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Surface and Intraparticle Diffusion of Crystal Violet Dye on Egyptian Doum Fruit from Aqueous Solutions

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Abstract

The adsorption of crystal violet (CV) dye from waste solution onto Doum Fruit (DF) using batch adsorption technique was investigated as a function of parameters such as initial pH, contact time, initial dye concentration, adsorbent amount, agitation speed and temperature. The DF was shown to be effective adsorbent for the removal of CV dye, and the equilibrium was reached in about 60 min. The experimental data were analyzed by Langmuir, Freundlich and Dubinin-Radushkevich isotherm models using linear regression analysis. The results of dsorption experiments indicate that the maximum sorption capacity (Q_{max}) of CV is 35.26 mg/g. Thermodynamic parameters such as ΔG°, ΔH° and ΔS° were also evaluated, the sorption process was found to be spontaneous and exothermic. The kinetic experimental data was analyzed using three kinetic models including pseudo-first order, pseudo-second order and intraparticle diffusion model to examine the mechanism of adsorption and potential rate-controlling step. The results indicated that the DF could be used effectively to adsorb CV dye from aqueous solutions.

Keywords- Crystal violet, low-cost adsorbent, Doum Fruit, batch study.

1. INTRODUCTION

Removing of the hazardous materials such as dyes and heavy metals from water is one of the most important environmental concerns especially with the increasing of industrial important environmental concerns especially with the increasing of industrial activities which considers one of the main sources of water pollution beside agricultural, domestic activities, and other environmental changes [1].

Using the adsorption onto solid phases as an extraction method for water purification is still attractive field. It has become one of the most important fields used to the removal of organic pollution, radionuclides, color, and odor, from waste water due to its simplicity, efficiency, fast, universal method and applicability, beside that it is inexpensive [2]. The main idea of the adsorption process is based on a partitioning of analyte between two phases, a solid phase (sorbent) and a liquid phase (sample matrix or solvent with analytes) [3]. The adsorption is influenced strongly by the used sorbent because it is controlled by many parameters such as selectivity, affinity and capacity [4]. So, the development of methodology of adsorption onto solid phases is connected by the introduction of novel types of sorptive materials.

A large number of sorbents are available now such as, polymer sorbents, graphitized or porous carbon and chemically modified silicagel. Due to the highly adsorption capacity of **A**ctivated **C**arbon (AC), it is used on a large scale for many years as an adsorbent for the removal of hazardous pollutants from water. The highly cost of producing and regeneration of AC encouraged the investigator on studying the possibility of using cheaper and available alternatives to AC adsorbent.

Low-cost, high distribution coefficients, high exchange capacity and availability, are the most important requirements for sorbents in the purification process. Up to day, the search focuses on developing low-cost adsorbents such as metal hydroxides sludge, natural materials, rock minerals, wood wastes, agricultural wastes or industrial to utilize as adsorbents [5]. Many agricultural waste materials have been extensively investigated [6-14]. Also, industrial wastes and natural substances are used [15-19]. The developing countries are needed to establish industries based on utilizing natural resources in various sectors. Doum palm (Hyphaenethebaica) is common in Upper Egypt, originally native to the Nile valley, bearing an edible fruit which has pharmacologic properties [20]. Extracts of Doum are used in the treatment of some diseases [21-23]. However, no researches have been carried on the ability of the DF to be a natural adsorbent to remove dyes from wastewater.

CV is a well-known triaryl methane cationic dye with molecular formula and molecular weight $C_{25}N_3H_{30}Cl$ and 407.979 gm/mole, respectively. It is used in various purposes in the industrial and medical fields [24]. In this research it is used as an adsorbate, a model molecule or as a representative for organic pollutants.

The main objectives of this study are to determine the effectiveness and feasibility of EDF in the removal of CV dye from aqueous solutions.

2. EXPERIMENTAL

2.1. Preparation of adsorbate

CV dye supplied by Aldrich was used as an adsorbate to determine the adsorption potential of EDF. The dye was used as such without any further purification. A stock solution of CV dye solution was prepared (1000 mg/L) by dissolving the 0.1 gm of dye powder in double distilled water then diluted with double distilled water to obtain desired dye concentration.

2.2. Preparation of adsorbent

DF was collected from a farm in Upper Egypt, Fig. 1a. It is washed several times with distilled water to remove any environmental contaminations and dried in an oven at 60°C overnight after cutting it into small parts to remove the seed, Fig.1b. To obtain powder, a ball milling method was used where the small pieces of DF were milled by a high energy ball miller with a speed 170 rpm for 10 h. 21 porcelain balls were used; 10 of them have 1.7 cm diameter and 9.9 g weight, the other 11 balls are 0.8 cm in diameter and 1.54 g weight. The DF was grounded and screened through a set of sieves to obtain particles of size 10-80 μm then kept dry in a closed container until required. No chemical or physical treatments were performed prior to adsorption experiments, see Fig. 1c.

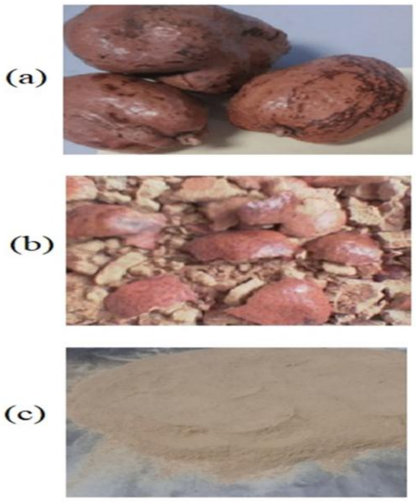

Fig. 1. a- DF b- DF after cutting to remove the seed c- DF powder.

2.3. Adsorbents characterization

The Fourier transform infrared (FT-IR) spectrum was recorded on a Vertex 70 FT-IR instrument (Bruker Company). The sample was thoroughly mixed with KBr as a matrix that grounded and pressed with a special press to give a disk of standard diameter. The formed disk was examined in between 4000 and 400 cm^{-1}.

X-ray diffraction (XRD) experiments were conducted on a PAN alytical (Empyrean) X-ray diffraction using Cu K_α radiation (wave length 0.154 cm^{-1}) at an accelerating voltage 40 KV, current of 35 mA, scan angle range 0f 20°-70° and scan step 0:02°.

The surface morphology of DF before and after adsorption of CV molecules from aqueous solution was analyzed by Scanning Electron Microscopy (SEM) Model Quanta 250 FEG (Field Emission Gun) attached with Energy Dispersive X-ray (EDX) unit analyses, with accelerating voltage 30 KV, magnification 14x up to 1000000 and resolution for Gun.1n), (FEI company, Netherlands), the same using sample in the SEM analysis is used in the qualitative analysis of DF composite by energy dispersive spectroscopy (EDS) in the same microscope, operating at an accelerating voltage of 15 kV.

The physical properties of sorbents were determined by nitrogen adsorption at 77 K using surface area and porosity analyzer Micromeritics-TriStar II- USA. N_2 adsorption isotherms were measured at a relative pressure range 0.0001-0.99. Then, the adsorption data was employed to determine surface area using Brunauer-Emmett-Teller equation and pore size distribution (including average pore diameter and pore volume) using Barrett- Johner- Halenda equation.

2.4. Batch Adsorption Experiments

A batch adsorption method was used in order to determine the kinetics pattern and the needed time to reach equilibrium state, samples of 30 mg of DF were transported into glass bottles containing 20 mL of 20 mg/L CV solution. Then, using a temperature- controlled shaker, the bottles were placed for a sufficient period to achieve equilibrium at 25ºC ± 0.1 and a constant speed. The samples were taken from the shaker at predetermined time intervals. Then the adsorbents were separated from the sample using centrifugation at 200 rpm for 5 minutes. Similar procedure was followed to find the effect of various important parameters as effect of pH, the amount of DF, agitation speed, temperature and the contact time between CV and DF. The absorbance of the supernatant solution was estimated spectrophotometrically at λ_{max} of 590 nm to determine the residual dye concentration, measured at any time, t. All adsorption experimental tests were made twice.

2.5. Data analysis

The following equations are used in calculations [25]:

$$R\% = \frac{C_o - C_t}{C_o} \times 100 \qquad (1)$$

$$q_t = \frac{(C_o - C_t)\,v}{m} \qquad (2)$$

$$q_e = \frac{(C_o - C_e)\,v}{m} \qquad (3)$$

Where R%, is the percentage removal, q_t and q_e are the amount of adsorbed CV on DF at time t and equilibrium, respectively. C_o, C_t and C_e are the concentrations of CV in the solution (mg/L) at initial time (t = 0), time (t) and equilibrium, respectively. V is the volume of solution (L) and m indicates the mass of adsorbent (g). In this work, our calculations of the considered kinetic and isotherm models were performed using Origin Software Version 9.0 (Microcal Software, Inc.)**.**

3. RESULTS AND DISCUSSION

3.1. Characterization

From FTIR spectra of DF, Fig. 2a, the broad band in the range 3000-3500 Cm^{-1} proves presence of OH^- of water molecules absorbed into a cellulose fiber structure of DF. The bands in the range of 1000-1300 Cm^{-1} can be attributed to the C-OH stretching and OH^- bending vibrations which suggest the existence of the hydroxyl group with large amount [26].The peak observed at 1634 cm^{-1} is the C=C stretch of DF. The peak located at 1426 cm^{-1} could be attributed to carbonyl groups. The bands at 1118 and 1034 cm^{-1} correspond to the Si–O and Si–O–Si vibrations, respectively [27]. By comparing FTIR spectra of DF after adsorption of CV dye, it is clear that the intensity of the bands decrease after adsorption which confirms the adsorption of dye with DF. The diffractogram of DF before adsorption of CV, Fig. 2b, appears sharp and most intense peaks that means increasing of particle size and purity of DF [28]. The morphology of DF surface before adsorption includes images at 1500×, Fig. 3a and 5000×, Fig. 3b magnification. These images show a considerable number of heterogeneous pores and presence of particles in different sizes and sharp edges that promote adhesion of CV molecules to be strongly adsorbed on cavities and pores of DF surface by means of physisorption. EDS spectra for DF, Fig.3c, confirms the presence of carbon, oxygen, silicon, chloride and potassium elements, which are characteristic of DF. It can be observed that carbon content was found more.

The Langmuir surface area was deduced from the analysis of the isotherms in relative pressure ranging from 0.00-1.0. It is found to be 0.051 m^2/g, the BET surface area is 0.168 m^2/g, the total pore volume (V_{total}) of the DF was 0.000246 cm^3/g and the average particle size 357,157.033 A°.

3.2. Adsorption studies

3.2.1. Influence of pH on the adsorption

For dye adsorption, acidity is very important parameter. Both the adsorbent and adsorbate may have functional groups that can be protonated or deprotonated to produce different surface charges in solutions at different pH, resulting in electrostatic attraction or repulsion between the charged adsorbates and adsorbents [29]. To study the effects of pH on the adsorption capacity of DF to CV, experiments were performed using different initial solution pH values, changing from 2 to 12, by the addition of 0.1M HCl or 0.1M NaOH at a fixed initial CV concentration of 20 mg/L. Each solution was treated with 30 mg of the adsorbent and kept at 25°C for one hour as a contact time and at agitation speed of 50 rpm. The residual CV dye concentration was measured. The adsorbed amount of CV was

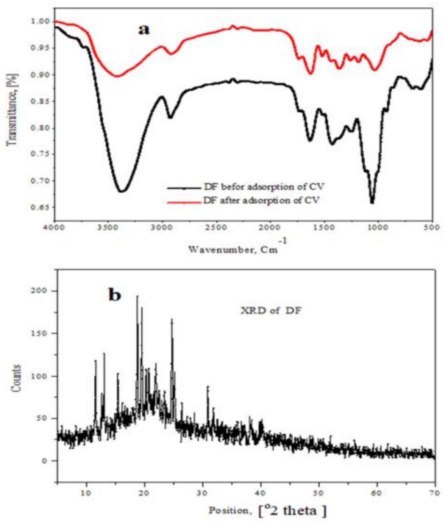

Fig. 2. a-FTIR spectrum of DF b- XRD of DF before adsorption of CV.

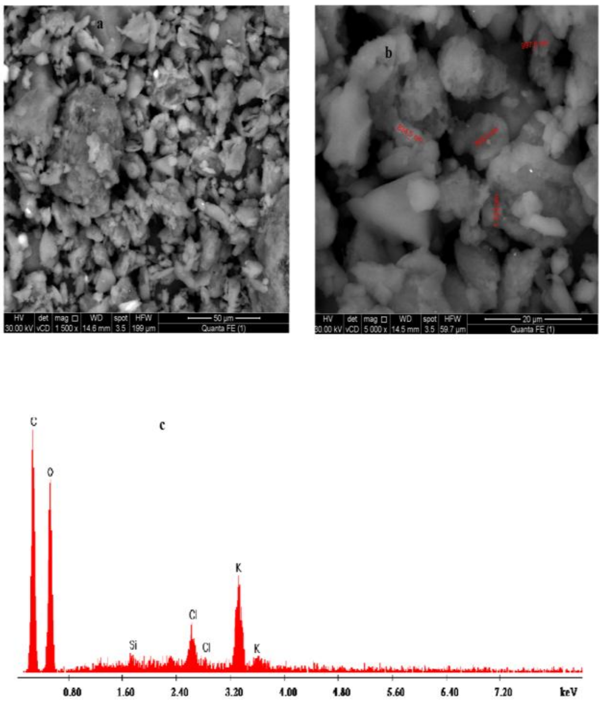

Fig. 3. **a-**SEM before adsorption of CV with1500× magnification **b-**SEM before adsorption of CV with 5000× magnification **c-** EDS spectra for DF.

plotted against the values of pH. It is founded that the amount of sorbed CV% increased as the pH value increased from 2 up to 7 and reached to maximum at pH = 7 followed by decreasing in the amount of q_t with increasing pH, Fig. 4a. Since CV dye molecule has different charged states depending on the acidity of the solution; at lower values pH (of range 1-2), the dye with two of the nitrogen atoms are positively charged. So, lower adsorption was expected due to the competition between excess H^+ ions with the two cation groups on the CV dye for adsorption sites causing little interaction between the CV molecules and DF. With increasing the pH value (up to 7), extra protons of CV molecule are lost to the solution leaving only one of the nitrogen atoms positive charges and more OH^- ions will accumulate on the adsorbent surface [30]. Meaning that, the electrostatic repulsion between the positively charged dye and the surface of the adsorbent is lowered causing more adsorption of CV molecules on the surface of adsorbent. In alkaline solution, value of the adsorbed amount of CV decreases where the excess OH^- ions of the solution may attack the electrophilic central carbon of the CV dye producing triphenyl methanol or carbinol form that lowering the chance CV molecules to adsorbed on the DF surface. The pH of sample of 20 ml of 20 mg/L CV solution after addition of 0.03 g of was 6.03 so, the other factories were studied at this value to avoid any addition of NaOH especially the increasing in the removal percentage from pH = 6.03 to pH = 6.03 is lower than 1%.

3.2.2. Contact time and initial concentration effects of on adsorption process

In the treatment of wastewater by sorption, the contact time between the sorbent with the organic pollutant is significantly more important. The highly efficiency of the sorbent is recognized when it's able to remove pollutants and reach the equilibrium in a short time [31]. Effects of contact time and initial concentration of CV on the sorption process were examined with 20 mL of CV concentrations of 20, 40, 60, 80 and100 mg/L at different times, over the range 0-120 min whereas the other remaining parameters were kept constants as; pH = 6.03, dosage of DF = 30 mg, and agitation speed of 50 rpm at 25ºC, Fig. 4b. From Fig. 4b, values of the adsorbed amount of CV found to increase in the initial stage of contact time from zero to 60 min followed by weakly increases that seemed to be a constant up to120 min. This behavior can be explained in the light of the following; in initial stage the unoccupied sites on DF surface are available by large numbers that allows adsorption of CV molecules fastly and the rate of diffusion of CV into the interior of the DF increases until all sites on the DF surface become occupied. This time is termed as the equilibrium time and the adsorbed amount of CV at this time refers to the maximum sorption capacity of DF under these operating conditions. After the equilibrium time, the rate of diffusion of CV into the interior of the DF becomes slower and/or constant in the later stage where the competition for the available active sites intensifies.

With respected to the effect of CV concentration, the amount of adsorbed CV dye increased with increasing the concentration of the dye that means dependence of the adsorption process on the initial concentration of CV. This may be attributed to highly driving force to overcome the resistance for mass transfer at a high initial dye concentration [32].

3.2.3. Effect of adsorbent dose

In order to assess the effect of adsorbent amount on CV removal, different masses on a wide range of 30- 100 mg of DF to 20 mL CV solution of concentration 20 mg/L was carried out where all other operating parameters were kept constant at pH = 6.03, contact time for one hour with agitation speed of 50 rpm and T = 25ºC. The results are depicted in Fig. 4c. It is obvious from Fig. 4c that the removal of CV decreases. This decrease is likely occurred due to the fixed volume of the used dye may lead to unsaturated adsorption sites during the adsorption process as the adsorbent mass increased [33]. In addition, the total surface area of the adsorbent may be reduced as a result of aggregation of the adsorbent particles as its mass increased that causing increase in the length of the diffusional path. Hence, the optimum dose from DF was found to be 30 mg/20 mL of CV.

3.2.4. Effect of agitation speed

This effect has an important role in the batch adsorption method due to its ability to affecting the distribution of the dye in the bulk solution in addition to the external boundary film [34]. Evaluation the effect of agitation speed on the adsorption process of CV on DF surface was studied at 25°C with an initial weight of 30 mg of DF in 20 mL of 20 mg/L of CV for one hour and pH = 6.03. It is founded that the adsorbed amount of CV are significantly increases from 8.85 up to 11.95 when the agitation speed increased from 20 to 100 rpm, Fig.4d. The removals of adsorbate molecules from aqueous solution onto solid phase surface follow the following mechanism; they are transported to the external surface of the adsorbent through migration from the bulk solution. Then, these molecules are diffusing the boundary layer of the external surface of adsorbent to adsorb on its pores site followed by diffusion into the interior surface of the adsorbent [35]. Then in adsorption of CV on DF, as the agitation speed increases as the resistance of the boundary layer decreases that forcing the adsorbate molecules strongly towards the external surface of adsorbent causing diffusion of adsorbate into the surface of the adsorbent on a large scale.

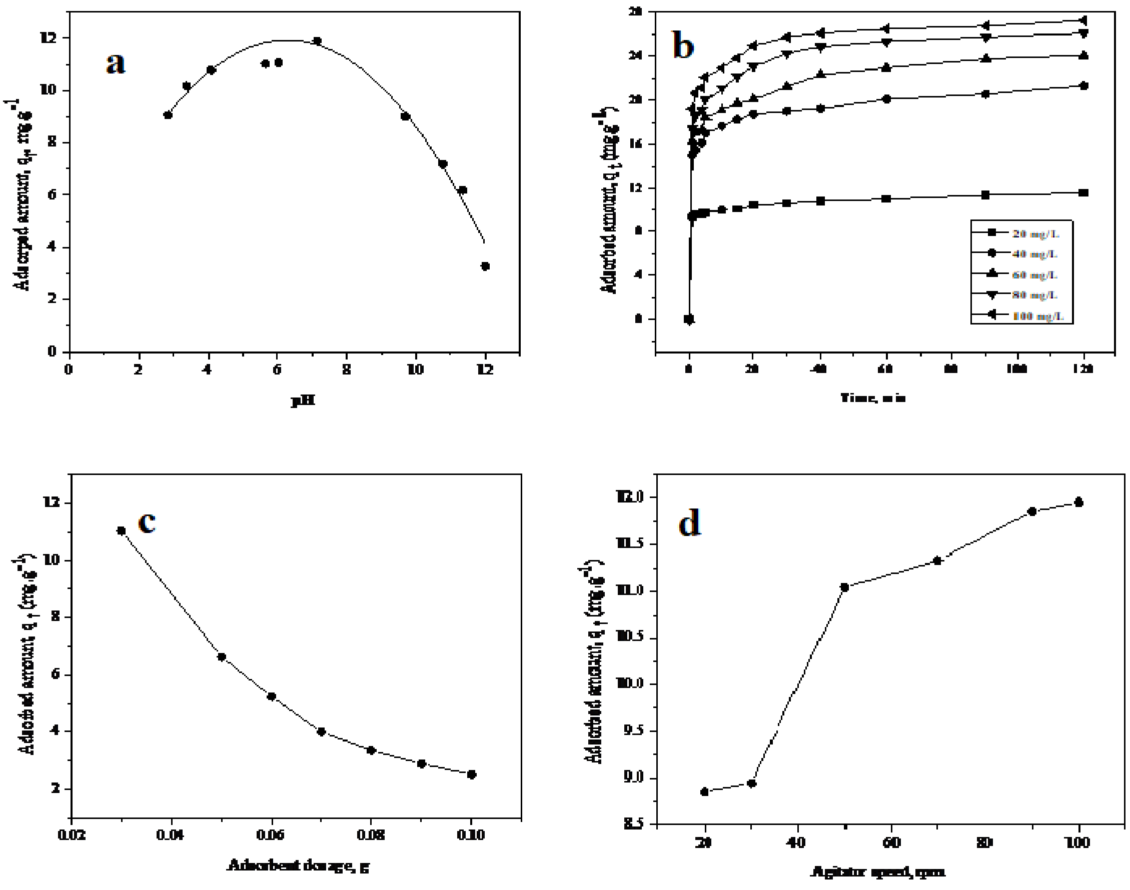

Fig. 4. a- Effect of pH on the adsorption of CV onto DF **b-** Effect of contact time and initial concentration of CV on adsorption of CV onto DF **c-** Effect of adsorbent dosage d- Effect of agitator speed on the removal process.

3.2.5. Effect of temperature and thermodynamic parameters

Temperature is an important parameter in adsorption processes where it can state the nature of adsorption either exothermic or endothermic process [36]. A series of experiments at 25, 30, 35, 40 and 45 °C was investigated to study the effect of temperature on the removal of 20 mg/L of 20 mL of CV dye on 30 mg DF within one hour contact time, pH = 6.03 and agitation speed = 50 rpm. The percentage removal of dye decreased from 82.85 to 58.20٪ when the temperature increased from 25 to 45ºC as shown in Fig. 5a. It is probably because of the weakness of the adsorptive forces between CV molecules and the active sites on the surface of DF that causes escaping of dye molecules from the DF surface to the bulk solution as the temperature increased. Also, this decreasing in the adsorption indicating that the process is exothermic in nature.

The temperature dependence of the adsorption process is associated with changes in several thermodynamic parameters. These parameters are very important because they give information about the spontaneity of the sorption processes. Parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes for the sorption of CV dye onto DF can be calculated using the following equations [37-38].

$$\text{Ln } K_d = -(\Delta G°/R\,T) \qquad (4)$$

$$\Delta G° = \Delta H° - T\Delta S° \qquad (5)$$

$$\text{Ln } K_d = (\Delta S°/R) - (\Delta H°/RT) \qquad (6)$$

Where R is the general gas constant and its value is 8.314 J/mol Kelvin, T is the absolute temperature (Kelvin) and K_d refers to distribution coefficient or adsorption equilibrium constant ($K_d = q_e/C_e$).

Plotting of $\ln K_d$ against 1/T gives a linear relation with $R^2 = 0.96$, Fig. 5b.Values of ΔH°, ΔS° was calculated from the slope and intercept of the plot, respectively. Values of ΔGº are calculated from equation 5 and listed with the other parameters in Table 1. From Table 1 value of ΔHº is negative that indicates liberation of the energy during adsorption process (exothermic nature), value of ΔSº is also negative one that enhancing presence the internal structure of the adsorbent without significant change during the adsorption process. Also, values of ΔGº are negative and lower than 40 KJ/mol, which confirms the physical adsorption, spontaneous nature of this adsorption and reflects the affinity of DF towards CV [39-40].

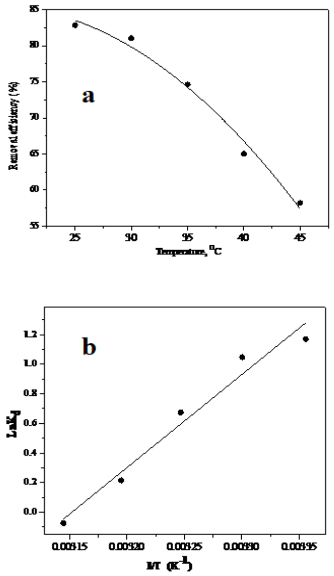

Fig. 5- a. Effect of temperature on adsorption of CV onto DF
b- Vant Hoff of adsorption of CV onto DF.

TABLE 1. Thermodynamic parameters for adsorption of CV onto DF.

Temp. (K)	**log K_d (L/g)**	**ΔH° (kJ/mol)**	**ΔS° (J/mol K)**	**ΔG° (kJ/mol)**
298	0.508	-52.239	-164.65	-2.89
303	0.455			-2.64
308	0.292			-1.72
313	0.093			-0.558
318	-0.032			0.196

3.3. Adsorption equilibrium isotherms

Analysis of data of the equilibrium adsorption by different isotherm models is important to determine the suitable model that can be used for design purposes. In addition, the adsorption isotherm is characterized by certain constants whose values give benefit information about the interaction between adsorbent and adsorbate such as adsorption capacity of the adsorbent and type of adsorption if physisorption or chemisorptions. Three different theoretical models were applied to the obtained experimental data to predict adsorption capabilities of CV on DF.

3.3.1. Langmuir isotherm model

Langmuir determines the maximum adsorption capacity of adsorbent surface to form monolayer. A basic assumption in the Langmuir model is that the adsorbates are adsorbed at a finite number of identical and equivalent sites on the outer surface of the adsorbent forming monolayer sorption with-out interaction between adsorbed molecules (i.e. the surface is homogenous)[41]. The following equation illustrates the linear form of Langmuir isotherm:-

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQ}\left(\frac{1}{C_e}\right) \qquad (7)$$

Where; q_e is the amount adsorbed per unit mass of CV at equilibrium (mg/g), Q is the theoretical monolayer capacity of the adsorbent (mg/g), C_e is the equilibrium concentration (mg/L) and b is the sorption equilibrium constant (called Langmuir constant) related to the energy of adsorption (L/mg). From b value, the equilibrium parameters (R_L) can be calculated. It is a dimensionless constant and considers one of the essential characteristics of the Langmuir model and can be calculated from the following equation [42]:-

$$R_L = \frac{1}{1+bC_0} \qquad (8)$$

Where C_0 is the highest initial concentration of CV. It is known that, the type of isotherm indicates according the value of R_L as follows; irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), and/or unfavorable ($R_L > 1$).

From plotting of $1/q_e$ against $1/C_e$, Fig. 6a, a straight line was appeared with correlation coefficient = 0.954. The maximum value of Q and b value were determined from the intercept and slope of Fig. 6a, respectively and collected in Table 2. The calculated R_L value is less than 1 and more than zero value indicating that the sorption isotherms is favorable.

3.3.2. Freundlich isotherm

The Freundlich isotherm is commonly used to describe the intensity of adsorption of the adsorbent for the adsorbate (multilayer adsorption). This model assumes that as the adsorbate concentration increases, its concentration on the surface of adsorbent will also increase. The logarithmic form of the Freundlich equation can be represented as the following [43]:-

$$\log q_e = \log K + \frac{1}{n}\log C_e \qquad (9)$$

Where K is an indicator constant for adsorption capacity of the adsorbent (mg/g) and 1/n is a function of the strength of adsorption in the adsorption process which depends on the nature of the both adsorbate and adsorbent [44]. It is reported that, value of n, between 1 and 10 (i.e. 1/n < 1, become closer to zero) refers to the surface is more heterogeneous than homogeneous and the adsorption is favorable [45]. From plots of log q_e against log C_e, a straight line with correlation coefficient 0.915 that indicates fitting of the isotherm to the experimental data, Fig.6 b. Value of K was calculated from the intercept of the straight line, Fig.6 b, as 8.52 then DF is thought to have a reasonable ability to sorbs CV dye. Value of n was determined from the slope as 2.64 which refers to the heterogeneity of the surface.

3.3.3. Dubinin- Radushkevich (D-R) isotherm

Both the characteristic porosity of the adsorbent and the heterogeneity of the surface energies from the adsorption can be recognized from applying the D-R isotherm to the data [46]. The D-R equation is more general than the Langmuir model because it doesn't assume a homogeneous surface, a constant sorption potential, or an absence of sterichindrance between adsorbed and incoming particles [47].The linear form of D-R isotherm is presented as the following equation:-

$$\ln q_e = \ln q_m - K_{D-R}\varepsilon^2 \qquad (10)$$

Where q_m is the theoretical isotherm saturation capacity (mg/g), K_{D-R} is the D-R isotherm constant and **ε** is another constant for D-R isotherm [48] which is described as;

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad (11)$$

Where T is the solution temperature (K), R is the gas constant (8.314 J/mol K) and C_e is the concentration of adsorbate at equilibrium (mg/L). Values of K_{D-R} and q_m represent the slope and intercept of the plot of $\mathrm{In} q_e$ against ε^2. From the value of K_{D-R}, means free energy, E, of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in solution (kJ/mol) can be calculated as follows [49];

$$E = \frac{1}{(2\,K_{D-R})^{1/2}} \qquad (12)$$

It is stated that, the adsorption process can be considered a physical adsorption when the value of E is below 8 (kJ/mg) and chemical adsorption when value of E is located in the range of 8 - 16 (kJ/mg). From Fig. 6 c, the value of R^2 is 0.901, reveals fitting the experimental data with the D-R isotherm model. The calculated value of E is 0.637 (kJ/mol) that gives indication on physisorption type between CV and DF.

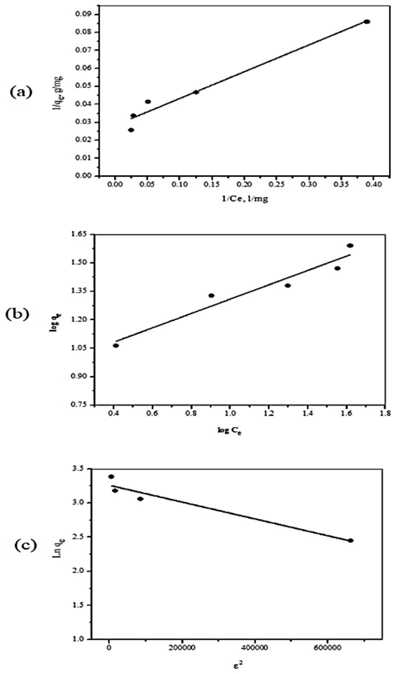

Fig. 6. a- Langmuir isotherm **b-** Freundlich isotherm **c-** Dubinin-Radushkevich.

Table 2. The parameters of Langmuir, Freundlich and Dubinin-Radushkevich isotherms at 298 K.

Isotherms	***R^2***	***Parameters***	***Values***
		(constant)	
Langmuir	**0.954**	**b (L/mg)**	**0.18**
		Q (mg/g)	**35.26**
		R_L (Unitless)	**0.050**
Freundlich	**0.915**	**K (mg/g)**	**8.52**
		n	**2.64**
Dubinin-Radushkevich	**0.904**	**q_m (mg/g)**	**25.96**
		E (kJ/mol)	**0.637**

From Table 2, values of correlation coefficient indicates fitting Langmuir isotherm with the experimental data with highly degree than Freundlich and D-R models.

3.4. Adsorption kinetic modeling

The importantly of the kinetic study is stating the rate and mechanism of the adsorption process. The rate of the adsorption is considered a good factor beside adsorption capacity for testing the availability of material to be used as an adsorbent; where the used adsorbent should have a fast adsorption rate and a large adsorption capacity [37].The adsorption mechanism was investigated to state the rate-limiting step to optimize the design of adsorbents and adsorption conditions. The rate-limiting step can be one or more of the following steps; 1- transportation of the dye from the bulk solution to the exterior surface of sorbent (called film or surface diffusion) 2- diffusion of dye molecules into the interior of sorbent particles (called intraparticle diffusion) 3- interior adsorption of dye onto sites of the sorbent. This third step is very rapid then; the adsorption process will be controlled by one of the two other steps or mixing of them. The obtained kinetic data for adsorption of CV onto DF was analyzed using different kinetic models as Lagergren's pseudo first-order kinetic model, pseudo second-order kinetic model and intra-particle diffusion model.

3.4.1. Pseudo-first order kinetic model

This model is presented by the Lagergren equation, which describe the rate of adsorption according the adsorption capacity. The integrated form of this equation can be represented as:

$$\mathrm{Log}(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \qquad (13)$$

Where q_e is the amount adsorbed at equilibrium (mg/g), q_t is the amount adsorbed at time t(mg/g) and k_1 is the rate constant of pseudo first- order sorption (g/mg min). Values of k_1 and q_e were calculated from slopes and intercepts of plots of log

(q_e- q_t) with time, respectively, Fig.7a and listed in Table 3. From Table 3, the adsorption of CV onto DF doesn't follow the pseudo first-order kinetic model although the correlation coefficients values are high considerable (in the range from 0.94 to 0.99), the calculated q_e values don't close to the experimental ones and lower.

3.4.2. Pseudo-second-order kinetic model

Using pseudo-second-order kinetic rate equation, the rate of sorption of CV onto DF was analyzed. The linear pseudo-second-order equation in the integrated form may be represented as the following;

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e{}^2} + \frac{1}{q_e} t \qquad (14)$$

Where k_2 is the rate constant of pseudo second-order sorption (gm/g min). From plots of t/q_t against t of Eq.14, straight lines should be obtained or (would be noticed) if the pseudo-second-order kinetics is applicable. From the slope and intercept of these plots, values of q_e and k_2 can be calculated, respectively. Plots of t/q_t versus t, Fig.7b, gives straight lines. Values of k_2 and q_e, Table 3. Values of the calculated adsorbed amount of CV (q_e calc.) are found to be closer to the experimental one (q_e exp.) with very higher value of correlation coefficients (≥ 0.998) for pseudo-second-order kinetic model. Then, the adsorption of CV onto DF is more favorably by the pseudo-second order model and this reinforcing the applicability of this model.

3.4.3. The intra-particle diffusion model

This model gives a relationship between the amounts of dye adsorbed at time t, q_t (mg/g) with the square root of the time $t^{\frac{1}{2}}$ rather than with the contact time t. This model neglected the film diffusion (or boundary layer diffusion) and takes in account the intraparticle diffusion step as the only rate controlling step. The linear form equation according Weber and Morrisis [50]:-

$$q_t \;=\; k_{id}\, t^{\frac{1}{2}} + C_i \qquad (15)$$

Where k_{id} (mg/g $min^{-1/2}$) is the rate constant for intra-particle diffusion at different initial concentrations, t is the time (min) and C_i (mg/g) is constant gives information about the thickness of the boundary layer: large the value of C_i suggests high boundary layer effect (i.e. the resistance to the external mass transfer will increase). From plot of q_t versus $t^{\frac{1}{2}}$ if only a straight line passing by the origin obtained this means that the intra-particle diffusion is the only mechanism controlling the sorption process and if multi-linear plots are obtained then, more than one step take place in the adsorption process [51-53]. The experimental data at various concentrations of initial CV were applied to the Weber and Morris model when other operating parameters are fixed as elucidate in Fig. 11c from which two parameters have been determined from the slopes and intercepts of Fig. 7c; k_{id} and C_i respectively, Table 3. From Fig. 7c, the lines are linear but don't pass through the origin that means the adsorption of CV onto DF isn't controlled by intraparticle diffusion only. Besides that, values of C_i are higher than zero and increases with increasing initial CV concentration that reflects increasing the resistance to dye molecules of the layer of liquid surrounding the particle of DF. Then we can be concluded that the adsorption process is a two-step mechanism involving film or surface diffusion and intraparticle diffusion.

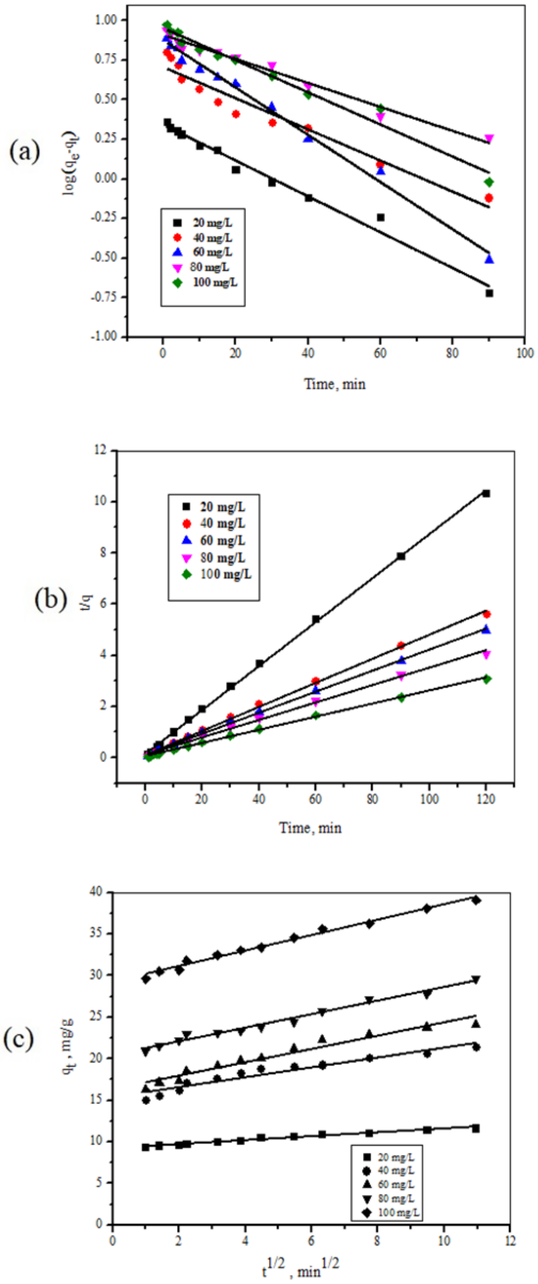

Fig. 7. a-Pseudo-first order model **b-** Pseudo-second order model **c-** The intra-particle diffusion model.

Table 4. Maximum adsorption capacity of various low-cost adsorbents with CV.

Conc. (mg/L)	**Pseudo-first-order**			**Pseudo-second-order**				**Intraparticle diffusion**		
	R^2	**q_e, calc. (mg/g)**	**k_1 (min^{-1})**	**K (g/mg min)**	**q_e, calc. (mg/g)**	**q_e, exp. (mg/g)**	**R^2**	**k_{id} (mg/g $min^{1/2}$)**	**R^2**	**C_i (mg/g)**
20	0.982	2.18	0.025	0.055	11.61	11.61	0.999	0.234	0.975	9.23
40	0.944	5.04	0.022	0.023	21.24	21.33	0.998	0.594	0.915	15.35
60	0.991	7.48	0.034	0.016	24.33	24.07	0.998	0.801	0.945	16.32
80	0.975	8.05	0.017	0.011	29.28	29.61	0.995	0.817	0.981	20.42
100	0.972	8.93	0.023	0.012	39.06	39.05	0.998	0.929	0.985	29.26

3.5. Comparison of capacities of various low-cost adsorbents for CV

The maximum adsorption capacities of different types of low-cost adsorbents are used for removal of CV available in the literature were reported in Table 4 to make comparison with the maximum sorption capacity of DF used in this work for CV. It shows that the performance of DF to remove CV from an aqueous solution is an excellent process.

Table 4. maximum adsorption capacity of various low-cost adsorbents with CV.

Adsorbents	**Q_{max} (mg/g)**	**References**
Acacia nilotica leaves (RVM)	**33**	**[54]**
Citrulluslanatus rind	**11.9**	**[55]**
Bottom ash	**12.1**	**[56]**
zeolites synthesized from fly ash (ZFA)	**19.6**	**[57]**
zeolites synthesized from bottom Ash (ZBA)	**17.6**	**[57]**
Leaf biomass of Calotropisprocera	**4.14**	**[58]**
Agricultural waste cocoa shell	**43.5**	**[59]**
Bagasse fly ash	**26.32**	**[60]**
Raw kaolin	**44.87**	**[61]**
Acacia nilotica leaves (RVM)	**33.0**	**[62]**
Jute fibre carbon	**27.99**	**[63]**
CAL BC	**40.49**	**[24]**
DF	**35.26**	**This study**

3. 6. Conclusions

In this study, employing of DF as available, environmentally safe and low-cost sorbent for the removal of CV from an aqueous solution improved that DF is an effective sorbent. The adsorption process reached to the equilibrium state after 60 min. It is increased as the dosage of CV increased that enhances the interactions between CV and DF. In addition, it is found to be effective in the acidic medium (pH<7), at room temperature (25°C), increased when the agitation speed increased and the optimum dose of DF was 30 mg per liter of CV. The adsorption process was spontaneous and exothermic. Also, the adsorption follows Langmuir with Q_{max} of 35.26 mg/g at 25°C and Freundlich isotherms (with lower degree than Langmuir) compared with D-R isotherm. The Lagergren first-order model, the pseudo-second order model and the intraparticle diffusion model were used to analyze the kinetics data. It is best fitted to the pseudo-second order model. Analysis of mechanism reveals that the adsorption process is a two-step mechanism involving surface (or film) diffusion with intraparticle diffusion.

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