

Synthesis of Nano-Titanium Tannate as an Adsorbent for Crystal Violet Dye, Kinetic and Equilibrium Isotherm Studies

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Abstract

The purpose of this study was to prepare nano-titanium tannate complex (TTC) and to investigate its adsorption capacity for removal of cationic dyes such as crystal violet (CV) dye. The morphology and the main elements of TTC adsorbent were characterized by scanning electron microscopy (SEM-EDS), while its crystal structure was characterized by X-ray diffraction (XRD). Also, FT-IR spectroscopy study structural aspects of TTC. A "cotton-ball"-like and porous surface structure of titanium tannate complex (TTC) with nanoparticle size of 16.18 nm show high capability for absorbing crystal violet dye. The effect of several parameters such as contact time, initial concentrations of CV, solution pH and the amount of TTC was investigated. Three different kinetic equations such as pseudo-first order, pseudo-second order and intraparticle diffusion were used to study the order and the mechanism of the adsorption process. The adsorption of CV dye followed pseudosecond order equation. Moreover, equilibrium data were tested with four adsorption isotherm models namely, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R). Langmuir was the best fit for the data with maximum capacity as 58.8 mg/g. The results of Separation factor, Surface coverage and standard free energy (ΔG°) indicated that adsorption of CV onto TTC was favorable with fast rate and spontaneous physical adsorption process.

Keywords

Titanium(III) Tannate Complex (TTC), Crystal Violet, Adsorption Kinetics, Adsorption Isotherms

1. Introduction

Due to the rapid growth of the need for water in different industries, huge number of different pollutants accumulated in water. In many cases, these pollutants make water unsuitable to be reused and become wastewater [1].

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2. Experiment

2.1. Chemicals

Analytical-grad that chemicals were used in this work without further purification. Crystal violet, a type of triphenylmethane dyes with molecular formula (C25H30ClN3), (aq. solubility 16 g/l; purity 80%) as shown in **Figure 1** was received from LOBA Chemie Company, India and used as received. To evaluate the significant of the adsorbent, stock solutions (1000 mg/L) of CV was prepared in double distilled water and further diluted to perform adsorption experiments in presence of titanium(III)-tannate complex (TTC) as an adsorbent. Dilute solutions of 1M HNO₃ and 1M NaOH (BDH) were used to adjust pH of CV solutions using a pH meter.



Figure 1. Crystal violet structure (mol. formula C₂₅H₃₀ClN₃).

2.2. Synthesis of Titanium(III) Tannate Complex (Adsorbent)

A Beaker with an amount of 50 ml (4%:1.0%, ethanol: water) of tannic acid (0.1 M) was placed in ultrasonic bath and sonicated for few minutes. Then a cretin volume of TiCl₃ was added drop wise with continuous sonication for 8.0 minutes. The molar ratio of tannic acid to titanium(III) chloride was chosen to be 1:20 according to R. Zhang *et al.*, [23]. The pH of the mixture was adjusted to 3.5 - 4.0 using tris-HCl to avoid precipitation of titanium ion in the form of hydroxide. The colorless solution of tannic acid turned to orange precipitate at the beginning of the addition of titanium(III) chloride then changed into dark red precipitate. Complete precipitation was tested by adding few drops of both tannic acid solution and titanium ion solution respectively. There was no more precipitate formed to indicate that the chosen molar ratio of tannic acid to titanium(III) chloride was optimal. The obtained product was separated through precipitation and washed several times with 30%:70% ethanol: water then dried in the oven overnight at 60°C before use in the adsorption experiments.

2.3. Characterization of Titanium(III) Tannate

To study the surface morphology and main elements present in the complex of titanium tannate, scanning electron microscopy (SEM) using SEM model Quanta 250 FEG attached with an energy dispersive X-ray spectroscopy (EDS) unit with accelerating voltage 30 K.V., magnification14x up to 1000,000 and resolution for Gun.1n was used. The crystal structure of titanium tannate was analyzed by X-ray diffraction (XRD) in scan mode with Cu-Ka radiation ($\lambda = 0.01542$ nm) in the 2θ range of 10° to 80°. The functional group in the synthesized complex was analyzed through the analysis of Fourier transform infrared spectrometry (FTIR) using KBr pellet in the range of 400 to 4000 cm⁻¹.

2.4. Adsorption Experiments

To evaluate the significant of titanium(III) tannate complex (TTC) as an adsorbent, CV dye solution was used in this study as an environmental pollutants. Stock solutions (1000 mg/L) of CV was prepared in distilled water and further diluted to the required concentration to perform the calibration curves and adsorption experiments. Serial dilutions (1.0 to 6.0 mg/L) of CV stock solutions were used to prepare the calibration curves. Batch adsorption experiments were performed by introducing known amounts of TTC into several glass tubes, each containing 5.0 mL (to minimize the waste) of CV solution with an initial concentration ranging from 40 to 150 mg/L. Tubes were agitated at 120 rpm using an electric shaker at room temperature. To ensure performing the adsorption experiments at known pH value, the pH was adjusted before starting the experiment using solution of either NaOH or HCl. At interval times, CV solutions were withdrawn and introduced into a centrifuge to separate TTC powder from samples. CV solutions of 50 mg/L with different amount of TTC powder (0.5 to 2.5 g/L) were used to study the effect of adsorbent dose on the adsorption process. The effect of pH was studied by performing similar experiments with 2.0 g/L of TTC powder at different pHs from 2.75 to 10. A known amount of TTC powder (2.0 g/L) were added to 5.0 mL of CV solution with different concentrations (40 to 150 mg/L) at room temperature to calculate the adsorption isotherm.

2.5. Analytical Methods

UV-vis spectrophotometer (Perkin Elmer) was used to determine the concentrations of CV solution before and after the adsorption experiments. Calibration curves were obtained and used to calculate dye concentrations during adsorption experiments at any time (C_t).

The amount of CV dye sorbed onto TTC powder at any time, q_t (mg/g), was calculated from;

$$q_t = \frac{V(C_0 - C_t)}{W} \tag{1}$$

At equilibrium, $q_t = q_e$ and $C_t = C_e$; therefore the amount of sorbed CV dye, q_e , was calculated from

$$q_e = \frac{V(C_0 - C_e)}{W} \tag{2}$$

where C_0 , C_t and C_e are the initial concentration, concentration at any time and equilibrium concentrations of CV dye solution (mg/L), respectively, V is the volume of the dye solution (L), and W is the mass of TTC (g).

Dye removal percentage can be calculated as follows:

$$\operatorname{Removal}_{\%} = \frac{\left(C_0 - C_t\right)}{C_0} \times 100 \tag{3}$$

2.6. Adsorption Kinetics

Kinetic Study will allow the determination of the rate of CV uptake by TTC adsorbent which in turn led to measuring the efficiency of the adsorption process. Three different kinetic models namely a pseudo-first order [24]-[26], a pseudo-second order [27] [28] and an intraparticle diffusion [29] were used in the current study. The linear form of Lagergren pseudo-first order model is represented as:

$$\log\left(q_e - q_t\right) = \log q_e - \left(\frac{k_1}{2.303}\right)t \tag{4}$$

where q_e and q_t are the amounts of the CV adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the rate constant of adsorption (min⁻¹).

While, the linear form of pseudo second-order developed by Ho [27] based on equilibrium adsorption can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 x q_e^2} + \left(\frac{1}{q_e}\right) t \tag{5}$$

where k_2 (g/mg·min) is the adsorption rate constant of pseudo second-order adsorption rate.

Also, intraparticle diffusion equation can be described by the following equation:

$$q_t = k_{id}\sqrt{t} + C \tag{6}$$

where, k_{id} the intraparticle diffusion rate constant (mg/g·min^{-1/2}) and *C* is the intraparticle diffusion constant (mg·g⁻¹). The plot of q_t versus $t^{1/2}$ is used to calculate the constants k_{id} and *C* from the slope and the intercept respectively. The relative values of *C* give an idea about the boundary layer thickness, *i.e.*, the larger the intercept value, the greater the boundary layer effect [22].

2.7. Adsorption Isotherm

The equilibrium state between the amount of adsorbed onto the adsorbent surface (q_e) and the concentration of adsorbate in solution (C_e) at a fixed both temperature and pH is described by adsorption isotherm. In this study, linear forms of four different adsorption isotherm equations were used to describe the equilibrium data. These equations are Langmuir [30] [31] and Freundlich [32] in addition to Temkin [33] [34] and Dubinin-Radushkevich (D-R) equation [35] [36]. The parameters of those equations can describe both the surface properties and the affinity of the adsorbent such as TTC to the adsorbate such as CV dye. Also, adsorption maximum capacity, adsorption intensity and the heat of adsorption (kJ/mol) which indicates the adsorption potential can be measured.

3. Results and Discussion

3.1. Characterization of Titanium(III) Tannate

SEM images of the morphology of the synthesized titanium tannate complex (TTC) is shown in **Figure 2** at two different magnification view as low (30,000×) and high (100,000×). The images show bladed crystals for TTC with "cotton-ball"-like morphology and porous surface structure. In addition, the average particle size was estimated from SEM image (**Figure 2(b)**) as 16.18 nm. The main elements present in TTC is determined by SEM-EDS spectrum and shown in **Figure 3**. The results indicated that the carbon, oxygen, titanium were the main elements present in TTC structure with percent composition as 21.07%, 48.95% and 28.75% by weight respectively. The calculated percent composition from the SEM-EDS spectrum shows that the ratio of carbon to oxygen is different from their ratio in the chemical formula of tannic acid (C76H52O46). Although previous research [23] proposes a possibility of hydrolysis of metal ions such as Ti(III) which led to increase the % of oxygen, further research is required to prove that. **Figure 4** shows the XRD patterns of 16.18 nm TTC with a diffraction peaks appear in the range of $2\theta = 30^{\circ}$ to 35° indicated that titanium tannate complex has an amorphous structure.



Figure 2. (a) Low (30,000×) and (b) high (100,000×) magnification SEM images of TTC.





Figure 4. XRD spectra of the titanium tannate complex.

The results in **Figure 5** show the FTIR spectra of tannic acid (TA) and titanium tannate complex (TTC). The results show that the main bands appeared in the spectrum of tannic acid are the stretching vibrations band of hydroxyl group (OH) of the phenolic ring which appeared as abroad band at 3700 cm^{-1} to 3000 cm^{-1} range due to the hydrogen bonding between OH. Also, stretching vibration carbonyl groups (C=O) appeared at $1730 - 1705 \text{ cm}^{-1}$, in addition to C-O bands at $1100 - 1300 \text{ cm}^{-1}$ as reported also previously [23] [37]. For FTIR spectra of TTC (solid line in **Figure 5**), the major difference was in the OH group region in addition to the C-O region where absorption was much less indicating that the C-O bonds had been weakened as would occur when chelated with titanium ion. Bonding therefore occurred between the metal ion and the hydroxyl groups. Accordingly, the suggested structure of titanium tannate complex is shown in **Figure 6**.

3.2. Effect of Contact Time and Initial Concentrations of CV Dye

A known amount of ttc powder 0.010 g (2.0 g/L) was added to 0.005 L of different concentrations of CV (from 40 - 150 mg/L). For a total period of 120 min at a temperature of 298 K, experiments were performed to evaluate the effect of contact time (0 - 120 min) and different initial concentrations (40, 50, 70, 90 and 150 mg/L) of CV dye on the adsorption process as shown in **Figure 7**. The obtained results in indicated that the curve of the adsorption rate of CV onto TTC powder was very rapid in the first 10 min confirming the presence of large number of readily accessible adsorption sites. For example at 40 mg/L of CV the adsorbed amount (q_i) reached



Figure 5. FTIR of tannic acid (TA) and titanium tannate complex (TTC).



Figure 6. Suggested chemical structure of titanium tannate complex.



of crystal violet dye onto TTC powder (T = 298 K, time = 120 min, [CV]0 = 40 - 150 mg/L, pHi = 7, V = 0.005 L, TTC dosage = 2.0 g/L).

16.85 mg/g, which represented about 78.11%, comparing to 19.91 mg/g (92.3%) at 120 min. Then, the adsorption of CV dye increased gradually during the following 40 min until reached equilibrium at about 120 min. Furthermore, the sorbed amount of CV dye was also increased from 16.85 to 42.10 mg/g by increasing the initial concentrations from 40 to 150 mg/L respectively. The results showed that the uptake of CV dye by TTC powder depends on the contact time and the initial concentration. This may be due to the time required for the CV dye to encounter the boundary layer effect, then diffuse to the surface of TTC powder and finally diffuse to the porous structure [38]. Also, it was noted that the time profile of the adsorption of CV dye reached saturation in a single, smooth and contentious curve which indicated the possible formation of monolayer of CV dye onto the surface of TTC powder [39]. To ensure complete equilibrium of the data, adsorption samples were collected at 120 min.

3.3. Effect of Solution pH on Adsorption of CV

Adsorption rate can be affected by the degree of ionization of adsorbate and the surface charge of adsorbent [40]-[42]. However, these two parameters were controlled mainly by the initial solution pH. To evaluate the effect of pH on the equilibrium adsorption capacity (q_e) of CV onto TTC surface, experiments were conducted at 50 mg/L [CV]₀, 2.0 g/L TTC dose, and 120 min contact time at a temperature of 298 K. Figure 8 indicated that the adsorption rate was slow in acidic medium at pH 2.75 with 64.46% removal. Then the % removal continue to be linearly proportional to the increase in the initial pH values until reached maximum removal of 94.33% in basic medium when the pH values increases from 8 to 10. It is known that crystal violet dye gives positively charged ion (colored cation) which can compete with H⁺ ions in solution at high pH value for the adsorption sites and lead to decrease the adsorption rate. Thus when the pH value of the solution increased from 2.75 to 7 lead to decrease the competition between H⁺ ions and cationic CV dye in solution and thus led to increase the adsorption rate. Moreover, increase the negative charge on the surface of TTC due to increase the concentration of OH-ions in basic medium, led to increase the electrostatic attraction of positively charged CV dye and increases the adsorption process [43]. Similar results were observed for our previous research on the adsorption of methylene blue dye, a cationic dye (MB dye⁺) onto miswak leaves [44]. In addition, the adsorption of crystal violet onto different adsorbents such as activated carbons derived from male flowers of coconut tree [28], tobacco stem [32] and some metal cations onto different adsorbents such as Cd(II) ion onto activated red mud [45] was previously reported with similar trend. These results on effect of pH indicate that the solution pH controls the electrostatic interactions between adsorbent surface and adsorbate in the solution which can have a profound effect on the adsorption process.



Figure 8. Effect of solution pH on the adsorption of crystal violet dye onto TTC (T = 298 K, time = 120 min, [CV]0 = 50 mg/L, V = 0.005 L, TTC dosage = 2.0 g/L).

3.4. Effect of Adsorbed Amount

To investigate the effect of adsorbent dosage on the adsorption of CV, different tubes filled with a specific volume of CV dye solution with [CV]0 (50 mg/L) at different amounts of TTC powder (0.25 to 2.5 g/L) at room temperature. **Figure 9** showed a general trend for the adsorption of CV onto the surface of TTC. The percent removal of CV increased rapidly in the first stage with the increase in the adsorbent dose then increased slowly until reached equilibrium with the further increase in the adsorbent dose. The solution of CV dye is decolorized by 31.63% by using 0.5 g/L of TTC dosage. The decolonization rate of CV solution increases dramatically by introducing more dosage of TTC to reach 96.27% at dosage of 2.0 g/L TTC. Furthermore, increasing the dosage of TTC to 2.5 g/L leads to decrease the % removal to reach 92.95%. Thus in further experiments 2.0 g/L of TTC were chosen as the optimum dose. It is clear that the increase in both the surface area and the adsorption sites which resulted by introducing more dosage of TTC adsorbent, lead to increase the % removal of CV from aqueous solution. On the other hand, % removal of CV decreased from 96.27% to 92.95% when introducing more amount of TTC as 2.5 g/L. It was reported that [46] increasing the amount of the adsorbent may led to increase the overlapping and/or aggregation of the adsorption sites on the adsorbent surface which can decrease the adsorption rate.

3.5. Adsorption Kinetics (Determining Adsorption Rate Constant)

Determining the kinetic parameter (such as the rate constant) and predicting information about adsorbent/adsorbate interaction it is significant for any adsorption experiments. As discussed above, three different models were used to study the kinetic of adsorption of CV onto TTC powder.

3.5.1. Pseudo First-Order Equation

Equation (4) expressed the linear form of Langergren pseudo first-order for the adsorption process of CV dye onto TTC adsorbent. Different concentrations of CV dye (40 - 150 mg/L) were used to calculate k_1 and q_e from the slope and the intercept of the plots of $\log(q_e - q_t)$ versus *t* as shown in Figure 10(a). The value of k1 and q_e determined from Equation (4) are presented in Table 1 along with the corresponding correlation coefficients (R^2). The low values of R^2 and the disagreement between the experimental and the calculated values of q_e indicated that the adsorption of CV dye onto TTC is not first-order kinetics.

3.5.2. Pseudo-Second Order Rate Equation

The kinetic data of the adsorption of CV onto TTC were further analyzed by the linear form of pseudo-second

order model (Equation (5)). The slope and the intercept of the plot of $\frac{t}{q_t}$ versus t is used to determine the value



Figure 9. Effect of adsorbent dose on the adsorption of crystal violet onto TTC (T = 298 K, time = 120 min, [CV]0 = 50 mg/L, pHi = 7, V = 0.005 L, ttc dosage = 0.5.0 - 2.5 g/L).



Figure 10. Pseudo-first order (a) and Pseudo-second order (b) kinetics for the adsorption of CV onto TTC (T = 298 K, time = 120 min, [CV]0 = 40 - 150 mg/L, pHi = 7, V = 0.005 L, TTC dosage = 2.0 g/L).

Table 1. Adsorption kinetic parameters for the adsorption of CV onto TTC (T = 298 K, time = 120 min, [CV]0 = 40 - 150 mg/L, pHi = 7, V = 0.005 L, TTC dosage = 2.0 g/L).

		First-order kinetic model			Se	Second-order kinetic model		
[CV]0 (mg/L)	$q_e, \exp (\mathrm{mg/g})$	q_e , cal (mg/g)	k1 (min ⁻¹)	R2	q_e , cal (mg/g)	k2 (g/mg·min ⁻¹)	R2	
40	20.060	5.370	0.035	0.807	20.41	0.040	0.999	
50	23.417	4.498	0.025	0.974	23.81	0.025	0.999	
70	30.671	11.117	0.012	0.947	28.57	0.010	0.997	
90	36.922	10.188	0.009	0.934	32.26	0.011	0.998	
100	51.502	0.012	0.012	0.988	50.00	0.010	0.998	

of both q_e and k_2 respectively. Table 1 presented both values of k_1 and q_e along with the value of R^2 . The results in Figure 10(b) show linear plots with very high values of R^2 (very close to unity) in addition to a good agreement between experimental and calculated values of q_e (Table 1). It is clearly indicated that the adsorption of CV dye onto TTC is greatly represented by the pseudo second-order kinetics which means the adsorption process may be chemisorption. Similar trends were shown for the adsorption of CV onto Zeolites from Coal Fly and Bottom Ashes [22]. It is known that one of the advantages of using the second-order equation is that there is no need to know the value of q_e from the experiments, as it can be calculated from the slope of its equation. Furthermore, second-order model allows to obtain the initial adsorption rate [47].

3.5.3. Intra-Particle Diffusion Study

It is proposed that the uptake of the adsorbate (such as CV dye) by the adsorbent (such as TTC) varies almost proportionately with the square root of the contact time $(t^{1/2})$ according to the Equation (6) [13]. In order to investigate the mechanism of CV dye adsorption onto TTC, intra-particle diffusion based mechanism was studied. The results indicated that the plot in **Figure 11** was not linear over the whole time range. Also, the plot indicated that the external surface adsorption (stage 1) is absent and it is finished before 10 min. Then after 10 min, the intra-particle diffusion control (stage 2) started and kept on to 60 min. Finally, the equilibrium step (stage 3) appeared after 60 min up to 120 min. It can be seen that the adsorption of CV dye onto TTC involved more than one process, and the intra-particle transport is not the rate-limiting step.

3.6. Adsorption Isotherms for Crystal Violet

The affinity of TTC adsorbent for the adsorption of CV dye was evaluated by using different adsorption isotherms such as Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R).

3.6.1. Langmuir Isotherm

The Langmuir isotherm model assumes that a monolayer of adsorbed material (in liquid, such as CV is adsorbed over a uniform adsorbent surface such as TTC. The Langmuir-I equation is derived by some mathematical manipulation as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{7}$$

where q_m (the maximum capacity of adsorption, mg/g,) and K_L (a constant related to the affinity of the binding sites, L/mg,) are the Langmuir isotherm constants. Both q_m and K_L can be determined from the linear form of Langmuir-I equation as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \tag{8}$$

Figure 11. Intra-particle diffusion plot for the adsorption of CV onto TTC (T = 298 K, time = 120 min, [CV]0 = 40, 70 and 150 mg/L (from bottom to top respectively), pHi = 7, V = 0.005 L, TTC dosage = 2.0 g/L).

Figure 12(a) shows the linear fit of Langmuir-I for the adsorption of CV onto TTC at room temperature. The value of q_m , K_L and R^2 are presented in **Table 2**. The high value of R^2 as 0.999 indicated minimal deviation from the fitted equation showing that the adsorption data would follow Langmuir-I equation. Also, the data in **Table 2** indicated that the maximum adsorption capacity of TTC for CV was calculated as 58.8 mg/g. Furthermore, the value of K_L gives indication for the affinity between the adsorbent surface (TTC) and the adsorbate (CV dye molecules). It can be mentioned that the surface of TTC is homogeneous and the adsorbent is energetically homogeneous [4] [24]. The adsorption of crystal violet dye also followed Langmuir-I model onto different adsorbents such as zeolites from coal fly ash (ZFA), bottom ash (ZBA) [4] and onto activated carbon derived from Gölbaşı lignite [48]. In addition, S. Patil *et al.* [48] also, found the adsorption of crystal violet dye onto different adsorbents followed Langmuir-I model and formed monolayer. On the other hand, comparison of maximum monolayer adsorption capacity (q_m) of CV dye onto various adsorbents obtained in the literature is presented in **Table 3** in order to compare the efficiency of TTC adsorbent. It can be seen that TTC is very effective adsorbent for CV dye with a relatively large adsorption capacity of 58.8 mg/g when compared with some other adsorbents.

Figure 12. Adsorption isotherm models, (a) Langmuir-I, (b) Freundlich, (c) Temkin and (d) D-R for the adsorption of CV onto TTC (T = 298 K, time = 120 min, [CV]0 = 40 - 150 mg/L, pHi = 7, V = 0.005 L, TTC dosage = 2.0 g/L).

Table 2. Langmuir,	Freundlich,	Temkin and D-	R constants for	r the adsorption	of CV onto	TTC $(T = 2$	98 K, time =	120 min,
[CV]0 = 40 - 100 m	g/L, pHi = 7	V = 0.005 L, c	losage = 2.0 g/l	L).				

Langmuir constants			Freundlich constants			
$q_m \pmod{g}$	K_{L} (L/mg)	R^2	$k_{\rm F}$ (L/mg)	Ν	R^2	
58.8	0.156	0.999	14.99	3.125	0.895	
Temkin constants			Dubinin-Radushkevich (D - R) constants			
b_{T} (kJ/mol)	k_{T} (L/mg)	R^2	q_s (mg/g)	$B \pmod{2/kJ^2}$	R^2	
0.236	2.24	0.962	44.345	2.220	0.953	

Table 3. Comparison of the maximum monolayer adsorption of CV dye onto various adsorbents.					
Adsorbent	$q_m \pmod{g}$	Reference			
Bottom ash	12.10	[49]			
TS, NaOH-TS	118, 195	[50]			
Ananas comosus (pineapple) leaf powder (PLP)	158.73	[51]			
Phosphoric acid activated carbons (PAAC)	60.42	[32]			
Sulphuric acid activated carbons (SAAC)	85.84	[32]			
Cocoa (theobroma cacao) shell (CSAC)	43.50	[52]			
Activated carbon	15.7 - 19.8	[53]			
ZFA	19.6	[22]			
ZBA	17.6	[22]			
Different natural materials	60.8 - 65.8	[48]			
TTC	58.8	present study			

Separation Factor and Surface Coverage (θ)

There are two factors such separation factor (R_L), and surface coverage (θ) can help and give significant information about the behavior of the interaction between the adsorbent and the adsorbate. Separation factor is a dimensionless constant which can be used as a characteristic for Langmuir isotherm [44] as shown by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \tag{9}$$

where C_0 (mg/L) is the initial concentration of CV dye and K_L (L/mg) is Langmuir constant. The value of R_L indicates the shape of the isotherm to be either linear ($R_L = 1$), unfavorable ($R_L > 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). Figure 13 representing the Plot of R_L versus C_0 of CV dye at room temperature. It can be seen that the R_L values were in the range of 0.04 to 0.14, which is less than unity, indicating that the adsorption of CV onto TTC is a favorable process and thus TTC is a good adsorbent for CV dye. Recently T. Depci et al. [48] found similar results for the adsorption of CV onto activated carbon derived from Gölbaşı lignite.

In addition, the surface coverage (θ) of the adsorbent (TTC) is related to the initial concentration of CV dye - (C_0) as a Langmuir type equation as follow:

$$K_L C_0 = \frac{\theta}{\left(1 - \theta\right)} \tag{10}$$

$$\theta = \frac{K_L C_0}{\left(1 - K_L C_0\right)} \tag{11}$$

where K_L is Langmuir constant (the adsorption coefficient), C_0 is the initial concentration of CV and θ is the surface coverage. The values of θ calculated according to Equation (11) and plotted against the values of initial concentrations (C_0) as shown in Figure 13. The results show that the adsorption of CV onto TTC was very fast in the beginning and the surface coverage (θ) increases rapidly with the increase of initial concentration. Then θ increases slowly when the initial concentration exceeds 30 mg/L until θ value is close to 1.0. This results show that TTC will be very effective adsorbent in removing CV ions from aqueous solutions.

3.6.2. Freundlich Isotherm

The adsorption process takes place on a heterogeneous surface when the resulted data followed Freundlich isotherm model. Freundlich equations (linear and nonlinear) can be expressed as:

Figure 13. Separation Factor (R_L) and Surface Coverage (θ) for the adsorption of CV onto TTC (T = 298 K, time =120 min, [CV]0 = 40 - 150 mg/L, pHi = 7, V = 0.005 L, dosage = 2.0 g/L).

$$q_e = K_F C^{1/n} \tag{12}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{13}$$

where K_F (L/mg) is an indicator of the multilayer adsorption capacity and $\frac{1}{n}$ is the adsorption intensity and indicates both the relative distribution of energy and the heterogeneity of the adsorbent sites. Plot of $\log q_e$ versus $\log C_e$ at constant temperature is shown in Figure 12(b). The value of K_F and $\frac{1}{n}$ (Table 2) was determined from the intercept and the slope respectively. Although, the value of R^2 (0.895) of Freundlich is lower than the value of R^2 (0.999) of Langmuir-I isotherm. This result indicates that Freundlich model is not a good model to describe the adsorption of CV dye onto TTC. The results of Langmuir and Freundlich implies that the adsorption of CVonto TTC show a mechanism involving only monolayer condition.

Recent reports for the adsorption of crystal violet dye onto different adsorbents found similar trends indicating that the equilibrium data were described well by Langmuir model and did not fit well with Freundlich model [54].

3.6.3. Temkin Isotherms

Equation (14) represented the linear form of Temkin isotherm model which can be used to test the adsorption potential of adsorbent to adsorbate. This equation supposes that increasing the coverage layer of adsorbate onto the surface of adsorbent makes the heat of adsorption (ΔH_{ads}) of all molecules in that layer decreased linearly by increase the coverage.

$$q_e = \frac{RT}{b_r} \ln K_T + \frac{RT}{b_r} \ln C_e \tag{14}$$

where, *R* is common gas constant (0.008314 kJ/mol K), *T* is the absolute temperature (K), $\frac{1}{b_T}$ is the Temkin constant related to the heat of sorption (kJ/mol) which indicates the adsorption potential (intensity) of the adsorption

bent and K_T (L/g) is Temkin constant related to adsorption capacity. The constants $\frac{1}{b_T}$ and K_T can be cal-

culated from the liner plots of q_e versus $\ln C_e$ as shown in Figure 12(c). The numerical values of correlation coefficient R^2 , in addition to both K_T and b_T of the Temkin equation for CV are represented in Table 2. Results indicate that the data of equilibrium isotherm of CVonto TTC ($R^2 = 0.971$) are also can be described by the Temkin model. Also, the slight fitting of Temkin isotherm model for the adsorption of CV ions by Anethum graveolens was reported [18].

3.6.4. Dubinin-Radushkevich (D-R) Isotherm Model

The adsorption data of CV dye onto TTC were also tested by Dubinin-Raduskevich (D-R) isotherm model in order to investigate the characteristic porosity and the apparent free energy of adsorption. Isotherm model of D-R (Equation (15)) does not assume constant adsorption potential or homogeneous surface for the adsorbent [13].

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{15}$$

where, β , a constant related to the mean free energy of adsorption (mol²/J) per molecule of CV dye (adsorbate) when transferred to the surface of TTC (adsorbent) from solution.

 $q_m \pmod{g}$ is the theoretical saturation capacity based on D-R isotherm and ε is the Polanyi potential (J/mol). ε is related to the equilibrium concentration C_e , (mg/L) and can be calculated from the following equation:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{16}$$

where *R* is common gas constant (8.314 J/mol K) and *T*(K) is the absolute temperature. Figure 12(d), representing the plot of $\ln q_e$ against ε for adsorption of CV onto TTC which allows for the determining q_m and β from the intercept and the slope respectively. Table 2 shows the numerical values of q_m and the correlation coefficient (R^2). The high value of R^2 indicated that the adsorption of CV onto TTC followed D-R isotherm model. Based on the value of β , (which is related to the mean free energy of adsorption), the mean free energy of adsorption (*E*) (KJ/mol) can be calculated as follow:

$$E = \frac{1}{\sqrt{2\beta}} \tag{17}$$

The results in **Table 2** show that the value of *E* is equal to 0.475 kJ/mol which is lower than 8 kJ/mol. It indicates that the adsorption of CV dye onto TTC complex is a physical adsorption process. Similar results were obtained by T. Chinniagounder *et al.* [52] for the adsorption of CV dye onto Cocoa (Theobroma cacao) Shell Activated Carbon (CSAC).

3.7. Standard Gibbs Free Energy Change (ΔG°)

The degree of spontaneity of the adsorption process is mainly determined from standard Gibbs free energy (ΔG°) equation. Increase the negative value of ΔG° represents the increase in the spontaneity and the favorability of the adsorption [55]. Equations (18) and (19) were used to calculate ΔG° .

$$\Delta G^o = -RT \ln K_C \tag{18}$$

$$K_C = \frac{q_e}{C_e} \tag{19}$$

where; *T* is the temperature (K), *R* is gas constant (kJ/mol·K) and K_c (dimensionless) is the standard thermodynamic equilibrium constant, hence both q_e and C_e are multiplied by the dosage of the adsorbent (g) used and is the amount of adsorbed CV per unit mass of TTC at equilibrium (mg/g) used and the volume (L) of the solution used. Calculation of ΔG° from previous equation was more negative and the average ΔG° was calculated as (-18.12 kJ/mol) which indicated that the adsorption of CV onto TTC adsorbent is spontaneous and favorably. It was noted that the absolute values of both ΔG° and K_c (equilibrium constant) decrease with the increase with the initial concentration of Crystal violet dye. These results were similar to the recent report for the adsorption of CV dye onto activated carbon derived from Gölbaşı lignite [48].

4. Conclusion

The main conclusions of this investigation indicated that Ti-tannate complex (TTC) could be used as an effective adsorbent for the removal of CV dye from aqueous solution. Also, the adsorption of CV dye onto TTC powder was found to depend on the contact time and the initial concentration in addition to the dosage of TTC. Furthermore, the electrostatic interactions between CV and TTC surface controlled by the value of pH and the maximum removal were observed at pH 7. Kinetic study of adsorption process showed that pseudo-second order was the best model to describe the rate of removal of CV dye with the correlation coefficient (R^2) of 0.999. Also, the intraparticle diffusion was not the rate determining step. The study of adsorption isotherm resulted in fitting the data well to three different models (based on the values of R^2) in the following order as Langmuir-I > Temkin > D-R, while Freundlich equations were not suitable to describe the adsorption process. The monolayer maximum capacity of CV onto TTC is 58.8 mg/g as obtained from Langmuir model. The removal of CV by TTC was favorable, rapid and effective. Hence, the value of separation factor (R_L) was less than unity and the value of surface coverage (θ) increased rapidly with the increase of [CV]₀ till became close to 1.0. In addition, the adsorption of CV is spontaneous and physical process indicating that TTC is valuable adsorbent for removing CV from water and wastewater.

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