



Removal of Methylene Blue And Indigo Carmine From Aqueous Solutions Using Couroupita Guianensis Leaves As An Adsorbent

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ABSTRACT

Present study focuses on the use of leaves of Couroupita guianensis (kailashpati) in powder form as natural bio adsorbent for removal of methylene blue and indigo carmine dyes. The study revealed that the methylene blue dye (15 ppm) showed maximum removal at pH 9, contact time 45min, particle size 140 μ m and adsorbent dose 0.15 g. Its adsorption followed pseudo first order kinetics. Thermodynamic studies revealed that adsorption of mb is a spontaneous process. Indigo carmine dye (5 ppm) showed maximum removal at pH 2, contact time 90 min, particle size 140 μ m and adsorbent dosage 0.3 g. Its adsorption followed pseudo second order kinetics. Thermodynamic studies revealed that process of adsorption of ic is a non-spontaneous process.

Keywords: Bioadsorbent, Couroupita guianensis, methylene blue, indigo carmine, thermodynamics.

INTRODUCTION

In industrial waste water treatment, dye removal is one of the major concerns. The industries such as textile, paper, plastic, paint etc contain a large quantity of synthetic dyes as pollutant. Most of the Industries release the effluent with a load of color with it and is released in nearby water bodies. Large amount of dyes and organic pollutants are released through textile industries. Now days, treating the textile effluents are becoming an environmental concern due to scarcity of water and chronic effects on human beings [1]. Various methods like ion exchange, reverse osmosis, ozonation, etc, are being used for treating the effluents but all these techniques have some or the other drawback [2]. These methods are costly and accumulation of concentrated sludge becomes a disposal problem. Among all the techniques adsorption is the best technique used for the purification of water effluent. Recently there is trend to use natural bio adsorbents for removal of dyes [3-5] and metal ions [6,7] as these are easily available, and are in abundance and the used powder can be easily disposed or used as fertilizer in agriculture and it degrades the dye naturally too. The present work is undertaken to study the potential of Couroupita guianensis (kailashpati) leaves as natural bio adsorbent for the removal of methylene blue (mb) dye and indigo carmine(ic) dye, from their aqueous solutions. The studies were carried out using batch adsorption process.

MATERIALS AND METHODS

Preparation of adsorbent and adsorbates used: The leaves of *Couroupita guianensis* (kailashpati) tree were collected from university garden and washed thoroughly with tap water. These leaves were then dried in oven at 353 K for 12 h and powdered. The powder was treated with water at 353 K for four hours and then filtered. 3g of powder was then treated with 250 mL of tap water for 4 hours. The procedure was repeated 5 times till the colour of the filtrate fades. It was then dried in oven for 4 h at 353K till the powder was free flowing and then stored until further use. The adsorbent was activated by heating it at 60°C for 2 h. Methylene blue (mb) and indigo carmine (ic) were obtained from selkrom and sd fine- chem limited respectively. 100ppm stock solution of dye was prepared and diluted according to the need.

Batch adsorption process: The removal of dyes was studied by batch adsorption process. The different parameters such as pH, concentration, adsorbent dose, particle size and contact time were optimized to get maximum removal of dyes. At these optimized conditions thermodynamic and kinetic studies were carried out.

Experimental procedure: Before the use of adsorbent, it was pre heated for two hours each time before use. 25 mL of 10ppm solution was continuously stirred at 1200 to 1300 rpm after addition of adsorbent. All the parameters were kept constant except one parameter to be optimized. After that the solution was centrifuged for 12 to 15 min at 2500 rpm and filtered through Whatman -41 filter paper. The filtrate was analyzed in U.V-Visible spectrophotometer and percent removal was calculated from following equation.

$$\% \text{ removal} = ((C_o - C_e)/C_o) \times 100 \dots\dots\dots (1)$$

Where C_o - initial absorbance of unadsorbed solution
 C_e - absorbance of solution after adsorption

RESULTS AND DISCUSSION

Effect of pH: pH of the solution was varied between 2-10 and the results are shown in the fig1(a) and (b)

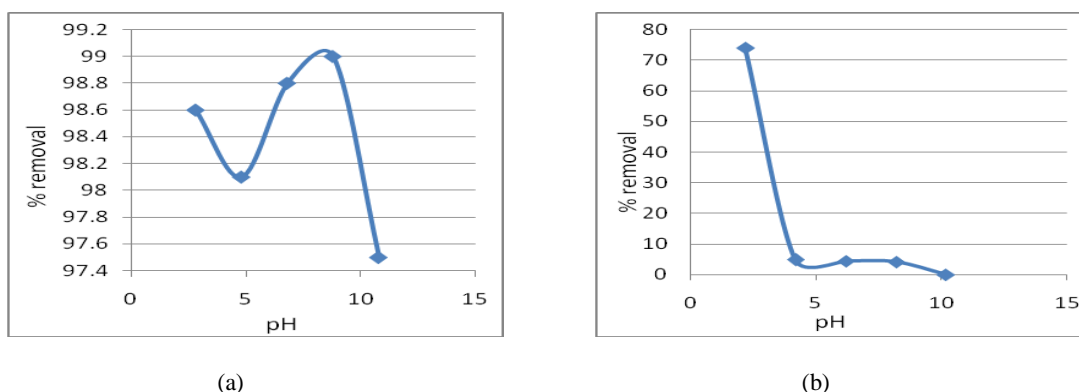


Fig 1: Variation of % removal of (a) mb, (b) ic with pH at concentration 10 ppm, adsorbent dose 0.2 g, contact time 30 min, particle size 140 μm .

As can be seen from fig.1 the maximum removal of methylene blue (mb) is obtained at pH 9 because the adsorbent surface is influenced by the surface charge on the adsorbent. The surface charge of Kailashpati powder is related with the pH of dye solution. The powder consists of polar functional groups such as hydroxyl (-OH) and carbonyl (>C=O) which will be influenced by the pH. As the pH of the solution increases, the number of negatively charge sites increased. This is because a strong electrostatic attraction exists between the positively charged cationic dye and the negatively charged powder surface due to the

ionization of kailashpati powder. As a result, a negatively charged surface site on the adsorbent favors the adsorption of dye [8]. In case of ic dye it is adsorbed at acidic pH where the negative charged sights at the surface are neutralized and positive charge is acquired by the surface. There is electroststic attraction between the positively charged surface and anionic dye [9].

Effect of Contact time: Contact time between adsorbate and adsorbent was varied between 15 min to 120 min. and results are shown in fig. 2.

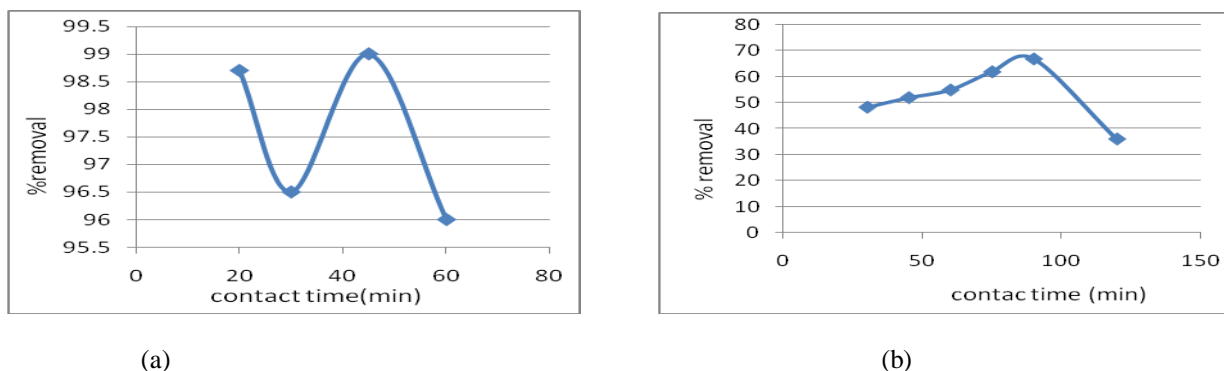


Fig 2: Variation of % removal of (a) mb , (b) ic with contact time at pH 9 for mb and 2 for ic, adsorbent dose 0.2 g, particle size 140 μm , concentration 10 ppm

In case of Methylene blue and Indigo carmine the %removal increases with contact time and then again decreases, this is due to the fact that as the contact time increases the interaction between the adsorbent and dye also increases but after a particular time interval the surface is completely covered by dye and no further adsorption can take place hence either the %removal remains constant or desorption might take place resulting in decrease in adsorption. At this point, the amount of dye desorbed is in dynamic equilibrium with the amount of dye being adsorbed on adsorbent [10].

Effect of Adsorbent dose: Adsorbent dose was varied between 0.05g to 0.4 g and results are shown in fig. 3. Adsorbent dose is an important parameter that strongly influences the adsorption process by affecting adsorption capacity of the adsorbent. As the adsorbent dose increases the percent removal increases because at lower adsorbent dose the adsorbent (dye) is more accessible [10], but after a particular amount of adsorbent saturation of adsorption sites occur due to particulate interaction such as aggregation takes place. Such aggregation would lead to a decrease in total surface area of the adsorbent and increase in diffusion path length. Hence the percent removal of the dye also decreases [11].

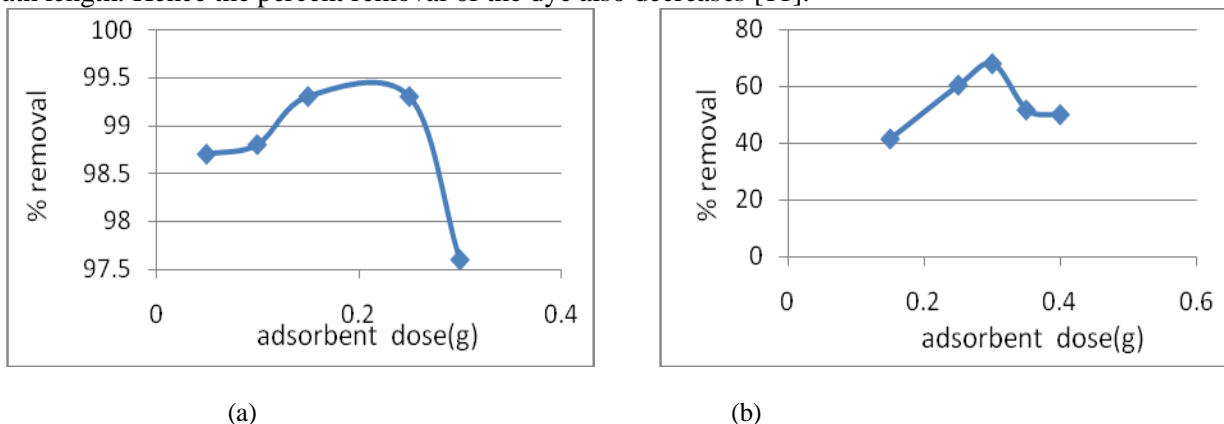


Fig 3: Variation of % removal of (a) mb , (b) ic with adsorbent dosage at pH 9 for mb and 2 for ic, contact time 45min for mb and 90 min for ic, particle size 140 μm , concentration 10 ppm

Effect of Particle size: The % removal of dye were studied at adsorbent particle size of 140, 250, and 420 (Fig. 4)

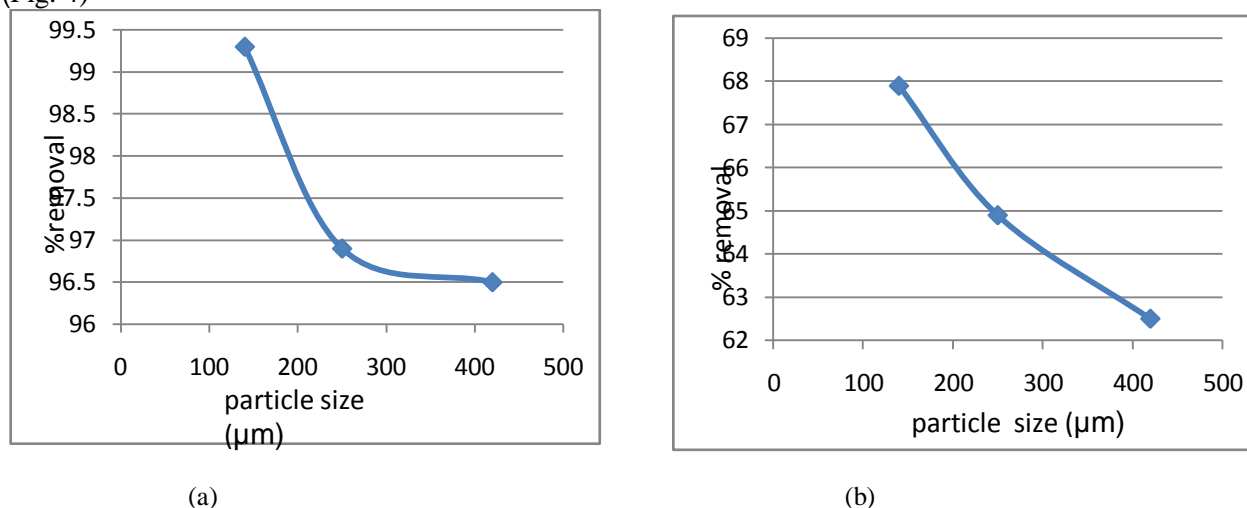


Fig 4: Variation of % removal of (a) mb , (b) ic with particle size at pH 9 for mb and 2 for ic, contact time 45min for mb and 90 min for ic, adsorbent dosage of 0.3g for ic and 0.15g for mb, concentration 10 ppm

From the graphs it can be seen that as the particle size increases the surface area decreases which results in the decrease in efficiency of adsorption. Same is the case for ic dye. With decrease in the particle size, the amount of the dye adsorbed was found to increase for both the dyes. This is mainly due to the increase in the surface area and accessibility of the adsorbent pores for the dye with the decrease in particle size i.e. as the particle size decreases the pores are easily available for adsorption of dyes [12].

Effect of Concentration: At the optimized conditions %removal of dyes was studied at various concentrations. These results are shown in fig. 5.

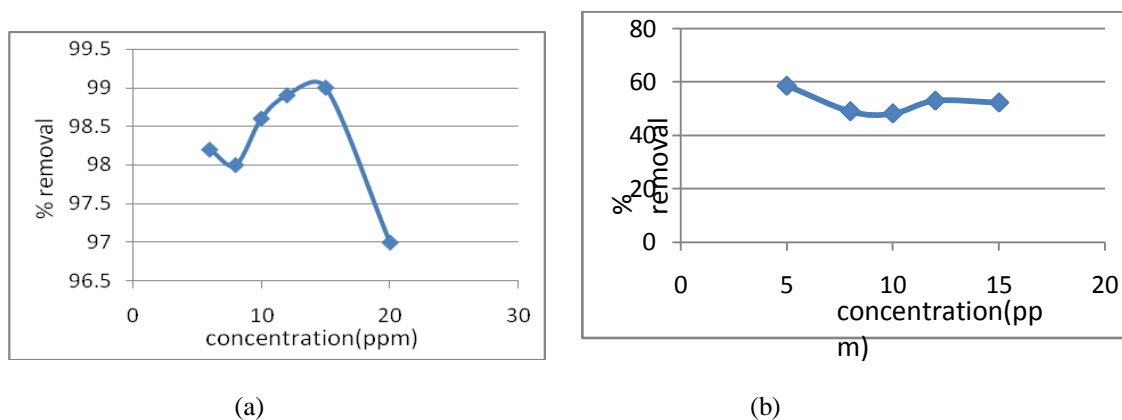


Fig 5: Variation of % removal of (a) mb , (b) ic with concentration at pH 9 for mb and 2 for ic, contact time 45min for mb and 90 min for ic, adsorbent dosage of 0.3g for ic and 0.15g for mb, particle size 140 μm.

As can be seen from Fig. 5 (a) that adsorption capacity increases from 98% to 99.5%, as the concentration increased from 5 ppm to 15 ppm. The higher the methylene blue concentration, the stronger is the driving forces of the concentration gradient so the adsorption capacity will be higher [8] this may also happen due to the fact that total adsorption sites available at the surface of the adsorbent remain fixed and invariable

for all concentrations. With increasing concentration the available adsorption sites become fewer and hence the percent removal of dye decreases with the initial concentration [10].

Characterization studies: The prepared adsorbent was characterized by FTIR and SEM techniques. FTIR spectrum of virgin adsorbent and loaded adsorbent is shown in fig 6.

FTIR studies:

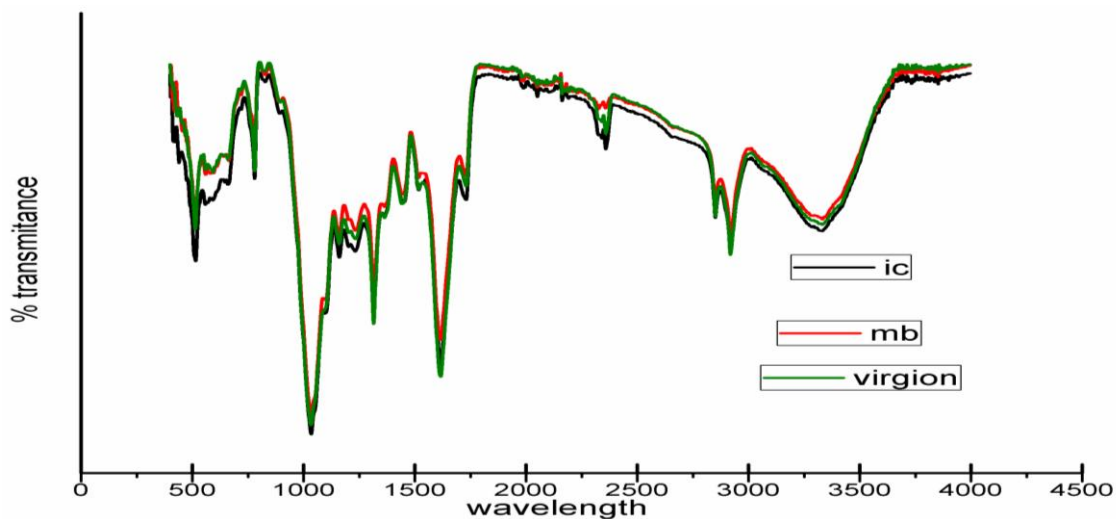
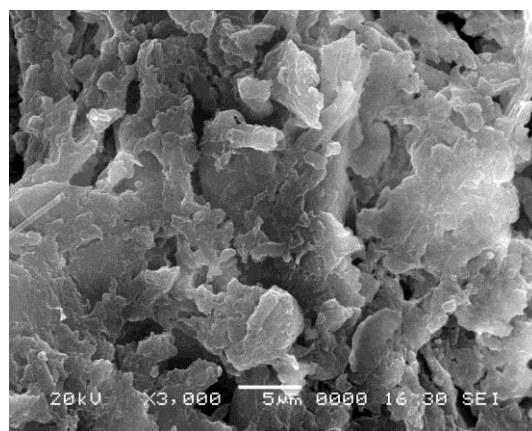
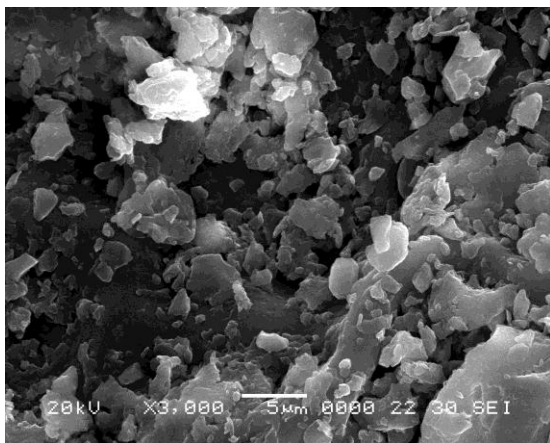
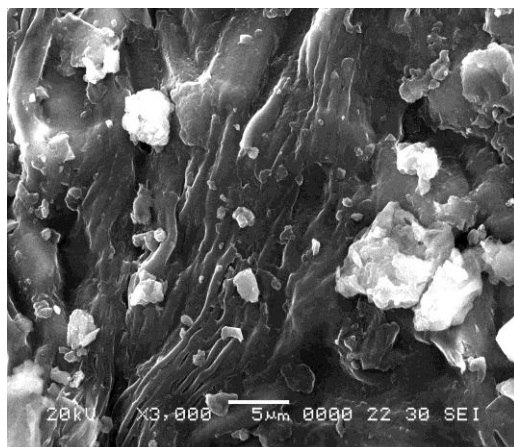


Fig 6: FTIR graph for virgin and powder adsorbed with mb and ic dye

As can be seen from the figure that %transmittance of the adsorbed dye virgin adsorbent show very slight difference from each other. The slight difference in intensities between the graphs confirms that the dye is adsorbed on adsorbent. Two peaks between the range of 3000 cm^{-1} to 2500 cm^{-1} indicates the presence of sp^2 hybridized carbon hydrogen stretching on adsorbent and the peaks in the range of 1000 cm^{-1} indicates the carbon oxygen bond stretching. The broad peak from 3000 cm^{-1} indicates presence of alcoholic group.

SEM studies: SEM micrographs for virgin adsorbent, adsorbed dye and adsorbed adsorbent are shown in fig 7





(c)

Fig. 7 SEM images of (a) Virgin adsorbent, (b) indigo carmine loaded adsorbent, (c) methylene blue loaded adsorbent

From these SEM images we can see that there are lots of active sites at the adsorbent surface present for adsorption as in (Fig 7(a) for virgin adsorbent). Fig 7 (b) shows the adsorbed indigo carmine dye but as the dye showed only 60 -65 % adsorption hence there are few void spaces on the surface of adsorbent. Fig 7 (c) shows the adsorption of methylene blue dye at the surface. There are no void spaces on the surface because this dye gets 99% adsorbed hence all the surface is covered by adsorption.

Effect of temperature on adsorption process: The effect of temperature on adsorption of mb and ic on powdered leaves of *Couroupita guianensis* was investigated by varying the temperature from 25 to 45°C. For this purpose experiments were carried out at the optimized parameters (indigo carmine: initial concentration 5ppm, pH 2, contact time 90 min, adsorbent dosage 0.3g, particle size 140 μm ; for methylene blue: 15ppm, pH 9, contact time 45 min, adsorbent dosage 0.15g, particle size 140 μm .) Thermodynamics provide valuable information on type of process and provides knowledge about standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°), standard entropy change (ΔS°) during adsorption. Gibbs free energy change can be given by $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. Where T is temperature in Kelvin. ΔS° and ΔH° can be calculated by van't Hoff equation [8].

Following graphs shows the plot of $\ln k$ Vs $1/T$. for methylene blue Fig.8 and indigo carmine Fig 9.

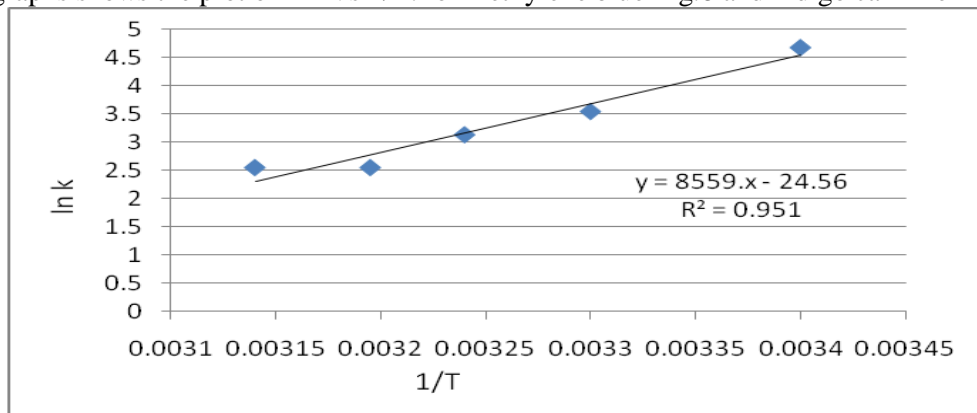


Fig 8: Variation of $\ln k$ with $1/T$ for methylene blue

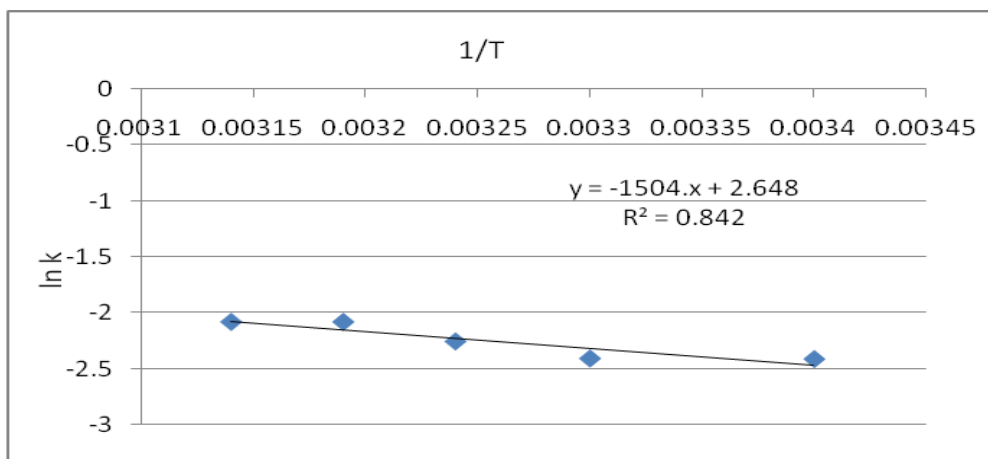


Fig 9: Variation of $\ln k$ with $1/T$ for indigo car

Thermodynamic parameters obtained from these plots are recorded in table 1.

Table 1. Thermodynamic parameters for adsorption of methylene blue and indigo carmine.

dye	ΔG° (kJ/molK)					ΔH° (kJ/mol)	ΔS° (kJ/molK)
	298 K	303 K	308 K	313 K	318 K		
mb	-10.310	-9.289	-8.268	-7.247	-6.226	-7.1159	-0.204
ic	5.944	5.834	5.724	5.614	5.504	12.506	0.022

As the temperature increases the % removal for indigo carmine increases from 70.6% to 74.1% because with increase in temperature, the rate of diffusion of adsorbate molecule across the external boundary layer and interval pores of the adsorbent particles increases. Changing the temperature will change the equilibrium capacity of the adsorbent for particular adsorbate [8]. As seen from the table the ΔG° values are positive for ic indicating the nonspontaneous nature and thermodynamically unfavourable adsorption. Negative values of ΔH° and ΔS° indicate exothermic process and decrease in randomness at liquid solid interface respectively [8].

As the temperature increases the % removal for methylene blue decreases slightly from 99.8% to 98.8%. The negative values of ΔG° indicate spontaneous nature and thermodynamically favorable adsorption for mb. The positive values of ΔH° and ΔS° indicate endothermic process and decrease in randomness at liquid solid interface respectively.

Kinetic study: The kinetics of adsorption of mb was studied for a contact time ranging from 10 to 45 min. the experimental data was fitted to pseudo second order kinetic model (Fig.10). The reported R^2 value indicates that the experimental results shows better fit to pseudo- second order.

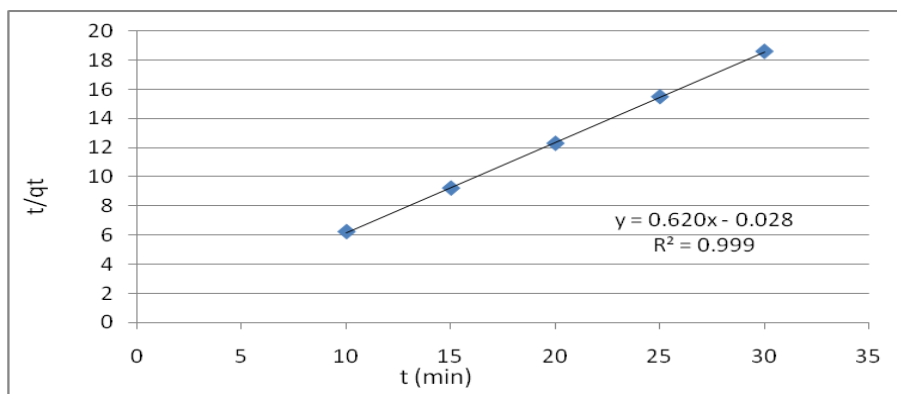


Fig.10: pseudo second order plot for adsorption of methylene blue on bio adsorbent

The kinetics of adsorption of ic was studied for a contact time ranging from 30 to 120 min. the experimental data was fitted to pseudo first order kinetic model (Fig.11). The reported R^2 value indicates that the experimental results show better fit to pseudo- first order.

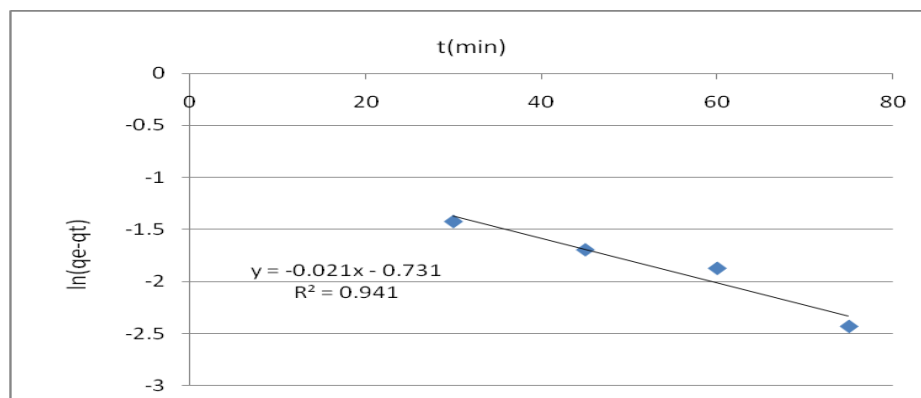


Fig. 11 .Pseudo first order plot for adsorption of indigo carmine on bio adsorbent

APPLICATIONS

Powdered leaves of kailashpati can be used effectively for the removal of methylene blue and indigo carmine from aqueous solution. The developed technique is cost effective and efficient and can be applied to other dyes also.

CONCLUSIONS

1. Maximum removal (99.7%) of methylene blue (15 ppm) was observed at pH 9, contact time 45min, adsorbent dose of 0.15 g, particle size of 140 μm .
2. Maximum removal (60%) of indigo carmine (5 ppm) was observed at pH 2, contact time 90min, adsorbent dose of 0.3 g, particle size of 140 μm ,
3. Thermodynamics study revealed that adsorption of methylene blue dye is a spontaneous and endothermic process which decreases the entropy of the system, while adsorption of indigo carmine dye is a non-spontaneous and exothermic process which increase the randomness of the system
4. Adsorption of methylene blue and indigo carmine follow pseudo second order and pseudo first order kinetics respectively.

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