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Kinetics and Isotherm Studies of Crystal Violet Adsorption from Aqueous Solution using Tomato Seeds

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Abstract: ***In this work, the feasibility of employing tomato seeds to remove crystal violet a cationic dye from its aqueous solutions was investigated. Parameters that influence the adsorption process such as particle size, pH, adsorbent dose, initial dye concentration, contact time and temperature were studied in batch experiments. The optimum conditions for removal of CV were found to be pH 1.48, equilibrium time 60 min, biosorbent dosage 1.4 g, initial dye concentration 4.4 mg L^{-1} and temperature 312K .The experimental equilibrium adsorption data fitted well to the Freundlich isotherm model. The kinetic data conformed to the pseudo-second-order kinetic model. Thermodynamic parameters such as Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) were also calculated and it was found that the adsorption of dye by tomato seeds was a spontaneous process. It was concluded that tomato seeds have thepotential for application as anadsorbent for removal of crystal violet from aqueous solution.***

Keywords: Adsorption; Crystal violet dye; Tomato seeds; Kinetics; Isotherm; Thermodynamics

1. Introduction

Several manufacturing processes utilize toxic chemicals for the production of finished products, the unused parts of which escape into the environment as industrial waste-wash [1]. Environmental scientists worldwide are thus faced with the daunting task of emerging cost-effective and efficient technologies for their treatment for various human activities [2]. Discharge of industrial effluents containing hazardous contaminants, such as phenol, toxic metals, and dyes, even at low concentrations, is a cause of negative impact on the environment[3,4].

Dyes are one of the main constituents of the wastewater produced from many industries related to textile, paint and varnishes, ink, plastics, pulp and paper, cosmetics, tannery etc., and also to the industries, which produce dyes. Colored dye effluents pose a main threat to the surrounding ecosystem. Many of the dyes are very toxic. Various treatment technologieslike adsorption [5-9], photodegradation [10-14], coagulation-flocculation [15], chemical oxidation [16,17], electrochemicaloxidation [18], biological process [19] etc. are obtainablefor the removal of dye from the wastewater.

Adsorption is a well-known and superior technique for dye and organic removal because of its easy operation, insensitivity to toxic substances, the ability to treat concentrated forms of the dyes, and thepossibility of reusing the spent adsorbent via regeneration [20]. In the process of adsorption, a solid adsorbent is employed in order toattract the dye component and finally leading to its removal fromthe water by the formation of physical and chemical bonds.Crystal Violet (CV), also known as Gentian violet is a triarylmethane dye, extensively used as a purple dye in the textile industry for dyeing of cotton and silk. It also finds application in the manufacture of paints and printing inks [21,22]. In the medical community, it is used as a biological stain and is the active ingredient in Gram’s stain. In animal and veterinary medicine, it is employed as a bacteriostatic agent [21]. The dye is also used as an external skin disinfectant in humans. It is used as an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus [23].

The present study has been designed to investigate the potential use of tomato seeds for the removal of crystal violet from aqueous solution. For this purpose, batch adsorption experiments have been carried out under varying experimental conditions such ascontact time, the initial concentration of crystal violet solution, pH and temperature of the solution

2. Materials and Methods

Adsorbent:

The Tomato seeds (SolanumLycopersicum) was used as an adsorbent which was obtained from local market. Tomato seeds were thoroughly washed with distilled water several times to remove any impurities if presented on thesurface, then soaks in 100 ml distilled water for at least 15 min. fig.1.


(a) (b)

Figure 1: a) dry seeds and b) socked in distilled water for 15 min

Adsorbate

Crystal Violet (CV) used in this study was of commercial quality (CI 42,555, MF: C25H30N3Cl, MW: 407.9, _max: 590 nm) and was used without further purification. Stock solution (40 mg L^{-1}) was prepared by dissolving accurately weighed thequantity of the dye in double-distilled water. Experimental dye solution of different concentrations was prepared by diluting the stock solution with asuitable volume of double-distilled water. The initial solution pH was adjusted using 0.1 M H_3PO_4 and 0.1 M NaOH solutions.The structure of C.V is given in fig.2.

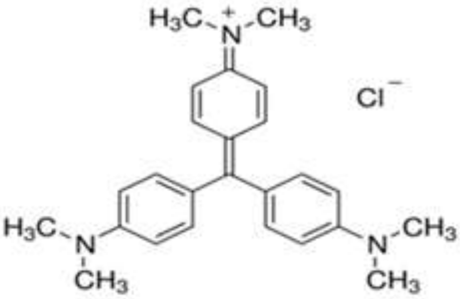

Figure 2: The structure of crystal violet

Adsorption studies

Batch adsorption studies were carried out in 500 mL round bottom with 350 mL of working volume, with a concentration of 40 mg L^{-1}. A weighed amount (1 g) of adsorbent was added to the solution. Theinfluence of initial solution pH (1.48, 2.1, 5.2, 7 and 9.3), adsorbent dose (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6 and 1.8 g), contact time (10, 20, 30, 40, 50, 60, 70, 80 and 90 min) and temperature (306, 312, 318, 328 and 338 K) were evaluated during the present study. Samples were collected from the flasks at predetermined time intervals for analyzing the residual dye concentration in the solution. The residual amount of dye in each flask was investigated using UV/VIS spectrophotometer (UV-1800 Shimadzu). The amount of dye adsorbed per unit adsorbent (mg dye per g adsorbent) was calculated according to a mass balance on the dye concentration using Eq. (1):

$$q_e = \frac{(C_0 - C_e)\,V}{w} \quad \text{.........} \quad (1)$$

The percent removal (%) of dye was calculated using the following equation:

$$\%R = \frac{C_0 - Ce \times 100}{C_0} \quad \text{.........} \quad (2)$$

3. Result and Discussion

Optimization

The adsorbent dosage

As the dose of theadsorbent can strongly affect the sorption capacity, the adsorption procedure was done with tomato seeds (0.2-1.8 g). Obtained results shown in Figure 3 indicated that increasing amount of the adsorbent increases the contact surface area and exchangeable sites, and then increases the percent removal of dye.

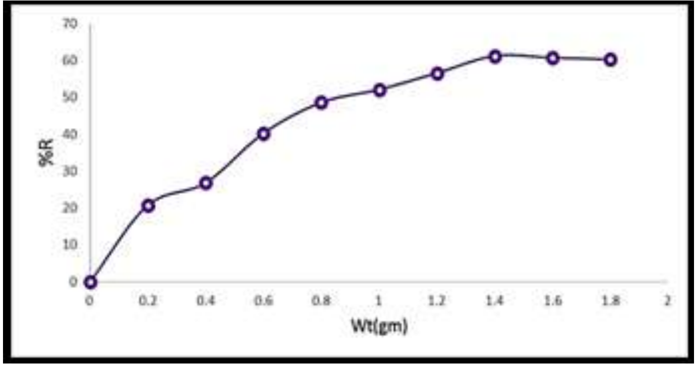

Figure 3: Effect of adsorbent dose on adsorption of CV dye onto tomato seeds.

The initial concentration

The rate of adsorption is a function of the initial concentration of the adsorbate, which makes it an important factor to be considered for effective adsorption. The effect of different initial CV concentration as (4, 4.4, 4.8, 5.3, 5.6, 6, 6.4, 6.8 mg/L) on adsorption of CV onto tomato seeds is presented in Fig. 4. The optimum initial concentration was found to be 4.4 $g.L^{-1}$ and was used for the successive experiments.

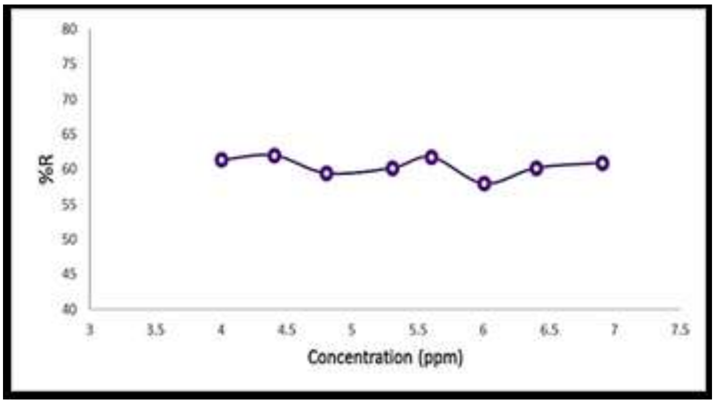

Figure 4: Effect of initial concentration on adsorption of CV dye onto tomato seeds

The contact time

For the estimation ofequilibrium time, the adsorption experiment was carriedout at pH 7and room temperature using the concentration of CVsolution 5.6 mg L^{-1}. The amount oftomato seeds taken for this experiment was 1 g.Very rapid adsorption was found during the adsorptiontime of 60 minute. Then the adsorption progresses very slowly shown in Figure 5.

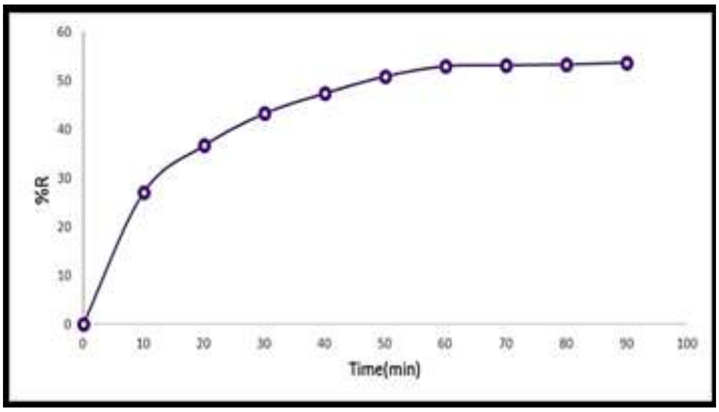

Figure 5: Effect of contact time on adsorption of CV dye onto tomato seeds

pH study

To study the effect of pH on the adsorption. The range of pH adjusted between 1.48 and 9.33. The experimental date indicates that the removal of dye was so effective at pH 1.48 but we used neutral pH because the puppies of our study to remove dyes from water and reduce the pollution and must occur in economic way,for that we chosepH7. Figure 6 shows the effect of pH on the removal of Crystal Violet on to tomato seeds [24,25].

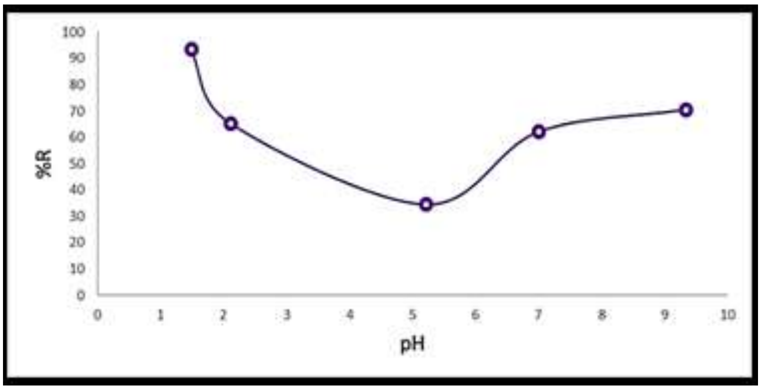

Figure 6: Effect of pH on adsorption of CV dye onto tomato seeds.

The effect of temperature

Dye removal was examined at different temperatures range started from 21C° (as ambient temperature) to 65C°. 38.5 ml of dye solution 4.4mg/l was contacted to 1.4 g of tomato seeds for 60 min at pH 7 at 21, 27, 33, 39, 45, 55 and 65C°.

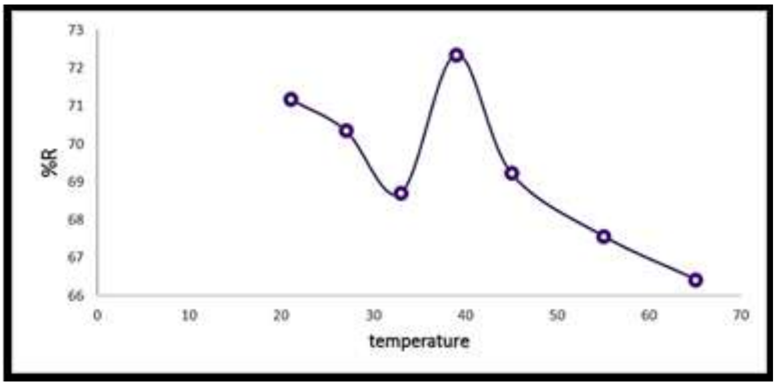

Figure 7: Effect of temperature on adsorption of CV dye onto DWM seeds.

Adsorption isotherms

Different isotherm models have been developed for describing sorption equilibrium. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms were used in the presentstudy.

Langmuir isotherm

The Langmuir sorption isotherm describes that the uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules and is commonly expressed as [26]:

$$C_e/q_e = 1/qmK_L + C_e/q_m \text{ ………. } (3)$$

whereq_e (mg g^{-1}) and C_e (mg L^{-1}) are the solid phase concentration and the liquid phase concentration of adsorbate at equilibrium respectively, q_m (mg g^{-1}) is the maximum adsorption capacity, and K_L (Lmg^{-1}) is the adsorption equilibrium constant. The constants K_L and qm can be determined from the slope and intercept of the plot between $C_e/q_e$and C_e.

Freundlich isotherm

The Freundlich isotherm is applicable to non-ideal adsorptionon heterogeneous surfaces and the linear form of the isotherm can be represented as [27]:

$$\ln q_e = \ln K_f + 1/n \ln C_e\text{……….. } (4)$$

whereq_e is the equilibrium dye concentration on adsorbent (mg g^{-1}), C_e is the equilibrium dye concentration in solution (mg L^{-1}), K_F (mg g^{-1}) (Lg^{-1})1/n is the Freundlich constant related to sorption capacity and n is the heterogeneity factor. K_F and 1/n are calculated from the intercept and slope of the straight line of the plot ln$q_e$versus lnC_e.

Dubinin–Radushkevich (D–R) isotherm

The Dubinin–Radushkevich (D–R) isotherm model envisages about the heterogeneity of the surface energies and has the following formulation [28]:

$$\ln q_e = \ln q_s – K_{ad}\, \varepsilon^2 \text{ ……… } (5)$$

whereq_m is the maximum adsorption capacity, ˇ is a coefficient related to the mean free energy of adsorption (mmol^2 J^{-2}), ε is the Polanyi potential (Jmmol^{-1}), R is the gas constant (8.314 Jmol^{-1} K^{-1}), T is the temperature (K) and $C_e$is the adsorbate equilibrium concentration (mg L^{-1}). The D–R constants q_m and ˇcan be determined from the intercept and slope of the plot between lnqe and ε^2. The constantˇgives an idea about the mean free energy E (kJ mol^{-1}) of adsorption per mole of theadsorbatewhen it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship [29]:

$$\varepsilon = RT \ln [1 + 1/C_e] \text{ ……… } (6)$$

If the magnitude of E is between 8 and 16 kJ mol^{-1}, the sorption process is supposed to proceed via chemisorption, while for values of E<8kJmol^{-1}, the sorption process is of physical nature [29].

$$E = 1/(2K_{ad})^{1/2} \text{ …….. } (7)$$

The Temkin isotherm

The Temkin isotherm model is based on the assumption that the decline of the heat of sorption as a function of temperature is linear and has the following formulation [30]:

$$q_e = B\, \mathit{ln} k_T + B\, \mathit{ln} C_e \text{ …….. } (8)$$

where q_e is the equilibrium adsorbateconcentration on the biosorbent(mg g^{-1}), C_e is the equilibrium adsorbate concentration in solution (mg L^{-1}) and KT(L g−1) and B_T are the Temkin constants. The isotherm constants determined at different temperatures are tabulated in Table 1. Shows the plots comparing theLangmuir, Freundlich,Dubinin–Radushkevich (D–R) and Temkin isotherm models with the experimental data for the biosorption of CV onto tomato seeds at a temperature of 312 K.

Table 1: Langmuir, Freundlich, DubininRadushKvich and Temkin isotherm model parameters and their respective correlation coefficients for the sorption of CV onto tomatobiosorbent.

Temperature (K)	Langmuir isotherm			Freundlich isotherm		
	q_m (mg/g)	K_L(L/mg)	R^2	n	K_f	R^2
306	3.1655	0.2378	0.6395	1.3442	0.5950	0.7969
312	2.5088	0.3505	0.9122	1.6276	0.6737	0.9594
318	4.8146	0.1278	0.5139	1.0612	0.5107	0.8921
328	1.3394	1.4071	0.8510	2.6659	0.7703	0.5396
338	4.2105	0.1539	0.5051	1.2388	0.5669	0.9293
Temkin isotherm			Dubinin – radushkevich isotherm			
b_T	K_T	R^2	$K_{D.R}$	E	q_s	R^2

J.mol^{-1}	(L mg^{-1})		Mol^2 KJ^{-2} ×10^{-7}	J/mol	mg.g^{-1}	
3488.3916	1.9928	0.8608	0.550	3042.90	2.1736	0.7789
4501.8535	3.0166	0.9711	0.413	3479.44	1.8789	0.9393
3208.1689	1.6639	0.8954	0.677	2717.63	2.7709	0.8742
8208.8862	10.3802	0.5175	0.291	4145.13	1.6457	0.6948
3958.4899	2.0422	0.9357	0.529	3074.38	2.5370	0.9599

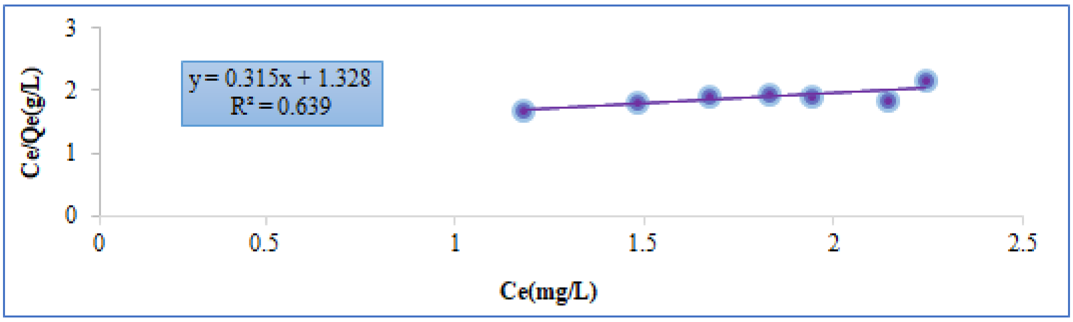

Figure 8: Langmuir's adsorption isotherm for the adsorption of CV onto tomato biosorbent at 312K.

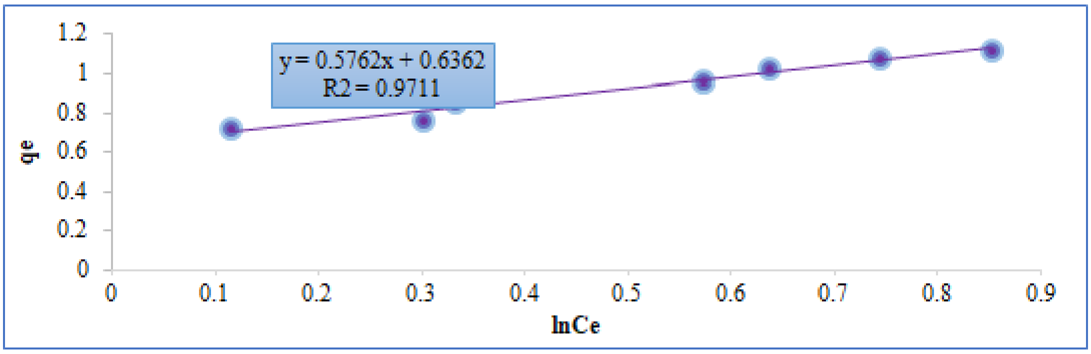

Figure 9: Temkinadsorption isotherm for the adsorption of CV onto tomato biosorbent at 312K

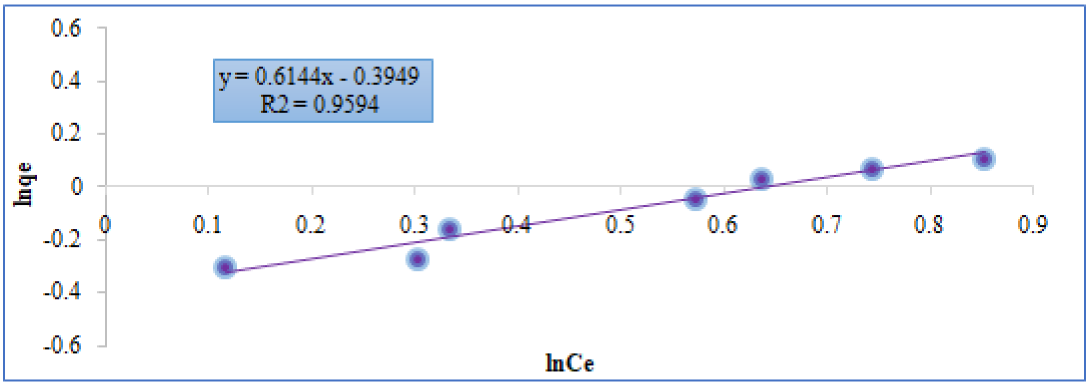

Figure 10: Freundlichisotherm model for the adsorption of CV by tomato biomass at 312K.

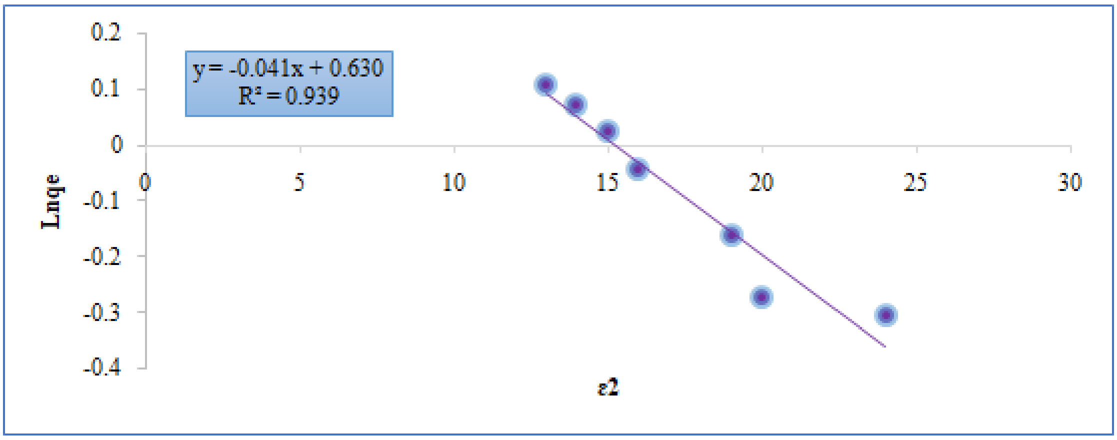

Figure 11: D-R isotherm model on the adsorption of CV onto tomatobiosorbent at 312K

Kinetic Adsorption

In the present investigation, three kinetic models namely, pseudo-first-order, pseudo-second-order and intraparticle diffusion model were tested to obtain rate constants, equilibriumadsorption capacity and adsorption mechanism at different temperatures.The pseudo-first-order rate constant, k_1, and the equilibriumadsorption capacity, q_e at different temperatures were determinedfrom the slope and intercept of the plots of ln $(q_e–q_t)$ versus t(Eq. (9)) (figure 12) and are listed in Table 2along with the correlationcoefficient, R^2. From the kinetic data in Table 2, it can be seen that at all studied temperatures, the correlation coefficients for the pseudo-first-order kinetic model are very low. Moreover, a large difference between theoretical and experimental equilibrium adsorption capacity, q_e is observed at all temperatures, indicating a poor fit of the pseudo-first-order equation to the experimental data.

$$\ln (q_e – q_t) = \ln q_e – K_1 t \quad …….. (9)$$

The kinetic data of CV adsorption onto tomato seedswere further analyzed using the pseudo-second-order equation (Eq. (10)). The pseudo-second-order model constants were determined from the slope and intercept of the plot of t/q_tversus t. The plot of t/q_tagainst t at different temperatures is shown in Fig. 13. Contrary to the pseudo-first-order equation, the fitting of the kinetic data in the pseudo-second-order equation showed excellent linearity with high correlation coefficient (R^2> 0.999) over the temperature range of 306–338 K.

$$t/qt = 1/K2qe2 + t/qe \quad ……… (10)$$

The intraparticle diffusion was investigated using the empiricalrelationship based on the model of Weber–Morris (Eq. (11)).

$$q_t = K_d t^{0.5} + C \quad …….. (11)$$

The Weber–Morris plots (q_e versus $t^{0.5}$) for adsorption of CV on tomato seeds at different temperatures were multimodal with three distinct regions (figure 14). The initial curved region corresponds to the external surface uptake, the second stage relates the gradual uptake reflecting intraparticle diffusion as the rate limiting step and final plateau region indicates equilibrium uptake. Based on these results it might be concluded that intraparticle diffusion was involved in CV adsorption onto tomato seeds, but it was not the sole rate determining step and that some other mechanisms also play an important role. A similar trend has already been reported for CV adsorption onto different low-cost adsorbents [31,32,33].

Table 2: Kinetic Parameters Of The Adsorption Of C.V Onto Tomato Seeds at 6.4 mg/L

Temperature (K)	First-order			Second-order			Intra-particle diffusion	
	q_e mg/g	K_1 Min^{-1}	R^2	qe mg/g	K_2 mg/g min	R^2	K_d mg/g min	R^2
306	0.9107	0.0540	0.9897	1.3727	0.0622	0.9979	0.1050	0.9925
312	0.9152	0.0560	0.9900	1.2943	0.0592	0.9987	0.1055	0.9810
318	0.9170	0.0600	0.9876	1.2569	0.0653	0.9997	0.1015	0.9686
328	0.8431	0.0557	0.9915	1.2786	0.0446	0.9989	0.1018	0.9880
338	0.9331	0.0590	0.9768	1.2671	0.0637	0.9980	0.0982	0.9782

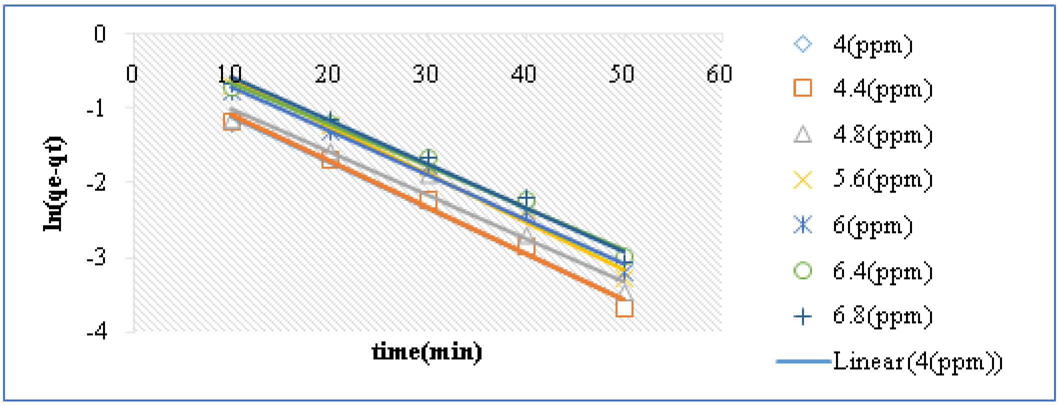

Figure 12: Pseudo-first-order kinetic model plots for adsorption of CV on tomato seeds at 312K

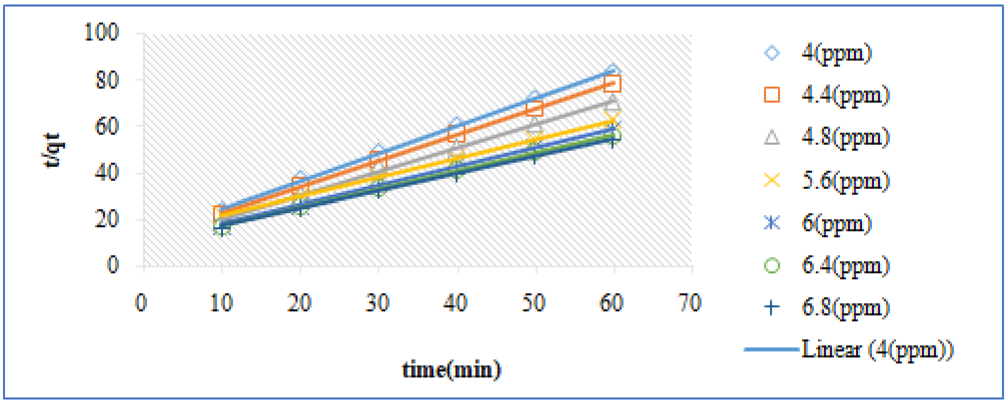

Figure 13: Pseudo-second-order kinetic model plots for adsorption of CV on tomato seeds at 312K

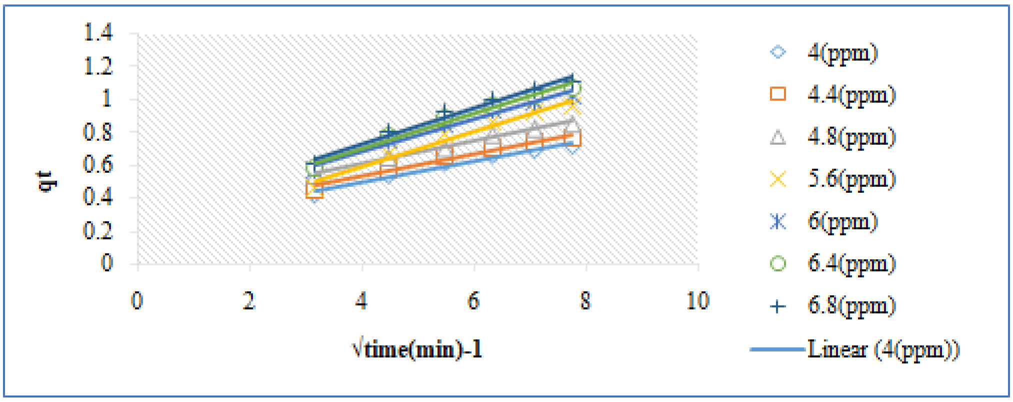

Figure 14: Intraparticle diffusion model plots for adsorption of CV on tomato seeds at 312K

Thermodynamic parameters

The thermodynamic parameters – Gibbs free energy change (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) for the biosorption process were calculated using the following equations for the temperature range 306–338K [34]:

$$\Delta G^\circ = -RT\ln K_{eq} \qquad \ldots\ldots\ldots\ldots(12)$$

$$K_{eq} = q_e / C_e \qquad \ldots\ldots\ldots\ (13)$$

$$\ln K_{eq} = \Delta S^0/R - \Delta H^0/RT \qquad \ldots\ldots\ldots\ldots\ (14)$$

The plot of ΔG^0 versus T (Fig. 15) gives a straight line with the slope and intercept giving the values of ΔH^0 and ΔS^0 respectively. Table 3 shows the value of the thermodynamic parameters of CVbiosorption on tomato seeds. The negative value of ΔG^0 at all temperatures confirms the spontaneous nature of the biosorption process. The increase in value of ΔG^0 with increasing temperature suggests areduction in spontaneous nature of the biosorption process. Thenegative value of ΔH^0 implies that the biosorption is exothermic. The positive value of ΔS^0 shows the process is enthalpy driven.

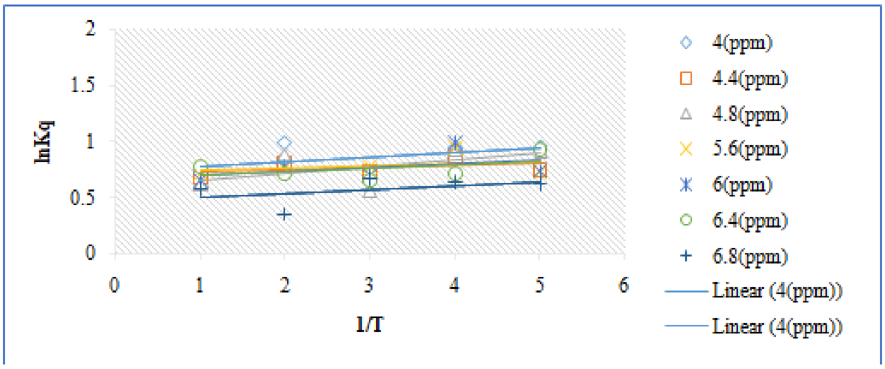

Figure 15: Plot of 1/T vs. lnkq for the adsorption of CV onto tomatobiosorben

Table 3: Thermodynamic parameters of CV adsorption onto the tomatobiosorbent at 6.4mg/L

$-\Delta H^0$(J/mol)	ΔS^0(J/K/MOL)	$-\Delta G^0$(J/mol)				
250.25	5.5329	306K	312K	318K	328K	338K
		1971.67	1851.65	1718.03	1954.35	1942.49
		K_{eq}				
		2.1706	2.0418	1.9152	2.0476	2.5201

4. Conclusion

Tomato seeds were tested and evaluated as a possible biosorbent for removal of CV from its aqueous solution, the removal efficiency approaches 90%. The temperature has a strong influence on the adsorption process and the maximum removal was observed at 312K. Experimental equilibrium data provide the best fit with freundlich isotherm with R^2=0.95, which signifies that a heterogeneous adsorption takes place between the dye and the surface of tomato seeds. The nature of adsorption was physical adsorption as inferred from the Dubinin-Radushkevich isotherm model. The thermodynamic study indicated that this adsorption is spontaneous and exothermic as evidenced by negative values of the changer in Gibbs free energy ΔG^0 and enthalpy ΔH^0. The pseudo-second order equation best describes the kinetics of adsorption system due do it, higher R^2 values than that of the pseudo first-order.

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