



## Insights into removal of Eriochrome Black-T dye from aqueous solution by Doum fruit as a natural dsorbent

Ahmed A. Abdel- Khalek<sup>1</sup>, Mahmoud M. Abdel- Hafeez<sup>2</sup>, Reham A. Mohamed<sup>1</sup>  
and Engy H. Gabrail<sup>3</sup>

<sup>1</sup>Chemistry Department, Faculty of Science, Beni-Suef University, Beni-Suef City,

<sup>2</sup>Forensic Medicine Authority, Ministry of Justice, Cairo, Egypt,

<sup>3</sup>General Director Of Environmental Projects Development, Beni-Suef University, Beni-Suef City, Egypt.



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### Abstract

Natural Doum fruit (DF) was prepared for studying its adsorption behavior as an effective natural adsorbent for removing Eriochrome black-T (EBT) dye. In this study the adsorption was performed with different variables like initial concentration of the dye, contact time, pH, adsorbent dose, temperature, and agitation speed. The prepared DF powder has been characterized before and after adsorption of EBT by many analyses like XRD (X-ray diffraction), SEM (Scanning Electron Microscopy), and FTIR (Fourier Transform Infrared Spectroscopy). Values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated as thermodynamic parameters. Langmuir, Freundlich and Temkin isotherm models are used to analyze the experimental data by using linear regression analysis. The  $Q_{max}$  (maximum sorption capacity) of DF is 24.68 mg/g as calculated from experiments of the adsorption process. pseudo-first order, pseudo-second order and intraparticle diffusion model were used to examine the mechanism of adsorption. The obtained result refers that; DF is an effective adsorbent for removal of EBT dye from aqueous solutions.

Keywords: Eriochrome black-T, low-cost adsorbent, Doum Fruit, batch study

### 1. Introduction

Azo compounds that containing one or more azo bonds ( $-N=N-$ ) or more linking as substitution on aromatic compounds are used on a large scale as organic dyes in the textile industries as organic dyes due to the reactivity of azo bonds [1]. These dyes are more stable and its degradation is difficult even at low concentration. Also, they exhibit a high resistance to water, heat, light, microbial and chemical attack [2]. EBT is one of the essential azo dyes which located more than 50% of manufactured dye in the world. For the last reasons in addition to the toxicity of their breakdown products, it is undesirable to release these compounds into the environment [3-4]. So, there is a continuous development of technologies to remove dyes from waste water efficiently. A lot of physico-chemical processes are developed nowadays involving reverse osmosis, coagulation, membrane separation, ozone oxidation, electrochemical, biological

treatments, adsorption, oxidation, photo catalysis, membrane filtration, etc. [5-7]. Adsorption is another technique different from the last ones due to its easy availability, its cost is lower, high efficiency, its design is simple, biodegradability, easy operation, and the ability to treat dyes in more concentrated forms [5, 8]. Activated carbon is one the famous adsorbent that used on a large scale in the adsorption of dyes is still an expensive material [9-13]. So, using available low-cost materials is more interesting in the research process [14-18]. Doum palm (*Hyphaenethebaica*) is growing in Upper Egypt native to the Nile valley and having an edible fruit which has pharmacologic properties [19]. However, no researches have been carried on the ability of the DF as a natural adsorbent to remove EBT as anionic dye from wastewater.

\*Corresponding author e-mail: [ewiesfawzy@yahoo.com](mailto:ewiesfawzy@yahoo.com); (Ahmed A. Abdel- Khalek).

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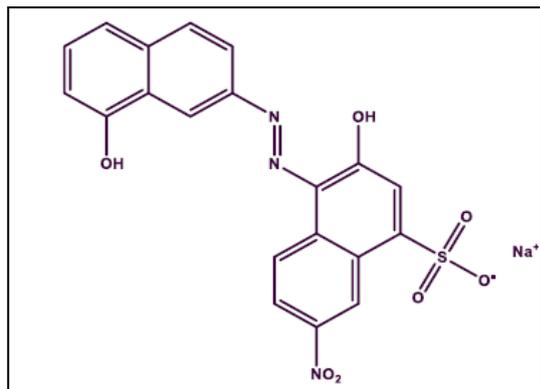
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## 2. Materials and methods

### Materials

Hydrochloric acid and Sodium hydroxide (Merk) are used as received without any further purification. EBT dye was obtained from Sigma-Aldrich; its molecular structure is given in (Fig. 1). EBT dye (Sigma-Aldrich); its molecular structure is given in Fig. 1. EBT dye was prepared in a stock solution of (1000 mg/L) where 1 g of the dye was dissolved in doubly distilled water to obtain the wanted concentration of the dye. Different concentrations of EBT were prepared.



**Fig. 1:** the molecular structure of EBT

### Methodology

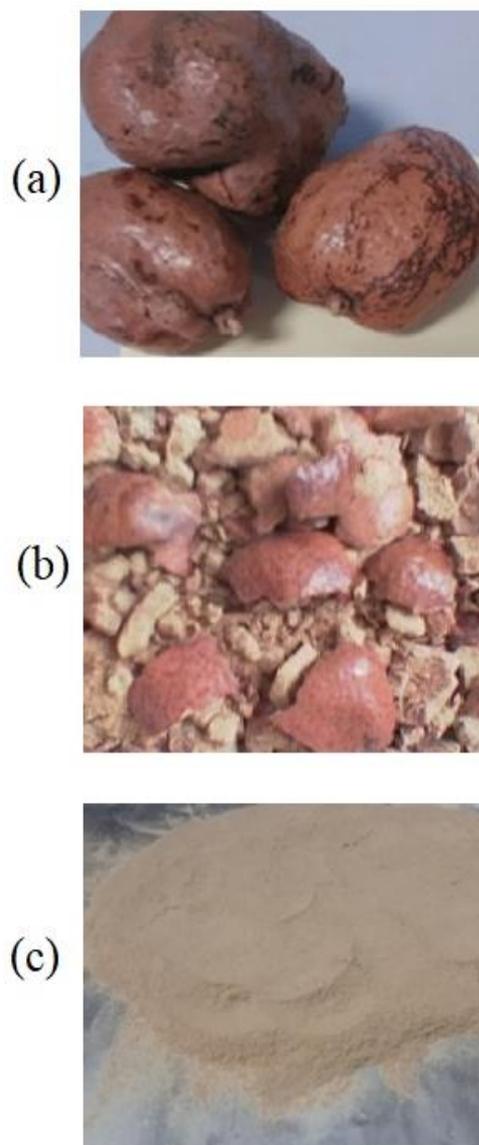
DF is collected from a farm in Upper Egypt, (Fig. 2. a). To remove any environmental contaminations, it was washed several times with distilled water then cutting into small parts to remove its seed, (Fig. 2. b). Its preparation was according our previous work [20]. The detailed preparation process is as follows. By using a ball milling method, the small pieces of DF were milled where a high energy ball miller with a speed 170 r/m for 10 h were used. An oven overnight was used at 60 °C to dry the DF powder, (Fig. 2. c). Then, the powder was grounded to obtaining size of 10-80 μm of the particles, (Fig. 2. c). No physical or chemical treatments were performed before the adsorption processes.

### Instrumentation

The experiments were equilibrated by mixing the solid phases with the aqueous one using shaker (Julabo SW-20C, Germany) supported with a mechanical thermostat controlled within  $\pm 1$  °C and i stirring range (20 -2000) rpm. A UV-vis spectrophotometer (Jenway Model UV-6300, USA) was used to measure adsorption spectra of the solutions. The Jenway pH-meter was used in pH measurements of the reaction mixture. Using a Vertex 70 FT-IR instrument (Bruker Company), the spectrum of Fourier transform infrared (FT-IR) was recorded. A disk of standard diameter was prepared by mixing the sample with KBr as a matrix then grounded and pressed with a special press and examined between 4000 and 400  $\text{cm}^{-1}$ . X-ray

diffraction (XRD) was performed on a PANalytical (Empyrean) using  $\text{CuK}\alpha$  radiation with wave length of 0.154  $\text{nm}$ , range of the scan angle is 20°-70°, voltage of the accelerating is 40 KV, scan step is 0:02° and the used current was 35 mA.

By using SEM (Model Quanta 250, Field Emission Gun), the morphology of the surface of DF before and after adsorption of EBT molecules from aqueous solution was analyzed. The microscope is attached with Energy Dispersive X-ray (EDX) unit analyses, the voltage of the accelerating is 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 where the voltage of acceleration was 15 kV.



**Fig. 2. a.** shape of DF, **Fig. b.** DF after cutting to remove the seed, and **Fig. c.** DF powder.

### Batch Adsorption Experiments

A batch adsorption method was used in order to determine the kinetics pattern and the needed time to reach an equilibrium state, samples of 0.03 g of DF were transported into glass bottles that contain 20 ml of 20 mg/L EBT solution. Then, using a temperature- controlled shaker, the bottles were placed for a sufficient period to achieve equilibrium at  $25^{\circ}\text{C} \pm 0.1$  and constant speed. The samples were taken from the shaker at predetermined time intervals. Then the adsorbents were separated from the sample using centrifugation at 50 rpm for 10 minutes. A similar procedure was followed to find the effect of various important parameters like the effect of pH, the amount of DF, agitation speed, temperature and the contact time between EBT and DF. The absorbance of the supernatant solution was estimated spectrophotometrically at  $\lambda_{\text{max}}$  of 520 nm to determine the residual dye concentration, measured at any time, t. All tests of the adsorption experimental were repeated another time.

### Data analysis.

The following equations are used [21]: -

$$q_t = \frac{(C_o - C_t) v}{m} \quad (1)$$

$$q_e = \frac{(C_o - C_e) v}{m} \quad (2)$$

$$R \% = \frac{C_o - C_t}{C_o} \times 100 \quad (3)$$

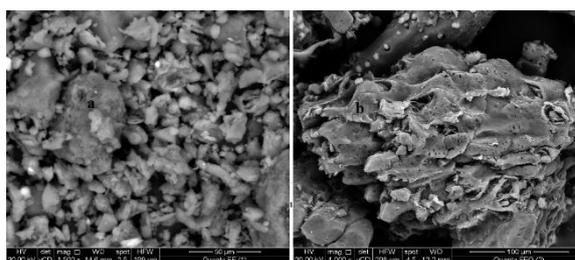
Where  $q_t$ ,  $q_e$  are the quantity adsorbed of EBT dye by the DF at time t and equilibrium, respectively and R is the removal efficiency.  $C_o$ ,  $C_t$  and  $C_e$  are the concentrations of EBT in the solution (mg/L) at initial time ( $t = 0$ ), time (t) and equilibrium, respectively. V (L) is the solution volume and m (gm) is the adsorbent mass. In this work, our calculations of the considered kinetic and isotherm models were performed using version 9.0 of Origin Software program.

## 3. Results and discussion

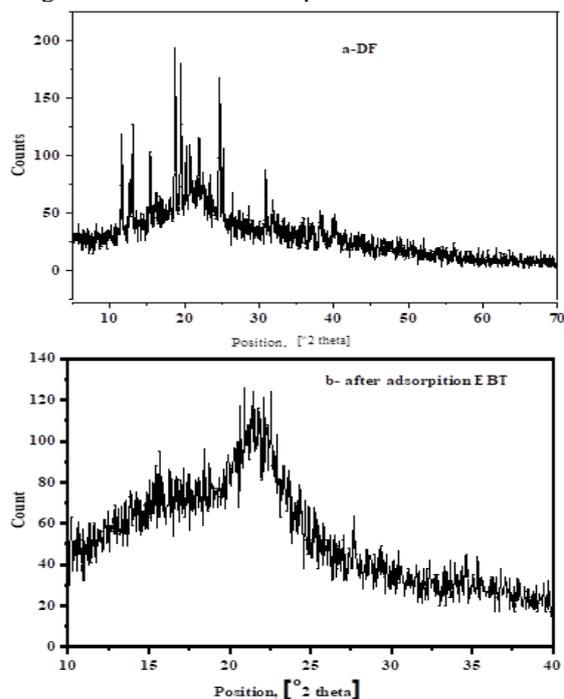
### Characterization of DF before and after adsorption of EBT dye.

The morphology of DF surface before adsorption includes image at  $1500\times$ , Fig. 3a magnification that reveals the surface texture and porosity of DF particles. The porosity of DF adsorbent can be seen easily in the micrograph in addition to presence a few porous with well -developed cavity which helping in the accommodation process of the dye molecules after migration from the liquid phase to a solid surface. From the SEM images of DF after adsorption EBT at  $1000\times$  magnification, (Fig. 3b), show an irregular and dispersed mass after occupation the available pores on DF surface with the dye molecules that indicating the adsorption process is occurred. An EDS spectrum 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 X-ray diffractogram of DF, (Fig. 4. a) shows the morphology future and characteristic of the DF surface which appears sharp peaks over arrange of  $2\theta$  of  $15\text{-}25^{\circ}$  that indicate the amorphous nature of the DF. (Fig. 4. b), represent diffraction peaks after EBT uptake [22]. It could be observed that the number of the peaks become lower and its intensity become slightly weaker which may be due to surface adsorption of EBT onto DF particles [23]. There are noticed change in the position of peaks was noted which suggests that phase transformation was observed after EBT dye adsorption [24].



**Fig. 3:** a-SEM before adsorption of EBT with  $1500\times$  magnification. b. after adsorption of EBT with  $1000\times$  magnification and c. EDS spectra for DF.



**Fig. 4.** a. XRD of DF before adsorption of EBT and b. XRD of DF after Adsorption of EBT.

The FT- IR spectra was done to analyze the composition change of adsorbent by the adsorption, a comparison between the FT-IR spectrum of DF before and after adsorption of EBT was done, (Fig. 5. a, b). From (Fig. 5. a) appears the spectra exhibited several peaks representing in the DF sample of different chemical groups which possibly help in bending of the EBT molecules. The appearance of peak in natural DF powder at  $1630\text{ Cm}^{-1}$  indicates to presence of C=C bond of alkenes, *i.e.* the characteristics of cellulose [25]. While presence of abroad peak at  $3406\text{ Cm}^{-1}$  is corresponding to the characteristic O-H groups [26]. The narrow peaks at  $2918.23\text{ cm}^{-1}$  correspond to the stretching of C- H group and  $1367\text{ Cm}^{-1}$  indicates presence of  $\text{CH}_3$  group [27]. At  $1259.65\text{ cm}^{-1}$  a small peak was appeared that related to C-O group [28], the peak of  $1546\text{ cm}^{-1}$  corresponded to N-O (nitro) and at  $1735.77\text{ Cm}^{-1}$  the peak corresponded to C=O stretching vibration to aldehydes and ketones [29]. Bands in (Fig. 5. b) were found shifted and intensity of peaks changed after adsorption of EBT dye on DF as compared to DF alone which refers to possibility of interaction of the active sites of DF for uptaking EBT dye ions.

### Adsorption studies

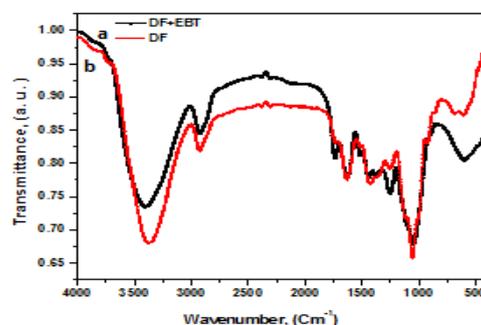
#### Influence of pH of the solution

The experiments were performed by using different initial solution pH values, varying from 2 to 12, by adding 0.1M HCl or 0.1M NaOH at a fixed initial EBT concentration of 20 mg/L, 30 mg of DF at  $25^\circ\text{C}$ , controlled shaker at speed of 50 rpm for 60 min and centrifuged for 15 min. The obtained results in Fig. 6a show a noticeable effect for pH variation on the adsorption process of EBT dye. Over pH range 2 -5.3, there is an increasing in adsorption process where in this range there is a strong electrostatic attraction between oppositely charge;  $\text{H}^+$  ion and sulphonate group ( $\text{SO}_3^-$ ) of EBT that gives the anionic nature of the dye and consequence ion lead to favor adsorption of EBT on to the DF surface [30]. After that as pH of the solution increased, the  $q_t$  began to decrease and a noticeable decreasing in  $q_t$  values up to pH = 12. This behavior can illustrate as follow; over pH 6, there is repulsion forces between  $\text{SO}_3^-$  and  $\text{OH}^-$  and competeion between these anions which decreases adsorption of dye. From the above illustration, it is evident that pH = 5.3 is beneficial for adsorption of EBT.

#### Influence of contact time and initial dye concentration

Effects of the contact time were studied from the begging of the adsorption process up to two hours at pH = 5.3, dosage of DF = 30 mg, and agitation speed = 50 rpm at  $25^\circ\text{C}$ . The obtained data are given in (Fig. 6. b), from which a sharp increase in the first 30 minutes of the adsorption process and the equilibrium

point is reached after 40 minutes. To ensure complete equilibrium time the test was completed up to 120 min. From 0 to 40 min, large numbers of unoccupied sites are present on the DF surface help EBT molecules to occupy most of these active sites and adsorb quickly on it and the adsorption process become faster until saturation of most active adsorption sites. After 40 min, a competition process between EBT dye molecules occurred to adsorbed on the sites of DF. Then, the adsorption processes reached to the equilibrium state at which the rate of diffusion of EBT from bulk of solution to DF surface becomes slower and/or constant [31]. The adsorbed amount of the EBT dye on the DF surface can be affected by the initial dye concentration directly. Also, (Fig. 6. b) demonstrates the initial concentration effects of EBT on its adsorption onto DF using different concentrations of EBT. Initial concentration has its own importance in adsorption process and variation in its concentration shows significant effect. At equilibrium time, the uptake of EBT was increased from 11.33 mg/g to 26.11 mg/g when the initial concentration of EBT increased from 20 to 100 mg/L, respectively. This increasing in the uptake amount of EBT may be due to migration of most EBT molecules towards the external surface of DF from bulk solution that provided an additional driving force to overcome the resistance of the mass transfer for EBT between the surface of DF and the solution.



**Fig. 5. a.** FTIR of DF before adsorption of EBT, and **b.** after adsorption of EBT

#### Influence of adsorbent dose

At constant conditions of at pH = 5.3, agitation speed = 50 rpm at  $25^\circ\text{C}$ , effects of DF dose on the adsorption of 20 ml of 20 mg/L of EBT dye was investigated using different dosage of DF over the range 0.01 - 0.1 gm. Fig. 6. c; shows that the percent of removal of EBT was increased from 16.7 to 83.3 %by increasing the dosage of DF from 0.01 - 0.03 gm. This increasing may be attributed to increasing the surface area of adsorbent then more adsorption sites and pores on DF surface are available leading to further increase in dye adsorption. No significant increment was observed in the removal tendency after increasing the dose more

than 0.03 gm where an aggregation for DF particles can expect leading to decreasing of the total surface area of DF. Therefore, the suitable dose of DF is 30 mg which has the highest removal efficiency of 83.3 % and considered the optimum condition for the adsorption process.

#### **Influence of agitation speed**

The effect of agitation speed on the adsorption process of EBT on DF surface was performed by changing the speed of rotation of adsorbate - adsorbent solution over agitation speed range from 10 to 100 rpm while keeping other parameters constant and samples withdrawn at different intervals. Fig. 6. d; appearing significantly increases the percentage of removal of EBT from 25.8 to 83.3 when the agitation speed increased from 10 to 50 rpm. This can attribute to forcing EBT towards DF causing rapidly diffusion for dye molecules into the surface of DF as results for decreases the boundary layer resistance. After increasing the speed of agitation more than 50 rpm, value of R % becomes almost constant.

#### **Influence of temperature and calculation the thermodynamic parameters**

The adsorbed amount of dye on the surface of DF may controlled by the temperature where temperature can be considered an important parameter in adsorption processes [27]. Effects of temperature factor on adsorption of EBT onto DF was carried out at 25, 30, 35, 40 and 45°C for an initial concentration of 20 mg/L, pH = 5.3, speed = 50 rpm and dosage of DF was 0.03 g/20 ml. The relation between the removal efficiency of EBT with different temperatures were illustrated in Fig. 7a. Increasing the temperature has significant effect on adsorption process; the R% value was increased linearly from 83.3 to 98.3 % when the temperature increased from 25 to 45°C that can be illustrate in light of the following; at higher temperature the kinetic energy of EBT molecules become higher and its approach to the DF surface became easier. Also, this behavior revealed the endothermic nature for the adsorption of EBT on DF. This fact was also confirmed from the positive value of enthalpy.

The thermodynamic activation parameters involving  $\Delta H^\circ$  (enthalpy),  $\Delta S^\circ$  (entropy) and  $\Delta G^\circ$  (Gibbs free energy) were calculated to state the thermodynamic nature of the sorption process of EBT onto DF.  $\Delta G^\circ$  was determined from this equation [28];

$$\ln K_d = (\Delta G^\circ / R T) \quad (4)$$

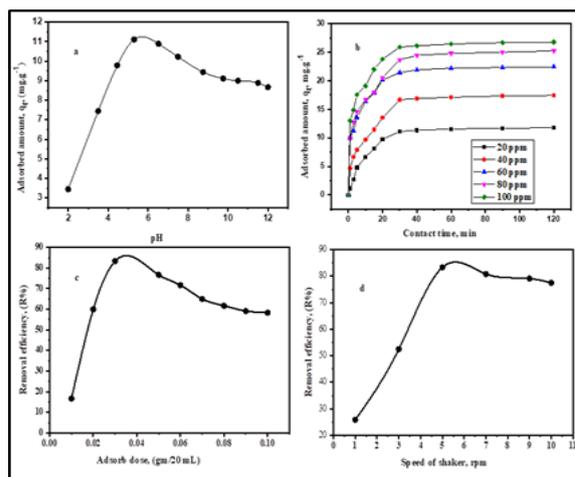
Where ( $K_d = q_e/C_e$ ) represent the distribution coefficient constant, R is the general gas constant (8.314 J/mol Kelvin) and T is the Absolut temperature (Kelvin). Since  $\Delta G^\circ$  can be also given as follow [27];

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

From equations 4 and 5:-

$$\ln K_d = (\Delta S^\circ / R) - (\Delta H^\circ / RT) \quad (6)$$

A linear relation was obtained from plotting of  $\ln K_d$  with  $1/T$  gives with  $R^2 = 0.99$ , (Fig. 7. b), from the slope and intercept of this plotting,  $\Delta H^\circ$  and  $\Delta S^\circ$  parameters were calculated, respectively and listed with the other parameters in Table 1. From Table 1, positive value of  $\Delta H^\circ$  appearing the endothermic nature of the adsorption process (withdrawing energy during adsorption process) whereas value of  $\Delta S^\circ$  is positive that reflects increasing the randomness at the solid solution interface.



**Fig. 6. a.** Effect of pH on the adsorption of EBT onto DF, **Fig. b.** Effect of contact time and initial concentration of EBT on adsorption of EBT onto DF, **Fig. c.** Effect of adsorbent dosage, and **Fig. d.** Effect of agitator speed on the removal process.

The negative  $\Delta G^\circ$  values, showing that the sorption process is possible and spontaneous in addition to the decrease in the  $\Delta G^\circ$  values with increasing temperature suggested that the dye uptake was more favourable. the value of  $\Delta G^\circ$  are lower than 40kJ/mol, which means the adsorption mechanism is phisorption, which are consistence with b value obtained from temkin model.

#### **Adsorption isotherm**

The distribution process for EBT molecules between the phases of DF surface (solid) and liquid can be understood from using Langmuir, Freundlich and Temkin isotherm models to analysis the equilibrium adsorption data and also to state the nature of interaction between EBT molecules with adsorbents. The more applicable isotherm model to the adsorption was stated according to values of  $R^2$  coefficients. The isotherm models were operated under conditions of; pH = 5.3, 0.03 g of DF, contact time = 30 min, agitation speed was 50 rpm using arrange initial concentration of EBT from 20 up to 100 mg/L at 25 °C.

### Langmuir isotherm model

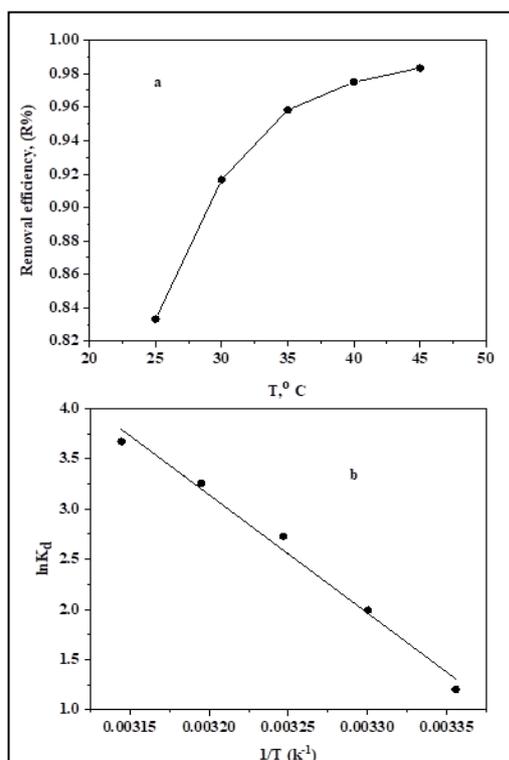
The linear equation for Langmuir isotherm was determined according considerations involving the active sites on the surface of the adsorbent are similar that leading to formation of monolayer adsorption without any interactions between the adsorbed molecules [32].

$$\frac{1}{q_e} = \frac{1}{Q_{\max}} + \frac{1}{bQ_{\max}} \left( \frac{1}{C_e} \right) \quad (7)$$

Where  $q_e$  is the adsorbed amount of EBT at equilibrium per unit mass of DF (mg/g) and  $C_e$  is the concentration of EBT in solution at equilibrium.  $Q_{\max}$  (mg/g) and  $b$  (L/mg) are theoretical constants represent the maximum adsorption capacity and Langmuir binding constant, respectively.  $Q_{\max}$  and  $b$  values can be determined from intercept and slope of plotting of  $1/q_e$  against  $1/C_e$ , respectively. From Fig. 8a a straight line was appeared with correlation coefficient = 0.945 and the calculated value of  $Q_{\max}$  and  $b$  were downed in Table 2. From value of  $b$ , the characteristics constant of Langmuir model,  $R_L$ , can be determined from the highest initial concentration of EBT,  $C_o$ , according this relation;

$$R_L = \frac{1}{1+bC_o} \quad (8)$$

Importantly of this constant is due to determination of the type of the isotherm as follow; the isotherm is irreversible when value of  $R_L$  equal zero, linear if  $R_L$  value equal one and favorable when  $R_L$  value more than zero and less than 1. The calculated  $R$  indicates favorable sorption isotherm, Table 2.



**Fig. 7. a.** Effect of temperature on adsorption of EBT onto DF and **Fig. b.** plots of  $\ln K_d$  against  $1/T$ .

**Table 1** Thermodynamic parameters for adsorption of EBT onto DF.

Temp. (K)	$K_d$ (L/g)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol K)	$-\Delta G^\circ$ (kJ/mol)
298	3.33	97.949	339.54	2.98
303	7.33			4.93
308	15.33			6.76
313	26.00			8.08
318	39.33			9.09

### Freundlich isotherm

This model assumed a multilayer adsorption on a heterogeneous surface where the adsorbed molecules can interact with each other's. The linear form can express as;

$$\log q_e = \log K_F + 1/n (\log C_e) \quad (9)$$

Where  $K_F$  (L/g) called Freundlich constant that gives indication for the adsorbent capacity for adsorption whereas  $n$  is the value of the intensity of adsorption that depicts the strength and capability of the uptake process where  $n$  value representing a beneficial adsorption if its values was in between 1 and 10. From plots of  $\log q_e$  against  $\log C_e$ , Fig.8b, a straight line was appeared with correlation coefficient value of 0.9945 that indicates fitness of this isotherm to the obtained data, from the intercept and slope of this plot, value of  $K$  and  $n$  were calculated and listed in Table 2. Also, the obtained value of  $K_F$  indicates that DF has a higher capacity to sorb EBT in addition to value of  $n$  is more than one (= 3.38) which indicating beneficial adsorption between EBT and DF [33]. Value of  $1/n$  was determined as 0.297 which refer to the heterogeneity of the surface where the adsorption is favorable and heterogeneous when the value of  $1/n$  more than zero and less than unit.

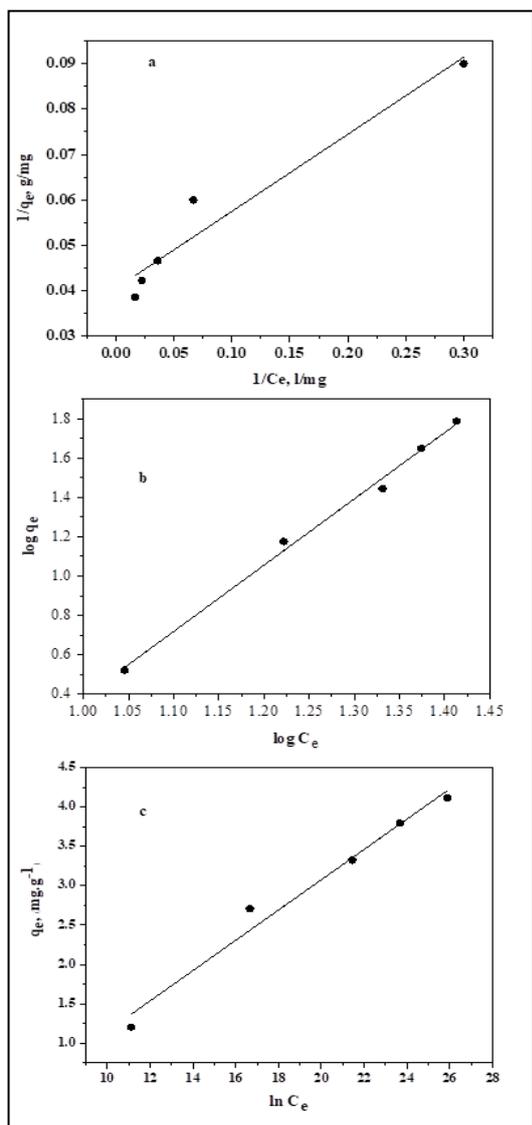
### Temkin model

This model assumed an interaction between adsorbate and adsorbent leading to decrease of the uptake heat of the adsorbate molecules linearly with the coverage meaning that the binding energies is distributed equally [34]. Using the linear form of this isotherm, the binding energies of the adsorption process can be determined as the following: -

$$q_e = \left( \frac{RT}{b} \right) \ln A + \left( \frac{RT}{b} \right) \ln C_e \quad (10)$$

Where  $R$  is the gas constant ( $8.314 \times 10^{-3}$  kJ/mol K),  $T$  is the absolute temperature (K),  $A$  is constant named equilibrium binding constant (L/g) and  $b$  is another constant related to the heat of adsorption energy (kJ/mol). The isotherm constants  $b$  and  $A$  were calculated from the slope and intercept, respectively of plotting of  $q_e$  against  $\ln C_e$  where a linear plot, Fig. 8c. constants  $b$  and  $A$  were calculated and listed in Table 2. The value of  $b$  was 2.055 (lower than 8kJ/ mol) that mean physisorption processes where a weakly interaction between adsorbate and adsorbent through

Van der Waals forces. From Table 2, a higher  $R^2$  value for the Freundlich isotherm than Langmuir one therefore, adsorption of EBT onto DF is more applicable to be described using Freundlich model. The obtained lower value of  $b$  of Temkin model supports this suggestion. Similar data were presented for the removal of EBT.



**Fig. 8:** a- Langmuir isotherm, b- Freundlich isotherm, and c- Temkin isotherm.

#### Adsorption kinetic modeling

Studying the kinetic modeling meaning that we can obtain an important factor that helps us to state if the selected material in the adsorption process benefit or not. Where the fast adsorption rate is preferred [35]. The kinetic data for adsorption of EBT onto DF were analyzed using Lagergren's pseudo first-order kinetic model, pseudo second-order kinetic model and intra-particle diffusion model as three different kinetic models.

**Table 2** The parameters of Langmuir, Freundlich and Temkin isotherms at 298 °K of EBT adsorption onto DF.

Isotherms Parameters	$R^2$ Values	(constant)
<b>Langmuir</b>	0.945	$b$ (L/mg)
0.239		$Q_{max}$ (mg/g)
24.68		$R_L$ (Unitless)
0.04		
<b>Freundlich</b>	0.9945	$K_F$ (L/g)
7.75		$n$
3.38		
<b>Temkin</b>	0.980	$b$
2.055		$A$ (L/mg)
36.23		

#### Pseudo-first order kinetic model

The integrated form of Lagergren equation was used widely to describe the pseudo-first-order kinetic adsorption model in which the adsorption rate is proportional to the difference between the capacities of adsorption in equilibrium state and actual one according the following equation [36];

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (11)$$

Where  $q_e$  (mg/g) is the adsorbed amount of EBT onto DF at equilibrium and  $q_t$  (mg/g) is the adsorbed amount at time  $t$  whereas  $k_1$  (1/min) is the rate constant of pseudo first-order sorption. From slopes and intercepts of plotting of  $\log(q_e - q_t)$  with time,  $k_1$  and  $q_e$  values were calculated, respectively. From Fig. 9.a and Table 3, the calculated  $q_e$  values don't close to the experimental ones and lower meaning that the adsorption of EBT onto DF doesn't obey the pseudo first-order kinetic model.

#### Pseudo-second-order kinetic model

Using pseudo-second-order kinetic rate equation, the rate of sorption of EBT onto DF was analyzed. The linear pseudo-second-order equation in the integrated form can be represented as [37];

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (12)$$

Where  $k_2$  (g/mg. min) is constant of the rate of pseudo second-order sorption. Application of the pseudo-second-order kinetics model meaning straight lines should be obtained from plots of  $t/q_t$  against of  $t$ .  $q_e$  and  $k_2$  values were stated from the slope and intercept of this plot, respectively, see Fig 9b and Table 3. Values of the calculated adsorbed amount of EBT ( $q_e$  calc.) were found to be closer to the experimental one ( $q_e$  exp) with very higher value of correlation coefficients ( $\geq 0.998$ ). Then, the adsorption of EBT onto DF is more

favorably by the pseudo-second order model and this reinforcing the applicability of this model.

### The intra-particle diffusion model

To state the type of the step that controlling the adsorption of EBT onto DF, the experimental data at various concentrations of initial EBT were applied to the Weber and Morris model when other operating parameters are fixed.

This model gives a relationship between the adsorbed amounts of dye at time  $t$ ,  $q_t$  (mg/g) with the square root of the time ( $t^{1/2}$ ). If a straight line passing by the zero point was obtained then, the thickness of the boundary layer surrounding the particle should be reduced and the film diffusion or the resistance of the boundary layer can be neglected (i. e. can't consider a major factor in the rate-controlling steps). The linear form equation according Weber and Morris is [38];

$$q_t = k_{id} t^{1/2} + C_i \quad (13)$$

Where  $k_{id}$  ( $\text{mg/g min}^{-1/2}$ ) is the rate constant for intra-particle diffusion at different used initial concentrations,  $t$  is the time (min) and  $C_i$  (mg/g) is constant gives information about the boundary layer thickness.

From plots of  $q_t$  against  $t^{1/2}$  for different initial EBT dye concentrations at 25 °C, Fig. 9c, it is noticed that there are linear regions at the beginning of the adsorption processes don't pass through the origin followed by a horizontal linear region representing equilibrium stage. Also, values of  $C_i$  are higher than zero and increases with increasing initial EBT concentration that reflects increasing the resistance to dye molecules of the layer of liquid that surround the particle of DF. Then we can be concluded that the contribution of the film diffusion in the rate controlling is greater and adsorption of EBT onto DF is controlled with film diffusion and intraparticle diffusion together.

### Comparison of capacities of various low-cost adsorbents for EBT

To make a comparison between availability of DF to remove EBT from an aqueous solution with different adsorbents types [39-43], the maximum

adsorption capacity was used. From Table 4, DF can be considering a succeeded adsorbent remove EBT from an aqueous solution.

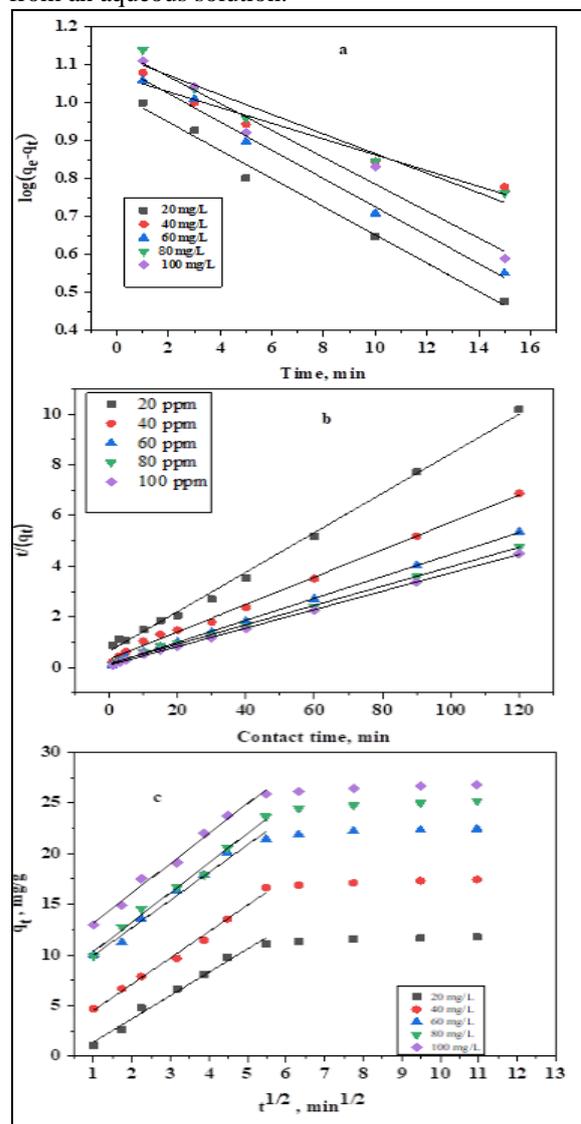


Fig. 9: a-Pseudo-first order model, b- Pseudo-second order model and c- The intra-particle diffusion model.

**Table 3;** The kinetic parameters of Pseudo-first-order, pseudo-second-order and intra-particle diffusion models

Conc. (mg/L)	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion			
	R <sup>2</sup>	q <sub>e</sub> , calc. (mg/g)	k <sub>1</sub> (min <sup>-1</sup> )	k <sub>2</sub> (g/m g min)	q <sub>e</sub> , calc. (mg/g)	q <sub>e</sub> , exp. (mg/g)	R <sup>2</sup>	k <sub>id</sub> (mg/g min <sup>1/2</sup> )	R <sup>2</sup>	C <sub>i</sub> (mg/g)
20	0.989	10.54	0.085	96.0	12.82	11.11	0.996	2.29	0.984	-0.887
40	0.962	11.74	0.047	0.0092	18.48	16.67	0.996	2.59	0.989	1.929
60	0.993	12.53	0.085	0.0147	23.05	21.45	0.999	2.72	0.981	7.234
80	0.954	13.30	0.059	0.0095	26.11	23.67	0.998	2.93	0.987	7.399
100	0.974	13.77	0.081	0.0137	27.39	25.89	0.999	2.95	0.987	10.228

**Table 4:** Maximum adsorption capacity of various adsorbents with EBT.

	$Q_{\max}$ (mg/g)	References Adsorbent
DF	24.86	This study
NiFe <sub>2</sub> O <sub>4</sub> magnetic nanoparticles	7.02	[39]
Waste rice hulls activated carbon	2.28	[40]
Bentonite carbon composite	2.89	[41]
H <sub>2</sub> SO <sub>4</sub> modified clay	16.50	[3]
Nteje clay	16.26	[3]
polyzwitterionic acid (HCPZA)	20.17	[42]
Untreated almond shell	18.18	[43]
Graphene	102.04	[4]

### 3. Conclusions

Natural DF as a locally low cost was used in our study to state its adsorption capacity and the ability for adsorption EBT dye from aqueous solutions. SEM, XRD and FTIR were used to characterize the DF. Effects of the experimental conditions on the performance of the adsorbent were investigated by studying the different effects of the experimental conditions on the adsorption. From the experiments results, the equilibrium state was reached at < 40 min. The effect of pH investigated for values ranging from 2 to 12, showed maximum adsorption of EBT on the DF for pH 5.3 at room temperature (25°C). The adsorption process increased when the agitation speed increased up to 50 rpm and the optimum dose of DF was 30 mg per liter of EBT. The adsorption process was spontaneous and endothermic. For knowing the quantitative description of the adsorption processes of EBT dye, the equilibrium adsorption isotherms models of Langmuir, Freundlich and Temkin, have been applied tested. The adsorption follows Langmuir with  $Q_{\max}$  of 24.68 mg/g at 25°C and Freundlich isotherms with higher degree than Langmuir. 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 appears a big role for the film diffusion process in the rate determining step and it controlling the adsorption of EBT onto DF in addition to the intraparticle diffusion process.

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