REMOVAL OF CRYSTAL VIOLET DYE FROM AQUEOUS SOLUTION BY ADSORPTION ON MIXTURE OF ACTIVATED CARBON: A KINETIC & EQUILIBRIUM STUDY

P.B. Wagh¹ and V.S. Shrivastava²

¹North Maharashtra University, Jalgaon, Maharashtra, Department of Chemistry, J.E.S. Arts, Science, and Commerce College, Nandurbar - 425412 (India).
²Nano Chemistry Research Laboratory, G.T.P. College, Nandurbar - 425412 (India).

Email: waghprakash2@gmail.com
Email: drvinod.srivastava@yahoo.com

ABSTRACT

The kinetics and equilibrium study of crystal violet dye adsorption on mixture of activated carbon (PWCAC) and (CSAC) was studied. The use of low cost ecofriendly adsorbent has been investigated as an ideal alternative to the current expensive methods of removing of dye from aqueous solution. This study was done by batch adsorption techniques. The quantitative adsorption kinetic and equilibrium parameter for crystal violet dye were studied using UV-visible adsorption spectroscopy. The effect of initial dye concentration, pH, adsorbent dose, temperature, particle size were determined to find the optimal condition for adsorption. The percentage removal of dye was found to be most effective at pH 10 and contact time 120 min and at an adsorbent dose 4 g/L of dye. The study indicates that the percentage removal of dye increases with increasing initial dye concentration, adsorption dose and contact time and attains equilibrium at optimum conditions.

The equilibrium study of adsorption of crystal violet dye on to mixture of activated carbon was investigated using pseudo first order and pseudo second order kinetic models. The adsorption kinetics was found to follow pseudo second order kinetic model. The equilibrium adsorption data of crystal violet dye on PWCAC and CSAC mixture was analyzed by Langmuir and Freundlich adsorption model. The results show that the Langmuir model provides the best correlation.

Keywords: Crystal violet adsorption kinetics; equilibrium study; and activated carbon mixture; FTIR; EDAX and SEM.
1. INTRODUCTION

The discharge of highly colored dyes effluents from dyes industries can disturb the aquatic life by decreasing sunlight penetration or by direct poisoning of living organism [1]. This problem is created due to non-degradable nature of synthetic dyes by chemical or photochemical process [2]. So for this the alternative procedure must be employed for the elimination of such a dyes before disposal. In this field the study and development of adsorption technique is very interesting approach. Different materials have been applied for the adsorption of different basic dyes from aqueous solution. The treatment processes like photo catalytic degradation, integrated chemical biological degradation, adsorption on activated carbon have been used to remove dyes from the dye waste water effluents [3-5]. A synthetic dye in waste water cannot be effectively decolorized by traditional method [6].

The high cost of removal of dye from aqueous solution using adsorption on commercial activated carbon though very effective has motivated the search for the alternative adsorbent. The agricultural byproduct is considered to be low value product. Due to their low utilization and most of the biomaterial are set to fire or discarded. This process creates resources losses and environmental pollution. The utilization of this material must bring economic and social benefit to the mankind. Recently an attention has been focused on the utilization and characterization of this native agricultural byproducts [7-8].The activated carbon perhaps the most widely used adsorbent for the removal of many organic dyes. Activated carbons exhibit an extended surface area, highly developed pore structure (in particular, microspores) and a high surface reactivity (Bansal and Goyal, 2005), so they are generally used to remove hazardous dyes and heavy metals from aqueous solution. The present study is undertaken to evaluate the efficiency of a mixture of activated carbon prepared from palm wood cellulose activated carbon (PWCAC) and coconut shell activated carbon(CSAC)[9]. The adsorption study was carried out involving various parameters as initial concentration, adsorbent dosage, agitation time and pH. The kinetics of the adsorption process and the thermodynamic parameters governing the adsorption process were evaluated and discussed. The data has been tabulated and discussed in the view of the above; the mixture is used in a definite proportion for the removal of basic dye (Crystal violet) from an aqueous solution.

2. MATERIALS AND METHOD

1.1 Preparation of adsorbent

The precursor material was collected from the local sources. The material was converted into small pieces and then washed several time by distilled water and then put in sunlight to dry for 24 hours. The small pieces are converted into different sized particles by grinding in ball mill. The material was sieved to an average particle size. The obtained material was activated chemically. A 50% zinc chloride solution was used for activation. The material was soaked in ZnCl₂ solution for 24hours. Then after decantation, the sample was pyrolyzed in Muffle Furnas in absence of air at 600°C for 60 min. The obtained material is used as an adsorbent [10]. The material is further used without purification as an adsorbent.

1.2 Adsorbate

The basic dye, crystal violate (C.I.42555) is colored water soluble powder. The crystal violate has molecular formula C₂₅H₃₀N₃C and molecular weight 408 gm⁻¹ and wave length 590 nm was used as adsorbate. It is supplied by SD fine chemicals Mumbai. The crystal violate has structure [11].

Fig.1: Structure of crystal violate

1000 ppm stock solution of crystal violate dye was prepared by dissolving 1gm of dye in double distilled water and from that stock solution a required ppm solutions were prepared for the experimental study.

3. RESULT AND DISCUSSION

The adsorption experiments were carried in a batch process at room temperature by using an aqueous solution of crystal violates dye. In each experiment an accurately weighed amount of PWCAC and CSAC mixture was added in 50ml of the dye solution in 100ml stoppered conical flask and then mixture was agitated in the mechanical shaker for a definite time at a
room temperature. The adsorbent was separated from the solution by centrifugation. The absorbance of the supernatant solution was estimated to determine the residual dye concentration. The residual dye concentration was determined before and after treatment at 590nm wave length with spectrophotometer (Systronics -118) using quartz’s cell of path length 1cm. The experiment were carried out at initial pH values ranging from 2 to 10 pH. The removal of dye from 2 to 10 pH were measured by using pH meter (Equitronics model EQ 607). The initial pH was controlled by addition of 0.1NHCl and 0.1NaOH solution. The kinetic of adsorption was determined by analyzing adsorptive uptake of dye from aqueous solution at different time intervals. The FTIR, SEM, XRD) of adsorbent was also carried

3.1 Adsorbent characterization

3.1.1. FTIR

The FTIR of mixed carbon fig (1) showed that the presence of peaks for a large number of functional groups. Viz 3432cm⁻¹ is due to O-H stretching frequency in alcohol or it may be due to –N-H stretching frequency in amines. 2852cm⁻¹ and 2926 cm⁻¹ is due to –C-H stretching frequency. 1570-1630 cm⁻¹ is due to aromatic >C= C< stretching frequency. 1270,1315,1384 cm⁻¹ is due to C-N stretching frequency in amines. 1111 cm⁻¹ is due to –C-O stretching frequency. 780 cm⁻¹ is C-H bending frequency in alkene or C-Cl stretching frequency. The FTIR of mixed carbon after the dye adsorption fig.(2) showed that the presence of peaks for the large no of functional groups. The 3407 cm⁻¹ is due to stretching frequency in alcohols, phenol or N-H stretching frequency in amines. The 2926-2852 cm⁻¹ is due to –C-H stretching frequency in alkanes. The 1581,1616,1413 cm⁻¹ may be due to aromatic >C= C< stretching frequency. The 1382,1315 cm⁻¹ is due to >C-N stretching frequency in amines. 1174 cm⁻¹ is due to –C-O stretching frequency. 779 cm⁻¹ is due to –C-H bending frequency in alkenes or –C-Cl stretching frequency. 568,673 cm⁻¹ is for C-Br stretching frequency. 1413 cm⁻¹ is for C-H bending frequency in alkane. 1174,1350,1382 cm⁻¹ is due to S=O stretching frequency in sulfonic acid.

Fig.2 FTIR spectra of pure adsorbent

Fig.3 FTIR spectra of dye adsorbed adsorbent
3.1.2. XRD Analysis

The XRD diagram of mixture of PWCAC and CASC is shown in (fig 3) The XRD of mixed adsorbent shows main peak 2θ of 24.44° and 2θ peak 26.73° and 2θ at 72.48° respectively. The high intensity of peaks indicates the highly crystalline nature of PWCAC and CSAC carbon. The average particle size is estimated by Scherer formula. The size of particle observed is 7.1 nm, 18.44 nm and 16.7 nm.

![XRD Spectra of mixed adsorbent PWCAC and CSAC](image)

3.1.3. SEM Analysis

The scanning electron microscope (SEM) is widely used to study the morphological features and surface characteristics of adsorbent material. It is useful to determine particle shape, porosity and appropriate size distribution of the adsorbent material.

![SEM micrograph of PWCAC and CSAC of mixed carbon](image)
3.1.4. EDAX

It is energy dispersive x ray spectroscopy and it is a chemical microanalysis techniques used in conjunctions with SEM.EDAX analysis was used to characterize the elemental composition of PWCA and CSAC. The EDAX of elemental analysis shows 28.51% of C, 21.8% H before adsorption and 88.40% C and 9.18% O after adsorption.

3.2. Effect of pH

The experiment were carry out at 60 mg of initial dye concentration with 4 g/L adsorbent dose for 120 min equilibrium time and in the range of pH change from 2 to 12. Initially when pH increases from 4 to 10 the percentage removal increases from 91.98% to 98.12% and it slightly decreases up to 91. % for pH 12 . The maximum percentage removal occurs at pH 10 and hence the pH 10 is selected as a optimum pH.

3.3.3. Effect of contact time

The amount of dye adsorbed qt (Mg/gm) increased with increasing in agitation time and reached to the equilibrium after 120 min, for the dye concentration 20, 30, 40 and 60 ppm/L. Thus time required to achieve a definite fraction of equilibrium adsorption was found to be 120 min and it is independent of dye concentration. The adsorption density qt (mg/gm) also increased with increasing dye concentration. The percentage of dye removal at equilibrium increases from 84.21 % to 96.96% as dye concentration increased from 20 to 60 mg/L for 4 g/L of adsorbent does at pH 10. This shows that removal of crystal violate depends on concentration of dye. The maximum % removal of dye occurs at 60 ppm and hence it is selected for further study [12-14].
3.4. Effect of adsorbent dose

The effect of adsorbent dose on the amount of dye adsorbed was studied. The equilibrium value of amount of dye absorbed was observed to be increased from 81.17% to 97.19% mg/L with increase in adsorbent dose from 0.02gm to 4 g/L for 60 mg/L dye concentration, contact time 120 min and pH10. The percentage removal of crystal violate increased with increasing dose of adsorbent and that is due to the increased in availability of surface active sites resulting from increased of dose and agglomeration of adsorbent. The increase in the extent of removal of crystal violate is found to be significant at the dose 4g/L and hence it is fixed as a optimum dose for adsorbent [15].

3.5. Effect of initial dye concentration

The adsorbent and dye solution of different initial dye concentration 20mg to 200mg/L was contacted for 120 min at pH10 and at a constant adsorbent dose 4 g/L. The result shows that the percentage removal of dye increases from 84.21% to 95.96% when initial dye concentration increases from 20 to 60 mg/L; this shows that the crystal violate gets Removed by adsorption[15].

![Fig.8: Effect of contact time and concentration of crystal violet on Percentage removal, adsorbent dose 4 g/L, PH10 and contact time 120 min.](image)

![Fig.9: Effect of adsorbent dose on percentage removal of crystal violet dye for initial dye concentration, Contact time 120min, pH 10.](image)

![Fig.10: Effect of initial dye concentration on percentage removal Crystal violate by PWCAC and CSAC Mixture, Adsorbent dose 4 g/L and pH10](image)
3.6. Effect of partical size

The adsorption experiment was carried out by using different mesh size partical ranging from 50 to 250 mesh size. It is observed that the adsorption of dye decrease with increase of particle size and increase with decrease in particle size that is due to large surface area availability. For 100nm particle size the 5 removal is maximum and it is 89.47%.

![Fig.11: Effect of particle size on removal of crystal violate (Co=60ppm) by PWCAC and CSAC.](image)

3.7. Effect of temperature

The experiment was carried out at three different temperatures i.e. from 40, 50 and 60°C. It is observed that the removal of crystal violate decrease with increase of temperature hence adsorption of crystal violate is an exothermic process [17].

![Fig.12: Effect of temp. On percentage removal of crystal violet dye, Initial dye concentration 60 ppm, contact time 120 min. at pH 10](image)

3.7. ADSORPTION KINETICS

The kinetics of adsorption study is quite significant as it decides the residence time of adsorbate at the rate of adsorption process. The dye concentration and adsorbent dose are the important parameter because they determine capacity of adsorbent for a given initial concentration of dye solution. The study includes adsorption rate study .The kinetics of adsorption of crystal violate on PWCAC and CSAC mixture were analyzed using pseudo first order (Lagergren), Pseudo 2nd order kinetic models. The conformity between experimental data and the model predicated values were expressed by Correlation coefficient (r^2).A relatively high r^2 value indicate that the model successfully describes the kinetics of crystal violate adsorption. The dye removal from the solution is through the mechanism of adsorption.

3.7.1 Pseudo first order equation

The Pseudo first order (Lagergren) equation is generally expressed as

\[
\log (q_e - q_t) = \log q_e - \left( \frac{K_1}{2.303} \right) t
\]

where \(q_e\) and \(q_t\) are the amount of dye adsorbed (mg/g) on PWCAC and CSAC mixture at equilibrium and at time 't', respectively. \(K_1\) is a rate constant of pseudo first order adsorption (min^{-1}).The rate constant \(K_1\) and \(q_e\) for first order equation are determined from the slope and intercept of the plot of log (qe-qt) vs. time respectively (fig.13)
Fig. 13: Lagergren 1st order plot for adsorption of crystal violate by PWCAC and CSAC mixture for different initial dye concentration adsorbent dose 4gm/L and pH10.

The linear relationship of the plot for 20, 30, 40 and 60 mg/L dye concentration indicates the validity of equation. The correlation coefficient $r^2$ of the first order equation is (0.967 to 0.99) the value of $q_e$ calculated from first order kinetics plots were not same as compared to experimental (Table 1). It shows that the rate constant $K_1$ is not the same with increase in initial dye concentration and adsorbent dose. It shows the inapplicability of Lagergren equation to describe the kinetics of crystal violate.

3.7.2 The pseudo second order equation

The kinetic data were further analyzed using Pseudo second order kinetic model which is expressed as (18)

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e} \quad (2)$$

Here $K_2$ is rate constant of second order.

Fig. 14: Plot of pseudo 2nd order model at different initial dye concentration for crystal violate, adsorbent dose 4g/L and pH10.

The plot of $t/q_t$ vs. (fig. 14) of the above equation gives linear relationship from which $q_e$ and $K_2$ can be determine from the slope and intercept of the plot respectively. The linear plot of $t/q_t$ vs. $t$ show a good agreement of experimental data with second order kinetic model for different initial dye concentration 20, 30, 40, 60 mg/L and for different adsorbent dose. The calculated $q_e$, $K_2$ and corresponding linear regression correlations coefficients $r^2$ value are sumrised in a table (2). The values are greater than 0.999 (Table 1) which indicate the applicability of kinetic equation and Pseudo second order nature of adsorption process of crystal violate on PWCAC and CSAC mixture. The $q_e$ value increases` with increase in initial dye concentration and adsorbent dose. The calculated $q_e$ values are agreed well with the experimental values.
3.8. ADSORPTION KINETICS

The distribution of the dye between the liquid phase and the adsorbent is a measure of the position of equilibrium in adsorption process and can be generally expressed in Freundlich and Langmuir isotherm.

3.8.1. Freundlich isotherms

The linear plot of log qe vs. log Ce (Fig.15) confirms the applicability of the model. The logarithmic form of Freundlich isotherms equation is (20)

\[ \log qe = \log k_f + \frac{1}{n} \log Ce \]

Where qe is the amount of dye adsorbed per unit mass of the adsorbent (mg/gm), Ce is the equilibrium concentration of the dye (mg/L), the \( k_f \) represent quantity of dye adsorbed in mg/gm for unit concentration of dye and \( 1/n \) is measure of adsorption density. There is a linear plot of log qe vs. log Ce for 10, 20, 30 and 40 mg/L dye concentration. The \( k_f \) and \( n \) values were calculated. From the intercept and slope of the plot are presented in table 2. The correlation coefficient of the graphs are \( r^2 < 0.9949 \) indicate the inapplicability of isotherms.

![Figure 15: Freundlich plot for adsorption of crystal violate by PWCAC and CSAC mixture, pH 10 and adsorption dose 4 g/L](image)

3.8.2. Langmuir isotherms

Langmuir isotherms is represented by the following equation [21]

\[ \frac{Ce}{qe} = \frac{1}{ab} + \frac{Ce}{b} \]

Where \( Ce \) is the concentration of the dye solution (mg/gm) at equilibrium. The constant \( a \) signifies the the adsorption capacity (mg/gm) and \( b \) is related to energy and adsorption (L/mg). The linear plot of Ce/qe vs. Ce shows that the...
adsorption follows the Langmuir isotherms (Fig.12). The values of 'a, and b' were calculated from the slope and intercept of the linear plots and represented in Table 3. The applicability of the Langmuir isotherms suggest the monolayer coverage of the dye on the surface of PWCAC and CSAC mixture. The essentials characteristics of the Langmuir isotherms can be expressed by the dimensional constant called equilibrium parameter RL and defined by the equation[22-23].

\[
RL = \frac{1}{1 + bC_i}
\]

Where \( b \) is the Langmuir constant and \( C_i \) is the initial dye concentration (mg/l). According to the values of the RL, The isotherms shape may be interpreted as if RL is>1, unfavorable. RL=1 Linear, RL>0 favorable and RL=0 irreversible adsorption [24-25]. The results given in Table 3 shows that the adsorption of crystal violate on PWCAC and CSAC mixture is favorable.

![Langmuir plot for adsorption of crystal violate by PWCAC and CSAC mixture pH10 and adsorbent dose 4g/L](image)

**Fig.16: Langmuir plot for adsorption of crystal violate by PWCAC and CSAC mixture pH10 and adsorbent dose 4g/L**

**Table 2** Freundlich and Langmuir coefficient for adsorption of crystal violate on PWCAC and CSAC mixture for different dye concentration and adsorbent dose from 4 gm/L and pH 10

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<th>Dye conc. In mg/L</th>
<th>K_f L/g</th>
<th>n</th>
<th>1/n</th>
<th>r2</th>
<th>a mg/g</th>
<th>b g/L</th>
<th>RL</th>
<th>r2</th>
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<tbody>
<tr>
<td>20</td>
<td>2.5118</td>
<td>2.0876</td>
<td>0.4790</td>
<td>0.930</td>
<td>2.439</td>
<td>0.7739</td>
<td>0.0606</td>
<td>0.998</td>
</tr>
<tr>
<td>30</td>
<td>5.0118</td>
<td>1.4285</td>
<td>0.7000</td>
<td>0.970</td>
<td>2.500</td>
<td>0.8000</td>
<td>0.0400</td>
<td>0.999</td>
</tr>
<tr>
<td>40</td>
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<td>2.0000</td>
<td>0.5000</td>
<td>0.9620</td>
<td>2.0408</td>
<td>0.8183</td>
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<td>0.9090</td>
<td>0.0183</td>
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</tr>
</tbody>
</table>

### 4. CONCLUSIONS

[1] The adsorption study indicates that, the agro based material palm wood cellulose activated carbon and coconut shell activated carbon can be used as an effective adsorbent for the removal of crystal violate dye from aqueous solution.

[2] The adsorption experiments were conducted in a batch mode for the concentration range 20 to 60 mg/L at pH10 and for an adsorbent dose 0.02 to 4 g/L and up to contact time 120 min.

[3] The equilibrium was achieved in 120 min and maximum adsorption capacities were observed at pH10 and adsorbent dose 4 g/L.
[4] The amount of dye uptake (mg/gm) was found to be increases with increase in contact time, initial dye concentration and it decreases with an increase in adsorbent dose.

[5] The adsorption rate was found to confirm to pseudo second order kinetics with good co relation.

[6] The equilibrium data fit very well in Langmuir isotherms equation. It confirms the capacity of Crystal violate dye on to PWCAC and CSAC with a monolayer adsorption capacity.

[7] The dimensionless separation factor (RL) called equilibrium parameter showed that PWCAC and CSAC could be used for the removal of Crystal violate from aqueous solution.

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Author biography

Full name: Wagh prakash bhila
Birth date: 4.3.1963
Educational qualification: M.Sc.
Principle subject: physical chemistry
Designation: Associate professor
Working place: Dept, of chemistry, JEEs Arts, Commerce and Science college Nandurbar, Maharashtra (India)
Affiliated university: North Maharashtra University Jalgaon, Maharashtra (India) 425412
Teaching experience: 27 years
Research experiences: 44 years
Project completed: 1
Research paper published: 03