

Removal of Cibacron Brilliant Yellow 3G-P Dye from Aqueous Solutions using Coffee Husks as Non-Conventional Low-Cost Sorbent

Ismail I. Fafous, Nedal Abu Farha

Abstract—The purpose of this research is to establish the experimental conditions for removal of Cibacron Brilliant Yellow 3G-P dye (CBY) from aqueous solutions by sorption onto coffee husks as a low-cost sorbent. The effects of various experimental parameters (e.g. initial CBY dye concentration, sorbent mass, pH, temperature) were examined and the optimal experimental conditions were determined. The results indicated that the removal of the dye was pH dependent and at initial pH of 2, the dye was removed effectively. The CBY dye sorption data were fitted to Langmuir, Freundlich, Temkin and Dubinin-Radushkevich equilibrium models. The maximum sorption capacity of CBY dye ions onto coffee husks increased from 24.04 to 35.04 mg g⁻¹ when the temperature was increased from 293 to 313 K. The calculated sorption thermodynamic parameters including ΔG° , ΔH° , and ΔS° indicated that the CBY dye sorption onto coffee husks is a spontaneous, endothermic and mainly physical in nature.

Keywords—Coffee husks, equilibrium, reactive dyes, sorption.

I. INTRODUCTION

DYE-RELATED industries such as textile, leather, paper, plastic and food generate large volume of dyes-containing wastewater, which poses serious environmental problems due to their persistent and the recalcitrant nature of some dyes [1]. Reactive dyes such as Cibacron Brilliant Yellow 3G-P are widely used in dyeing processes due to their favourable characteristics of strong interaction with the substrate, bright color, water-fastness, simply application techniques and lower energy consumption [2]. The presence of very small quantities of dyes in water causes a highly visible and undesirable color, has a significant effect on the photosynthesis activity and thus affecting the aquatic ecosystem [3], and may cause damage to human beings such as liver, brain and dysfunction of the kidneys[4]. Thus, the removal of color from textile industry and dyestuff manufacturing industry effluents is of a high environmental concern. Many wastewater treatment methods such as chemical oxidation, coagulation, filtration, adsorption, and electrolysis have been used for dye removal from wastewater effluents prior to discharge [1],[4]. Among above mentioned methods, adsorption process is still the most common method due to its simplicity of design, cheapness and applicability for removal of wide range of pollutants [5].

This work was financially supported by Deanship of Scientific Research and Graduate Studies at the Hashemite University, Zarqa, Jordan.

Ismail I. Fafous and Nedal Abu Farha are with the Department of Chemistry, Hashemite University, Zarqa, Jordan (corresponding author, Ismail Fafous, phone: +962 5 390 3333 ext. 4738; fax: +962 5 382 6613; e-mail: ismailf@hu.edu.jo.)

Activated carbon has been the most popular and widely used as a versatile adsorbent for removal of various types of pollutants such as dyes[6],[7] metal ions [8], pesticides [9], and many other chemicals. Nevertheless, in recent years and due to the high cost, non-renewable source, and lack of reversible sorption (e.g., regeneration) of commercially available activated carbon, researchers have made great efforts towards developing low-cost alternative adsorbents [5]. Coffee is one of the most popular beverages in the world in terms of consumption. World coffee production was 6.7 million metric tons annually in 1998-2000, and rose to 7 million metric tons annually in 2010 [5]. However, significant amount of solid wastes generated from coffee industry such as coffee husks, defected coffee beans (low quality coffee) and spent coffee grounds (from soluble coffee production), have been explored as adsorbents for water treatment [5]. To the best of our knowledge, there is no studies were conducted to investigate the interaction of anionic dyes in particular CBY dye with coffee husks.

In the present work, experiments were performed to remove an anionic Cibacron Brilliant Yellow 3GP reactive dye as a model pollutant from aqueous solutions by an adsorption technique using coffee husks as an adsorbent. Characterization of coffee husks was studied by measuring the surface area, micropore volume, particle size distribution, surface oxide, and the point of zero charge. The CBY sorption was studied as a function of the following parameters: sorbent mass, initial CBY concentration, pH, and temperature. Different sorption isotherms and thermodynamic parameters have been investigated and their role in the interpretation of the mechanism of sorption has been discussed. The results will provide a better understanding with respect to treatment of dye-contaminated waters and dyes mobility in the environment.

II. EXPERIMENTAL

A. Chemicals and Reagents

Cibacron Brilliant Yellow 3G-P (C₂₅H₁₅C₁₃N₉Na₃O₁₀S₃) was purchased from Aldrich Chemical Company Ltd. As shown in Fig. 1, CBY has three sulfonate groups (a trivalent anion), which have negative charges in aqueous solution. The general characteristics of CBY are molecular weight 872.97 g mol⁻¹, color index number 18972, and λ_{\max} = 404 nm [10]. Double distilled water was used throughout the work. Nitric acid (Tedia, USA) and sodium hydroxide (GCC, UK) were used to adjust the pH. The dye was used without further purification. All other chemicals were of analytical grade unless stated otherwise.

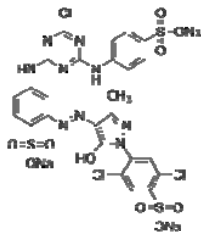


Fig. 1 Chemical structure of CBY dye

B. Preparation of Coffee Husks as a Sorbent

Coffee husks were purchased from Brazilian Coffee House (International Mill Company), Amman, Jordan. The coffee husks were washed several times with double distilled water to remove color, foreign impurities and soluble compounds, and dried in an oven at 97 °C for 24 hours. Then they were treated with 2% (v/v) formaldehyde solution for 24 hours to reduce organic leaching and avoid mould formation during batch sorption experiments as described elsewhere [11]. The resultant coffee husks were washed thoroughly several times until no color was released and then dried in an oven at 97 °C for 24 hours. The dried coffee husks were grinded by a mixer, sieved to particle size of 1 mm, stored in a brown glass bottle and kept in the desiccators until use. The particle size distribution of the treated coffee husks was determined by Mastersizer 2000 particle size analyzer (Malvern Instruments Ltd., Malvern, UK). The average particle size of a sample was quantified by a volume-weighted mean diameter $D[4,3]$ and found to be 113.0 μm .

C. Characterization of Coffee Husks

Textural characteristics of the coffee husks were determined by nitrogen adsorption at 77.3 K using a Micrometrics Gemini 2390t surface area analyzer. The Brunauer Emmett-Teller (BET) surface area, micropore volume, and micropore surface area of the coffee husks were determined using BET method and the software available with the instrument. The Barrett-Joyner-Halenda (BJH) method was used to calculate pore size distribution. The determination of surface oxides was performed as described by Bohem [12]. pH value at the point of zero charge, pH_{PZC} , of the coffee husks was determined by mass titration procedure as described by Valdés et al.[13]. Elemental analysis of the coffee husks was performed using a EURO EA 3000 elemental analyzer (EuroVector, Italy). Results of these analyses are presented in Table 1.

D. Determination of CBY Dye Contents in Solution

A stock solution of CBY (1000 mg L^{-1}) was prepared by dissolving a 1.000 g of CBY dye in double distilled water. The solution was then diluted with double distilled water to one liter in a volumetric flask. A series of standard solutions was prepared by diluting the stock solution. The dye concentrations were determined spectrophotometrically by measuring the absorbance at maximum wavelength (λ_{max}) of 404 nm against the reagent blank using CECIL 2011-visible spectrophotometer, after separating the sorbent from the dye solution by filtration.

Analytical calibration curve of CBY was found to be linear within the range of 2–100 mg L^{-1} (with correlation coefficient, R^2 , of 0.9998) and samples of higher concentrations were further diluted to fit into the dynamic range of the calibration curve. All samples were adjusted to the same pH prior to the analysis.

E. Batch Experiments

Batch-equilibration sorption experiments were carried out in duplicate in all experiments under variation of the pH and/or the CBY dye concentration. 0.200 g of coffee husks was added to 100 mL solution containing various concentrations of CBY (15–550 mL^{-1}) in 250 mL Erlenmeyer flasks with screw caps.

The pH values of the samples were adjusted to 2.0 ± 0.1 by adding negligible volumes of 2 mol L^{-1} NaOH or 2 mol L^{-1} HNO_3 . The flasks were then capped tightly and were agitated in an isothermal water bath shaker (GFL 1083, Germany) with reciprocating motion at three temperatures 20 ± 1 , 30 ± 1 and 40 ± 1 °C for one week until equilibrium was achieved.

After shaking, all flasks were filtered at the set temperature. The final pH values of the solutions were then measured after all sorption tests. It was found that the final pH of the solution increases towards the coffee husks point of zero charge value.

The filtered solutions were adjusted to the same pH value, and the remaining concentrations of the CBY dye after equilibrium were determined.

Blank experiments were performed using the same procedure but without adding coffee husks. The amount of CBY dye sorbed at equilibrium, q_e (mg g^{-1}), by coffee husks was calculated from the mass difference between initial concentration, C_o (mg L^{-1}), and final equilibrium concentration, C_e (mg L^{-1}), as shown in the following equation.

$$q_e = \frac{(C_o - C_e)V}{m_{\text{husks}}} \quad (1)$$

Where V (L) is the volume of the solution and m_{husks} (g) is the mass of the dry husks used.

The effect of pH on the sorption capacity of CBY onto coffee husks was investigated using 100 mL of 100 mg L^{-1} CBY and 0.200 g coffee husks.

The pH values of samples were adjusted to a pH range of 2–12 at 303 K. The samples were subjected to the same procedure described previously; equilibrium concentrations and sorbed amounts were determined.

The final pH values of the solutions were then measured after all sorption tests. It was found that the final pH of the solution varies towards the coffee husks point of zero charge value.

The isotherm data were fitted to four isotherm models using Linear Regression Analysis using Excel program.

All the experimental data were the average of duplicate determinations, and the average uncertainties were < 3.4%.

III. RESULTS AND DISCUSSION

A. Physical and Chemical Properties of Coffee Husks

The chemical and physical properties of coffee husks including functional groups and elemental analysis were determined using standard techniques and presented in Table 1. The BET surface area of the coffee husks is found as $0.41 \text{ m}^2 \text{ g}^{-1}$. BJH adsorption cumulative surface area of pores (17 Å to 3000 Å diameter) is $0.39 \text{ m}^2 \text{ g}^{-1}$, whereas BJH adsorption of cumulative volume of pores (17 Å to 3000 Å diameter) is $0.003 \text{ cm}^3 \text{ g}^{-1}$. BJH adsorption average pore diameter is 313.0 Å.

Bohem's titration revealed that the coffee husks have both acidic and basic properties. The acidic functional groups are carboxylic, lactonic, and phenolic. The basic functional groups include oxygen-containing moieties such as ketonic, pyronic, chromenic [12]. The coffee husks have acidic surface properties and a relatively high density of surface functional groups due to the low surface area. In fact, carboxylic group attracted to coffee husks surface has a pK_a value within 4-5. Therefore, this functional group would accrue different charges with respect to the studied solution pH while phenolic groups (1.12 mmol g^{-1}) will be deprotonated after pH 10. The distribution of the functional groups and chemical composition in the surface of the coffee husks play a major role in determining its sorption capacity, affinity and selectivity towards specific analytes (e.g., dyes). However, the interaction of the CBY dye with all functional groups on the surface of the coffee husks is possible *via* many mechanisms such as physisorption, chemisorption, ion exchange or surface complexation.

B. Point of Zero Charge

The experimental titration curves for point of zero charge (pH_{PZC}) determination are presented in Fig. 2. The pH_{PZC} of coffee husks is around 5.2 and therefore pH values should be carefully controlled in order to have a predominant positively ($\text{pH} < 5.2$), neutral ($\text{pH} = 5.2$) or negatively charged surface ($\text{pH} > 5.2$) of the sorbent. Oliveira et. al. [11] have reported the pH_{PZC} values in the range of 4.3-4.5 for untreated coffee husks.

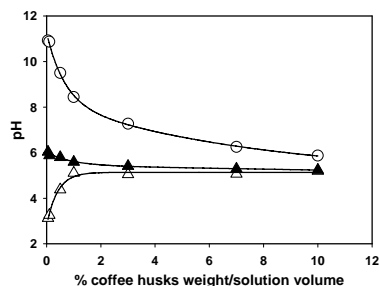


Fig. 2 Experimental curves for point of zero charge determination. (Δ), initial pH 3; (▲), initial pH 6; (○), initial pH 11

C. Effect of pH

The sorption capacity of coffee husks for CBY dye was significantly affected by the initial pH of aqueous solution.

Fig. 3 presents the influence of pH value on the equilibrium concentration of CBY dye sorbed to coffee husks from aqueous solution of an initial concentration of 100 mg L^{-1} . The pH was varied in this experiment between 2 and 12, while keeping all other parameters constant. The sorption capacity (q_e) was found to decrease with increasing pH, exhibiting a maximum of 21.34 mg g^{-1} at pH 2.0. A further increase in pH inversely affected the sorption capacity, and hence, pH 2.0 was selected for performing the subsequent experiments.

As mentioned in section A, coffee husks have both acidic and basic functional groups, at lower pH value ($< \text{pH}_{\text{PZC}}$) more protons will be available to protonate some functional groups of coffee husks to form positively charged sorption sites, thereby increasing the electrostatic attraction between negatively charged CBY dye anion and positively charged sorption sites causes an increase in the dye sorption capacity. The similar pH effects were also observed by the adsorption of some anionic dyes on cross-linked chitosan beads[14], coffee husk-based activated carbon[2], waste biomass from lysine fermentation process [10], de-oiled soya[15], and sugar beet pulp [16].

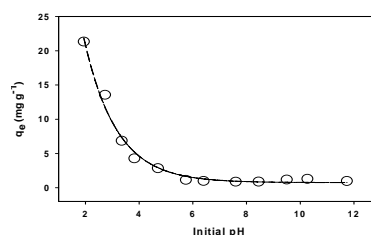


Fig. 3 Effect of initial pH on CBY dye sorption onto coffee husks.

D. Effect of Sorbent Mass

Fig. 4 shows the effect of the sorbent mass on dye removal. Experiments were done at 100 mg L^{-1} of CBY dye, 100 mL solution, equilibrated for a week. The dye removal increases when the mass of coffee husks increases because the ratio of the active sites of the coffee husks surface to the CBY dye molecules increases.

CBY dye sorption rate is shown to be high when the mass increases 0.050 to 0.500 g. The prompt increase in the removal with the increase in the mass of the sorbent can be attributed to the greater surface area and availability of new active sites. After mass of 0.500 g (loading dose 5 g L^{-1}), the rate of CBY dye removal becomes very slow and reaches a steady state (dye removal 98.72%).

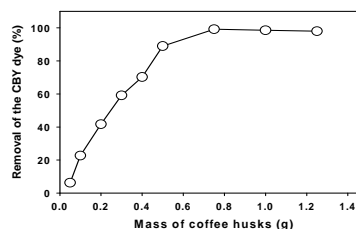


Fig. 4 The effect of coffee husks mass on the percent removal of CBY dye from aqueous solution

E. Sorption Isotherms

In this study, four popular equilibrium isotherm models were tested for their ability to describe the experimental data, namely Langmuir isotherm model [17-19], Freundlich isotherm model [18], [20], Temkin model [19], [21] and Dubinin-Radushkevich (D-R) isotherm model [18], [22], [23].

Langmuir sorption model [17-19] is based on the assumption that the maximum sorption capacity corresponds to full monolayer coverage of the solute molecules on the adsorbent surface, with no interaction between sorbed molecules. The linear form of Langmuir model is

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (2)$$

where q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amounts of sorbed CBY dye per unit mass of sorbent and CBY dye concentration at equilibrium, respectively. q_m (mg g^{-1}) is the maximum amount of the CBY dye per unit mass of sorbent to form a complete monolayer on the surface. K_L is a constant related to the affinity of the binding sites (L mg^{-1}).

The linear plot of ($\frac{C_e}{q_e}$) versus C_e shows (Fig. 5 (a)) that the

sorption process adequately obeys the Langmuir model. The K_L and q_m were determined from the slope and intercept of the plot, respectively and presented in Table II. The essential characteristics of Langmuir isotherm can be described by the dimensionless equilibrium constant or separation factor, R_L , as follows [24]:

$$R_L = \frac{1}{1 + K_L C_o} \quad (3)$$

where C_o is the highest initial concentration of CBY dye (mg L^{-1}), and K_L (L mg^{-1}) is Langmuir constant. The value of R_L indicates isotherm shape and whether the sorption is favourable or not, as per the following criteria: unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The values of R_L in this work were found to be 0.061, 0.040 and 0.030 at 293, 303 and 313 K, respectively, indicating that the sorption of CBY dye is favourable.

The Freundlich isotherm model [18], [25] is an empirical equation and used to describe heterogeneous surfaces. The linear form of Freundlich model is

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

where K_F is an empirical constant related to the sorption capacity of the sorbent (L mg^{-1})(L g^{-1}) $^{1/n}$ and constant n is an empirical parameter related to the intensity of sorption and varies with surface heterogeneity and affinity. The value of n gives an indication of the favourability of the sorption. Fig.5 (b) shows the plot of $\ln q_e$ versus $\ln C_e$, n and K_F values were calculated from the slope and intercept of the plot, respectively and listed in Table 2. According to Treybal [25], n values between 1 and 10 represent favourable sorption conditions. In this study, the values of n are 2.99, 4.55 and 5.30 at 293, 303 and 313 K, respectively, indicating that the

sorption is favourable at the described experimental conditions, which is consistent with Langmuir model findings.

Temkin isotherm model [19], [21] is generally used in the linear form as shown in (5)

$$q_e = B \ln A + B \ln C_e \quad (5)$$

where A is the Temkin isotherm constant (L g^{-1}), $B = \frac{RT}{b}$, b is

the Temkin constant related to the heat of sorption (J mol^{-1}), and R is universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature in Kelvin. The Temkin constants were calculated from the slope and intercept of the regression line of the plot of (q_e) versus $\ln C_e$ (Fig. 5 (c)) and listed in Table 2.

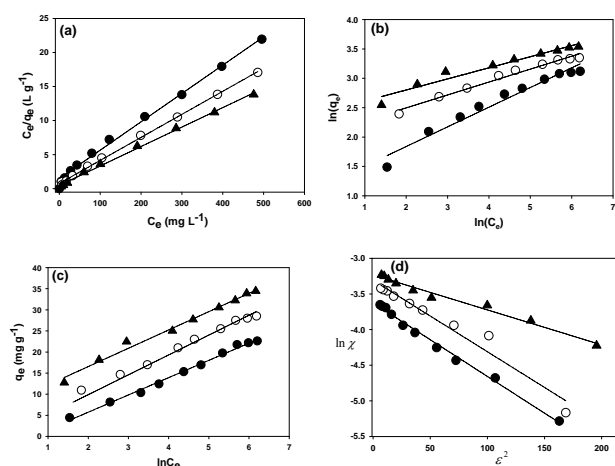


Fig. 5 Sorption isotherm models of CBY dye onto coffee husks at three temperatures. (a), Langmuir isotherm model; (b), Freundlich isotherm model; (c), Temkin isotherm model; (d), Dubinin-Radushkevich isotherm model. ●, 293 K; ○, 303 K; ▲, 313 K. The solid lines represent least squares linear curve fitting

Dubinin-Radushkevich (D-R) [22,23] developed the following isotherm in accounting for the effect of the porous structure of an adsorbent

$$x = x_m \exp(-K_{D-R} \epsilon^2) \quad (6)$$

where ϵ is Polanyi potential and is equal to

$$\epsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (7)$$

x is the amount of CBY dye sorbed per mass of coffee husks (mol g^{-1}), x_m is the theoretical sorption capacity (mol kg^{-1}), C_e is the equilibrium concentration of CBY dye (mol L^{-1}), K_{D-R} is the constant related to the adsorption energy ($\text{mol}^2 \text{ kJ}^{-2}$), R is the universal gas constant ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$), and T is the temperature in Kelvin.

The D-R equation can be linearised by taking the natural log of both sides of (6)

$$\ln x = \ln x_m - K_{D-R} \epsilon^2 \quad (8)$$

Fig. 5 (d) shows the plot of $\ln x$ against ε^2 , D-R isotherm constants, K_{D-R} and x_m were evaluated from the slope and intercept of the plot, respectively. The mean free energy of sorption (E_{D-R}) [23] required to transfer one mole of ions from bulk solution to the surface of the sorbent was then calculated from the following (9):

$$E_{D-R} = \frac{1}{\sqrt{2K_{D-R}}} \quad (9)$$

The magnitude of E_{D-R} (kJ mol^{-1}) may provide useful information with regard to whether or not sorption is subject to a chemical or physical process [23,26,27]. The D-R parameters and the mean free energy were evaluated and presented in Table 2. The values of E_{D-R} are 6.97, 7.06, and 10.10 kJ mol^{-1} at 293, 303 and 313 K, respectively. The typical range of bonding energy for ion-exchange mechanisms is 8–16 kJ mol^{-1} , indicating that physical adsorption may play a significant role in the adsorption process [18]. The values of x_m are $2.66 \times 10^{-2} \text{ mol kg}^{-1}$ (23.22 mg g^{-1}), $3.66 \times 10^{-2} \text{ mol kg}^{-1}$ (31.91 mg g^{-1}) and $3.94 \times 10^{-2} \text{ mol kg}^{-1}$ (34.43 mg g^{-1}) at 293, 303 and 313 K, respectively. These values are close to q_m values previously determined from the Langmuir isotherm model.

As shown in Table II, the regression correlation coefficients (R^2) exceed 0.9499 for Langmuir, Dubinin-Radushkevich, Temkin and Freundlich models, suggesting that the four models closely fitted the experimental data.

At the same time, the regression analysis results showed that the Langmuir isotherm was able to describe the sorption equilibrium data slightly better than Temkin, Freundlich and Dubinin-Radushkevich isotherm models in the concentration ranges studied in terms of R^2 . This is probably due to the homogenous distribution of the available active sites onto surface of coffee husks because Langmuir model assumes that the surface is homogenous. Similar results were reported for adsorption of several dyes from aqueous solution on activated carbon prepared from coffee husks[2] and untreated coffee husks[28], beech wood sawdust [29] sugar beet pulp[16]. Table 3 compares the sorption capacity of various types of agricultural solid wastes used for removal of some anionic dyes. The value of q_m in this study is larger than those in the most of the previous studies. This suggests that coffee husks are potential sorbents for CBY dye removal from aqueous solutions.

As shown in Table 2, the values of K_L , K_F , n , E_{D-R} , and q_m are increased with the increase in the temperature, revealing that the sorption capacity, q_m , of CBY dye onto coffee husks increasing with the increase in the temperature. The CBY dye equilibrium adsorption capacity obtained from the Langmuir equation increased from 24.04 to 35.04 mg g^{-1} when temperature was increased from 293 to 313 K. This may be due to increasing the mobility of the CBY dye molecules and an increase in the number of the accessible active sites on the surface of coffee husks [4].

F. Thermodynamic Analysis

Thermodynamic parameters improve our understanding regarding the inherent energetic changes involved during the sorption process. Changes of thermodynamic parameters of free energy of sorption (ΔG°), standard enthalpy (ΔH°), and standard entropy changes (ΔS°) were calculated from the variation of the Langmuir constants, K_L (L mol^{-1}), with the change in temperature based on the following equations [35].

$$\Delta G^\circ = -RT \ln K_L \quad (10)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

All terms have been defined previously. By plotting a graph of $\ln K_L$ versus $(1/T)$, the values of ΔS° and ΔH° can be estimated from the intercept and slope (Table 4), respectively. Thermodynamic parameters (ΔG° , ΔS° , and ΔH°) were calculated using (10), (11) and (12) and presented in Table 4.

The values of ΔG° were negative at the three temperatures, confirming that the sorption of CBY dye onto coffee husks was spontaneous and thermodynamically favourable. As sorption temperature increases the magnitude of ΔG° shifts to higher negative values. This agrees with the result that the maximum sorption capacity of coffee husks, q_m (as well as x_m), increases with increasing the sorption temperature.

Generally, the values of the ΔG° are in the range of 0 to -20 kJ mol^{-1} and -80 to -400 kJ mol^{-1} for physisorption and chemisorption, respectively [48]. In this study, the values of ΔG° are within the range of -24.6 to -28.3 kJ mol^{-1} , indicating that the physisorption is predominant mechanism of sorption. The observed positive ΔH° suggested an endothermic sorption, which supports the result that CBY dye sorption increased with temperature. Liu [35] reported that ΔH° ranges of physisorption and chemisorption are 2.1-20.9 and 80-200 kJ mol^{-1} , respectively. In this study the magnitude of ΔH° is 29.1 kJ mol^{-1} indicating that the sorption process is mainly of physical nature. The positive value of ΔS° indicated increased randomness at the solid-liquid interface during the sorption process. It thus contributed to the increase of CBY dye sorption capacities at higher temperature.

IV. CONCLUSIONS

This study investigated the potential use of coffee husks as a low-cost sorbent for removal of CBY dye from aqueous solution. The extent of the CBY removal decreases with the increasing of the solution pH, and hence the anionic dye was effectively removed under extremely acidic conditions (pH 2). The equilibrium data were fitted to Langmuir, Temkin, Freundlich, and Dubinin-Radushkevich isotherm models and the sorption data were best described by the Langmuir model.

The values of the dimensionless separation factor calculated from the Langmuir constants confirmed the favourable sorption of CBY dye onto coffee husks. The maximum sorption capacity of CBY dye ions onto coffee husks was 35.04 mg g^{-1} at 313 K and pH 2.0. The calculated sorption thermodynamic parameters (ΔG° , ΔH° , and ΔS°) indicated that the CBY dye sorption onto coffee husks is a spontaneous, endothermic, and mainly physical in nature.

TABLE I
SURFACE OXIDES AND ELEMENTAL ANALYSIS OF COFFEE HUSKS

Adsorbent	Elemental analysis				Bohem titrations (mmol g ⁻¹)				
	%C	%H	%N	%O ^f	a	b	c	d	e
Coffee husks	44.73	6.24	2.30	46.73	0.80	2.31	1.12	0.83	0.36

(a), total basic groups; (b), total acidic groups; (c), phenolic groups; d), lactonic groups; (e), carboxylic groups; ^f, estimated by difference

TABLE III
REPORTED SORPTION CAPACITIES, Q_m , OF VARIOUS AGRICULTURAL SOLID WASTES FOR SOME ANIONIC DYES

Sorbents	Dye	Q_m (mg g ⁻¹)	Reference
Sugar beet pulp	Gemazol	256.4	[16]
De-oiled soya	turquoise blue-G	176.8	[15]
Coffee husks	CBY	24.04	This study
Orange peel	Acid violet 17	19.88	[30]
Peanut hull	Amaranth	14.90	[31]
Coir pith	Acid violet	7.34	[32]
Banana pith	Direct acid	5.92	[33]
Sunflower seed shells	Reactive black 5	0.873	[34]

TABLE IV
THERMODYNAMIC PARAMETERS FOR CBY DYE SORPTION ONTO COFFEE HUSKS

Temperature (K)	K_L (L mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)	R^2
293	2.42×10^4			-24.6	
303	3.82×10^4	29.1	183.5	-26.5	0.9912
313	5.19×10^4			-28.3	

TABLE II
PARAMETERS OF THE FOUR EQUILIBRIUM ISOTHERM MODELS AND MEAN FREE ENERGY OF SORPTION (E_{D-R}) FOR SORPTION OF CBY DYE ONTO COFFEE HUSKS AT THREE TEMPERATURES

Model parameters	Temperature (K)		
	293	303	313
Langmuir Model			
q_m (mg g ⁻¹)	24.04	29.59	35.04
K_L (L mg ⁻¹)	2.77×10^{-2}	4.38×10^{-2}	5.95×10^{-2}
R^2	0.9970	0.9986	0.9975
Freundlich Model			
n	2.99	4.55	5.30
K_F (L mg ⁻¹)(L g ⁻¹) ^{1/n}	3.2	7.8	11.3
R^2	0.9641	0.9804	0.9499
Temkin Model			
A (L g ⁻¹)	0.55	2.04	6.13
B	4.10	4.22	4.34
R^2	0.9940	0.9955	0.9881
Dubinin-Radushkevich Model			
K_{D-R} (mol ² kJ ⁻²)	1.03×10^{-2}	1.00×10^{-2}	4.91×10^{-3}
x_m (mol kg ⁻¹)	2.66×10^{-2}	3.66×10^{-2}	3.94×10^{-2}
E_{D-R} (kJ mol ⁻¹)	6.97	7.06	10.10
R^2	0.9930	0.9605	0.9817

ACKNOWLEDGMENTS

The authors wish to thank Dr. Ayoup Ghrair (Royal Scientific Society, Amman, Jordan) for coffee husks surface area and pore size distribution analyses, and the administrations of Vegetarian Agricultural Production Company/VAPCO (Zarka, Jordan) for the use of their particle size analyzer.

REFERENCES

- [1] T. A. Khan, V. V. Singh, D. Kumar "Removal of some basic dyes from artificial textile wastewater by adsorption on akash kinari coal," J. Sci. Ind. Res., vol. 63, pp. 355-364, 2004.
- [2] M. A. Ahmad, N. K. Rahman "Equilibrium, kinetics and thermodynamic of remazol brilliant orange 3r dye adsorption on coffee husk-based activated carbon," Chem. Eng. J., vol. 170, pp. 154-161, 2011.
- [3] L. S. Oliveira, A. S. Franca, T. M. Alves, S. D. F. Rocha "Evaluation of untreated coffee husks as potential biosorbents for treatment of dye contaminated waters," J. Hazard. Mater., vol. 155, pp. 507-512, 2008.
- [4] M. A. M. Salleh, D. K. Mahmoud, W. A. W. A. Karim, A. Idris "Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review," Desalination, vol. 280, pp. 1-13, 2011.
- [5] A. Bhatnagar, M. Sillanpää "Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment-A review," Chem. Eng. J., vol. 157, pp. 277-296, 2010.
- [6] V. Gómez, M. S. Larrechi, M. P. Callao "Kinetic and adsorption study of acid dye removal using activated carbon," Chemosphere, vol. 69, pp. 1151-1158, 2007.
- [7] M. F. R. Pereira, S. F. Soares, J. J. M. Órfão, J. L. Figueiredo "Adsorption of dyes on activated carbons: Influence of surface chemical groups," Carbon, vol. 41, pp. 811-821, 2003.
- [8] M. Sanchez-Polo, J. Rivera-Utrilla "Adsorbent-adsorbate interactions in the adsorption of Cd(II) and Hg(II) on ozonized activated carbons," Environ. Sci. Technol., vol. 36, pp. 3850-3854, 2002.
- [9] K. Y. Foo, B. H. Hameed "Detoxification of pesticide waste via activated carbon adsorption process," J. Hazard. Mater., vol. 175, pp. 1-11, 2010.

- [10] Sung Wook Won, Y.-S. Yun "Biosorptive removal of reactive yellow 2 using waste biomass from lysine fermentation process," *Dyes Pigm.*, vol. 76, pp. 502-507, 2008.
- [11] W. E. Oliveira, A. S. Franca, L. S. Oliveira, S. D. Rocha "Untreated coffee husks as biosorbents for the removal of heavy metals from aqueous solutions," *J. Hazard. Mater.*, vol. 152, pp. 1073-1081, 2008.
- [12] H. P. Boehm "Surface oxides on carbon and their analysis: A critical assessment," *Carbon*, vol. 40, pp. 145-149, 2002.
- [13] H. Valdes, M. Sanchez-Polo, J. Rivera-Utrilla, C. A. Zaror "Effect of ozone treatment on surface properties of activated carbon," *Langmuir*, vol. 18, pp. 2111-2116, 2002.
- [14] M.-S. Chiou, P.-Y. Ho, H.-Y. Li "Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads," *Dyes Pigm.*, vol. 60 pp. 69-84, 2004.
- [15] A. Mittal, J. Mittal, L. Kurup "Batch and bulk removal of hazardous dye, indigo carmine from wastewater through adsorption," *J. Hazard. Mater.*, vol. 137, pp. 591-602, 2006.
- [16] Z. m. Aksu, I. A. Isoglu "Use of agricultural waste sugar beet pulp for the removal of gemazol turquoise blue-g reactive dye from aqueous solution," *J. Hazard. Mater.*, vol. 137, pp. 418-430, 2006.
- [17] I. Langmuir "The adsorption of gases on plane surfaces of glass, mica and platinum," *J. Am. Chem. Soc.*, vol. 40, pp. 1361-1403, 1918.
- [18] Y. Ho, J. Porter, G. McKay "Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, nickel and lead single component systems," *Water Air Soil Pollut.*, vol. 141, pp. 1-33, 2002.
- [19] B. H. Hameed, J. M. Salman, A. L. Ahmad "Adsorption isotherm and kinetic modeling of 2,4-d pesticide on activated carbon derived from date stones," *J. Hazard. Mater.*, vol. 163, pp. 121-126, 2009.
- [20] H. Freundlich "Über die adsorption in lösungen (adsorption in solution)," *Z. Phys. Chem.*, vol. 57 pp. 384-470, 1906.
- [21] V. I. Temkin, V. Pyzhev *Acta Physicochim. URSS*, vol. 12, pp. 217-222 1940.
- [22] M. M. Dubinin, L. V. Radushkevich "Equation of the characteristic curve of activated charcoal," *Chem. Zentr.*, vol. 1 pp. 875-890, 1947.
- [23] Y. Liu, Y.-J. Liu "Biosorption isotherms, kinetics and thermodynamics," *Sep. Purif. Technol.*, vol. 61, pp. 229-242, 2008.
- [24] K. R. Hall, L. C. Eagleton, A. Acrivos, T. Vermeulen "Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions," *Ind. Eng. Chem. Fundam.*, vol. 5, pp. 212-223, 1966.
- [25] R. E. Treybal, "Mass transfer operations". third ed. New York: McGraw Hill. 1980.
- [26] K. Vijayaraghavan, T. V. N. Padmesh, K. Palanivelu, M. Velan "Biosorption of nickel(II) ions onto sargassum wightii: Application of two-parameter and three-parameter isotherm models," *J. Hazard. Mater.*, vol. 133, pp. 304-308, 2006.
- [27] B. Canan Akmil "Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared waste apricot," *J. Hazard. Mater.*, vol. 135, pp. 232-241, 2006.
- [28] L. S. Oliveira, A. S. Franca, T. M. Alves, S. n. D. F. Rocha "Evaluation of untreated coffee husks as potential biosorbents for treatment of dye contaminated waters," *J. Hazard. Mater.*, vol. 155, pp. 507-512, 2008.
- [29] V. Dulman, S. M. Cucu-Man "Sorption of some textile dyes by beech wood sawdust," *J. Hazard. Mater.*, vol. 162, pp. 1457-1464, 2009.
- [30] R. Sivaraj, C. Namasivayam, K. Kadirvelu "Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions," *Waste Management*, vol. 21, pp. 105-110, 2001.
- [31] R. Gong, Y. Ding, M. Li, C. Yang, H. Liu, Y. Sun "Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution," *Dyes Pigm.*, vol. 64, pp. 187-192, 2005.
- [32] C. Namasivayam, M. Dinesh Kumar, K. Selvi, R. Ashruffunissa Begum, T. Vanathi, R. T. Yamuna "'waste' coir pith-a potential biomass for the treatment of dyeing wastewaters," *Biomass and Bioenergy*, vol. 21, pp. 477-483, 2001.
- [33] C. Namasivayam, D. Prabha, M. Kumutha "Removal of direct red and acid brilliant blue by adsorption on banana pith," *Bioresour. Technol.*, vol. 64, pp. 77-79, 1998.
- [34] J. F. Osmá, V. n. Saravia, J. L. Toca-Herrera, S. R. g. Couto "Sunflower seed shells: A novel and effective low-cost adsorbent for the removal of the diazo dye reactive black 5 from aqueous solutions," *J. Hazard. Mater.*, vol. 147, pp. 900-905, 2007.
- [35] Y. Liu "Is the free energy change of adsorption correctly calculated?," *J. Chem. Eng. Data*, vol. 54, pp. 1981-1985, 2009.

Ismail Fafous is as an assistant professor in the Department of Chemistry, Hashemite University/ Jordan. He received his B.Sc degree. in Chemistry from the Hashemite University/ Jordan in 1999, M.Sc. degree in Chemistry from University of Jordan/Jordan in 2001, and Ph.D. degree in Chemistry from Carleton University/ Canada in 2005. Dr. Fafous has published eighteen research papers in national and international reputable journals. His research interests include metal speciation, sorption, wastewater treatment and method developments.

Nedal Abu Farha received his B.Sc. degree in Chemistry from the Yarmouk University / Jordan. He is working as a laboratory technician in the Department of Chemistry/, Hashemite University/ Jordan. His research interests include analytical instrumentation and pollutants monitoring in the environment.