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Removal of Crystal Violet from Aqueous solutions using Chitosan and *Saraca Indica* leaves

N .S .Rajurkar* and Asha Desai

*Department of Chemistry, Savitribai Phule Pune University, Pune 411007, **INDIA**

Email: nsraj@chem.unipune.ac.in

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ABSTRACT

Present study focuses on the use of conventional and novel adsorbent for removal of crystal violet from aqueous solution by batch adsorption process using chitosan and saraca indica (Ashoka) leaves as adsorbents. The study revealed that the crystal violet (10 ppm) showed maximum removal (98%) at pH 3, contact time 40 min, adsorbent dose 0.6 g and particle size 250 µm. The adsorption of dye has been described by Langmuir and Freundlich Isotherms. Its adsorption followed second order kinetics..The bioadsorbent (Asoka leaves) have been tested for the removal of color from the aqueous solution containing crystal violet. The study revealed that crystal violet (10 ppm) showed maximum removal at pH3, contact time 30 min, adsorbent dose 0.2 g and particle size 105µm. The adsorption of dye has been described by Langmuir Isotherm. Its adsorption followed second order kinetics.

Keywords: Chitosan, Bio adsorbent, *Saraca indica leaves*, crystal violet, Adsorption Isotherm, Kinetics, Thermodynamics.

INTRODUCTION

In industrial waste water treatment dye removal is one of the major concerns. Textile industries discharge a large quantity of highly colored waste water effluent which are released into nearby land or rivers. Treating the textile effluents is becoming an environmental concern due to scarcity of water [1]. Various methods like ion exchange, reverse osmosis, ozonation, photodegradation, chemical oxidation, electrocoagulation-electrofloatation and adsorption etc are being used for treating the effluents but all this techniques have some or other drawback [2].

These methods are costly and accumulation of concentrated sludge becomes disposal problem. Recently there is a 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. 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 *saraca indica* (Ashoka) leaves as bioadsorbent for the removal of crystal violet (CV) dye from its aqueous solutions and compare the results with conventional adsorbent chitosan. The studies were carried out using batch adsorption process.

MATERIALS AND METHODS

Crystal violet was obtained from Molychem chemicals ltd Mumbai, India and Chitosan was purchased from Otto Company with degree of deacetylation of 80%. The stock solution (500ppm) of the dye was prepared in distilled water and diluted as per requirement .The leaves of Ashoka tree were collected from M M college campus Pune city and washed thoroughly with tap water. These leaves were then dried in air for 72 h powdered and treated with water at 363K for 4 h and then filtered. The procedure was repeated till the color of the filtrate fades and then powder is used as bioadsorbent.

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

25mL of 10ppm solution was used to study different parameters for both adsorbents (Chitosan and Bioadsorbent). The solution along with each adsorbent was continuously stirred at 1100 to 1200 rpm. All the parameters were kept constant except one parameter to be optimized. After that the solution was centrifuged for 10 to 15 min at 1200 rpm and filtered through whatman-41 filter paper. The filtrate was analyzed in U.V-visible spectrometer and percentage removal was calculated from following equation-

$$\textbf{\% removal} = (C_0 - C_e) / C_0 \times 100$$

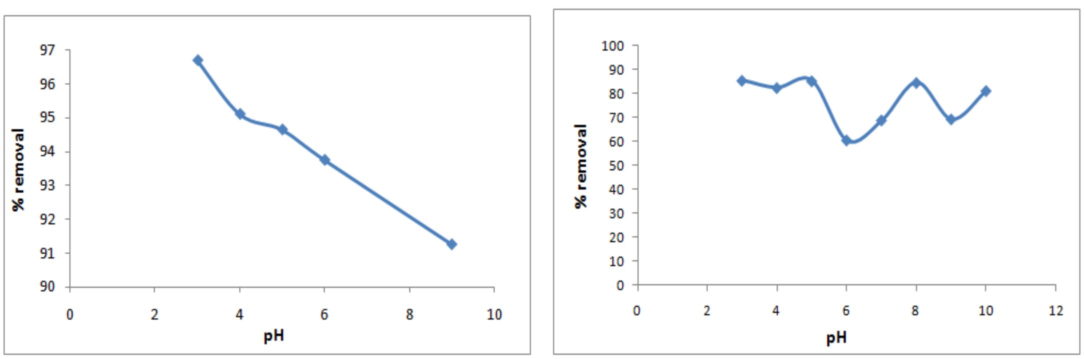
Where,

C_0 = Initial absorbance of unabsorbed solution

C_e = absorbance of solution after adsorption

RESULTS AND DISCUSSION

Effect of pH: The effect of pH on % removal of CV was studied by varying pH between 3 to10. The results are shown in fig.1

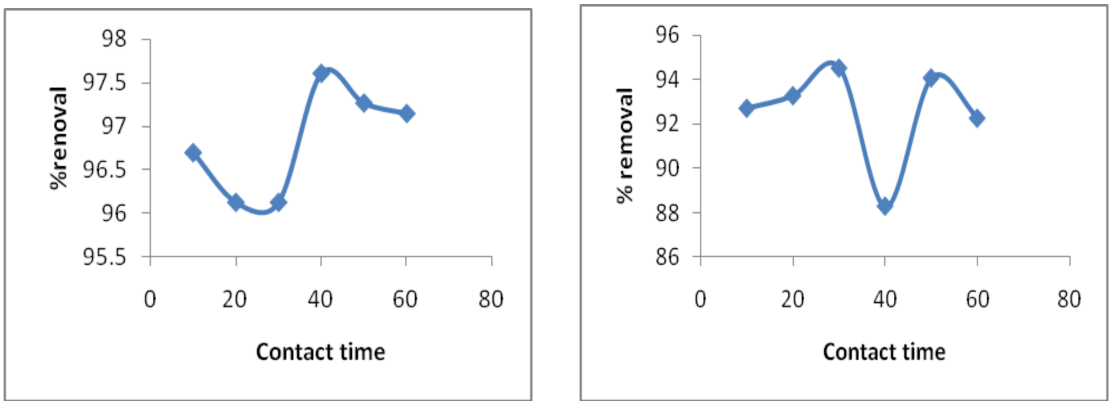


(a) (b)

Fig 1: Effect of pH on % removal of **(a)** C.V. chitosan **(b)** C.V. with bioadsorbent with pH at concentration 10ppm, adsorbent dose 0.5g contact time 30 min, particle size 420µm.

From fig.1 It is seen that maximum removal of crystal violet (CV) is observed at pH 3. Acidity is very important in the adsorption process, especially for dye adsorption. The pH of a medium will control the magnitude of the electrostatic charges imparted by the ionized dye molecules. Both the adsorbent and adsorbate may have functional groups that can be protonated or deprotonated to produce different surface charges in solutions at different pH, resulting in electrostatic attraction or repulsion between the charged adsorbates and adsorbents. Therefore, the effect of pH on the adsorption behavior of the dye on the adsorbent was studied by observing the percentage of dye removal over a wide pH range of 3-10[8]. The variation in the removal of CV with pH is shown in Figure 1. As presented in the figure, the obtained results show that the percentage removal of dye decreases slightly with increasing basicity up to pH 7.0 after which it remains almost constant. This behavior may be due to the increase in negative charge density of surface at acidic pH, resulting in a attraction between the positively charged dye molecule and adsorbent. As the pH increases, the surface changes density on the adsorbent decreases, resulting in electrostatic repulsion from the positive charge of the dye molecule [9].

Effect of Contact Time: The effect of contact time on % removal of CV was studied by varying time between10-60 min. The results are shown in fig.2

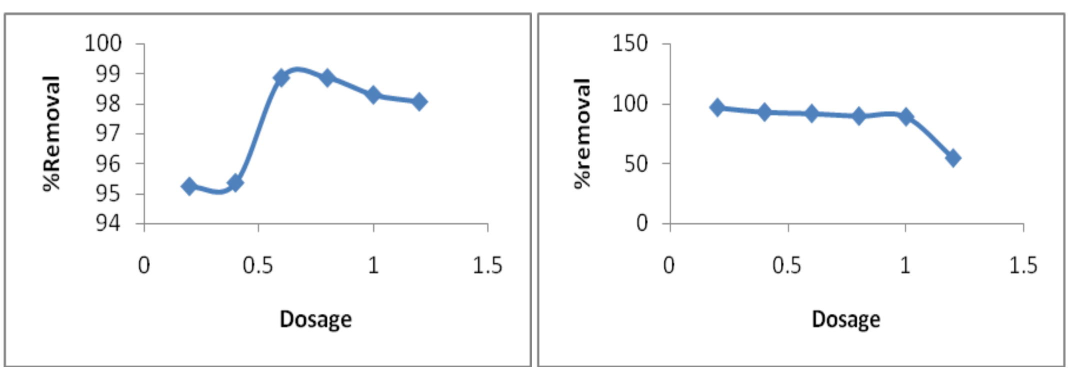


(a) (b)

Fig 2: Effect of contact time on % removal of **(a)** C.V. with Chitosan **(b)** C.V. with bioadsorbent with contact time at pH 3 for both adsorbent, dose 0.5g, particle size 420µm, concentration 10 ppm

Crystal violet shows increase in % removal with increase in contact time and then again decreases. As 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 takes place or desorption might take place resulting in decrease in adsorption. It shows constant % removal. At this point the amount of dye desorbed is in dynamic equilibrium with amount of dye being adsorbed on adsorbent [10].

Effect of Adsorbent Dose: The effect of adsorbent dosage on % removal of CV was studied by varying dose between 0.2-1.2 g. The results are shown in fig.3

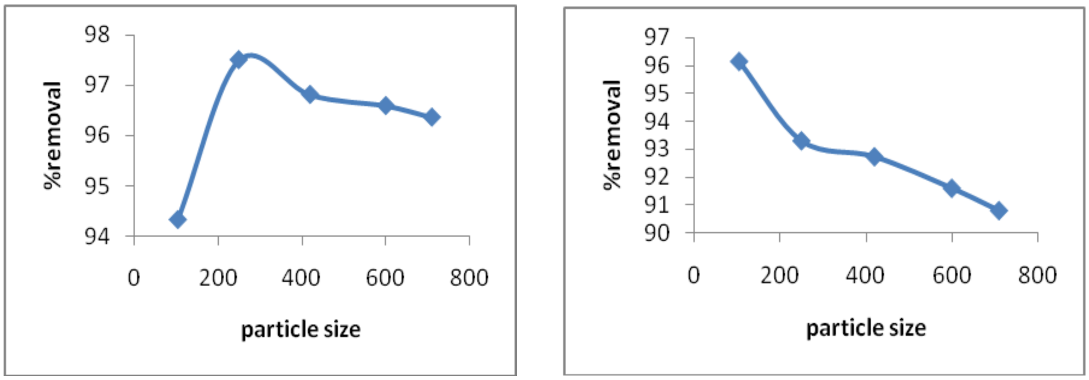


(a) (b)

Fig 3: Effect of adsorbent dosage on % removal of **(a)** C.V. with Chitosan **(b)** C.V. with bioadsorbent with adsorbent dose at pH3, contact time 40min and 30min respectively, particle size 420 µm, concentration 10 ppm

Adsorbent dose is an important parameter that strongly influences the adsorption process by affecting adsorption capacity of the adsorbent. The increase in removal of dyes with adsorbent dose is due to the introduction of more binding sides for adsorption [11]. After a particular amount of adsorbent dose saturation occurs due to particulate interaction leads to aggregation. It causes reduction in surface area of adsorbent. It decreases %removal of dye [12].

Effect of Particle size: The effect of particle size on % removal of dye was studied at adsorbent particle size of 105,250 and 420, 610, 700 µm. The results are shown in fig.4

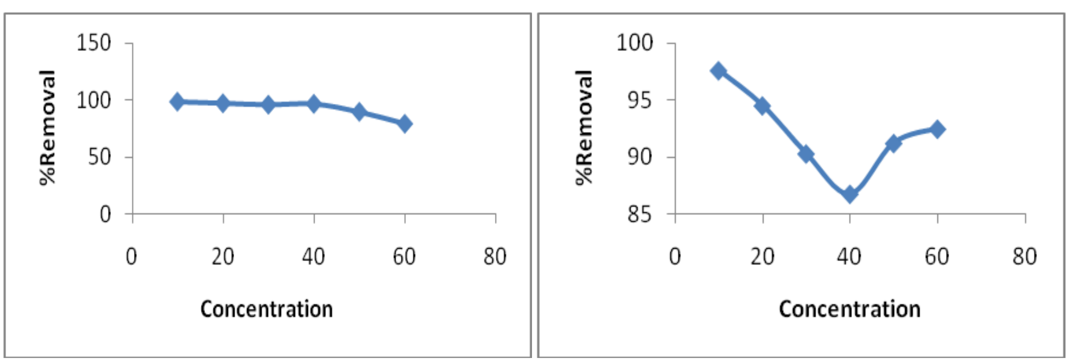


(a) (b)

Fig 4: Effect of particle size on % removal of (a) C.V. with Chitosan (b) C.V. with bioadsorbent with particle size at pH 3, contact time 40 min and 30 min respectively, adsorbent dose 0.6 g and 0.2 g, concentration 10 ppm.

From the graph it can be seen that as the particle size increases the surface area decreases which results in the decrease in efficiency of adsorption. With chitosan the efficiency of adsorption decreases with particle size initially and then increases. But with decrease in particle size CV with bioadsorbent shows maximum adsorption. 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 [13].

Effects of Concentration: At the optimized conditions of various parameters studied % removal of dyes was studied at various concentrations. The results are shown in figure 5



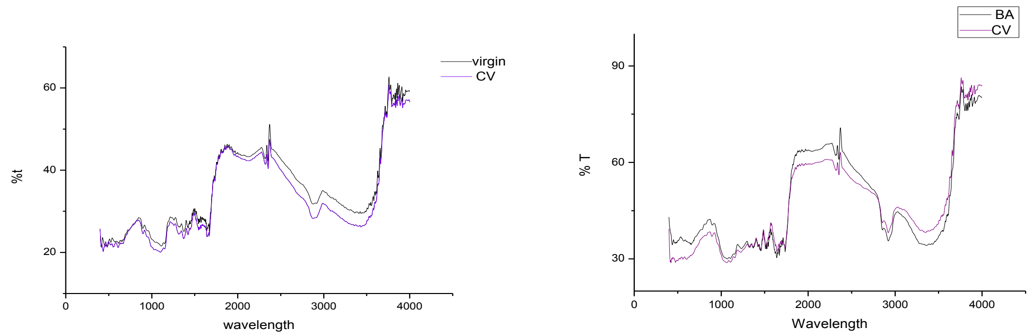
(a) (b)

Fig 5: Variation of % removal of **(a)** C.V. with Chitosan **(b)** C.V. with bioadsorbent with concentration at pH 3, contact time 40 min and 30 min respectively, dose 0.6 g and 0.2 g respectively, Particle size 250 µm and 105 µm respectively.

It can be seen from fig. 5 (a) and 5(b) as concentration increases % removal of dye decreases. With increasing concentration the available adsorption sites become fewer and hence the % removal of dye decreases in both the cases [14].

Characterization Studies: Studied adsorbents were characterized by FTIR and SEM techniques. FTIR spectrum of virgin adsorbent and dye loaded adsorbent is shown in fig. 6

FTIR studies:

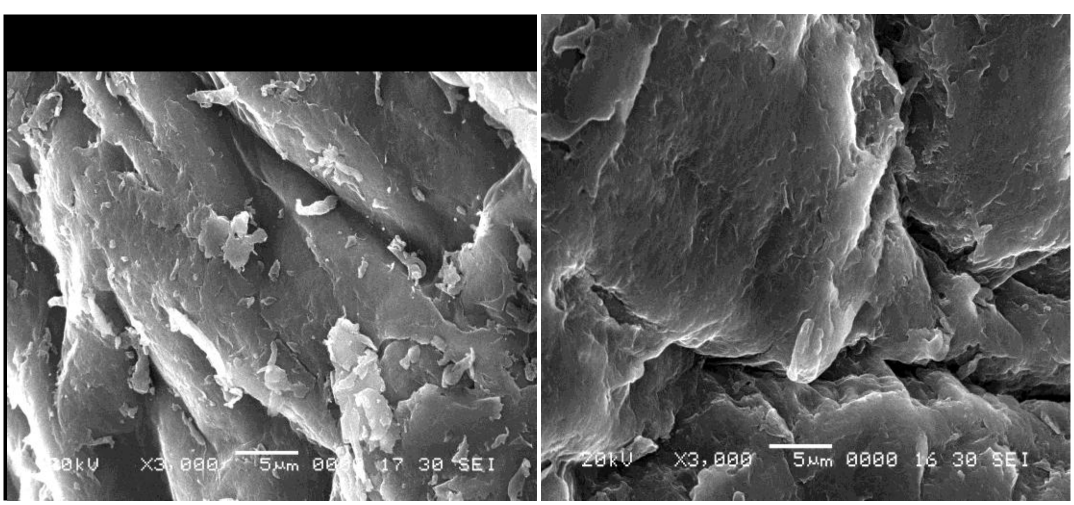


(a) (b)

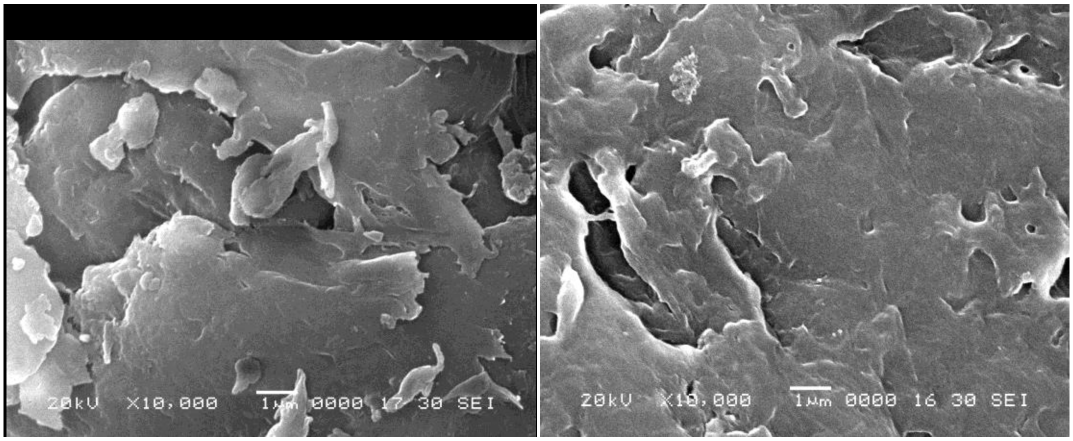
Fig 6 (a) indicates FTIR graph for virgin (Chitosan) and virgin loaded with crystal violet dye.
Figure 6(b) indicates FTIR graph for virgin (Bioadsorbent) and virgin loaded with crystal violet dye.

Fig.(a) indicates a sharp peak at 3000 to 3500 cm^{-1} indicates presence of alcoholic group. Peak at1100 cm^{-1} indicates presence of C-N Stretching. Fig.(b) Indicates FTIR graph for virgin (Bioadsorbent) and virgin loaded with crystal violet dye. A sharp peak at 3500 cm^{-1} indicates presence of alcoholic group. Peak at 1000 cm^{-1} indicates presence of C-O Stretching and peak at 1100 cm^{-1} indicates C-N stretching Bond in the figure.

SEM Studies: SEM Results for virgin adsorbent (Chitosan) and along with adsorbed dye (CV) is shown in figure 7.



(a)SEM of chitosan before adsorption (b) SEM of chitosan with cv after adsorption

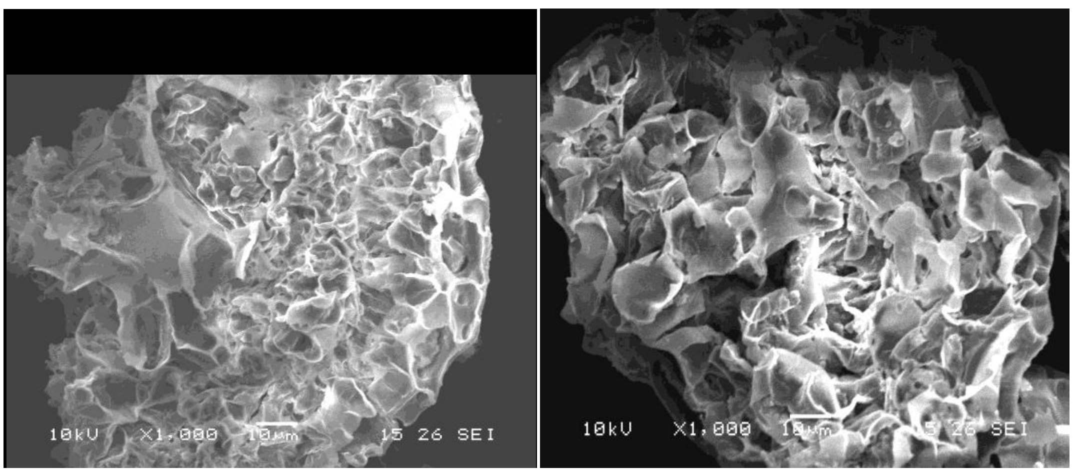


(c)SEM of chitosan before adsorption (d) SEM of chitosan with cv after adsorption

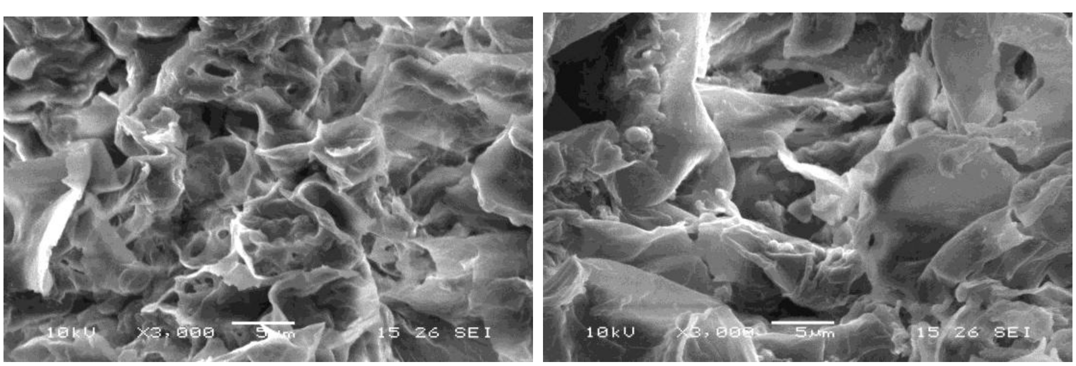
Fig. 7

Above SEM images show that there are many active sites at the surface available for adsorption for virgin adsorbent. But after adsorption with CV it indicates entire surface is covered by adsorption.

Virgin adsorbent (Bioadsorbent) and along with adsorbed dye (CV) is shown in figure 8.



(a) SEM of bioadsorbent before adsorption (b) SEM of bioadsorbent with cv after adsorption



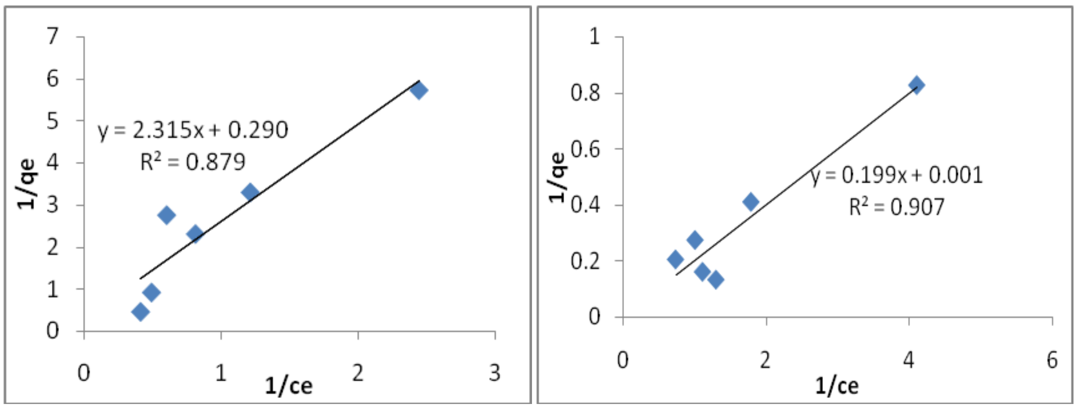
(c)SEM of bioadsorbent before\adsorption (d) SEM of bioadsorbent with cv after adsorption

Fig. 8

Above SEM images show that there are few void spaces at the surface available for adsorption for virgin bioadsorbent (Powdered Ashoka leaves). But after adsorption with CV it indicates void spaces are covered by adsorption of CV.

Adsorption Isotherms: An adsorption isotherm is the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium and constant temperature the equilibrium adsorption is important to study different isotherms such as Langmuir Isotherm and Freundlich Isotherm.

Langmuir Isotherm:



(a) Chitosan with CV (b) Bioadsorbent with CV

Fig 9: Langmuir Isotherm is studied by plotting the graph of 1/Ce against $1/q_e$

Figure 9 (a) indicates chitosan with crystal violet gave good result (R^2 = 0.879). Figure 9 (b) indicates Bioadsorbent with crystal violet gave very good result (R^2 = 0.907). Hence we can conclude that CV dye with both chitosan and bioadsorbent favors Langmuir Isotherm at equilibrium. It can be studied by the following equation-

$$\mathbf{1/q_e = 1/ab \times 1/c_e + 1/b}$$

q_e= Dye Adsorbed or per unit mass of Chitosan(mg g^{-1})
Ce= Adsorbed dye concentration at equilibrium.
a= Constant related to affinity of binding sites (L g^{-1})
b=Maximum amount of dye concentration per unit g of Chitosan (mg g^{-1})
These parameters are recorded in table. 1

Table 1. Parameters for Langmuir Isotherm

Dye	a	b	R^2
CV with Chitosan	**0.1256 mg g^{-1}**	**3.44 mg g^{-1}**	**0.8799**
CV with Bioadsorbent	**6.5×10^{-3} mg g^{-1}**	**769.2 mg g^{-1}**	**0.907**

Freundlich Isotherm: The Freundlich model assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases. The linear form of the Freundlich isotherm model yields a straight line. The slope and intercept are obtained from graph (Figure. 10) are used to calculate the Freundlich constants n and K_f

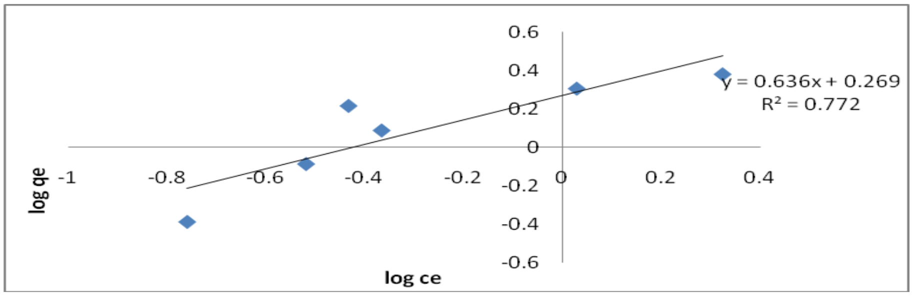


Fig 10: Freundlich Isotherm is studied by plotting the graph of log ce against log q_e.

Figure 10 indicates chitosan with crystal violet gave good result ($R^2 = 0.772$). It can be studied by following equation

$$\log q_e = (1/n) \log C_e + \log kF$$

where q_e is the amount of adsorbed mg g^{-1}.
kF is Freundlich constant related to adsorption capacity
n is Freundlich constant related to adsorption intensity
C_e = Adsorbed dye Concentration at equilibrium.
These parameters are recorded in table 2.

Table 2. Parameters for Freundlich isotherm

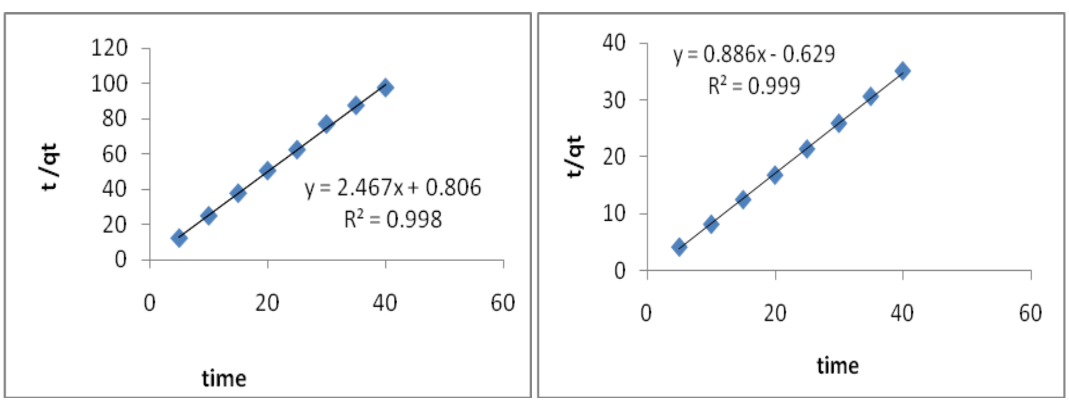
Dye	kF	n	R^2
CV with Chitosan	**1.8578 mg g^{-1}**	**1.572 mg g^{-1}**	**0.7728**

Kinetics of the Reaction: Kinetics studies are necessary to optimized different operation condition for the sorption of dyes. The kinetics of cv onto chitosan and saraca indica leaves powder was studied using pseudo second order kinetics

Pseudo second order Reaction: The adsorption mechanism over a complete range of the contact time is explained by pseudo second order kinetic model. The integrated linear form of the model is as follows:

$$\frac{t}{qt} = \frac{1}{k_2\, qe^2} + \frac{t}{qe}$$

A plot of t/qt versus t gives a linear relationship fig.11, from which q_e and k_2 were determined from the slope and intercept of the plot respectively and presented in table 3.



(a) Chitosan with CV (b) Bioadsorbent with CV

Fig 11: Pseudo second order Reaction is studied by plotting the graph of time against t/qt. (a) Indicates chitosan with crystal violet followed second order kinetics as R^2 gives very good result ($R^2 = 0.998$). (b) Indicates Bioadsorbent with crystal violet also followed second order kinetics as R^2 gives very good result ($R^2 = 0.999$)

Hence we can conclude that CV dye with both chitosan and bioadsorbent favors pseudo second order kinetics for a contact time ranging from 5 to 50 min.
The following table gives the values of q_e, k_2 and R^2. k_2 which indicates pseudo second order constant. It is recorded in table 3.

Table 3. Kinetic parameters for study of CV with chitosan and bioadsorbent

Dye	q_e	K_2	R^2
CV with Chitosan	**0.405**	**7.55**	**0.9986**
CV with Bioadsorbent	**1.12**	**-1.2476**	**0.999**

APPLICATIONS

Powdered leaves of Ashoka can be used for removal of crystal violet from aqueous solution effectively. The source is available abundantly in nature. The method of using bioadsorbent for removal of the dye is easy, less time consuming, cost effective and can be applied to other dyes also.

CONCLUSIONS

- Efficiency of removal of crystal violet with Chitosan is maximum (98.29%) at 10 ppm of concentration, pH 3, contact time 40 min, dosage 0.6 g and particle size 250µm,
- Percent removal of crystal violet with bioadsorbent is maximum (97.61%) at 10 ppm of concentration, pH 3, contact time 30 min, dosage 0.2 g and particle size 105µm,
- Adsorption of crystal violet with both chitosan and bioadsorbent follow Langmuir isotherm while adsorption of crystal violet with only chitosan follow Freundlich isotherm.
- Crystal violet with Chitosan and Bioadsorbent follow pseudo second order kinetics.

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AUTHORS' ADDRESSES

1. **Prof. (Mrs.) N.S. Rajurkar**
   Head, Department of Chemistry,
   Savitribai Phule Pune University,
   Pune- 411007, India
   Tel No: 912025601399
   Email: nsraj@chem.unipune.ac.in
2. **Asha. D. Desai**
   Department of Chemistry,
   Savitribai Phule Pune University,
   Pune- 411007, India
   Email: adchem@india.com