Evaluation of Uptake of Methylene blue dye by Sulphonated biomass of Cicer arientinum: Batch Study.

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Abstract: The uptake of methylene blue by sulphonated biomass of *Cicer arientinum* is conducted in batch mode. The effect of parameters like contact time, sorbent dose, pH and temperature has been studied. The value Kp is found to be 0.1928 and 0.8727 for initial and final concentrations respectively. The kinetics of biosorption results indicate that sorption process follows pseudo–second order model with determination coefficients greater than 0.988 for sorbent under all experimental conditions. Thermodynamic parameter via KD, and ΔG are calculated indicates, rise in KD, negative ΔG values determine the spontaneity of the process and significantly shows that sorption process is time, temperature and concentration dependant. The adsorption obeys the Langmuir isotherm, Hall separation factor values less than unity and low value of activation energy indicate that sorption is an activated and favorable physical process. The phenomenon of sorption includes liquid-film, mass transfer mechanism is well described by Weber and Morris intraparticle diffusion model. Thus sulphonated biomass of Cicer arientinum(S-III) is a low cost and easily available good sorbent for the removal of MB^+ from wastewater.

Key words: *Methylene blue, biosobent, adsorbent, adsorption, Sulphonated biomass (S III)*

I. Introduction

A variety of carbons have been prepared using different agricultural by products such as coconut shell, walnut shell, rice husk ,cotton stalks,nuts,grapes seeds, sugar cane bagass and many more. Bengal gram, pulses maize, wheat, bajara are the major crops of Maharashtra, agricultural waste from these crops are available in ample amount. Adsorbents with a wide variety of surface structure and pore size distribution are obtained by modifying the preparation conditions of either physical and or chemical activation processes. Literature available revealed that a large number of researchers are working to tap the scope of various cheaper biomaterial like crushed coconut shell , treated saw dust' peanut hull[1] baggase pith biomass, sawdust red onion skin[3,] new pods of tur[4], coir pith,fibres of wool,cotton,jute,bamboo as biosorbents.Removal abilities of various biosorbent like sorghum straw, fly ash, banana pith, charoli bark, bacteria, algae, fungi, yeast and dead biomass[5],have also been investigated. In both the methods there is a reaction of the precursor with the activating agent to develop the porosity.[6-7] Pseudo-activated carbon prepared by treating the lignocellulosic precursor with concentrated sulphuric acid showed adsorptive and ion exchange properties[8]. The process followed by carbonization and neutralization by washing, yields the activated carbon [9-10] acids, alkalis, salt solutions have been used for chemical activation. . Growing interest has been focused for the use of phosphoric acid as an activating agent in the production of activated carbon from minerals and botanical sources. Effect of temperature, pH, and concentration of the adsorbate solution on adsorption capacity was studied on activated alumina**,** sorption and desorption characteristics of the methylene blue have been studied on kaolinite. The adsorption behavior of the cationic dye ethylene blue on cellulose[22] from its own solution and from its mixture with an anionic dye, methyl orange has been investigated. The physical and chemical surface characteristics of activated carbon and adsorption of methylene blue from waste water. Kinetics and equilibrium studies of adsorption of methylene blue on jute fiber[23] carbon have also been reported. Leaves of cauliflower were used for the removal of dyes like crystal violet, malachite green, rhodamine B, and methylene blue. Equilibrium kinetic modeling of Methylene blue biosorption by pretreated streptomyces vimosus[24] indicated that there is an increase in % dye adsorption with increase in temperature. Study of kinetics and mechanism of methylene blue sorption on to palm kernel fiber reveals that sorption of methylene blue on to kernel fiber follows a chemical activation mechanism. The adsorption study of azo dyes with similar structures was carried out on neutral alumina[25] and the difference in adsorption of dyes has been explained on the basis of their molecular weight and structural complexity. In the late 1970 chemical activation of charcoal using KOH was reported[17-18]. In chemical activation process the lignocellulosic precursor is mixed with a chemical reagent for restricting the formation of tar. The adsorption was found to obey Langmuir and freundlich adsorption models. Literature survey also reveals that cotton seeds hulls, peat[19], walnut shell[20], cherry stone, apricot stone nut, grapes seeds[21], eucalypts[22], olive and peach stone[23], wood saw dust have been found to be suitable precursors owing to their high carbon and low ash contents. Newer adsorbent materials like tree barks**,** cotton capsule shells**,** cauliflower[24]saw dust[25], rice straw, ground nut husk carbon' tea leaves, waste wool**,** have been, investigated for removal of pollutants from waste

water in the last two decades Methylene blue is widely released as waste from industry and can be harmful for the environmental flora and fauna. Furthermore, in humans, it will cause stomach upset and ulcer, mental retardation, liver, and brain damage. Therefore, removal of methylene blue from effluents is essential.

II.   Materials and Methods
2.1 Sorbate and Chemicals
The solutions of methylene blue[MB] $^+$ (3, 9 bis – diamino phenathionium chloride) (All Chemicals used Merck Chem.) sorbate having molecular formula $C_{16}H_{18}N_3SCl$ were prepared by dissolving appropriate amounts of dry powdered dye stuff in bidistilled water. The different concentrations of the solutions 0.799 mg/L., 7.99 mg/L, 39.9 mg/L and 79.99 mg/L. were prepared.

2.2 Sorbent

The dried material of cicer arientinum was crushed, powdered and then soaked in AR conc. Sulphuric acid for 2 hours. The biomass was then heated on a water bath till the fumes ceased then washed thoroughly with distilled water till the black mass was acid free. It was then dried at 110 ^{0}C in the oven for 3 hours and passed through 0.63 mm mesh to get particles of uniform size sorbent and stored in vacuum desiccators.

2.3 Sorption Kinetics
The experiments is carried out in three sets and each set contain 50 mg of sorbent in different conical flasks, to each flasks 25 ml of freshly prepared methylene blue dye solution of initial concentration (Co= 0.799 mg/L) was added. The volume was made up to 100 ml by adding distilled water. The flasks were protected from sunlight and stirred on magnetic stirrer with constant speed400 rpm for a period of 2,4,6,8,10,12,14,30,and 60 minutes respectively and filtered through whatmann filter paper. The absorbance of the filtrate was measured using systronic -112 photoelectric colorimeter at wavelength 640nm filter. The same procedure repeated to study the effect of different variables mentioned in work. The dye uptake capacity for the adsorbate was calculated by simple concentration method.

$$q= \frac{(Co-Ct)\ V}{100}$$

Where q is the quantity of sorbate (dye) uptake by biomass, Co and Ct are the initial and final concentrations respectively. V is the volume of solution in ml and W is the dry weight of the biomass added. Calibration and actual experiments were carried triplicate and mean values are presented. The removal percentage is calculated by equation: PR (%) = [1- Ce/Co] x 100

Where PR % = removal percentage of dye from static system after agitation Co= of initial metal ion concentration, Ct with fixed dosage of adsorbent and Ce = sorbate concentration at experimental equilibrium stage.

2.4 Langmuir isotherm model:
Langmuir isotherm was applied for adsorption equilibrium data. The unmodified Langmuir equation is as follows
Qe= abCe/ 1+bCe   Where a= maximum adsorption capacity (mg/g)
        b = Langmuir isotherm parameter related to the energy of adsorption (1/mg)

2.5 Freundilich isotherm model:
Freundlich equation is used for heterogeneous surface energy term. Freundlich isotherm can also be used to explain adsorption phenomenon as given:
Qe= Kf Ce $^{1/n}$
The linearized freundlich model isotherm is represented by equation
 Log10qe= Log 10 Kf + 1/n Log 10 Ce
Where, Kf and n are constants incorporating all factors affecting the adsorption capacity and an indication of the favorability of metal ion adsorption onto carbon respectively.

2.6 Adsorption thermodynamic equation:
Value of the thermodynamic parameter free energy ΔG ^{o} were calculated using following thermodynamic equation (Sarin and Pant, 2006)
ΔG ^{o} = - RT ln K ; where ΔG^o change in free energy (KJ/mol); T = Absolute temperature (K) , R (Universal gas constant) = 8.314 J/mole . K; K is the equilibrium constant at temperature, T The equilibrium constant, K can be calculated from.   K= qe/Ce

2.7 Kinetic models:

The kinetics of dye adsorption on sorbent can be modeled by the pseudo first order Lagergren equation and Pseudo second order model. The rate constant of adsorption from the first order rate expression. Log (qe-qt=Log qe – (Kt/2.303) t

Where qe and q are the amount of dye adsorbed (mg/g) at equilibrium and K1 is the rate constant. The second-order kinetics model is expressed as $t/q = 1/k_2 qe_2 + t/qe$

The initial adsorption rate (mg/g) to can be defined as $n = k_2 qe_2$

The initial adsorption rate (h) equilibrium adsorption capacity (qe) and 2nd order rate constant K2 (g/mg min) are determined experimentally, from the slope and intercept of the plot.

2.8 Intra particle diffusion study: The adsorption by porous particles is a process which involves a number of steps. The most common empirical function which explains adsorption is that the uptake varies almost proportionally with t ½ and rather than contact time. Qt= k id1/2+C

According to the equation the plot of qt vs. t $^{1/2}$ should be a straight line passing through origin, when the intraparticle diffusion is the rate controlling step. If the plot of qt vs. t $^{1/2}$ is non linear it indicates the adsorption is not governed by a single mechanism.

III.   Result and Discussion

3.1 Characterization of biosorbents.

The physical testing Bulk density is 0.42 g / cc, Moisture content 4.5 %, Volatile material 10.2 %, and Ash Content 5.1% and IR spectrum for sorbent shows absorption peaks at 3340 cm^{-1} broad –OH, 2924 cm^{-1} –NH, 1725cm^{-1} COOH respectively.

I Effect of parameters on uptake of S-III

3.2 Effect of Contact Time

Effect of time on adsorption of Methylene blue on S-III indicates that at all the concentrations of the dye rate of adsorption is quite high and the process reaches equilibrium within 30 seconds. For an initial concentration of 0.799 mg/L the minimum amount adsorbed on S-III is 42.55% within 10 seconds. and the maximum adsorption is 89.54% in one minute. While for an initial concentration of 79.9 mg/L the minimum amount adsorbed is 88.42 % within 10 seconds and the maximum adsorption 96.31% within one minute. Out of the total amount adsorbed at equilibrium, more than 60% is seen to be adsorbed within the initial 30 seconds itself **(Fig-1)**. The plots of % adsorbed vs. time shows two distinct regions one clearly indicating rapid adsorption and the other indicating the slowed down rate .This can be caused due to strong attractive forces between the dye molecules and the sorbent; fast diffusion onto the external surface followed by fast pore diffusion into the intra particular matrix to attain rapid equilibrium.
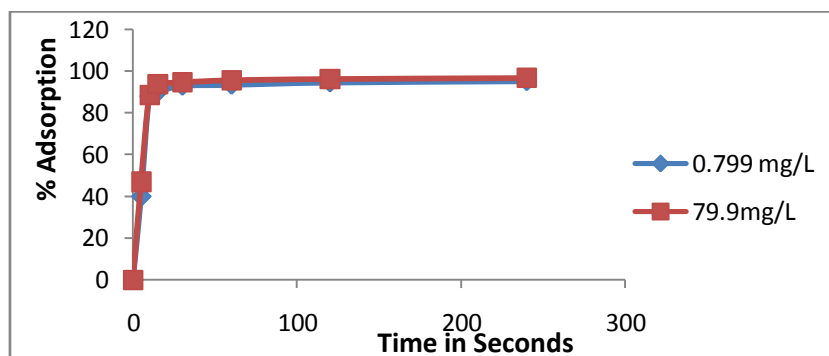

Fig-1. % Adsorption   vs. time S- III (Co = 0.799 mg/Ltr.&79.9mg/Ltr.)

3.3 Effect of Adsorbent dose:

When higher adsorbent dose there is an increase in the surface area and also the number of available sites, resulting in an increased and rapid uptake of the dye. Although the %age removal increases with the adsorbent dose, the adsorption capacity shows significant decrease at equilibrilium, for the dose of 50mg/100ml the adsorption capacity is found to be 1.012mg/g while it decreased to 0.635mg/g, 0.335mg/g and 0.133mg/g for the doses of100mg/100ml, 200mg/ 100ml&500mg/100ml of S-III**. (Fig.2)**
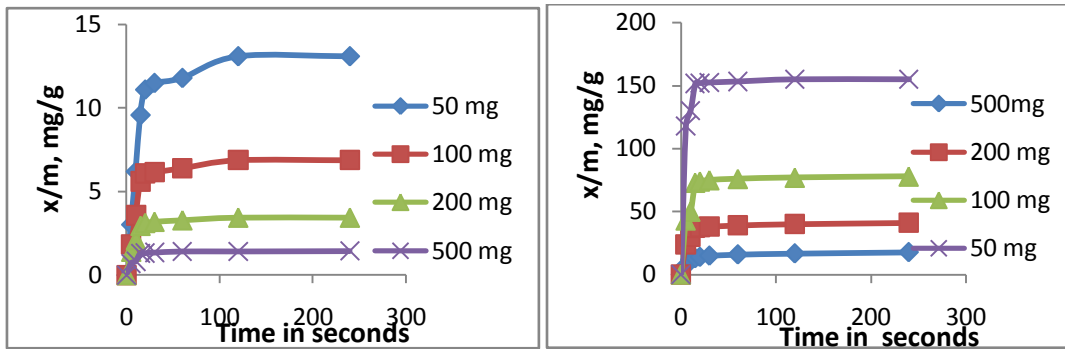
Fig-2 Adsorption Capacity vs. time S- III (Co = 0.799 mg/Ltr. and 79.9mg/Ltr.)

3.4 Effect of pH on adsorption of MB by S- III

The pH of a solution is an important factor which controls any adsorption process. The dye binding sites on the surface of the adsorbent are often modified by change in the pH of the solution. Methylene blue is cationic dye and exists as methylene blue $[MB]^+$ in solutions. Initially there is a competition for H^+ and $[MB]^+$ ions , to attach to the adsorption sites However as pH increases the number of H^+ ions in solution decreases till pH 4 , and a slight increase is observed in adsorption of the dye . As the pH increases beyond 6, it is observed that the adsorption falls and nearing the equilibrium maximum dye cations are on the surface of the sorbent. As pH increases the $[OH]^-$ and the remaining $[MB]^+$ cations appear to form pairs due to electrostatic attraction and the $[MB]^+$ ions are held back in solution.
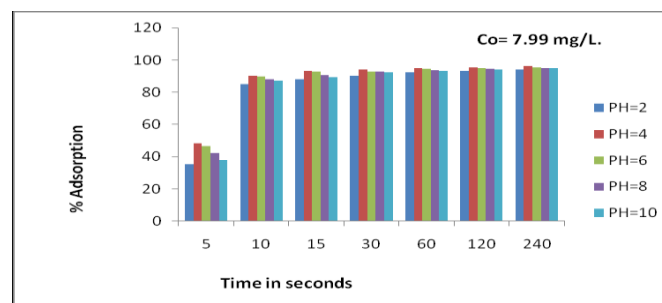

Fig. 3 Plot of effect of pH on % adsorption S-III (Co= 7.99 mg/L)

3.5 Effect of Initial concentration

Initial concentration affects the uptake capacity of the biosorbent to a large extent. For a fixed dose of S-III (50 mg/ 100 ml) it shows increases adsorption from 20 % to 90% for initial concentration (0.799 mg/Ltr.) and 48 to 96% (79.9 mg/Ltr.) fig. 4 of the dye. At a higher biomaterial to solute ratio a fast superficial sorption on sorbent surface takes place producing a lower solute concentration in the solution. A fixed mass of sorbent can sorb only a certain amount of dye, therefore larger the sorbent mass, larger the amount of sorbate that can be removed. The concentration of the dye at the surface of the sorbent differs from that in the solution; there exists a concentration gradient in the solution & at the surface. As dose increases the amount of dye sorbed per unit gram of sorbent gets reduced thus causing a decrease in the adsorption capacity.
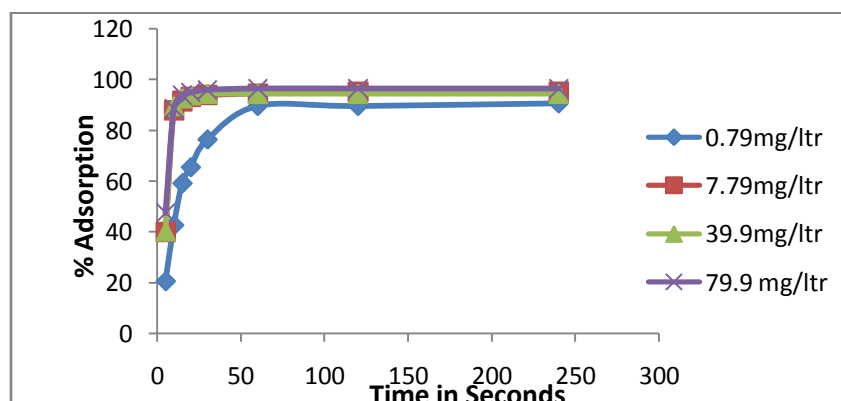

Fig. 4 Effect of initial concentration on sorption of M.B. by S-III

3.6 Effect of Temperature

To study the effect of temperature on adsorption of $[MB]^+$ by S-III experiments were carried out at four temperatures 15^{0}c, 25^{0}c, 35^{0}c and 45^{0}c using thermostat to maintain the temperature. The plots of % adsorption vs. time **(fig. 5)** using S-III indicates that maximum amount of $[MB]^+$ are adsorbed at 45^{0}c. Similar shapes were observed for the kinetic curves at all the temperature studied. The curves indicate that as temperature increases the sorption capacities also increases The rate of adsorption is much less at 15^{0}c (KD=3.88) for the same concentration at 45^{0}c (KD=26.08) **Table -1**.The increase in sorption capacities with temperature indicates that with increasing temperature mobility of the $[MB]^+$ ions increases. It can also be said that with rise in temperature the interaction between the dye molecules and the sorbent surface become more effective, the increase in the value of x/m with temperature also indicates the sorption process to be endothermic. ΔG values are a measure of the spontaneity of any process. For the sorption of the methylene blue on the biosorbent S- III the ΔG values are negative indicating the spontaneity of the reactions, these values indicate the favorable adsorption at elevated temperatures.
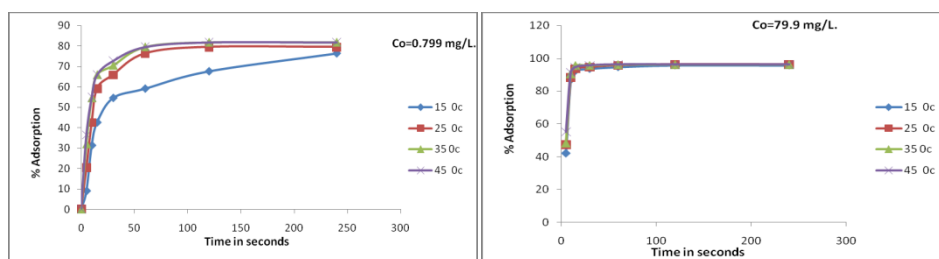

Fig. 5 % Sorption of M.B. by 50 mg S-III at different temperatures (Co=0.799mg/Ltr., 79.99 mg/Ltr.)

II Adsorption isotherm modeling

The data obtained on adsorption of $[MB]^+$ cation on the sorbent S-III was analyzed in the light of the Langmuir and Freundlich model of isotherms.

3.7 Thermodynamic parameters at 298°C
Effect of initial concentration and sorbent material on KD

Table-1

Co mg/Ltr.	KD	ΔG J/mole/K
0.799	3.886	-3361
7.99	17.58	-7099
39.99	17.30	-7077.90
79.99	26.08	-8075.8

Effect of temperature and sorbent material on KD (Co mg/Ltr. =0.799)

Table-2

Temperature	Co mg/Ltr. =0.799		Co mg/Ltr. =79.99	
	KD	ΔG J/mole/K	KD	ΔG J/mole/K
288	2.99	-2621.2	22.5	-7451.5
298	3.886	-3361	26.08	-8075.8
308	4.47	-3832	26.08	-8346.8
318	4.47	-3956.9	26.08	-8617.8

3.8 Langmuir model of isotherm

The linear plots for Ce *vs.* Ce/qe **(fig.6)** for S-III were straight lines indicating the applicability of the Langmuir adsorption isotherms. This is also indicative of the formation of monolayer coverage on the surface of the sorbent in the concentration range studied. Values of a and b were found to be 48.8 and 1.20, Hall separation factor RL is o.11 for S-III. RF was evaluated for the sorption process and was found to be less than 1 indicating favorable adsorption. Langmuir model is applicable to sorbent S-III in the concentration range studied. The coefficient of determination was much less than 0.5 in all cases.
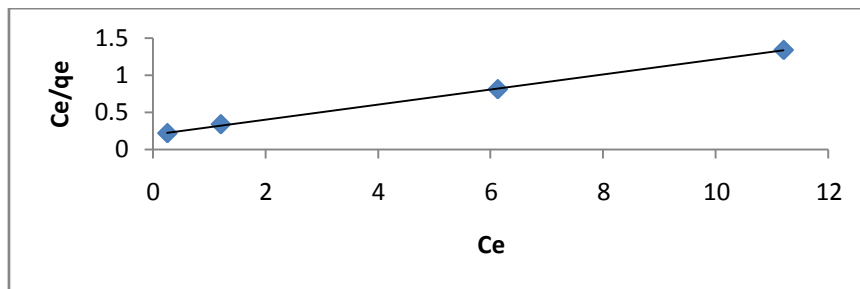
Fig .6 A Plot of Ce vs. Ce/qe for S-III

3.9 Freundlich model of isotherms:

The Freundlich isotherm coefficient **Table-3** for the adsorption capacity Kf and intensity of adsorption (1/n) have been evaluated from fitting of the data given in the tables below. Kf   gives an idea about the rate of adsorbate removal while 1/n gives an indication of the sorbate -sorbent bonds.

Table-3: Kf and n for adsorption on (S-III)

Temperature	Kf	n	R^2
298	25.11	0.6269	0.956
308	33.37	0.62632	0.9569
318	33.81	0.681	0.9529

The coefficients of determination are much better than those obtained from the Langmuir model. This indicates that the Freundlich is a better model to explain the adsorption of methylene blue on sulphonated of C. arientinum.
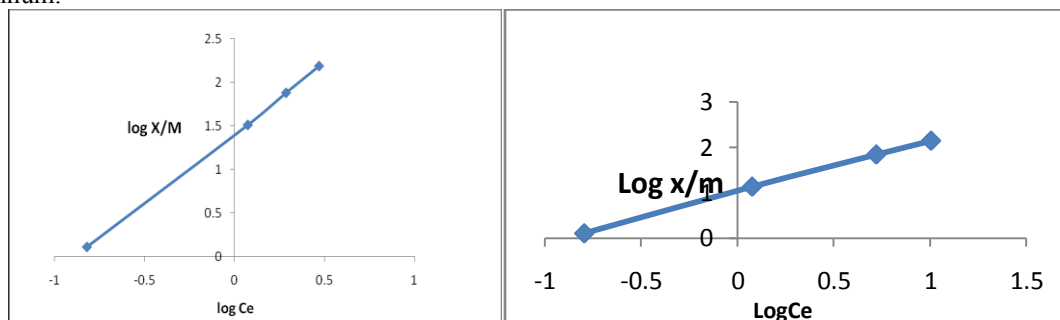

Fig.7 Plot of log x/m vs. log Ce   (S-III, dose= 50 mg, 500 mg.)

III Kinetic study

The majority research on dye adsorption systems revealed that two mechanism controlled dye adsorption 1) external 2) Internal diffusion. Some of the kinetic models used to assess the order of reaction are: 1) Pseudo–first order kinetic model by Lagergren, this is based on solid capacity 2) Pseudo second order kinetic model by Ho's and McKay is based on solid phase adsorption and external diffusion 3) Intraparticle diffusion model of Weber Morris. In order to describe the adsorption kinetics using S-III as adsorbents for removal of MB. Initial concentrations 0.799, 7.99 39.9 and 79.99 mg/Ltr. were used. The pseudo1[st] order model was applied. The plots of log (qe-qt) vs. t for all values of Co are shown in **(fig-8)**. The plots are expected to yield the straight lines if this model is applicable .Since straight lines are not obtained, the values of slopes are negative and R^2 values also found to be 0.95 it has been concluded that this model is not applicable. Modeling has been done using the pseudo second order equation developed by Ho and MacKay. The plots of t/qt vs. t yield straight lines indicating that the sorption process follows the pseudo second order kinetics. The values of rate constants K_2 were found to be 5.76, 0.144, 0.024 and 0.0108(g/mg/min) for initial dye concentration 0.799, 7.99, 39.99 and 79.9 mg/L.respectively for adsorption on S-III. A similar decrease in K_2 has been reported by Hamdaovi et al. for adsorption of [MB] $^+$ on wheat bran. The decrease in the values of K_2 for various initial concentrations is quite significant. The values of equilibrium sorption capacity obtained from the plot were found to vary from the experimental values, indicating non ideal adsorption and that removal off the dye involved number of processes such as adsorption, ion exchange etc. The coefficients of determination as obtained from the plots were found   to be very close to unity for all initial dye concentrations.

Table-4

Co mg/Ltr.	K_2	R^2
0.799	5.736	0.9989
7.99	0.1474	0.999
39.99	0.241	0.9996
79.99	0.0108	0.999

To be very close to unity for all initial concentrations. **Table-4** gives the values of K_2 and R^2 for these results. The plots of log (qe-qt) vs. t indicated the non applicability of the pseudo first order model. The plots of t/qt vs. t for initial concentrations 0.799, 7.99, 39.99 and 79.99 mg/Ltr. gave straight line plots. The K_2 values were found to have decreased with increasing Co (**Table-4**) R2 values as given in table are very close to unity indicating the validity of the model.
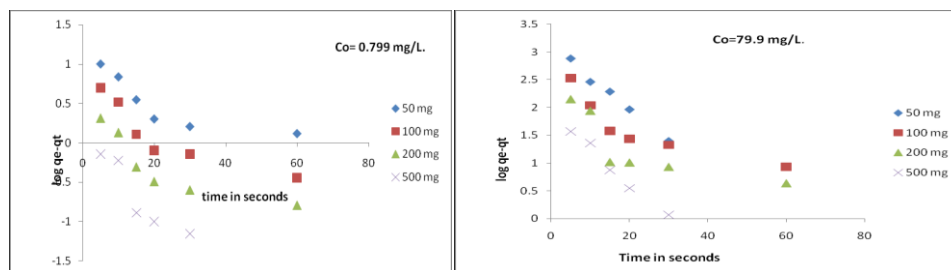

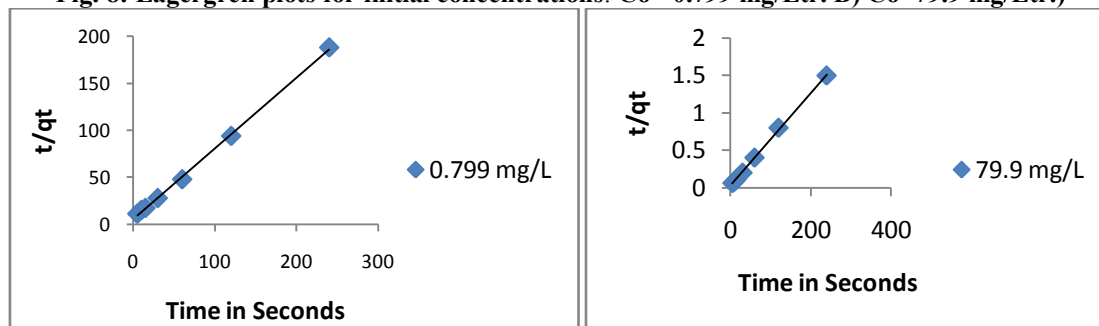**Fig. 8: Lagergren plots for initial concentrations**. Co= 0.799 mg/Ltr. B) Co=79.9 mg/Ltr.)

Fig.9 Pseudo second order plots (sorbent III) Plot of t/qt vs. T for S-III (Co= 0.799 mg/Ltr. Co= 79.9 mg/Ltr. 50 mg dose)

IV Intraparticle diffusion model
Table -5

Initial concentration mg/Ltr.	S-III Kp mg/Ltr.	S-III Intercept
0.799	0.1928	10.41
79.99	0.8727	142.84

The mechanism involved in the sorption process is determined by an intraparticle diffusion model. Plots of q vs. t$^{1/2}$ (**fig. 10)** gives an idea of the mechanism involved. In a batch reactor pore distribution and intraparticle diffusion are often the rate determining steps. The plots of q vs. t$^{1/2}$ show separate regions. The initial parts of the curve can be attributed to mass transfer effects. While the next linear portion indicates intraparticle or pore diffusion. The initial portion is also indicative of surface sorption and the boundary layer effect. Slope of the 2nd linear portion of the plot is defined as the intraparticle diffusion parameters Kp or Kid while the intercept of the plots gives an idea about the boundary layer. Larger the intercepts greater is the contribution of surface sorption in the rate limiting step. Intercept of the plots q vs. t$^{1/2}$ for 0.799 mg/Ltr. and 79.9 mg/Ltr. are found to be 10.41 and 142.84 for S-III. These results clearly indicate that boundary layer effect increases with the initial concentration of the dye. As observed in the graph we can see an initial curved portion which can be attributed to liquid –film mass transfer, while the latter portion reveals linearity which is characteristic of sorption processes where intraparticle diffusion is controlling step such phenomenon have been observed for the adsorption of the dye on activated carbon**.**
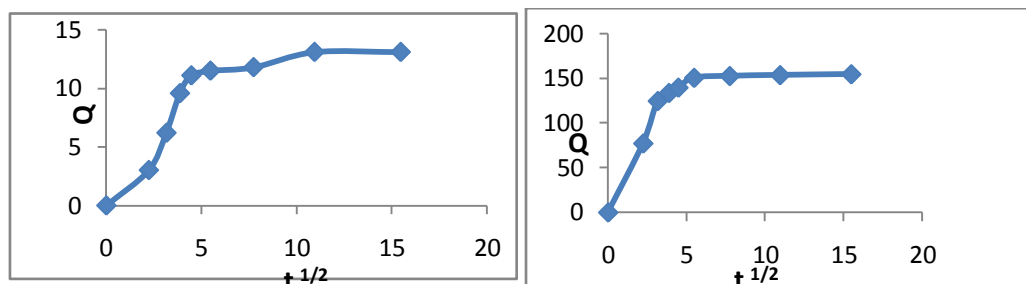
Fig. 10 Plots of Q vs. t ½ for S-III, (Co=0.799 mg/Ltr., 79.9 mg/Ltr.)

V.   Conclusions

Adsorption of $[MB]^+$ on sorbent S-III is a time dependent process, equillibrium is attained within one minute . Although the adsorption is very fast for S-III, there does not seem to be a significant contribution of temperature on the rate of   adsorption. The adsorption is initially very rapid and the rate then slows down. The sorbent dose has a substantial effect on the percentage of adsorption, as the sorbent dose is increased from 50mg/100ml to 500mg/100ml the initial adsorption increases from 44.4% to 72.78% and the % adsorption at equilibrium is found to increase from 68.7% to 87.4%. The increase in the value of x/m with temperature also indicates the sorption process to be endothermic. The adsorption capacity is found to increase up to pH 4 and afterwards decreases. At higher pH the increased OH^- concentration in the solution hold back the $[MB]+$ in solution and hence a reduction in % sorption and sorption capacity. For S-III the Kp values were found to 0.1928, 0.8727 mg/Ltr. for Co= 0.799 and 79.9 mg /L respectively, values of Kp indicate that the structures of S-III is not micro porous. With the increase in temperature the sorption capacities also increase. The increase in sorption capacities with temperature indicates increasing mobility of the $[MB]^+$ ions. For experimental concentration the KD values vary between 2.99 to 4.77& 22.5 to 26.08 for S-III over the initial and final temperature range studied. The value of KD is found to increase with rise in temperature. The ΔG values at the different temperature studied have negative values indicating spontaneity of the process for **S**- III. Kinetic modeling suggests that the process follows the pseudo second order kinetics. The values of Kf range between and 25.11& 33.81 and the values of 1/n are less than unity for indicating good intensity of adsorption for temperature 15, 25, 35 and 45^0C. The adsorption obeys the Langmuir isotherm. The Hall separation factor values indicate favorable adsorption. The intraparticle diffusion studies indicate that intraparticle diffusion is not the rate determining step and adsorption may be controlled by mass transfer mechanism.

Acknowledgement

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