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Adsorption of Crystal Violet Dye onto Tamarind Seed Powder

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Abstract: The present investigation describes adsorption of crystal violet dye from its aqueous solution onto tamarind (*Tamarindus indica*) fruit shell powder. Initial concentration, agitation speed and pH with various temperature have been studied, in which pH was found to be most effective. The adsorption data were mathematically analyzed using adsorption isotherm like Freundlich and Langmuir isotherm to study adsorption mechanism of crystal violet onto this seed powder. Freundlich isotherm was found to be most applicable. The equilibrium data were applied to intra-particle diffusion and adsorption kinetics. The reaction was found to be pseudo second order.

Keywords: Tamarind, Crystal violet, Langmuir, Freundlich isotherm.

Introduction

Textile industry uses large volumes of water in wet processing operations and thereby, generates substantial quantities of wastewater containing large amounts of dissolved dyestuffs and other products, such as dispersing agents, dye bath carriers, salts, emulsifiers, leveling agents and heavy metals¹. Majority of this dyes are synthetic in nature and are usually composed of aromatic rings in their structure, inert and non-biodegradable when discharged into waste streams. Therefore, the removal of such colored agents from aqueous effluents is of significant environmental, technical and commercial importance². Highly colored wastes are not only aesthetically displeasing but also hinder light penetration and may in consequence disturb biological processes in water-bodies. Moreover, dyes itself are toxic to some organisms and hence disturb the ecosystem. In addition, the expanded uses of dyes have shown that some of them and their reaction products such as aromatic compounds are highly carcinogenic, which make the removal of dyes before disposal of the wastewater is necessary³.

The studies have been performed in order to remove color and other contaminations using various types of methods include adsorption⁴, coagulation⁵, nano-filtration and ozonolysis⁶, membrane filtration⁷, oxidation process⁸ etc., in which adsorption is most useful due to its efficiency and visibility. The use of low-cost, easy obtained, high efficiency and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive

methods of removing dyes from wastewater. These adsorbents were prepared from natural materials such as plant roots, leaf and seed like neem leaf powder^{10,11}, gulmohar plant leaf powder¹², shells of hazelnut and almond¹³, shells of lentil, wheat and rice¹⁴, orange peel¹⁵, Banana peel¹⁶, guava leaf powder¹⁷ used for removal of color.

Investigations were carried to adsorb different types of metals on tamarind seed powder¹⁸⁻²⁰. Also, it is evident that, they were utilized to adsorb crystal violet (CV) using various types of adsorbents²¹⁻²³.

The present study was performed to investigate the surface morphology of tamarind seed powder (TSP) using various methods *viz.* particle size, FT-IR spectroscopy and SEM analysis and exploitation for removal of CV from aqueous solution. The parameters such as pH, contact duration and adsorbent dosage with different temperature were studied. Adsorption isotherm (Freundlich and Langmuir) and adsorption kinetics (Pseudo first-, second-order and intra particle diffusion) were also analyze in this explored.

Experimental

The tamarind, a family of Fabaceae, has used for preparation of medicines for internal and external applications and as condiment in many dishes. The major application of seed is commonly lies in the manufacturing of textile sizing powder. Tamarind fruit seed, collected near Navyug Science College, Gujarat and a waste product of tamarind pulp, are washed, dried and pulverized. This powder was further washed with distilled water till the washings were free of color and turbidity and then after, dried in the oven for 2 h at 60 °C. Sympatic, Germany (Model: Helos-BF) was use to analyze the TSP particle size. The Fourier transform analysis was carried out using instrument Shimadzu, Japan (Model: 8400S) at wave length of 400-4 000 cm⁻¹. SEM image were taken using Philips, The Netherlands (Model: XL-30 ESEM).

Adsorbate

The dye, crystal violet (CI 42555, Class: basic dye 3) having chemical formula: C₂₅H₃₀N₃Cl and molecular mass: 407.98 g/mol, used in this study was supplied by Merck, India. Structure of crystal violet molecule is shown in Figure 1.

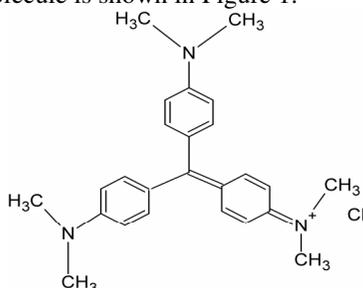


Figure 1. Structure of crystal violet.

Experimental details

Effect of initial concentration was studied by treatment CV solutions containing different concentration (2.0 to 14 × 10⁻⁶ M) with TSP at shaking speed of 300 rpm at different temperatures of 310, 320 and 330 K. To determine the effect of different agitation speed, the CV solution (concentration: 6.0 × 10⁻⁶ M) was treated with TSP at different temperatures of 310, 320 and 330 K and different agitation speed *i.e.* 100 to 1000 rpm. pH studied was conducted by treating TSP was treated with TSP at range of pH values from 3 to 11 at shaking speed of 300 rpm. The pH of the solutions was adjusted with 1 N HCl or NaOH solution by using a pH meter.

All the above experiments were carried out at adsorbent (TSP) dosage of 5.0 g/mL and time duration at 4 h. The concentration of the dye was measured by a spectrophotometer (ELICO SL 164 Double Beam UV-VIS Spectrophotometer) at $\lambda_{\text{max}} = 584 \text{ nm}$ and percentage of removal and quantity of dye adsorbed, q_e (mol/g) was calculated using the following formula:

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

$$q_e = (C_o - C_e) \times V / W \quad (2)$$

Where, C_o and C_e are initial and equilibrium concentration of dye respectively. V the volume of the solution and W the weight of the TSP used.

Adsorption isotherm

The analysis and design of adsorption separation processes requires the relevant adsorption equilibria, which is the most important piece of information in understanding an adsorption process. It is also important for designing an adsorption system. The adsorption equilibrium indicates how the adsorbate molecules distribute between the liquid phase (solution) and the solid phase (adsorbent) when the adsorption process reaches an equilibrium state. To describe the adsorption equilibrium data of crystal violet dye on adsorbent, TSP, Langmuir and Freundlich isotherm models were used. The Freundlich isotherm can be efficient on multilayer and also, heterogeneous surface and is expressed by the following equation.

$$q_e = K_F C_e^{1/n} \text{ or } \log q_e = \log K_F + 1/n \log C_e \quad (3)$$

Where, q_e and C_e is the amount of adsorbed adsorbate per unit weight of adsorbent and unadsorbed adsorbate concentration in solution at equilibrium, respectively and K_F and $1/n$ are Freundlich constant characteristics of the system, which are determined from the $\log q_e$ vs. $\log C_e$. Also, Langmuir adsorption is very useful for predicting adsorption capacities and also interpreting into mass transfer relationship. The isotherm can be written as follows:

$$q_e = q_m Q_0 C_e / (1 + b C_e) \text{ or } (C_e/q_e) = (1/Q_0) + (b/K_L) C_e \quad (4)$$

Where, Q_0 and b were the Langmuir constants, which measures of monolayer (maximum) adsorption capacity (in mg/g) and energy of adsorption (in g/L) respectively. The Langmuir parameters were obtained from the linear correlations between the values of C_e/q_e and C_e^{24} .

Adsorption kinetics

In order to investigate the mechanism of adsorption and potential rate controlling steps such as mass transport and chemical reaction processes, kinetic models have been used to test experimental data. These kinetic models include the pseudo-first-order equation, pseudo-second-order equation, and intraparticle-diffusion equation. The pseudo first-order equation of Lagergren is given by

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

Where q_t and q_e are the amounts of TBC adsorbed at time t and equilibrium (mg/g), respectively, and k_1 is the pseudo first-order rate constant for the adsorption process (1/min). The linear graph of $\ln(q_e - q_t)$ vs. t shows the applicability of first order kinetic. Also, the pseudo second-order chemisorption kinetic rate equation 5 is expressed as

$$t / q_t = 1 / k_2 q_e^2 + (1/q_e) t \quad (6)$$

Where k_2 is the equilibrium rate constant of pseudo second order equation (g/mg min). The linearity of t / q_t vs. t suggests the best fitted with pseudo second order kinetic. The kinetic data can also be analyzed by an intra-particle diffusion kinetic model, formulated as

$$q_t = k_p t^{1/2} + C \quad (7)$$

Where k_p ($\text{mg.g}^{-1}.\text{minute}^{-1/2}$) is the intra-particle diffusion rate constant and C is the intercept of the plot of q_t versus $t^{1/2}$. If this linear plot passes through the origin, then intraparticle diffusion is the rate-controlling step. The plots of intra-particle diffusion do not pass through the origin²⁵.

Results and Discussion

Surface morphology of TSP

The particle size of TSP was observed to be 100 - 120 μm (Average: 110 μm), which is used as adsorbent in many experiments^{2,26}. Figure 2 depicted FT-IR spectra of TSP, in which the bend near bend near 3600 cm^{-1} was revealed, is due to hydroxyl group, a broad bend near $3000 - 3200\text{ cm}^{-1}$ of amino and carboxylic acid group, a 1653 and 1541 cm^{-1} are due to primary amine and nitro compound and also, 1064 cm^{-1} of primary alcohol (C-O) stretching. The adsorbent containing these bends are usually utilized for color removal^{27,28}. The SEM images of TSP (Figure 3) at higher magnifications 350X and 500X shows that the surface of materials is porous.

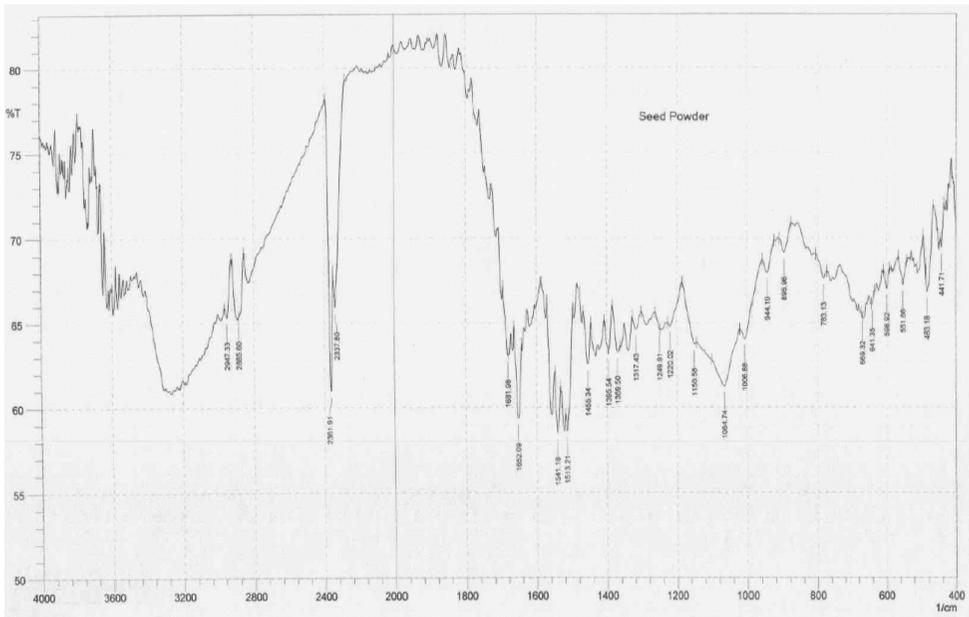


Figure 2. Depicted FTIR spectra of TSP.

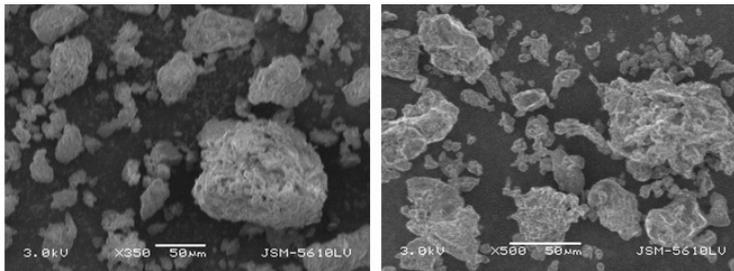


Figure 3. SEM images of TSP.

Effect of initial concentration

Figure 4 depicted the effect of initial concentration with different temperature ranges. It shows the percentage removal of dye decreases from 8.6% up to 65.4% with an increase of initial concentration even though adsorption density increases. The mass of the given adsorbent can adsorb only a fixed amount of dye. Therefore, the more concentrated an effluent, the smaller is the volume of effluent that a fixed mass of adsorbent can purify²². Also, it was observed that sorption of TSP for CV increased with increasing temperature indicating that the sorption process was endothermic in nature. The increase in uptake of dye molecules with temperature may be due to the desolvation of the sorbing species and change in the size of the pores and further evidence that intraparticle diffusion plays an important role in the rate-determining step in the adsorption of CV on TSP is confirmed by the temperature dependence of the rate of adsorption².

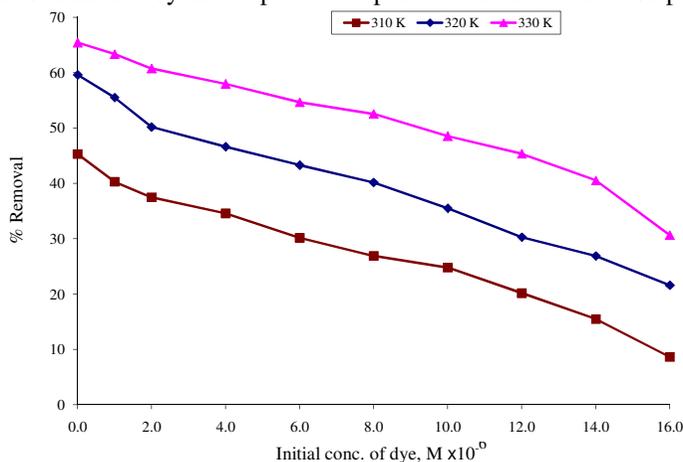


Figure 4. Effect of initial concentration of TSP with different temperatures.

Effect of agitator speed

The variation of percentage adsorption of CV with agitator speed and temperature at initial concentration of CV using concentration of 6.0×10^{-6} M and pH of 7.0 is shown in Figure 5. As agitator speed increases, percentage adsorption significantly also increases up to 15.5 to 50.0, 20.5 to 60.0 and 25.5 to 69.7% at 50 to 900 rpm respectively with different temperatures (310, 320 and 330 K), but then gradually approaches a constant value after 900 rpm. So, the equilibrium attained at 900 rpm for adsorption of CV onto TSP. The mechanism of adsorbate removal involved four steps: (i) migration of adsorbate molecules from the bulk solution to the surface to the surface of the adsorbent; (ii) diffusion through the boundary layer to the surface of adsorbent; (iii) adsorption at a site; and (iv) intraparticle diffusion into the interior of the adsorbent. Increasing agitation speed decreases the boundary layer resistance of the transfer of adsorbate molecules from the bulk solution to the adsorbent surface. Due to this, the adsorbate is forced towards the adsorbent surface and leads to an increases in the diffusion of adsorbate into the surface of the adsorbent²⁹. Further, it was verified that percentage of removal is increasing with increasing temperature.

Effect of pH

Figure 6 shows the dynamic adsorption of CV on TSP at different initial pH values with variable temperatures at initial dye concentration of 6.0×10^{-6} M. When the pH is changed from 1 to 7, the adsorption was slowly increase from 25.2 to 86.6% respectively and from 7 to 11, it was drastic increased up to 63.3 to 95.5% respectively. For cationic dyes, lower adsorption of

CV at acidic pH is probably due to the presence of excess H^+ ions competing with the cation groups on the dye for adsorption sites. As surface charge density decreases with an increase in the solution pH, the electrostatic repulsion between the positively charged dye and the surface of the adsorbent is lowered, which may result in an increase in the extent of adsorption³⁰. It was confirmed that when temperature of system was increases, adsorption also increasing.

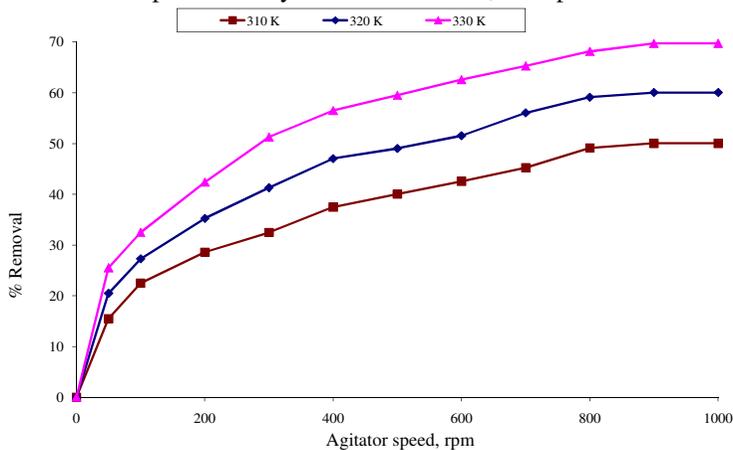


Figure 5. Effect of agitator speed with various temperatures.

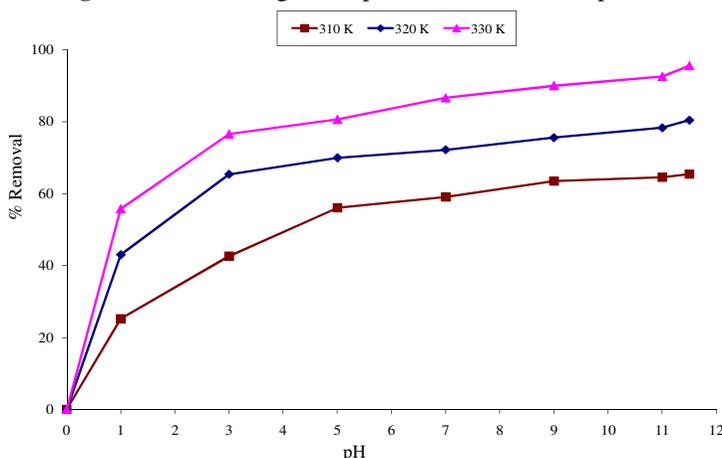


Figure 6. Effect of pH with different temperatures.

Isotherm date analysis

Figures 7 depicted the non-linear graph of amount of CV adsorbs *vs.* equilibrium concentration at dye concentration of 6.0×10^{-6} M at pH 7 and agitator speed of 500 rpm at temperatures of 310 and 320 K. Experimental values obtained for Langmuir parameters *i.e.* adsorption capacity (K_L) and intensity (Q_0) and Freundlich parameters *i.e.* capacity (K_F) and intensity (n) are represented in Table 1. The correlation coefficient values obtained from the Freundlich and Langmuir isotherms are also presented. The values indicate that the adsorption pattern followed Langmuir isotherm then Freundlich isotherm. The same results were obtained by adsorption of dye from its aqueous solution onto different adsorbents³¹⁻³³.

Kinetic model

The kinetic models, pseudo first-, second-order and intra-particle diffusion graphs were mentioned

in Figures 8(a), (b) and (c) respectively. All straight line graphs suggested to follow all these kinetics model. Table 2 depicted the correlation coefficient (r^2) values of kinetic models at different temperatures, indicates that pseudo second-order was greater than others two kinetics models, pseudo first-order and intra-particle diffusion for all temperatures. So, the results were best to pseudo second-order kinetic model. The trend was observed using various types of adsorbents^{34,35}.

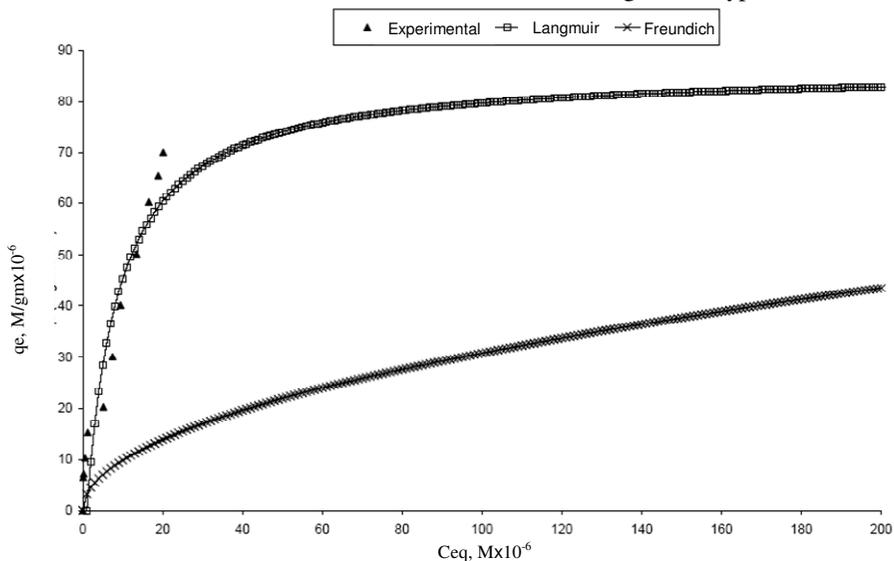


Figure 7. Non-linear graph of Freundlich and Langmuir isotherm.

Table 1. Isotherm parameters for adsorption of CV onto TSP.

| Temperature, K | Freundlich Isotherm | | | Langmuir Isotherm | | |
|----------------|------------------------|-------|--------|------------------------|-----------------------|--------|
| | K_F (mol/g) | n | r^2 | K_L (mol/g) | Q_o (mol/g) | r^2 |
| 310 | 3.079×10^{-5} | 2.047 | 0.9989 | 0.219×10^{-5} | 7.06×10^{-6} | 0.9991 |
| 320 | 3.499×10^{-5} | 1.838 | 0.9913 | 0.516×10^{-5} | 7.35×10^{-6} | 0.994 |

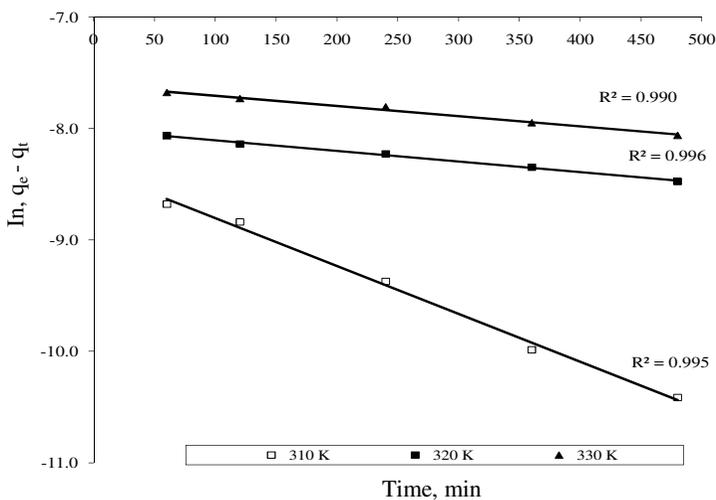


Figure 8 (a). Pseudo-first order equation.

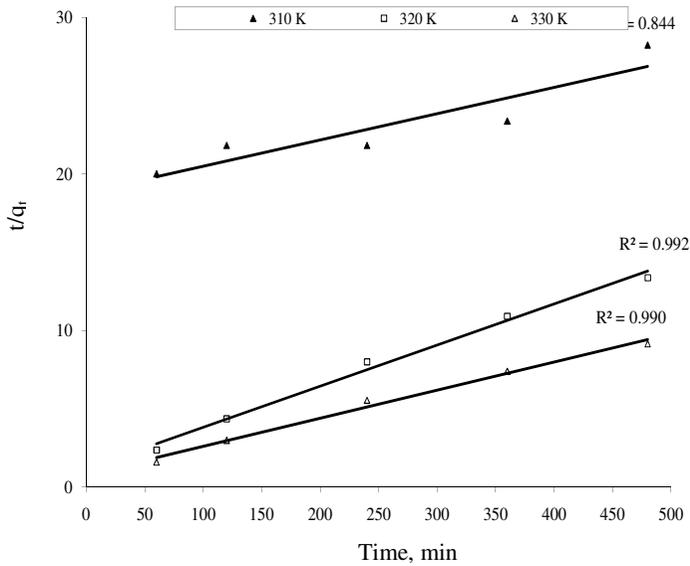


Figure 8 (b). Pseudo-second order equation.

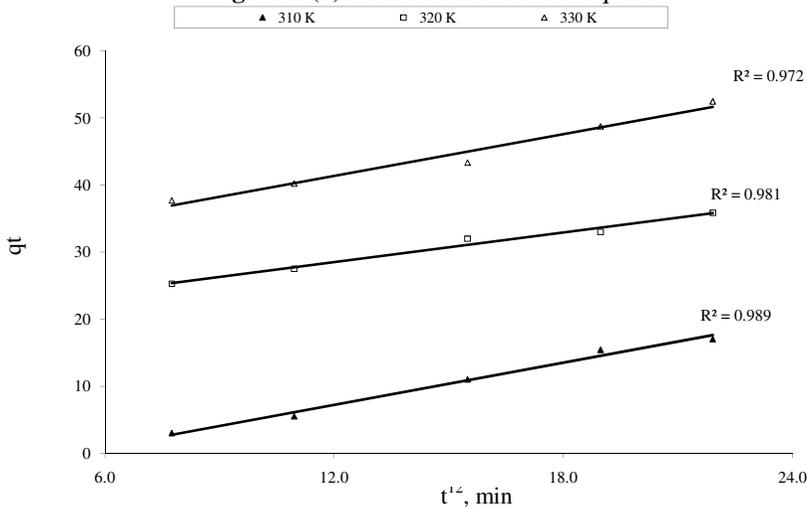


Figure 8 (c). Intra-particle diffusion equation.

Figure 8. Plots of adsorption kinetic equations for adsorption of TBC onto NLP at different contact duration, (a) pseudo first-order equation, (b) the pseudo second-order equation and (c) the Intra-particle diffusion equation.

Table 2. Kinetic parameters for the adsorption of CV onto TSP.

| S. No. | Temperature K | r ² Value | | |
|--------|------------------|----------------------|---------------------|-------------------------|
| | | Pseudo first-order | Pseudo second-order | Intra-particle equation |
| 1 | 310 | 0.9951 | 0.9907 | 0.9728 |
| 2 | 320 | 0.996 | 0.992 | 0.9818 |
| 3 | 330 | 0.9904 | 0.8446 | 0.9893 |

Conclusion

A significant adsorption of Crystal Violet dye onto Tamarind Seed Powder was found using different variables like initial concentration, pH and adsorbent dosage with various temperature, in which pH was found to be most effective. The maximum removal of crystal violet is found to be 95% at pH of 11 maintaining parameters like adsorbent dosage, initial concentration of dye, temperature, which were 5 g/L, 0.000005 M and 323 K respectively. The isotherm models were analyzed using the Langmuir and Freundlich for equilibrium data and kinetic models, pseudo first- order, second-order model and intra-particle diffusion equation to describe the kinetic data. The adsorption capacities were obtained from Freundlich and Langmuir isotherm plot were 3.499×10^{-5} and 0.516×10^{-5} mol/g. From coefficient correlation (r^2), we concluded that the experimental data were well fitted with Langmuir adsorption isotherm model and pseudo second order kinetic model.

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