RESEARCH PAPER

Study of Adsorption for Rose Bengal and Nile Blue Dyes on the Nano/Micro-Surface of Walnut Shell-Derived Coal

Estabraq Arif Mohammed, Lekaa Hussain Khadim *

Department of Chemistry, College of Education for Women, University of Kufa, Al Najaf Al-Ashraf, Iraq

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ABSTRACT

Since water pollution constitutes a large proportion of the pollutants spread on the surface of the earth, pollution is unfortunately the most dangerous silent weapon in the world today, especially in light of technological progress. Great efforts have been made to get rid of this pollution. Dyes, which are colored substances that can somehow bind to materials and give them bright colors, are considered water pollutants and have toxic effects on humans. The adsorption of the dyes Indigo Blue and Rose Bengal from their aqueous solutions on the surface of coal derived from walnut shells activated with phosphoric acid was studied as an economical method. Measurements of the surface of the coal derived from walnut shells were made, including SEM, and TEM. Many parameters were studied to determine the best conditions that improve the adsorption process. The results obtained after conducting many effects showed that the contact time for Indigo Blue dye was (150 minutes) and for r Bengal dye was (120 minutes), and the pH function as well as different temperatures (298 to 328 K).

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INTRODUCTION

One of the biggest issues affecting both people and the environment is pollution, particularly in light of the advancements in technology that have come with modern living. Pollution can take many different forms, including contamination of water, air, or soil, the presence of toxic organic or inorganic compounds, or changes in the proportion of certain fundamental elements in the environment relative to their normal levels. Either natural events or human initiatives are to blame for this. [1] In general, the existence of living cells, organisms, plants, and animals is threatened by water scarcity. Since it serves as the structural and functional foundation for all living things, water is fundamentally important. Furthermore, water is a necessary element of all living things and plays a unique part in the growth of critical functions. Because water covers two-thirds of the earth's surface, the planet Earth is thought to contain 1.4 cubic kilometers of water. Water's composition and quality naturally change as a result of consumer usage, making it unfit for the things it was used for before to pollution. Material and actions that alter the original composition of [2] Many researchers began considering appropriate and adequate methods to eliminate these pollutants when the pollution issues grew worse in the past few years. These pollutants have become a genuine problem, especially at low levels and concentrations. The most crucial methods for cleaning up pollution are

* Corresponding Author Email: liqaa.aljailawi@uokufa.edu.iq

adsorption.[3].

Adsorption definition A physicochemical phenomena known as adsorption often happens when liquid or gaseous components come into contact with solid solids. The surface on which the adsorption takes place is referred to as the adsorbent, and the substance that is adsorbed on it is known as the adsorbate[4]. One of the most significant areas of surface chemistry is adsorption. Nowadays, it is impossible to find an industry that does not profit from them. The oil, dairy, dye, and petroleum sectors are excellent illustrations of the value of adsorption and the mechanism that supports their expansion. The advantages of adsorption applications are not just found in the industrial sector; they also extend to other industries, the most significant of which are environmental pollution and the medical domain, as well as the uses of these domains in the treatment of poisoning cases and drug preparation [5].

Their molecules contain groups called chromophores that are, as well as other combinations called (auxochromes) of an acidic or basic nature that intensify and fix the color. [6] Rose bengal is used as an antioxidant to keep medications effective, cure skin conditions like psoriasis and eczema, shield the skin from infections, help prevent wrinkles and other symptoms of age, and leave the skin feeling fresh for a long time[7] It is a common medicinal dye that contains halogen and is soluble in

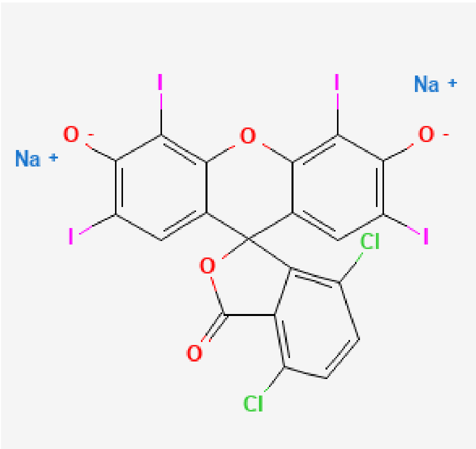

Fig. 1. Structure of Rose Bengal.

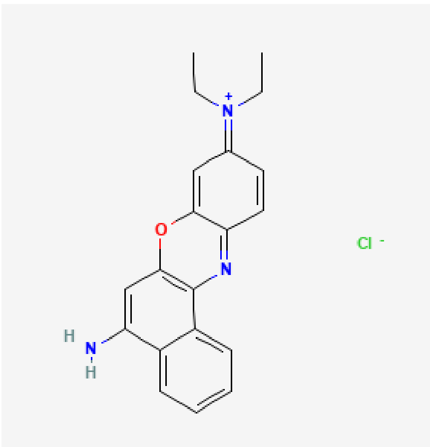

Fig. 2. Structure of Nile blue.

water. However, human skin and eyes may get irritated, itchy, etc. due to this dye's toxicity[8] The benzophenoxazine family of organic dyes includes the extremely fluorescent, photostable dye known as nile blue, chemical structures are shown in Figs. 1 and 2. Lipids and lysosomes have been imaged in vitro using it as a tissue dye. The dye is a perfect substrate for the construction of pH sensors and local polarization indicators due to its high quantum yield and solvent-dependent optical characteristics. Histology and biology also make use of it. It gives cell nuclei a blue hue and can be applied to both living and fixed cells[9].

Some common types of sorbents are alumina oxides, activated carbon . Every kind of sorbent has characteristics that make it beneficial in some situations but inefficient or unfeasible in others.

Carbon that has been activated A popular and reasonably priced adsorbent that is widely used in the pharmaceutical sector is activated carbon. Commercially, activated carbon comes in a wide variety of forms; some manufacturers produce more than 150 grades for a variety of uses.40 Carbon sources (e.g. coconut shell, and coal), physical forms (power, granular, and pellets), activation methods (chemical or steam), and any post-treatments that may be used can all be used to categorize the many types of activated carbons. The number of active sites, pore size, pore size distribution, particle size, surface area, and density are significant factors that can impact absorbent effectiveness. [10]

Used to make activated alumina, an adsorbent. It serves as a fluoride filter for drinking water and a desiccant for drying gasses and air. Because of its physical stability in water and resilience to heat shock, it can be used specifically in some settings as a silica gel alternative. [11]

MATERIALS AND METHODS

Material Walnut shells, citric acid, sodium hydroxide and sodium nitrite were purchased from CDH, India, and nitric acid and hydrogen chloride were obtained from Himedia (India).

Surface preparation of the absorbent material Walnut shells are used in the manufacture of carbon charcoal by first washing them repeatedly with distilled water, then leaving them to dry at 100 °C for 2 hours, and then placing them in an oxygen-free oven at 500 °C for 2 hours. Then the charcoal is finely ground and passed through a 0.1 µm sieve. After that, it is cleaned five times with distilled water and dried for 2 hours at (50 °C) [12]. As shown in Fig. 3.

Preparation of Standard Solutions and Calibration Curves

Preparation of standard solutions and calibration curves The standard solution of the dyes Rose bengal and Blue Nile was prepared at a concentration of (500 ppm) by dissolving (0.250 g) in (500 ml) of distilled water. Then, different concentrations of Rose bengal dye were prepared from (5 to 50 ppm) while in the case of Blue Nile dye, it was also prepared from (5 to 50 ppm). The spectrum of both dyes was taken using UV-Vis spectrometer to obtain lambda max where the maximum absorption was exploited using distilled water as a raw sample. Then, the absorbance of each of the ten samples was measured by UV-Vis spectrometer to determine the calibration curve of the dyes. (Rose bengal and Blue Nile dye).

Effect of Contact Time

This study was conducted at a temperature of 298 K between activated carbon and dye, and the volume of all samples was 20 ml with a

A B

Fig. 3. real images of A) Walnut shells B) Activated carbon derived from Walnut shells.

concentration of 50 ppm for the dyes Rose bengal and Nile Blue, and the weight of activated carbon was (0.2 g) and at different time periods (0.5, 1, 1.5, 2, 2.5, 3, 3.5 hours), after which the samples for both dyes were placed in a shaking water bath, then the samples were filtered with filter paper, then the filtered absorbance was measured by UV-visible spectroscopy [13].

The effect of surface weight on the adsorption capacity of Rose bengal and Nile blue dyes

The effect of surface weight on the adsorption capacity was studied to calculate the best contact time for Rose bengal and Nile blue dyes at a constant temperature (298) K and with different weights (0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5, 1) g and volume (20 ml). The prepared samples were placed in a shaking water bath for 120 minutes and 150 minutes for Rose bengal and Nile blue dyes respectively, then they were filtered with filter paper, and the absorbance was measured by (UV-vis) spectrometer [14].

Effect of Acid Function (pH)

The pH meter was used to evaluate the pH function in this research by taking six distinct concentrations of the two dyes (Nileblue and Rose Bengal) at their highest concentrations (2, 4, 6, 8, 10). Then each of these samples was given a constant surface weight, and a UV-Vis spectrometer was used to measure the absorbance [15].

Effect of Zero Point

To find the surface charge on which the adsorption process takes place, this study was conducted by taking ten samples of 20 ml of each of the two dyes at a concentration of (50 parts per million) for two dyes, Rose bengal and Nileblue.

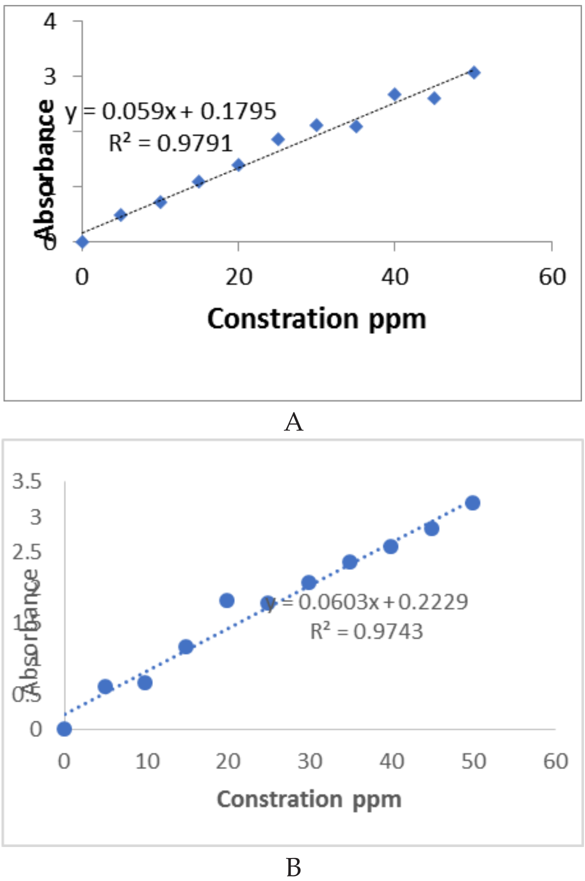

Fig. 4. UV-visible spectra of (A)Rose bengal and (B)Nile blue in distil water pH(6).

Then, a fixed weight of the surface (activated charcoal) in the amount of (0.3 g) was added to each of the ten samples of each of the two dyes, then 40 ml of sodium nitrate solution was added and left for 24 hours. After that, the absorbance was recorded, and from knowing the initial and final pH, the surface charge was calculated [16].

ΔpH=pHf-pHi (1)

pHf= After Adsorption, pHi= before adsorption

Adsorption Isothermal

Ten samples of each of the two dyes Rose Bengal and Nile Blue were prepared at concentrations of (5-50 ppm) respectively, with an amount of 20 ml of each concentration of the two dyes, and the fixed surface was added. These samples were placed in a shaking water bath, and after a specific period of time (Rose Bengal for 120 minutes and Nile Blue for 150 minutes), the samples were filtered with filter paper and the absorbance was measured in the UV spectrometer at the maximum corresponding to each of the two dyes, and the concentration after adsorption (Ce) was revealed through the calibration curve with the following equation [17].

$$Q_e = \frac{C_0 - C_e \, V_{Sol}}{m}$$

Where qe: The amount of adsorbent (mg/gm)

C0: The initial concentration of the dye (mg/l)

Ce: Concentration at equilibrium for the dye (mg/l)

Vsol: The total volume of the adsorbent, m: The weight of the adsorbent (gm)

RESULTS AND DISCUSSION

Calibration curve of Rose bengal and Nile blue dyes

The maximum absorption wavelength was obtained after measuring each dye, and it was found to be (544 for Rose bengal dye and 575 for Nile blue dye) as shown in Fig. 4. In the meantime, dual spectrum UV-Vis spectroscopy was used

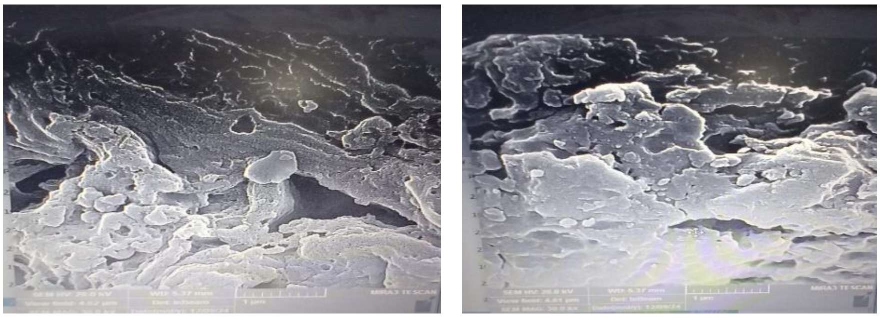

Fig. 5. SEM of the surface of charcoal derived from walnut shells. from walnut shells.

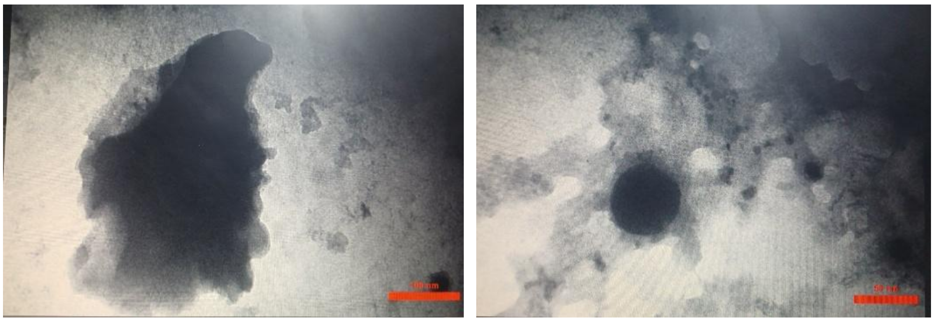

Fig. 6. TEM of the surface of charcoal derived from walnut shells. d from walnut shells.

to generate the calibration curves of the dyes described, with λmax for each dye.

Scanning electron microscope(SEM) of the surface of charcoal derived from walnut shells

A concentrated electron beam is used to scan a sample in a scanning electron microscope (SEM), which creates images of the sample. The sample's atoms and electrons interact to produce a variety of signals that reveal details about the composition and topography of the surface, results shown in Fig. 5.

Transmission electron microscop of the surface of charcoal derived from walnut shells

By focusing an electron beam onto a subject, transmission electron microscopy (TEM) creates an enlarged image that can be seen on a fluorescent screen or layer of photographic film, results shown in Fig. 6.

The effect of contact time

This experiment was conducted to determine the ideal contact time between the dye and the activated surface made of walnut shells. The results based on calculations indicated that the ideal contact time between the Nile blue and the surface was 150 minutes, while the ideal contact time between the rose bengal dye and the surface was 120 minutes. The maximum adsorption of the dye will occur there, which explains the high adsorption quantity (Qe). Because the active

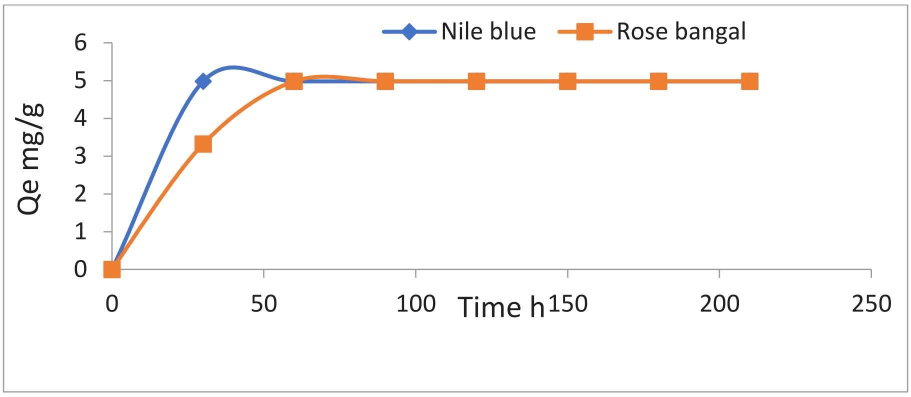

Fig. 7. Effect of contact time for adsorption of each of the dyes on the surface of activated carbon derived from walnut shells at pH = 6 and temperature 298 K.

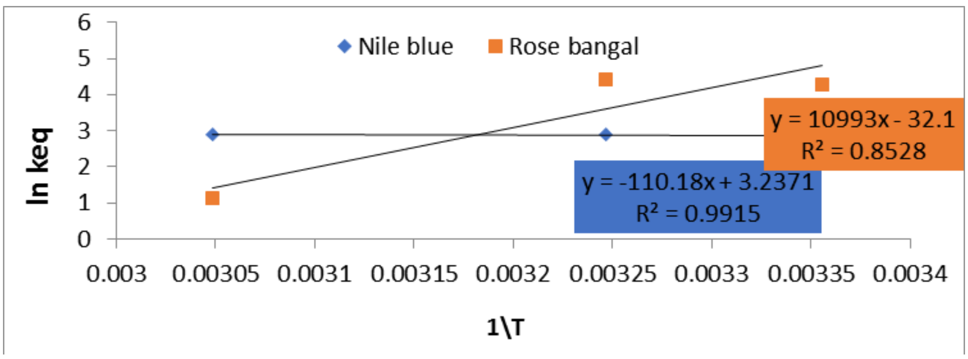

Fig. 8: shows the relationship between the reciprocal of temperature and the equilibrium constant for the adsorption of dyes on the surface of activated carbon derived from walnut shells at pH values of 298, 308, 318, 328 K and pH values of 6.

sites on the surface are unoccupied, the highest adsorption of the dye will occur on the active sites on the surface. After that, the adsorption capacity decreases due to the occupation of these sites, i.e. it reaches a saturation state with time and the adsorption is low. At the specified contact time with this dye, the adsorption capacity increases and the active sites of the activated surface are occupied, [18], results shown in Fig. 7. Also the effect of the weight of the activated surface was studied, which is an important factor in determining the adsorption capacity of dyes from their aqueous solutions. The results showed that the best weight for both Nile blue dye (0.3 gm) and Rose bengal dye is (0.05 gm). When the results of the adsorption amount on the surface of activated carbon were compared, at first it was high due to the availability of active sites, i.e. the availability of surface area. After that, the adsorption amount gradually begins to decrease with the increase in the weight of the surface on the one hand, and on the other hand, the decrease in the adsorption amount is attributed to the accumulation of the adsorbed material (the dye) in the aqueous phase.

Thermodynamics of Absorption

The following equations were used to assess the thermodynamic behavior [20] of Rose Bengal and Nile blue adsorption on activated charcoal, as stated in Fig. 8.

$$\Delta G = \Delta H - T\Delta S \qquad (3)$$

$$\mathrm{Ln}\ KC = -\Delta H/RT + \Delta S/R \qquad (4)$$

Enthalpy and entropy are obtained by plotting Ln Xeq against 1/T, where ΔH represents the enthalpy, ΔS the entropy, and ΔG the free energy change.

Adsorption Isotherm Model Study

Freundlich, Langmuir, Temkin, and Harkins-jura isotherms are among the different types of sorption isotherms; the last two are the most commonly used. Depending on the type of data being presented, any one of them can be used to best fit the data. The relationship between the amount of adsorbent adsorbed on the surface of the adsorbent and the amount of adsorbent adsorbed on the surface of the adsorbent is generally depicted graphically by sorption isotherms. There are different types of isotherms based on criteria [21].

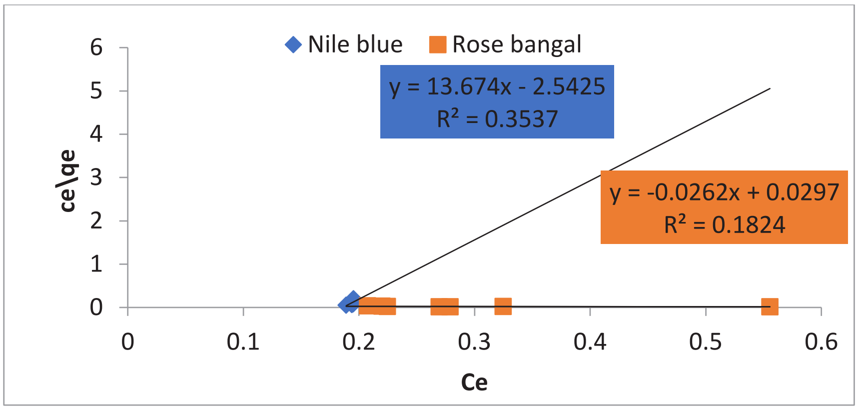

Fig. 9 shows the relationship between the Langmuir lines for the adsorption of dyes on the surface of activated carbon derived from walnut shells at pH 298 K and pH 6.

Table 1. Langmuir model constant for both dyes.

Dyes	Qm	Kl	R^2
Nile blue	0.0731	5.3804	0.3537
Rose bengal	-38.167	-0.8821	0.1824

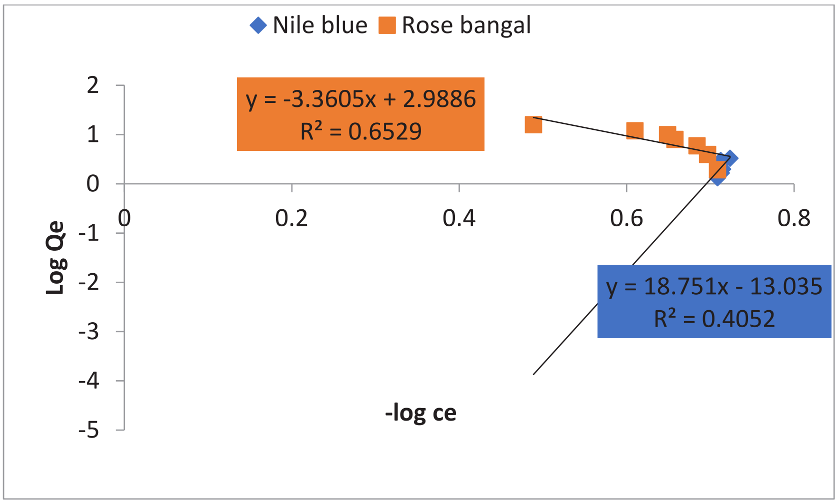

Fig. 10: shows the relationship between the Freundlich lines for the adsorption of dyes on the surface of activated carbon derived from walnut shells at pH 298 K and pH 6.

Table 2. Freundlich model constant for both dyes.

Dyes	K_f	N	R^2
Nile blue	10.839	-0.0533	0.4052
Rose Bengal	8.59013	4.45037	0.1254

Langmuir models

According to the isothermal Langmuir model, adsorption takes place on the absorbing materials' homogenous surfaces; in other words, it is single-layer adsorption. Sequential experiments were carried out using varying beginning concentrations of the two dyes (Nile blue and rose bengal) at varying temperatures (298 to 328 K) [22]. Fig. 9 below illustrates these findings.

$$Ce/Qe= 1\backslash Km.qm +Ce/qm \quad (5)$$

where Ce (mg/L) is the equilibrium concentration, qe (mg/g) is the mass of Nile blue and Rose bengal adsorbed at equilibrium, qm (mg/g) is a concentration parameter related to the adsorption capacity of the monolayer of the adsorbent, and KL (L/mg) is the Langmuir constant related to the adsorption efficiency of the solute. Fig. 9, shows a straight-line plot of Ce/qe versus Ce with a slope equal to Ce/qe and an intercept equal to (1/qm)(1/KL) [11]. The values of KL, qm, and the linear correlation coefficient, R2, are given in Table 1.

Freundlich model

Adsorption takes place on surfaces that are diverse and multilayered, as seen in Fig. 10. Both Rose Bengal and Nile blue dyes were applied to the surface of walnut shell-derived charcoal between 298 and 328 K using the Freundlich adsorption equation, results are shown in Table 2. The calculated Freundlich constants are denoted by (n), which indicates the degree of adsorption, the amount of curve curvature that the surface is saturated with, and (Kf), which indicates the surface's adsorption capacity from the slope and the intersection.

$$\text{Log Qe} = \text{Log Kf} + 1/n \text{ Log Ce} \quad (6)$$

where Kf and n are the system's Freundlich

Constants property.

CONCLUSION

The results showed that the activated charcoal derivative from the Cores of Iraqi dates is a good adsorbent with highly property of nano/micro-surface for removing both fast-green and malachite-green dyes from their aqueous solutions, even if the dyes concentration was very low by (0.05). Moreover, from the analysis of the outcome and fitness to the isothermal equations, the mechanism of adsorption are physical type can be predicted.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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