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Biosorption of Methylene Blue dye using low cost Azadirachta indica adsorbent in Batch Process

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Abstract : In the present study, methylene blue (MB) dye was removed by *Azadirachta indica* which was prepared using raw Neem leaves through successive unit operation in a batch process. The effect of various operating parameters like inlet concentration of MB dye, adsorbent dose, pH of solution, and contact time were studied on percentage removal of MB dye. It was observed that the percentage removal increased on increasing the adsorbent dose, pH and contact time. However, it decreases on increasing the dye concentration. The maximum removal was found to be 93.11 % at 1 gmof NLP dose under 180 minute of contact time for 10 mg/l MB dye solution. Moreover, various isotherm models *viz* Langmuir, Freundlich and Temkin were fitted through regression on batch experimental data and it was found that Freundlich isotherm model best fits since the value of R^2 (0.996) is maximum as compare R^2 value of other models. Further, the unsteady state kinetic models were fitted on experimental data for understanding the phenomena of type of adsorption and it was observed that Pseudo second order model was in close agreement with experimental data .The theoretical equilibrium adsorption capacity was also found to be well validated with experimental equilibrium adsorption capacity. The maximum adsorption capacity of NLP adsorbent was found to be 5.7 mg adsorbate adsorb/gm of adsorbent. The SEM images of new brand prepared adsorbent and used adsorbent after 180 minute of contact time shows that the NLP is an effective adsorbent for MB dye removal.
Keywords : Methylene Blue, Isotherm models, equilibrium, kinetic models, adsorption capacity , SEM.

1. Introduction

Various industries such as textile, leather, food, pharmaceutical, paper, printing, rubber and cosmetics [1-6] utilizes different types of synthetic dyes to provide aesthetic appearance to final product.Also various applications of synthetic dyes found in the field of groundwater tracing, sewage and waste water treatment [7-10]. The industries prefers the usage of synthetic dyes since it reduces the production time and increases the variety of color combination of end product as compare to the natural dyes. Approximately 1 lakh different commercial dyes are produced with an annual capacity of $8x10^5$tonnes[11]. To process 1000 kg clothes for coloring, 1 m^3 water is required which when discharged to the water bodies creates hazard to the environment

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and ecosystem due to the toxic nature of the dyes in the effluent [12]. The textile industries consumes about 10000 tonnes/year worldwide and discharged 100 tonnes/year into water bodies[13]. The permissible limit for the colour in drinking water should be below 25 Hazen as prescribed by various regulating bodies in India (*http://hspcb.gov.in/dwater.pdf)*.Various techniques such as adsorption, advanced oxidation, reverse osmosis, membrane distillation and coagulation[14-23] etc. are find extensive use in the treatment of dyes and other contamination like metal ions in the water bodies. Among the different removal processes, adsorption techniques found to be most effective for wastewater treatment which industries utilizes for the reduction of toxic organic/inorganic pollutants from the effluent[24-25]. Various adsorbents such as activated carbon[26], flyash[27], zeolite[28], gulmohar[29], walnutshell[30], etc. are used for the removal of different kind of dyes available in the wastewater from textile industries. Use of neem leaf powder as an adsorbent found to be limited for the dye removal from waste water. Therefore,in this study, neem leaf powder (NLP) as an adsorbent was prepared from the neem (AzadirachtaIndica) leaves in the laboratory for the adsorption of Methylene Blue Dye (MBD) and its adsorption capacity is evaluated for effective adsorption . The experiments on parameters like pH, initial concentration of MBD, adsorbent dose and contact time were performed and the data analyzed using isotherms (Langmuir, Freundlich and Temkin) and kinetic models (Pseudo first order, Pseudo second order and Elovich equation).The BET analysis is also performed to determine the surface area of prepared NLP.

2. Experimental

2.1 Adsorbent Preparation

The block diagram of the preparation method of NLP adsorbent is shown in Figure 1. Initially, the definite amount of neem leaves from local place is taken and water washed for removal of moisture and adhere impurities. Thereafter, it was dried in a tray dryer for 2 hours at 80 ^{o}C. The dried leaves were crushed and screen to 100 mesh number (0.149 mm). Further, the powder was rewashed to remove the moisture and liberated free acid and tray dried for 30 minutes. The dried sample was placed in a crucible and heated in a furnace at constant temperature of 220 ^{o}C for 15 minutes. The heated sample was cooled and washed several times for removal of moisture followed by drying. The obtained sample was NLP adsorbent. The prepared NLP characteristics like porosity, pore volume, pore diameter were determined by porosimeter. The effective surface area was evaluated by Brunauer-Emmett-Teller (BET) technique.

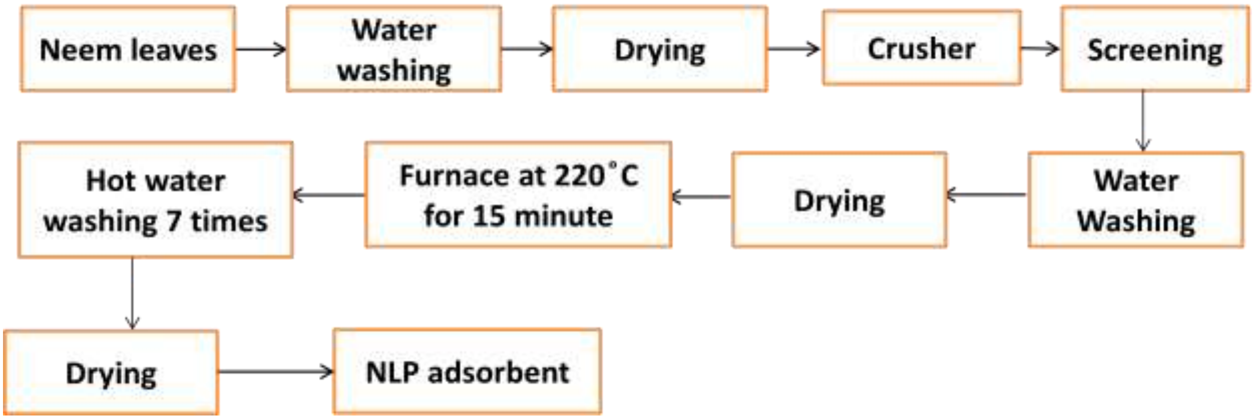

Figure 1: Block diagram for preparation of NLP adsorbent

2.2 Adsorbate

Methylene blue powderbasic in nature (Code: M0230) of Molecular Formula ($C_6H_{18}ClN_3S$), molecular weight (319.851 g/gmole) was purchased from Rankem Chemicals India. The stock solution of MB dye of concentration 500 ppm was prepared by dissolving MB powder as per stoichiometry in double distilled water. From the prepared stock solution, the various concentration range of MB from 10 to 150 ppm is prepared by dilution.

2.3 Experimental Methods

The experiments were performed for batch adsorption of MB solution onto NLP adsorbent surface at different parameters such as pH (2-10), adsorbent dose (0.2-1.0 gm), adsorbent concentration (10-150 mg/l) and contact time (0-180 minutes). During the experiment, the pH of the solution was maintained using 1N NaOH. Solution of various concentrations were prepared in a conical flask of 250 ml and adsorbent was added of various doses from 0.2 to 1 gm.The sample was placed inaorbital shaker which was maintained at constant temperature of 25±2^{0}C under constant RPM of 150. After definite interval of time the aqueous samples were taken from solution and the concentration were analyzed using a double beam UV spectrophotometer at 665 nm wavelength. Each experiment was performed three times and the average values taken for calculation of different parameters.The percentage removal and equilibrium adsorption capacity of adsorbent were calculated using the equations:

$$\%\mathrm{Re}moval = \left(1-\frac{C_e}{C_0}\right)\times 100 \quad (1) \qquad q_e = \frac{(C_0 - C_e)\times V}{W} \quad (2)$$

$$q_t = \frac{(C_0 - C_t)\times V}{W} \tag{3}$$

where C_0 ,C_e ,$C_t$$V$, W, $q_e$and q_t are the initial liquid phase MB dye concentration in mg/l, liquid phase equilibrium concentration of MB dye in mg/l , liquid phase MB dye concentration at any time t, volume of the solution in ml and weight of adsorbent doped in the batch process in gm, equilibrium adsorption capacity inmg/g and adsorption capacity at any time t in mg/g respectively.

2.4 Adsorption Isotherm

The response of NLP adsorbent on MB dye in batch mode was studied by evaluating the equilibrium isotherms and percentage removal of MB dye. Adsorption isotherm describes that how the adsorbate molecules are distributed between the bulk phase and on the adsorbent surface under equilibrium[31]. The experimental isotherm data were analyzed by comparing it closeness with three different isotherm models *viz* Langmuir, Freundlich, Temkin on the basis of correlation coefficient (R^2).

Langmuir Isotherm

The Langmuir isotherm model is mostly used because of its thermodynamic basis. This isotherm assumes monolayer adsorption of adsorbate on the homogeneous adsorbent surface containing fixed number of adsorption sites, and after reaching equilibrium point no adsorption can occur on the surface. The linear Langmuir isotherm model is expressed as [31]:

$$\frac{C_e}{q_e} = \frac{1}{q_L b_L} + \frac{1}{q_L} C_e \tag{4}$$

where q_L (mg/g)and b_L (l/mg) are Langmuir constant related to adsorption capacity and rate of adsorption relate to affinity of the binding sites and energy of adsorption respectively which are calculated from slope and intercept of the plot between C_e/q_e versus C_e.

Freundlich Isotherm

The Freundlich isotherm based on empirical equation which assumes heterogeneous surface energy system and is expressed by following equation [31]:

$$\log q_e = \frac{1}{n_F}\log C_e + \log k_F \tag{5}$$

where, n_F is the adsorption intensity and k_F is the rough indicator of adsorption capacity[(litre/mg)$^{1/n}$ mg adsorbate /gm adsorbent] which are calculated from the slope and intercept of the plot logq_e versus logC_e.The value of 1/ n_F provides the idea of favorable adsorption. It value (slope) ranges from 0 to 1 and the adsorption is more heterogeneous when n_F approaches to zero [31]. The favorable adsorption represent under the condition when n_F >1 or ranges between 1 to 10.

Temkin Isotherm

Temkin considered the effect of indirect adsorbate/adsorbate interaction on adsorption isotherm.The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interaction. The Temkin isotherm is expressed in the form as[32]:

$$q_e = \frac{RT}{b_T} \ln A_T C_e \tag{6}$$

where the constant$RT/b_T=B$ and $A_T=K_T$are calculated from slope and intercept by plotting the data between q_e *and* $\ln C_e$

2.5 Kinetics

Different kinetics models such as Pseudo first order, Pseudo second order and Elovich modelhave been used to investigate the mass transport mechanism, diffusion control and chemical reaction using the experimental data.

The pseudo first order equation is expressed as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

where q_e and q_t(mg/g) are the amount of MB dye adsorbed at equilibrium and time t. k_1 is the pseudo first order rate constant (l/min).

The pseudo second order equation is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{8}$$

where k_2 is pseudo second order rate constant (g/mg min).

The Elovic equation is written as

$$q_t = \frac{1}{B} \ln(AB) + \frac{1}{B} \ln t \tag{9}$$

where A is the initial rate of sorption (mg/g min) and B is extent of surface coverage and activation energy for chemisorptions (g/mg).

3. Result and Discussion

3.1 Surface analysis of adsorbent

The surface analysis of prepared NLP adsorbent and spent NLP adsorbent are performed using BET model. and their characteristics like particle size, pore diameter, pore volume, porosity and surface area is shown in Table 1.

Table 1:BET Analysis of NLP and Spent NLP adsorbent

Analysis	NLP	Spent NLP
Pore Diameter (µm)	0.2	0.16
Pore Volume (cm^3/gm)	0.003	0.001
Porosity (%)	30	25
Surface Area (m^2/g)	813.	402

3.2 Effect of Initial Dye concentration

The trend of variation in percentage removal with variation in initial MB dye concentration at different adsorbent dose of NLP is shown in Figure 2. It can be observed that the percentage removal decreases on increasing initial dye concentration. Further, It was depicted form the Figure 2 that on increasing in the initial concentration of MB dye solution from 10 to 150 mg/l, the percentage removal was decreased from 93.11 to 63.85 % for 1 gm adsorbent dose of NLP at 25±2 ºC. The possible reason for decrease in percentage removal with increase in initial MB dye concentration at constant pH of 10and temperature of 25±2 ºC might be at low concentration the availability of adsorption sites is high and the concentration of dye increases than the number of adsorption sites is not sufficient enough to accommodate the dye ions on to the adsorbent surface. It can also be seen that the percentage removal decreases linearly with increase in initial dye concentration This linear decrement in percentage removal were also reported by other [33].

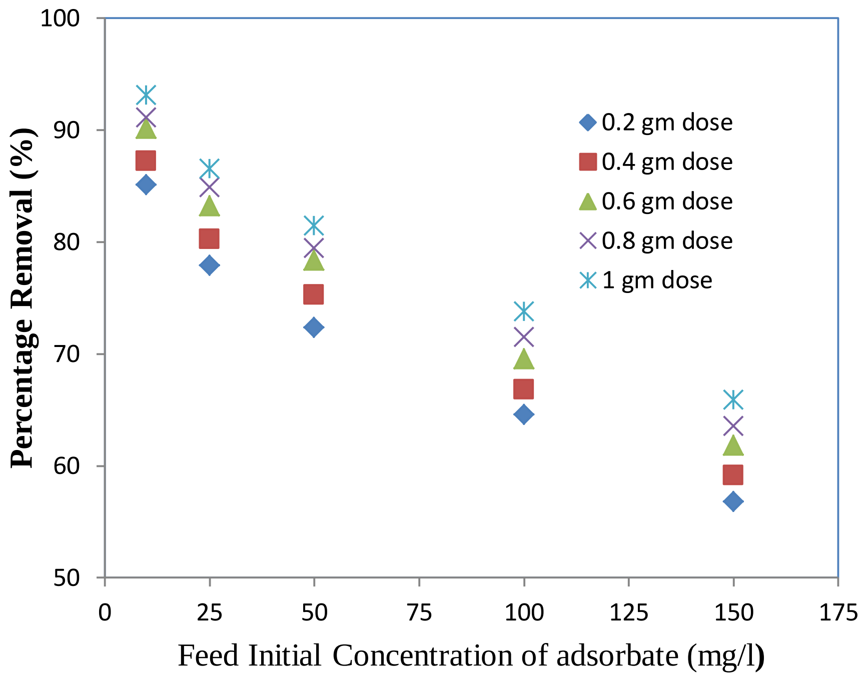

Figure 2: Effect of initial MB dye Concentration on Percentage Removal

3.3Effect of Contact Time

The effect of variation in contact time on percentage removal at different adsorbent dose of NLP is illustrated in Figure 3. Firstly, it wasfound that the experimental percentage removal increases steeply and thereafter gradually with increasing the contact time under different varied adsorbent dose of NLP. Moreover, It was observed that percentage removal increased from 68 to 91.5 % on increasing in the contact time from 15 to 90 minute for 1 gm adsorbent dose of NLP at 25±2 ºC. This may be due to the fact that initially adsorption site on adsorbent surface are more vacate for uptake of MB adsorbate on the adsorption site of NLP. However, from contact time of 90 to 180 minutes the percentage removal found to be increased from 91.5 to 93.11 %. This shows negligible significant effect of contact time on percentage removal. It can be attributed that the adsorbent sites with due course of time got brimmed results in lesser uptake of MB dye. Similar trend were reported by other researchers [32].

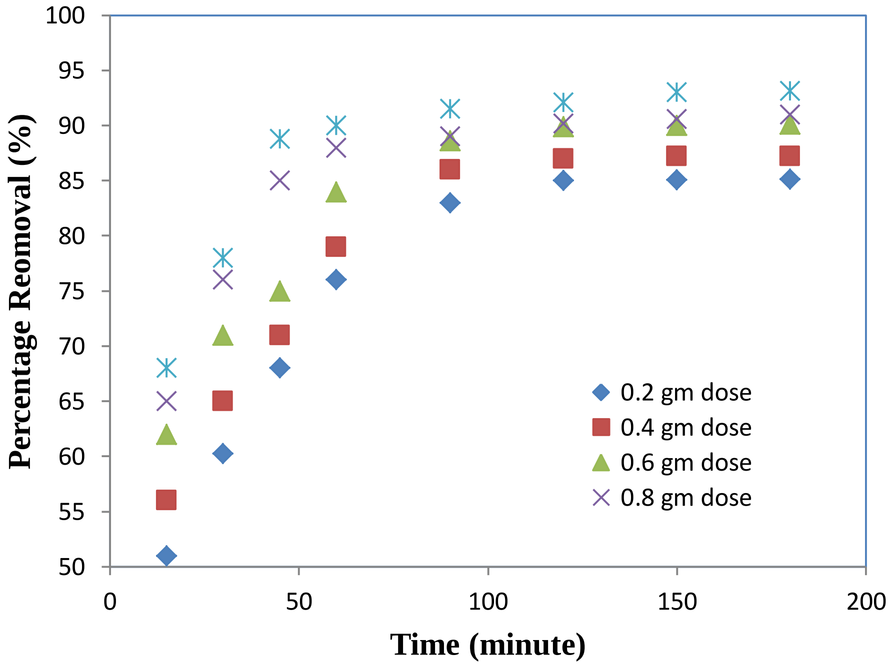

Figure 3: Effect of Contact Time on Percentage Removal

3.4 Effect of NLP adsorbent mass

The adsorption of MB dye on the NLP was performed by varying the adsorbent dose of NLP from 0.2 to 1 gm atconstant pH of 10 and temperature of 25±2 ^{o}C.It was observed from Figure 4 that the percentage removal of MB dye was increased from 85.11 % to 93.11% , 83% to 91.5 %, 68% to 88.8 % and 51% to 68% on increasing the adsorbent dose from0.2 to 1 gm at 180, 90,45 and 15 minutes respectively. This increment in the percentage removal can be attributed as the adsorbent dose is increased, the active sites are unsaturated initially since the large surface area is available during the adsorption reaction. Further, the available surface area of the adsorbent decreases due to the overlapping of adsorbate particles at higher doses. The same pattern has been reported by other authors [33].

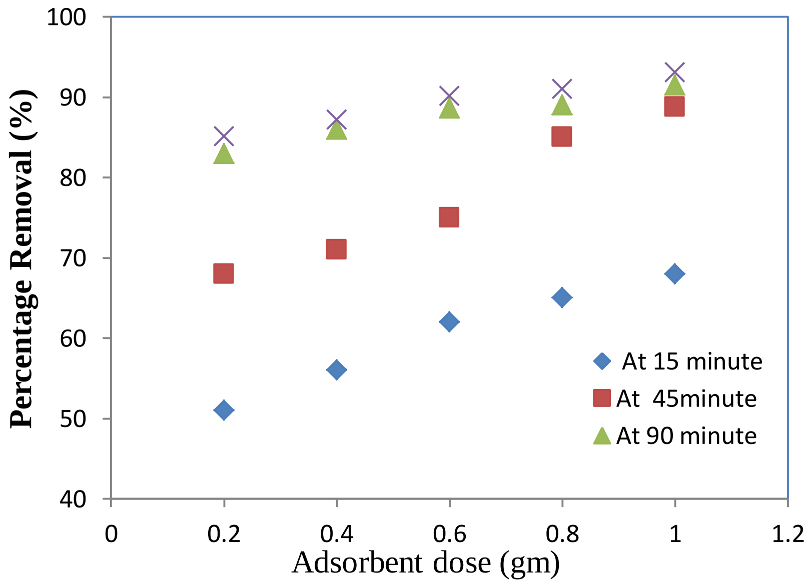

Figure 4: Effect of Adsorbent dose on Percentage Removal

3.5 Effect of pH

The effect of pH on percentage removal for batch process is represented in Figure 5. It was observed that the percentage removal increases from 37 % to 93.11 % with increase in pH from 2 to 10. Moreover, it can be seen that the percentage removal increases at a slower rate in acidic region while it increases rapidly in basic medium. Therefore, it can be concluded that the best adsorption of MB dye is found to be at basic pH which may be due to the release of protons (cation) from the adsorbent surface due to deprotonation of acidic groups on increasing the pH as a result cation exchange took place between adsorbent and the MB dye solution by leaving the negative sites onto adsorbent surface for adsorption of cationic form of MB dye .

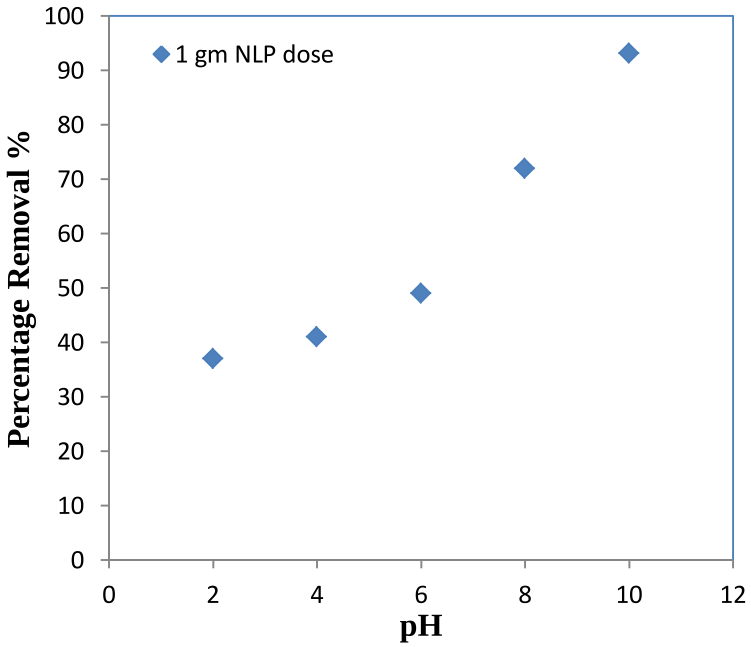

Figure 5:Effect of pH on Percentage Removal

3.6 Kinetic Studies

The experimental data for batch adsorption of MB dye onto NLP were fitted using various kinetic models *viz* Pseudo First Order, Pseudo second order and Elovich model for estimation of kinetic parameters using non linear regression technique are listed in Table 2 at MB dye initial concentration of 10 mg/l and 0.2 gm NLP dose. It was observed that Pseudo second order kinetic model found to be well validated with experimental data as its coefficient of correlation value (R^2), 0.998 is maximum in comparison to other kinetic models. It implies that chemisorption may take place in case of MB dye adsorption onto NLP adsorbent**.** Moreover, it was depicted that the experimental adsorption capacity is in close agreement with the theoretical adsorption capacity obtained from Pseudo second order. Furthermore, the experimental data were validated for different adsorbent dose of NLP ranges from 0.2 to 0.6 gm as shown in Figure 6.

Table 2: Kinetic Parameters for adsorption of MB dye onto NLP

Kinetics Model	Equilibrium Experimental Adsorption Capacity $q_{e,exp}$ (mg/gm)	Parameters	
Pseudo First Order	4.255	K_1(l/min)	0.132
		$q_{e,\,theoretical}$ (mg/g)	8.390
		R^2	0.962
Pseudo Second Order		K_2 X10^{-2}(g/mg·min)	1.403
		$q_{e,\,theoretical}$ (mg/gm)	4.73
		R^2	0.998
Elovich Model		α (mg/g·min)	1.25
		1/β = $q_{e,\,theoretical}$ (mg/g)	0.811
		R^2	0.971

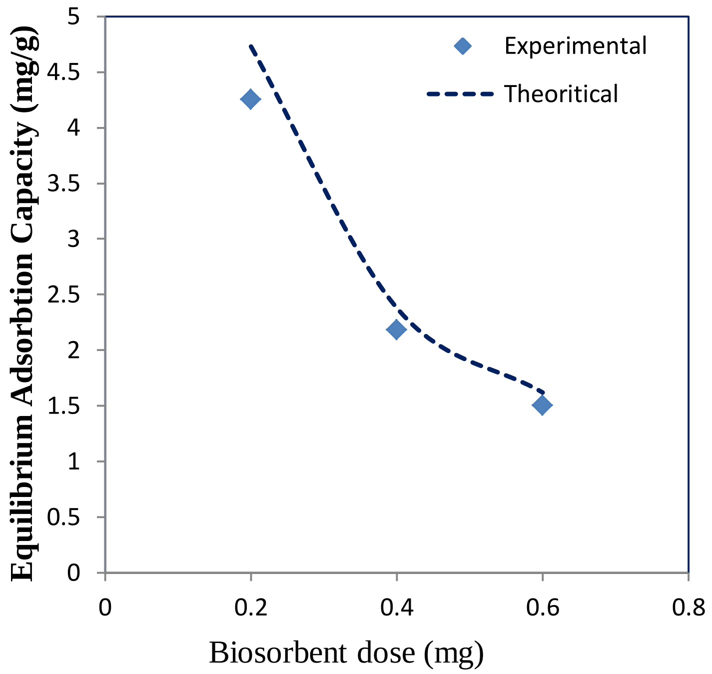

Figure 6:Effect of adsorbent dose on Adsorption Capacity

3.7 Isotherm Study:

Adsorption isotherm study was carried out for three isotherm models: Langmuir, Freundlich and Temkin. The relevancy of various isotherm for adsorption were examined by comparing the coefficient of correlation value (R^2). It can be depicted from Table 3 that Freundlich isotherm best fit the experimental data in comparison to Langmuir and Temkin isotherm since the R^2 value is high for Freundlich. Furthermore, the value of n_F is 5.701 which is greater than 1 clearly proclaim the multilayer adsorption phenomena in adsorption of MB dye on NLP adsorbent. The same paradigm was also acclaimed by different authors [31,32] on adsorption of numerous dyes on adsorbents.

Table 3: Isotherms Constants

Langmuir Constants		Freundlich Constants		Temkin Constants	
q_L (mg/gm)	57.800	k_F [(litre/mg)$^{1/n}$ mg adsorbate /gm adsorbent]	3.922	k_T=(A_T)litre/gm	0.669
b_L (l/mg)	0.039	n_F (favourable if n lies between 1 and 10)	5.701	RT/b_T	10.212
R^2	0.970	R^2	0.996	R^2	0.930

4. Conclusion

The NLP adsorbent was prepared for MBD removal and its surface characterization was performed using BET analysis. The effect of various parameters *viz* feed concentration of MBD, adsorption time, adsorbent dose of NLP and pH was exploited in detail and comprehended that percentage removal of MBD decreases on increasing the feed dye concentration. However, it increases upon increasing the activated adsorbent dose, pH and time.The maximum percentage removal of MBD was found to be 93.11% after 180 hour of adsorption time at 1 gm of adsorbent dose and 10 mg/l of initial dye concentration. Various isotherm were fitted on batch experimental data and it was found that Freundlich isotherms fits best. Kinetic study was also performed and it was observed that Pseudo second order model found is in well agreement with batch experimental data as a result it confirms the chemisorption of methylene blue onto activated NLP surface. Moreover, experimental adsorption capacity was in close agreement with the theoretical adsorption capacity obtained from Pseudo second order. The maximum adsorption capacity was found to be 4.25 mg/g. The reason of percentage removal decrement of MBD with time was understood by surface analysis of prepared NLP adsorbent and spent NLP adsorbent BET model. It was observed that the BET surface area, porosity, pore diameter and pore volume of spent NLP decreased with coarse of time.

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