer coverage (mg/g)

Plot of $1/q_e$ verses $1/C_e$ of langmuir adsorption isotherm ($R^2 \neq 1$) **(Fig.8),** showed non-Linearity. Hence Langmuir adsorption isotherm does not fit well for adsorption of MB on studied adsorbent[13].

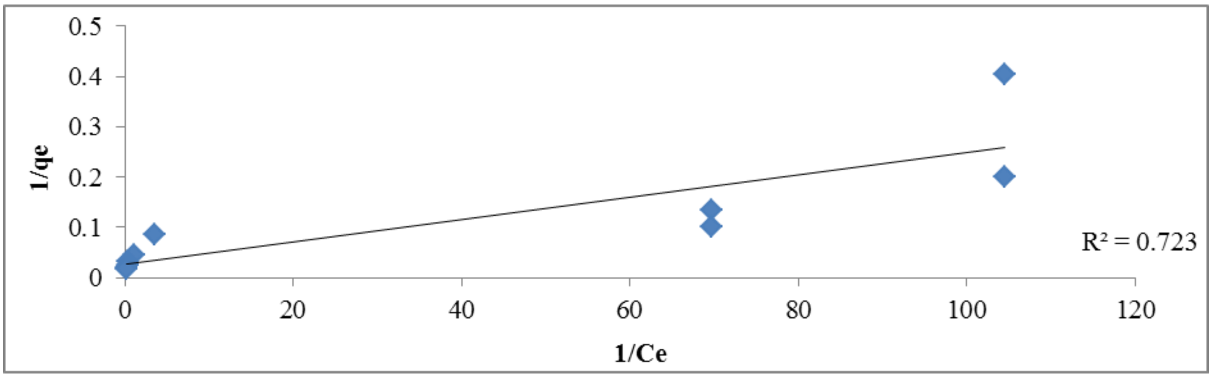

Fig.8: Langmuir isotherm plot for adsorption of MB on *Cestrum nocturnum* under optimized condition.

4.3 Temkin isotherm: Temkin isotherm suggest the distribution of uniform binding energy, it is expressed as,

$$qe = B \ln A + B \ln Ce \qquad \ldots (5)$$

Where: B=RT/b,

A and B are the Temkin isotherm constants ,b is the constant related to heat of adsorption, R is the gas constant (8.314 j/mole/K),T is the absolute temperature (K), qe is the amount of metal ions adsorbed at equilibrium(g/g) , Ce is the concentration of the dye at equilibrium (gL^{-1}).

The isotherm constant A and B are obtained from the plot of qe verses ln Ce **(Fig.9).** The linearity of graph indicates that the adsorption process obeys Temkin isotherm.

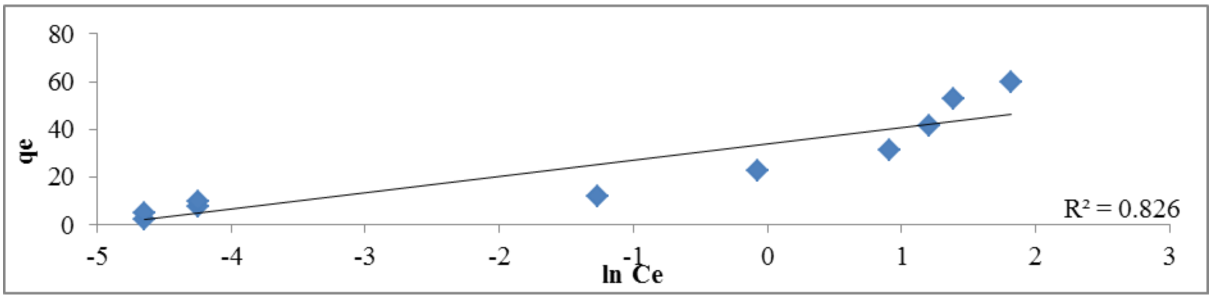

Fig.9: Temkin isotherm plot for adsorption of MB dye on *Cestrum nocturnum* under optimized condition.

4.4 Dubinin-Radushkevich (D-R) isotherm: This isotherm distinguishes between physical and chemical adsorption. D-R isotherm is stated by the following equation,

$$\ln qe = \ln q_{DR} + K\varepsilon^2 \qquad \ldots(6)$$

Where qe=the amount of dye adsorbed (g/g), Q_{DR} is the maximum adsorption capacity of dye (g/g), K is the Dubinin-Radushkevich constant (kJ^2/mole) and ε is Polanyi potential given by the equation

$$\varepsilon = RT\ln(1+1/Ce) \qquad \ldots(7)$$

Where R is the gas constant in J $mol^{-1}K$. T is the temperature in kelvin and Ce is equilibrium concentration of dye solution. (gL^{-1})

A plot of ln qe verses ε^2 (**Fig.10**) gives a straight line with a slope of K and an intercept of q_{DR}, Biosorption mean free energy E (kJ/mole) is calculated from D-R constant K and is determined as follows

$$E = 1/\sqrt{-2k} \qquad \ldots(8)$$

Where: E is the biosorption mean free energy (kJ/mole) and K is the D-R constant.

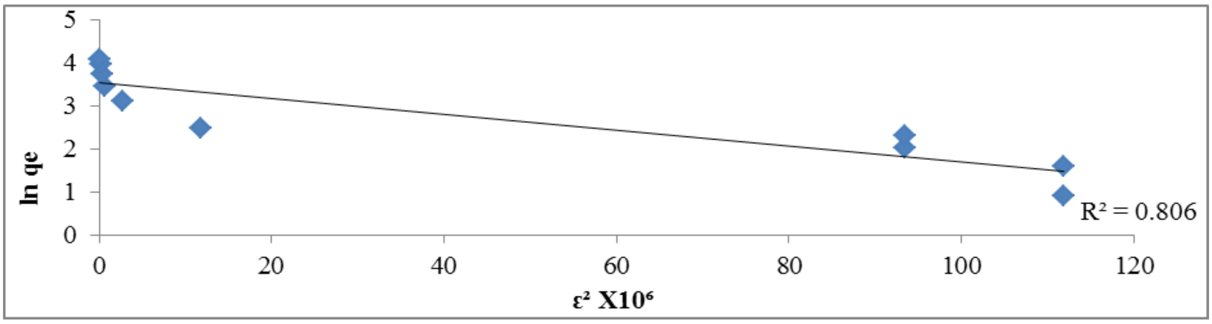

Fig.10: D-R Isotherm plot for adsorption of MB dye on *Cestrum nocturnum* under optimized condition.

The biosorption mean free energy (E) is involved the transfer of one mole of solute from infinity (in solution) to the surface of the adsorbent. Mean free energy describes the adsorption behavior. If its value is less than 8 it indicates physical adsorption and if greater than 8 indicates chemical adsorption[14]. The value of the mean free energy of MB dye is 5.19 kJ/mole which suggests physical adsorption process.

Table 1 reveals that adsorption of MB on the *Cestrum nocturnum* leaf powder follows Freundlich and Dubinin-Radushkevich (D-R) isotherm.

Table 1: Isotherm constant for MB dye adsorption onto the *Cestrum nocturnum* leaf powder.

Adsorption isotherm	Constants	Values
Freundlich Isotherm	R^2	0.896
	K_f	1.56
	n	2.73
Temkin Isotherm	R^2	0.826
	A	144.3
	B	6.807
D-R Isotherm	R^2	0.806
	q_{DR} (g/g)	34.87
	K (kJ/mol)	-0.019
	E (kJ/mol)	5.19

4.5 Adsorption Kinetic studies: A kinetic study of adsorptions provides information about its mechanism. For this purpose various kinetic models were observed.

Following equation was used for the adsorption kinetics of MB onto the adsorbent.

$$\log (q_e - q_t) = \log q_e - K_1 / (2.303)t \qquad \ldots(9)$$

Where:

q_e and q_t are amount of dye adsorbed (mg g^{-1}) on adsorbent at equilibrium and at time t respectively,

K_1 is rate constant of pseudo –first order adsorption (min^{-1}).

The slope and intercept values give pseudo–first order rate constant (k_1=0.031min^{-1} and

qe =0.61g/g respectively). Largergen pseudo –first order kinetic does not fit well ($R^2 \neq 1$) for whole range of contact time[2].

Largergen pseudo –second order rate expression is as follows[2].

$$t/q_t = 1/(K_2 qe^2) + t/q_e \qquad \ldots(10)$$

Where, K_2 is rate constant of second order adsorption (g mg^{-1} min^{-1}).

The plot of 't/qt' verses 't' (Fig.11**)** is used to determine second order rate constant. Value of Rate constant (K_2 =0.21, qe=9.78) and R^2= 0.999 showed that Largergen pseudo –second order adsorption equation fit well for whole range of contact time. The R^2 value indicates that the experimental results shows better fit to pseudo –second order. The equilibrium data was fitted to pseudo –second order kinetic model.

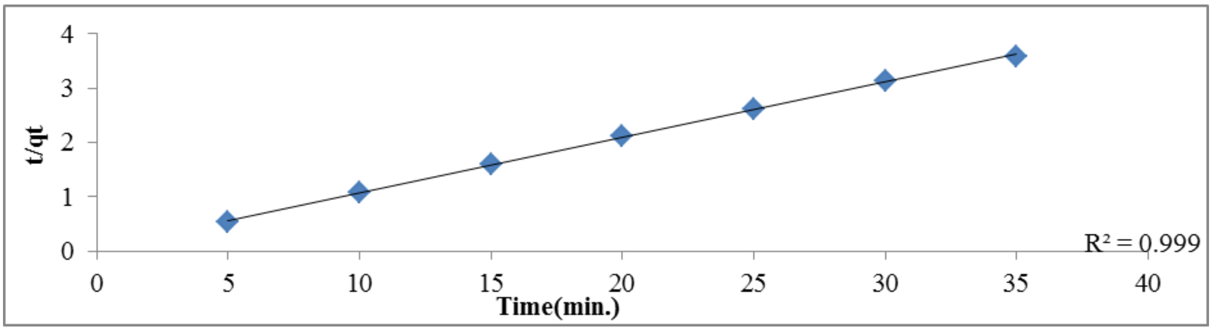

Fig.11: pseudo –second order plot for adsorption of MB dye on *Cestrum nocturnum* under optimized condition.

4.6 Intraparticle diffusion model: Diffusion of the adsorbate from the outer surface into the pores of the adsorbent is described by this model. From **Fig.12**, it was noted that the sorption process tends to be followed by two phases. The two phases in the intraparticle diffusion plot suggest that the sorption process proceeds by surface sorption and intraparticle diffusion. The intraparticle diffusion equation is given by

$$qt = k_{id} t^{0.5} + C \qquad \ldots(11)$$

Where: k_{id}=Particle diffusion rate constant in mg/g/$min^{0.5}$; and C is intercept.

A plot of qt verses $t^{0.5}$ gives values of k_{id} (slope) and C (intercept) from the equation.

From **Figure 12**, it is revealed that the value of k_{id} and C is 0.124 and 8.938 respectively.

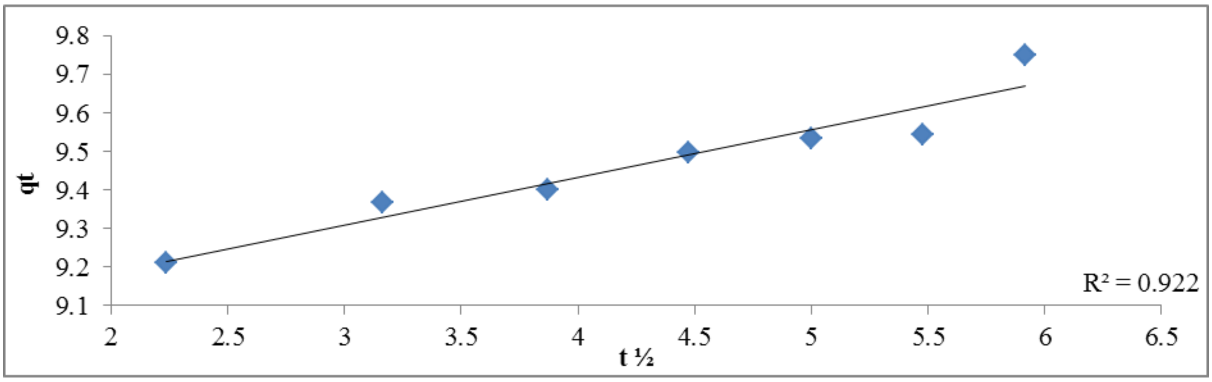

Fig.12: Intraparticle diffusion plot for adsorption of MB dye on *Cestrum nocturnum* under optimized condition.

4.7 Adsorption thermodynamic studies: The thermodynamic parameter reflects the feasibility and spontaneous nature of the process. The following equation is used to calculate various thermodynamic parameters such as change in free energy (ΔG^o) kJ/mole K, enthalpy (ΔH^o) kJ/mole, and entropy (ΔS^o) kJ/mole K.

$$\Delta G^o = \Delta H^o - T\,\Delta S^o \qquad \ldots (12)$$

$$\Delta G^o = -RT\ln K_0 \qquad \ldots (13)$$

$$K = \frac{q_e}{C_e} \qquad \ldots (14)$$

$$\ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad \ldots (15)$$

Where: K is equilibrium constant, R is gas constant, T is temperature in K, ΔG^o,ΔS^o and ΔH^o can be calculated by van't Hoff equation (10).ΔG^o is calculated from equation (10), ΔH^o and ΔS^o value obtained from the slope and intercept of plot ln K verses 1/T, The negative value of ΔG^o indicates the adsorption is spontaneous and thermodynamically favorable adsorption for MB. The very low negative value of ΔH^o indicates physiorption and reaction between dye and adsorbent is endothermic in nature. The negative value of ΔS^o indicates change in surface morphology and increase in randomness at solid liquid interface[14].

A plot of ln K verses 1/T is shown in **Fig. 13**

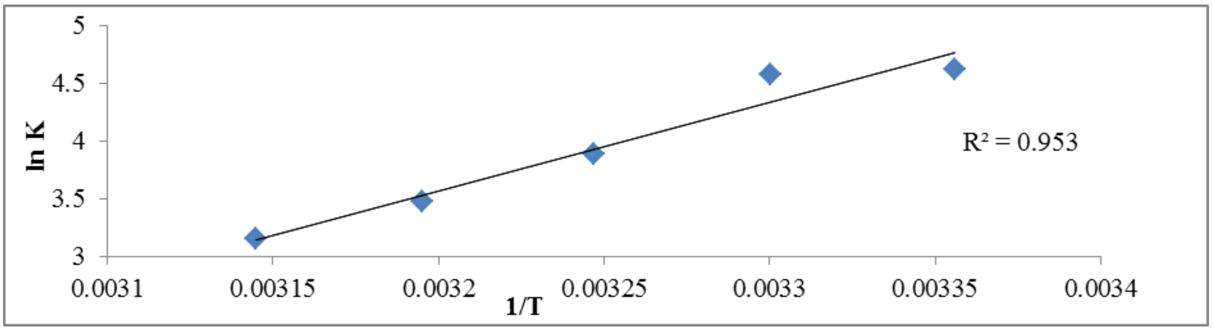

Fig.13: Plot of ln K verses 1 /T for adsorption of MB dye on *Cestrum nocturnum* under optimized condition.

Thermodynamic parameters obtained from these plots are recorded in **Table: 2.**

Table-2: Thermodynamic parameter for MB sorption by *Cestrum nocturnum* adsorbent

Temp. (K)	ΔG°(kJ/mol K)	ΔH°(kJ/mol)	ΔS°(kJ/mol K)
298	−11.80	−63.76	−0.17
303	−10.93		
308	−10.06		
313	−9.19		
318	−8.32		

From above table, the ΔG° values are negative indicating the spontaneous nature and thermodynamically favorable adsorption for MB[14]. The negative value of ΔH° indicates exothermic process[15]. The negative value of ΔS° indicates decreased disorder at liquid solid interface[16].

4.8 Recovery of dye: Dye recovery was carried out using various solvents (25 ml); water, 0.1N NaCl, 0.1 N NaOH and 0.1 N HCl solutions. The results are shown in **Fig.14** as HCl showed good efficiency of recovery, it was used for further recovery of dye (4 ppm) loaded on adsorbent at optimized conditions using various volumes of 0.1N HCl (Fig.15). 83.1 % MB dye was recovered by using 25 ml of 0.1N HCl. The results show that the depleted dye can be effectively recovered.

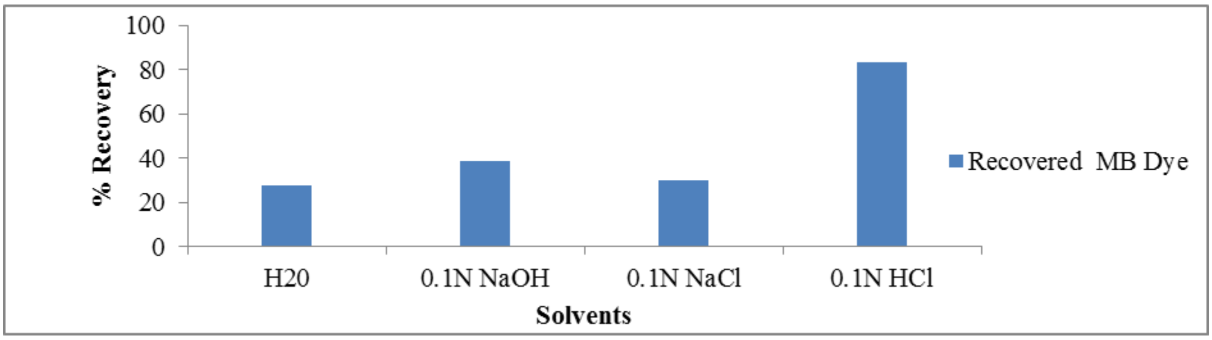

Fig.14: Dye recovery using various solvents.

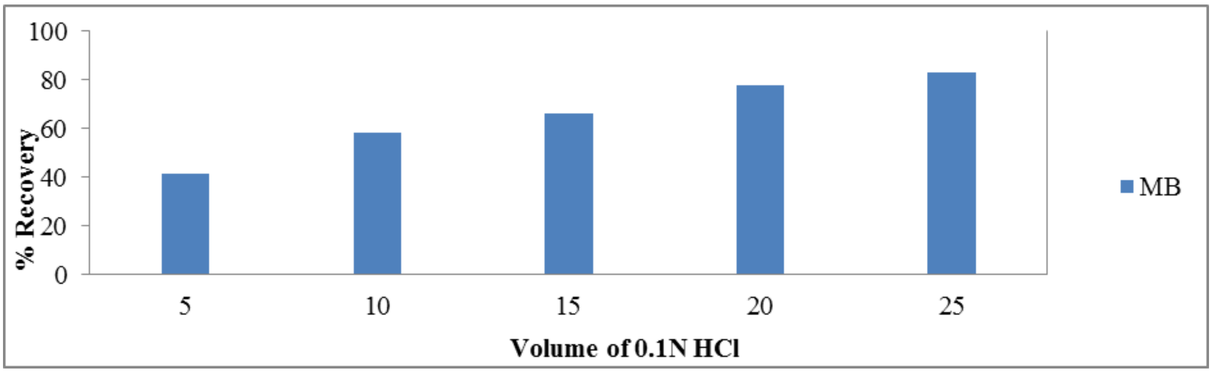

Fig.15: Recovery of dye loaded on adsorbent using 0.1 N HCl.

5. CHARACTERIZATION STUDIES

5.1 FTIR Studies: The I.R. absorption spectra of the *Cestrum nocturnum* (a) and MB adsorbed on *Cestrum nocturnum* (b) is shown in **Fig.16**. FTIR spectrum of novel adsorbent (a) shows a peak at 3774 cm^{-1} which indicates the presence of H –bonded –OH stretching vibration in phenolic compound present in cellulose of adsorbents. In spectrum (b), Strong broad band at 3750 cm^{-1} due to -OH stretching vibration, peak at 2917cm^{-1}, 3558cm^{-1}, 3627cm^{-1}indicates the presence –NH stretching vibration. The absorption band at 2917 cm^{-1} can be assigned to symmetric and asymmetric stretching vibration of the C–H_3 bonds in the dimethylene amino groups of MB molecule[17]. It is seen from figure that the peak intensity of spectrum (a) and (b) was changed considerably. The change in intensity indicates MB is adsorbed on to the adsorbent by adsorption process.

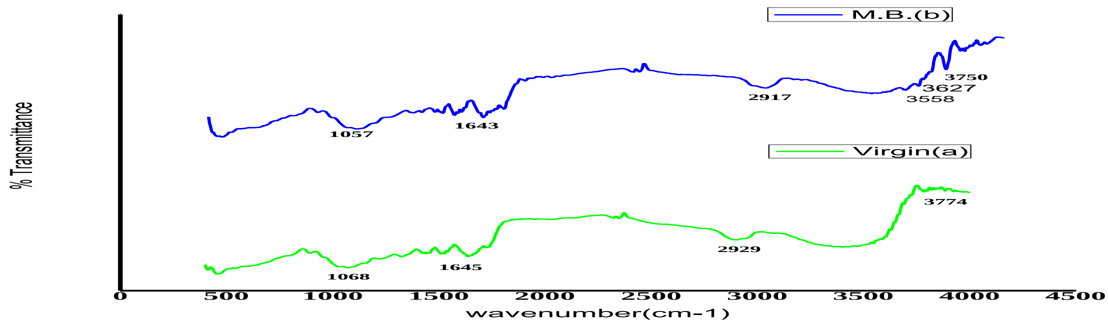

Fig.16: FTIR Spectrum of *Cestrum nocturnum* leaves powder **(a)** and MB loaded *Cestrum nocturnum* leaves powder **(b)**.

5.2 FESEM Studies: The morphological characteristics of adsorbent were studied using field emission scanning electron microscope.The FESEM micrograph are shown in Fig.17a and 17b.

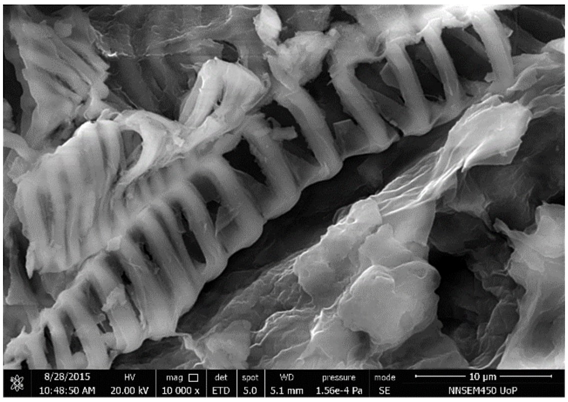

Fig.17a: FESEM micrograph of Cestrum nocturnum.

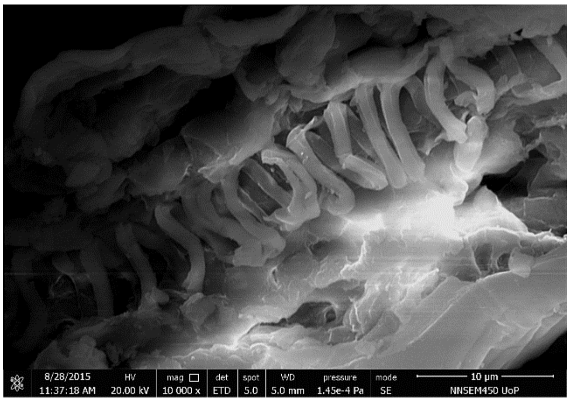

Fig. 17b: FESEM micrograph Cestrum nocturnum loaded with MB.

SEM micrograph of virgin adsorbent, shows irregular, rough and highly porous surface indicating the possibility of good adsorption. The appearance of a molecular cloud (darkness) over the surface of the dye loaded adsorbent **(Fig.17b)** confirms the adsorption of dye on to the surface of adsorbent. There are no porous (void) spaces on the surface of adsorbent because 99.6% dye adsorbent on to the surface of adsorbent.

5.3 EDX studies: The EDX spectrum of *Cestrum nocturnum* leaves powder and MB loaded *Cestrum nocturnum* leaves powder is shown in **Fig. 18a & 18b** respectively.

Energy dispersive spectrum of adsorbent (18a) shows the elements S, C, O, Fe, Si, P, S. While Energy dispersive spectrum of adsorbent loaded with MB (18b), shows additional element 'N'. From figure, it was concluded that adsorbent loaded with MB shows presence of 'N' which was present in the dye.

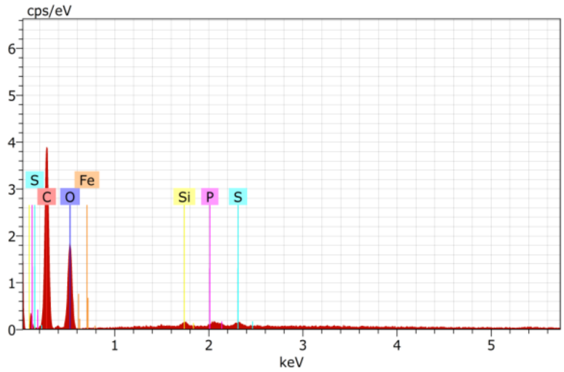

Fig. 18a, EDX of *Cestrum nocturnum*

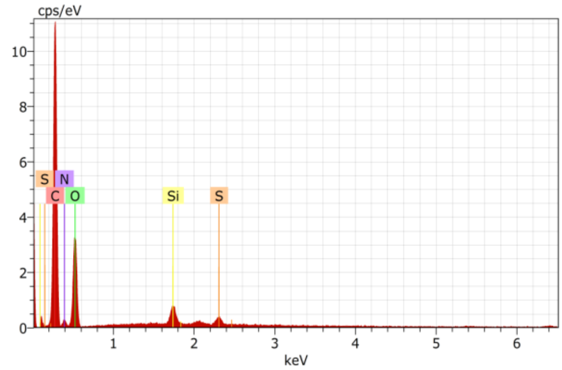

Fig. 18b, EDX of *Cestrum nocturnum* loaded with MB

APPLICATIONS

Cestrum nocturnum leaves powder can be used for effective removal of MB from aqueous solution. The technique is most efficient and cheap, novel adsorbent is easily available and can be applied to other dyes also.

CONCLUSIONS

- From the data of the present study, it is concluded that, the adsorption process is a very effective method for removal of MB from aqueous solution.
- Maximum removal (99.6%) of MB (4 ppm) was observed at pH 5, Contact time 35 min, adsorbent dose of 0.010g, particle size of 105 µm.
- Thermodynamic study revealed that adsorption of dye is a spontaneous and exothermic processs.
- Isotherm study states that adsorption of MB on *Cestrum nocturnum* leaves powder follows Freundlich, Dubinin-Radushkevich and Temkin Isotherms.
- Adsorption of MB follows pseudo –second order kinetics and Intraparticle diffusion model.
- Acid treated powdered leaves of *Cestrum nocturnum* act as an effective adsorbent for removal of MB dye.
- Adsorbed dye can be effectively recovered by using 0.1 N HCl solution as eluent.

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