Sorptive Removal of Crystal Violet from Aqueous Solution Using Spent Tea Leaves: Part I Optimization of Sorption Conditions and Kinetic Studies

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Abstract

The low cost adsorbent, spent tea leaves (STL) has been tested for the effectiveness in decolorization of wastewater containing crystal violet dye in batch experiments. Effect of various parameters such as agitation time, pH, temperature and adsorbent dose has been investigated. The dye uptake has been found to increase with pH and temperature. The kinetic uptake data, obtained at different sorbate concentrations, is best interpreted by pseudo second order model and rate constants for adsorption are found to be 8.5×10^{-3}, 22.2×10^{-3} and 42.0×10^{-3} g mg^{-1} min^{-1} for initial dye concentrations of 10, 20 and 30 mg L^{-1} respectively. The dye uptake was found to increase with temperature and the activation energy for adsorption process was found to be 10.45 ± 0.89 kJ mol^{-1}.

Keywords: Spent tea leaves, adsorption, Langmuir isotherm, pseudo second order, dye

1. Introduction

The discharge of synthetic dyes into wastewaters from the textile industries has raised much concern because of potential health hazards associated with entry of toxic components into the food chains of human and animals. Over 10,000 dyes with an annual production of over 7×10^5 metric tons world wide are commercially available and 5–10% of the dye stuff is lost in the industrial effluents.[1] The coloration of water by the dyes may have an inhibitory effect on photosynthesis, thus affecting aquatic eco-systems. Dyes may also be problematic if they are broken down anaerobically in the sediment as toxic amines which are often produced due to incomplete degradation by bacteria. Some of the dyes or their metabolites are either toxic or mutagenic and carcinogenic.[2] Crystal violet (CV), a basic dye, is most widely used for the dyeing of cotton, wool, silk, nylon, paper, leather etc., among all other dyes of its category.[3] In fact, basic dyes, such as crystal violet, are the brightest class of soluble dyes whose tinctorial values are very high; less than 1 mg L^{-1} of the dye produces an obvious coloration. Hence, it is needed to remove these dyes from textile effluent before it is discharged into receiving water bodies. Consequently, many processes have been applied for the removal of synthetic dyes from wastewater. These include: solar photo-fenton degradation,[4] photo catalytic degradation,[5] integrated chemical-biological degradation,[6] electrochemical degradation,[7] and adsorption.[8] Although, activated carbon adsorption appears to be the one of the most widely used techniques for dye removal,[9] but in view of the high cost and associated problems of regeneration, there has been a constant search for alternate low adsorbents. Such type of adsorbents include bentonite clay,[10] montmorillonite clay,[11] coconut husk,[12] Moroccan clay,[13] sawdust,[14] palm ash,[15] pumpkin seed hull,[16] activated desert plant,[17] rice straw,[18] etc.

Tea is the dried and processed leaves of *camellia sinensis* and is consumed by the largest number of people in the world. Only water is rated higher in the world consumption than tea. After hot water extraction of tea leaves, the residual mass is of no use and hence is disposed off. The utilization of such a waste product for the purpose of removing toxins from wastewater may be the most desirable. Therefore, in the present study, an attempt has been

made to remove cationic dye crystal violet from synthetic wastewater using spent tea leaves (STL) as a potential sorbent.

2. Experimental

2. 1. Materials

To prepare spent tea leaves (STL), tea leaves were purchased from a local shop (Flora Tea Company, Jabalpur; super dust quality, wilted finally grinded and fully oxidized as per manufacture specifications) and the continuous hot extraction of tea leaves was carried out until the supernatant was totally colorless. After each extraction fresh water was used. Finally, the tea leaves were allowed to dry at 70 °C in an electric oven (Tempstar, India) and then grinded to obtain finely divided powder which was passed through standard seives to obtain particles with average geometrical diameter of 250–211 μm tem. The dried sorbent was kept in air proof container for further use. The cationic dye, crystal violet (mol wt = 408, λ_{max} = 583 nm for 100 mg L^{-1} solution at 27 °C), sodium hydroxide and HCl were obtained from Hi Media Chemicals, Mumbai, India. The double distilled water was used throughout the investigations.

2. 2. Batch Mode Adsorption Studies

The stock solution of crystal violet (0.1g L^{-1}) was diluted to required concentrations. Batch mode adsorption studies were carried out with a pre-calculated amount of sorbent and 75 ml of sorbate solution of desired concentrations, taken in an Erlenmeyer flask, and agitated for a definite time period under a constant stirring speed of 100 rpm at room temperature (29 ± 0.2 °C) in a thermostated flask shaker (Rivotek, India). Here it is to be noted that the embient temperature was nearly 28 °C and therefore to maintain uniformity we performed all experiments at 29 ± 0.2 °C, although ±0.2 °C was relatively large uncertainity associated with thermostated shaker used. After agitation, the sorbent and sorbate were separated through centrifugation and supernatant was analyzed spectrophotometrically at 583 nm to determine concentration of dye in the solution. The amount of dye sorbed per gram of sorbent (i.e.x/m) and percent sorption were calculated using following two equations respectively.[19]

$$\frac{x}{m} (mg \; g^{-1}) = \frac{(C_o - C_e)V}{m} \qquad (1)$$

where
    C_o means initial concentration of dye solution (mg L^{-1}),
    C_e is equilibrium concentration of dye solution (mg L^{-1}),
    V is the volume of sorbate solution (L) taken for
       sorption study,
    m is amount of sorbent (g).

$$Sorption \; \% = \frac{(C_o - C_e)}{C_o} \; x \; 100 \qquad (2)$$

Here, sorption is defined as the process which involves accumulation of molecules or atoms from one phase onto active sites of other phase.

All the experiments were done in triplicate and average data have been reported.

3. Results and Discussion

3. 1. Effect of Sorbent/sorbate (g L^{-1}) Ratio on Dye Uptake

In order to get optimum dye uptake, different amounts of sorbent, in the range of 5 to 50 mg, were added into 75 ml of dye solution of definite concentration and agitated for 2 h under constant stirring. The results, as depicted in Figure 1, clearly shows that as the sorbent/sorbate g L^{-1} ratio increases, percent dye uptake also increases and finally it attains optimum sorption of 48 percent for the g L^{-1} ratio of 0.53. The observed increase in dye uptake may be attributed to the fact that with increase in the amount of sorbent number of active sites available for sorption also increases, thus resulting in enhancement in percent CV uptake. Optimum STL dose was found to be 0.2 g of sorbent per liter of dye solution. A similar observation has also been reported for the adsorption of malachite green dye from aqueous solution by bagasse fly ash and activated carbon.[20]
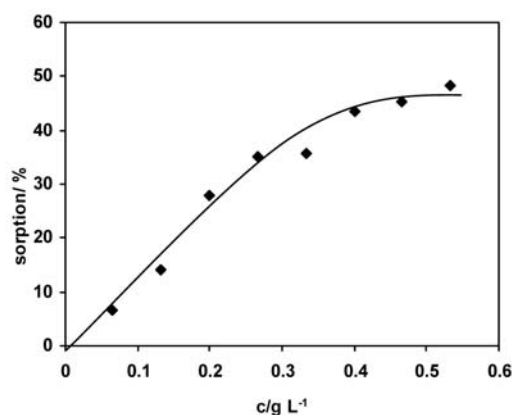

Figure 1. Sorption of crystal violet as a function of the concentration of crystal violet at 29 °C.

3. 2. Effect of Solution pH on Dye Uptake

The effect of solution pH on CV adsorption was studied by carrying out adsorption of dye onto STL sorbent, at different pH values of the sorbate solutions in the range of 2.0 to 8.5 at 29 °C under constant stirring conditions.

The results, as depicted in Figure 2, reveal that the dye up-take increases with the pH and it attains almost saturation value of 70.95 mg g^{-1} as the pH of the solution becomes 8.3, The observed finding may be explained on the basis of the fact that when the pH of the solution is quite low (i e. 2.0), the presence of excess H$^+$ ions compete with the cationic dye molecules in the solution and preferably occupy the binding sites available in the sorbent particles. As the pH of the sorbate solution increases number of H$^+$ ions decreases thus making the adsorption process more favorable .In the vicinity of pH value of 8.0, optimum dye uptake is obtained. Similar results have also been reported elsewhere.[21]
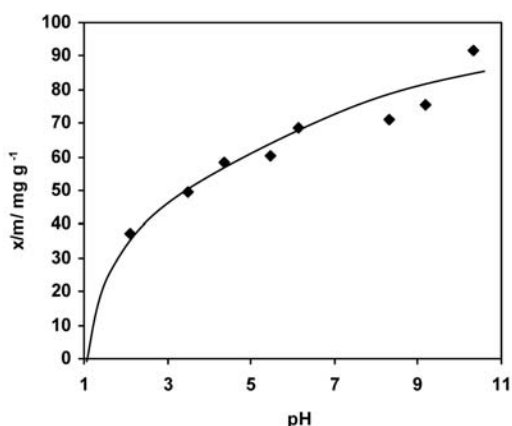
netics of dyes by various adsorbents have shown a wide range of adsorption rates. For example,[11] have reported a contact time of less than 30 min. as sufficient for attainment of equilibrium for adsorption of methylene blue onto montmorillonite clay for initial concentrations of drug solutions in the range of 200 to 1000 mg L^{-1} Likewise,[22] have studied adsorption of methylene blue onto activated carbon and reported a contact time of nearly 5 min as enough for equilibrium dye uptake. On the other hand,[23] studied adsorption of orange G and methyl violet onto fly ash bagasse and reported that after 4 h of contact a steady state approximation was assumed and a quasi-equilibrium situation was accepted.
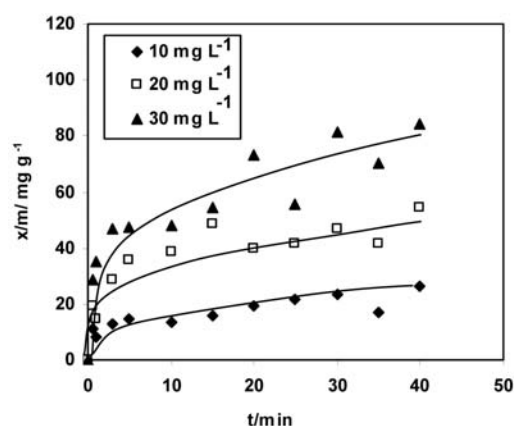

Figure 2. The amount of adsorbed dye in dependence of pH value of the system.

Figure 3. Dynamic uptake of crystal violet as a function of time for sorbate solutions with initial concentrations of 10, 20 and 30 mg L^{-1} at 29 °C.

3. 3. Effect of Sorbate Concentration and Contact Time

Sorbate solutions, with different concentrations, in the range of 10 to 30 mg L^{-1} were agitated with definite quantity of sorbent and the residual dye concentrations were monitored at different time intervals till the attainment of equilibrium. The results, as depicted in Figure 3, indicate that amount of CV sorbed per unit mass of sorbent (i e x/m) increases with initial dye concentration. The amount of CV sorbed at equilibrium (q$_e$) increased from 26.2 to 84.4 mg g^{-1} as the initial concentration was increased from 10 to 30 mg L^{-1}. The initial concentration provides an important driving force to overcome all mass transfer resistances of the CV between the aqueous and solid phases. Therefore, a higher initial dye concentration of dye will enhance the sorption process. A close look at the Figure 3 also reveals some facts regarding the time required in uptake process. The dye uptake process appears to be rapid in first five minutes and nearly 60% of total dye uptake appears to have been absorbed in this duration. Later on the process becomes relatively slower and equilibrium conditions are reached within 45 to 65 minutes. Here, it is also worth mentioning that data on adsorption ki-

3. 4. Kinetic Models

In order to search for an appropriate sorption mechanism, it is required to select a mathematical model that not only fits the data with fair accuracy, but also complies with a reasonable sorption mechanism. In this study, the dynamic uptake data was analyzed using three different kinetic models, namely pseudo first order, pseudo second order and simple Elovich equation.[24] However, the pseudo first order kinetic model was found to be almost unfit as the regression values were less than 0.70, and so it was discarded.

The pseudo-second order equation, developed by,[25] can be written as

$$\frac{dq}{dt} = k_2 (q_e - q)^2 \qquad (3)$$

where q is the amount of crystal violet sorbed at different time interval, q$_e$ is the amount of crystal violet sorbed at equilibrium, k$_2$ (g mg^{-1} min^{-1}) is the rate constant of the pseudo second order. Integrating Eq.(3) for the boundary conditions t = 0 to t = t and q = 0 to q = q$_e$ gives

$$\frac{t}{q} = \frac{1}{k_2\, q_e^2} + \frac{1}{q_e}t \qquad (4)$$

where k_2 and q_e can be obtained from the intercept and slope of t/q versus t.

For example Han et al[26] have reported pseudo second order uptake of methylene blue onto natural zeolite and found that for the initial dye concentration of 30 mg L^{-1}. The second order rate constant K_2 was 0.00978 mg gm^{-1} min^{-1} and in additionthe experimental and theoretical equilibrium uptake values ie qe where found to be 5.19 and 4.81 mg g^{-1} min^{-1} respectively showing a fair agreement between the two values.

The simple Elovich model,[27] is used to describe second-order kinetic, assuming that the actual solid surface is energetically heterogeneous, and is given as

$$q = \alpha + \beta \ln t \qquad (5)$$

where α and β are constants. The constant β is related to the extent of surface coverage.

The graphical representation of these two models has been well shown Figure 4 and Figure 5 respectively. The kinetic parameters, determined using slopes and intercepts of linear plots obtained, have been given in the Table 1.

A close observation at the regression values obtained clearly reveals that pseudo second-order model has fairly higher regression values than Elovich model, thus indicating that the dynamic uptake of crystal violet can be best interpreted by the pseudo second-order model. It can also be seen that the experimental equilibrium sorption values, obtained with 10, 20 and 30 mg L^{-1} dye solutions are in close agreement with the theoretical values given by pseudo-second-order kinetic model. It is also to be noted that second-order rate constant k_2 increases with initial concentration of the sorbate solution which is quite expected as the increase in concentration enhances the driving force responsible for sorption.

3. 5. Intraparticle Diffusion

As the above kinetic models were not able to identify the diffusion mechanism, the probability of intraparticle diffusion phenomenon could not be ruled out. As a first test to confirm the possibility of occurrence of intraparticle diffusion, curves were plotted between log [sorption/%] and log [t/min],[27] using the kinetic uptake data as displayed in Figure 6. The plots obtained were fairly linear thus indicating the occurrence of intraparticle diffusion phenomenon.

Finally, the intraparticle diffusion model, given by Weber and Morris was explored by using following equation.
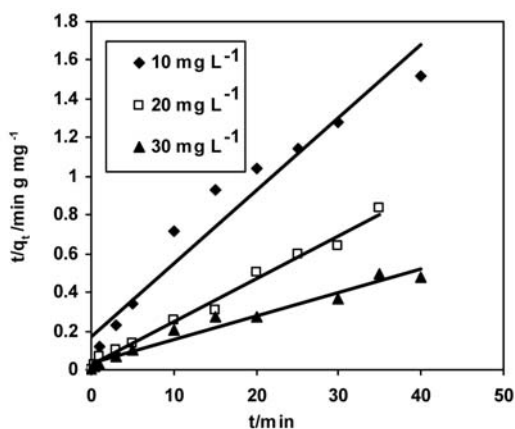
$$q_t = k_{id}\, t^{0.5} + c \qquad (6)$$

Figure 4. Pseudo second order kinetic plots for crystal violet uptake from crystal violet solutions with initial concentrations of 10, 20 and 30 mg L^{-1} at 29 °C.
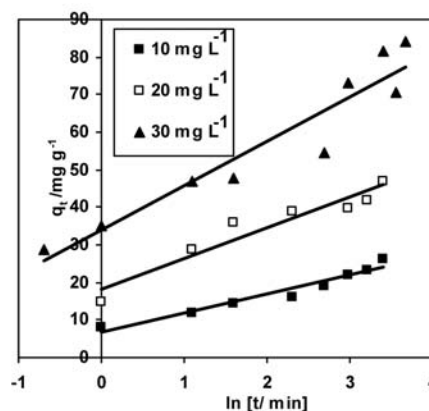

Figure 5. Simple Elovich model plots for crystal violet uptake from crystal violet solutions with initial concentrations of 10, 20 and 30 mg L^{-1} at 29 °C.

Table 1. Various kinetic parameters obtained for Pseudo second order and the Elovich model using kinetic uptake data for crystal violet solutions at 29 °C

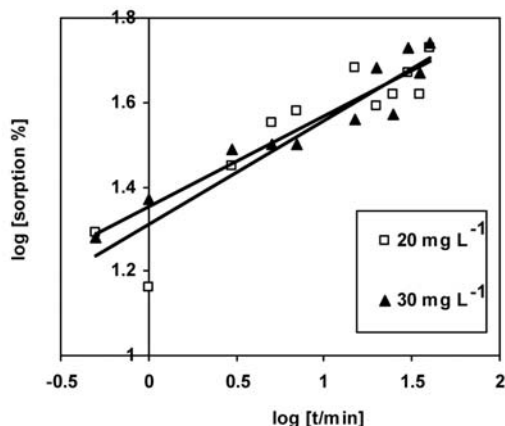| c(CV)/ mg L^{-1}	Pseudo second order model					Simple Elovich model		
	$k_s \times 10^2$	h (min^{-1} mg g)	R^2	$q_{e, exp}$ (mg g^{-1})	$q_{e, theor}$ (mg g^{-1})	α	β	R^2
10	0.85 ± 0.04	5.917 ± 0.26	0.9421	26.20 ± 1.10	26.38 ± 1.42	6.7405 ± 0.42	5.065 ± 0.285	0.944
20	2.22 ± 0.03	44.23 ± 2.46	0.9885	44.3 ± 1.82	44.64 ± 2.02	18.198 ± 0.926	8.1578 ± 0.962	0.9165
30	0.42 ± 0.04	28.68 ± 1.02	0.9619	84.4 ± 2.62	82.64 ± 2.16	33.86 ± 1.023	11.854 ± 1.062	0.9057

Figure 6. Time dependence of sorption in the logarithmic scale for the intraparticle diffusion conformation.

where q_t is the amount of crystal violet sorbed at different intervals, k_{id} (mg g^{-1} min$^{-1/2}$) is intraparticle diffusion coefficient. It is the proportionality constant, which relates the drug uptake with respect to square root of time and c is intercept, measuring the boundary layer thickness. In case, the plot is a straight line passing through origin, the uptake process is totally controlled by intraparticle diffusion. Figure 7 shows plots of q_t versus $t^{0.5}$ which are biphasic in nature. A close observation reveals that first part of the curves is almost smooth followed by a linear portion, thus indicating that although intraparticle diffusion is involved in the sorption process but it is not the only rate limiting mechanism but that some other mechanisms are also involved.[28] Such a deviation of linear plots from the origin may be attributed to the difference in the rates of mass transfer in the initial stage of sorption. Moreover, the intercept of the plots gives an idea about boundary layer thickness; the larger the value of the intercept, greater is the boundary layer effect. For initial concentrations of 10, 20 and 30 mg L^{-1}, the intercepts were found to be 17.8, 26.5 and 30.2 respectively. It seems that the boundary la-
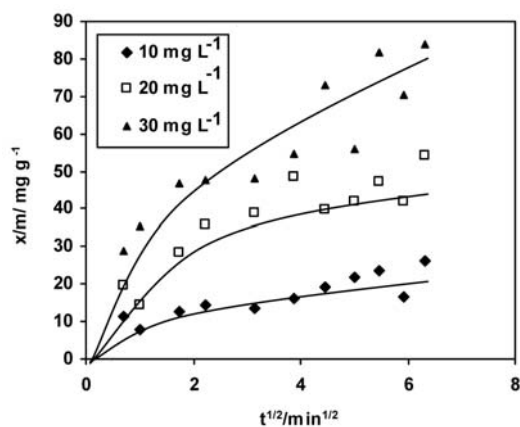
yer effect increases with the initial concentration of dye. Intraparticle diffusion rate constants, obtained using slopes of the linear parts, were found to be 243.0×10^{-2}, 690.1×10^{-2} and 754.2×10^{-2} mg g^{-1} min$^{-1/2}$ for 10, 20 and 30 mg L^{-1} dye solutions respectively. The initial curved portions, obtained in all three profiles, may be attributed to the liquid-film mass transfer. It is also evident that values of diffusion coefficients increase with initial concentrations of dye solutions as also reported by other workers.[29]

3. 6 Effect of Temperature

In order to study the effect of solution temperature on dynamic uptake of dye, the kinetic studies were carried out at three temperatures, namely 29, 37 and 50 °C. The results, as depicted in Figure 8, clearly indicate that dye uptake increases with temperature. This may be explained on the basis of the fact that increase in temperature enhances the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles as a result of the reduced viscosity of the solution.[30] In addition, the mobility of sorbate molecules also increases with temperature, thereby facilitating the formation of surface monolayers.
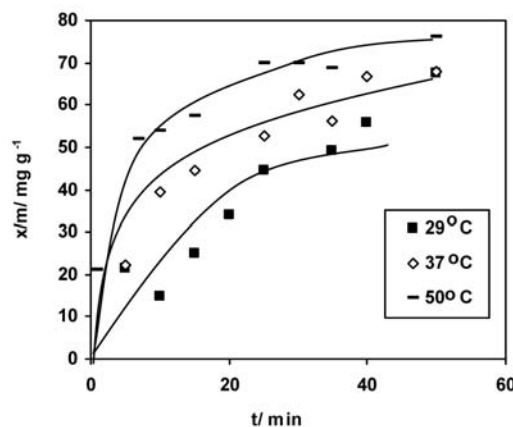

Figure 8. Dynamic uptake of crystal violet by sorbent at different temperatures.

Furthermore, the energy of activation for adsorption process was calculated by using Arrhenius equation as shown below.

$$\ln k_{id} = -\frac{E_a}{RT} + \text{constant} \qquad (7)$$

where k_{id} intraparticle diffusion rate constant as mentioned earlier and E_a is activation energy for adsorption.

In order to calculate E_a, graph was plotted between $\ln k_{id}$ and $1/T$ (see Figure 9) which was a straight line with the fairly higher regression value of 0.9980 using the slope of the linear plot, the activation energy was found to be

Figure 7. Dye uptake versus t1/2 plots for sorbate solutions with initial concentrations of 10, 20 and 30 mg L^{-1}.

nearly 10.450 ± 0.89 kJ mol^{-1}. The fairly lower value of activation energy suggests that adsorption at dye onto spent tea leaves is by an activated or diffusion-controlled process.
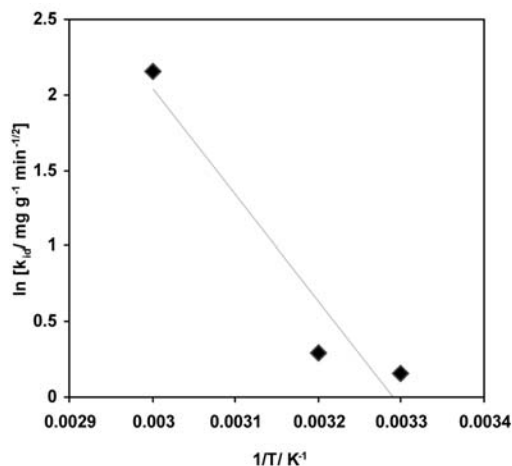

Figure 9. Evaluation of activation energy for adsorption.

4. Conclusions

From the above study it may be concluded that spent tea leaves (STL) has great potential to be used as low cost sorbent for effective removal of dyes. The process is favored at higher temperature and is completed within 1h. The easy availability of sorbent, with almost no cost and the no pre-treatment are the additional features of sorbent material. The studies regarding the equilibrium uptake of crystal violet are under progress and shall be in the next part of this communication.

5. Acknowledgements

6. References

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Povzetek

V tem delu smo proučevali možnost aplikacije uporabljenih čajnih listov kot adsorbenta za razbarvanje odpadnih voda. Na primeru barvila kristal vijolično smo merili odvisnost adsorpcije od časa mešanja, pH, temperature in doze adsorbenta. Ugotovili smo, da adsorpcija barvila narašča s pH in temperature. Kinetiko procesa lahko opišemo kot proces psevdo drugega reda s konstantami hitrosti adsorpcije 8.5×10^{-3}, 22.2×10^{-3} in 42.0×10^{-3} g mg^{-1} min^{-1} za začetne koncentracije barvila 10, 20 in 30 mg L^{-1}. Aktivacijska energija adsorpcije je 10.450 kJ mol^{-1}.