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Textile Dye Removal by Activated Date Seeds

Abstract- The objective of the study was to prepare activated carbon from date seeds (ADS) and use it as a medium for textile dye adsorption. Batch adsorption of reactive green dye showed that dye adsorption depends on the contact time, the dye concentration, and the pH equilibrium. Different concentrations of the prepared activated carbon were used with different dye concentrations and evaluated for dye removal efficiency. The maximum dye adsorption in this study was achieved after 270 min at a pH range of 5-9. In this study, the functional groups in the prepared ADS were identified using Fourier transform infrared (FTIR) while the crystal size was determined using an X-ray diffractometer (XRD). The Langmuir and Freundlich isotherm equation were used to study the adsorption kinetics, isotherms, and dye desorption while the pseudo-second-order kinetics was used to analyze the equilibrium adsorption data of the reactive green dye on the prepared ADS. The dyes' adsorption kinetics followed pseudo-second-order kinetics, which is adjudged as the best in adsorption studies. The equilibrium data were best fitted with the Freundlich isotherm model. Conclusively, the adsorption of dye onto the prepared ADS was observed to be an endothermic physical adsorption process.

Keywords- Activated carbon, Adsorption, Freundlich isotherm, kinetics, Langmuir isotherm, Reactive green dye.

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1. Introduction

Wastewater effluents are made up of toxic synthetic dyes which, when discharged into the environments, becomes a major concern due to esthetical and toxicological reasons [1]. The removal of color (a visible pollutant) is a difficult problem because such a process is only effective and economical in high solute concentrations. Charcoal adsorbents sourced from agricultural wastes can achieve an acidic dye adsorption within 4 to 5 h in solutions with a pH range of 8-10 [2]. Most industrial products are colored with dyes and pigments, and the dyeing process results in the generation of effluents whose discharge into the environment poses a danger to both human and the ecosystem [3].

The development of economical dye pretreatment methods for the removal of color from effluents has been a major challenge to the dyestuff production units. The processes for the removal of dyes can either be biological, chemical, or physical in nature; the physical dye removal methods include ion exchange, adsorption, and filtration or coagulation [1]. The adsorption method is the commonest dye removal method because of its effectiveness in dye removal from waste effluents. Batch kinetic, isotherm and column studies were carried out in this study; the obtained data were evaluated for fitness to the Langmuir-Freundlich isotherm model [2].

Activated carbon was prepared from date seeds and used for color removal from wastewater through an adsorption process. The prepared activated carbon has a large adsorption capacity due to its porous structure; its chemical structure influences its interaction with both polar and nonpolar adsorbates. Thus, the surface area and pore size distribution of the activated carbon cannot serve as a basis for the determination of its adsorption behavior [4].

Most activated carbons are composed of oxygen molecules (called functional groups) which are sourced from either the parent material or through oxidation processes during the activation phase. These surface oxides incorporate polar ends to the activated carbons. The adsorption equilibrium of a material (the ratio of the adsorbed amount to the residual amount in the solution) is determined when an adsorbate that contains a phase has been contacted with an adsorbent for a sufficient time, having its adsorbate concentration in the bulk solution in a dynamic balance with the interface concentration [5].

Heavy metals such as lead, chromium, cadmium, and copper are mainly to produce the color pigments of textile dyes. When these heavy metals are discharged to the environment, they are highly toxic and can accumulate in the human body or in water bodies over time [5]. Most industrial products are colored with dyes and this

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coloring process results in the generation of heavy-metal contaminated wastewater. During the dyeing processes, about 50 % of the dye concentration is lost to the wastewater due to the low levels of dye-fiber fixation [6, 7]. Color removal from waste effluents has become an important area of study because of the relative toxicity of even a minute quantity of dye in water [8]. Therefore, the adsorption of different pollutants using agricultural waste products has been one of the economic and realistic approaches for wastewater decontamination from dyes and heavy metals before discharging into the environment [9]. To different methods have been used enhance the adsorption capacity of enhance the adsorption capacity of adsorbents and such methods have often used the Langmuir isotherm to determine the effectiveness of an activation process. These activation processes involve the use of physical (such as material carbonization) and chemical (such as the use of chemical activating agents) activations. Wastewater from the textile plants is a mixture of heavy metals, dyes, organic compounds, surfactants, total dissolved solids (salts, chlorinated compounds, biological oxygen demand, and chemical oxygen demand [10].

Studies have investigated the efficacy of agricultural wastes as pollutant adsorbents. Industries, such as dyestuffs, paper, textile, plastics, paint, and tannery plants depend on dyes to color their products; they also utilize a substantial amount of water during the coloring process and as a result, generates a huge amount of colored wastewater [11]. The removal of dyes and heavy metals from wastewater can be achieved through various methods, including chemical precipitation, biochemical degradation, coagulation, chemical degradation, solvent extraction, photocatalytic degradation, electrochemical degradation, enhanced micellar ultrafiltration, ozone oxidation, adsorption, and ion exchange [12]. The use of low-cost adsorbents for the metal ions and dyes removal has been recently reviewed and among such methods, the use of GNC and BCC activated carbons has been proven to be efficient and simple, as well as economical and feasible for the decontamination of wastewater from metal ions and dyes [13].

The adsorption isotherm is an empirical relationship used for the prediction of the amount of a solute that can be adsorbed by activated carbon [14]. It is defined as a graphical depiction of the relationship between the amount adsorbed by a unit weight of an adsorbent and the amount of adsorbate left in the test medium at

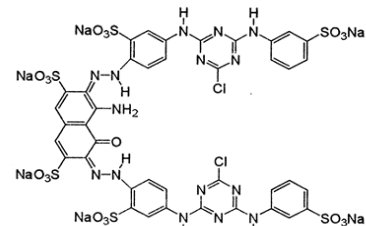
equilibrium. It shows the distribution of the absorbable solute between the solid and liquid phases at various equilibrium concentrations [15]. Freundlich and Langmuir are the two well-known isotherms that are commonly used in adsorption studies.

2. Materials and Methods

I. Reactive green dye

The reactive green dye used in this study was supplied by the Department of Dying of Kadhimiya Textile Factory, North of Baghdad. A 1000 mg/L stock solution of the dye was prepared by dissolving 1 g in 1 L of distilled water. The stock solution was further diluted to a concentration of 50 mg/L and used in the subsequent experiments. Table 1 showed the characteristics of the reactive green dye and its chemical structure.

Table 1: Characteristics of the reactive green dye

Item	Reactive green RR
Trade name	Drimarene brilliant green Z-3G
Origin	Switzerland
Phase	Solid /power
Molecular formula	$C_{60}H_{29}Cl_3N_{17}NaIO_{21}S_7$
Wavelength (nm)	660
Molecular weight (g/mol)	1839.4499
pH	6.5
Solubility (g/L at 25 °C)	92
Structure	

II. Preparation of the activated carbon

Figure 5 showed the process of preparing the ADS. The date seeds were washed, dried, and pulverized to a regular diameter of approximately 1.18mm. The granules were calcined in a furnace (Electrical furnace, Carbolite, S/N; 20-601148, UK.) at a temperature of 350 °C for 5 h [16], about 15 g of the calcined granules was activated by mixing with 60 mL of 98 wt % sulfuric acid at room temperature for 1 h (oxidation process). The sample was filtered with filter paper (Model 102) and washed with distilled water thoroughly before being dried in an oven (Mettler,

Germany) at 120 °C for 2 h; then a 250 mL conical funnel was filled with 120 mL of polluted water at different initial concentrations and at different temperatures. At 25 °C, the dose of 0.1 gm. was taken because it gave good results. To find the time required to reach the adsorption equilibrium, different concentrations (0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 g) of prepared activated carbon were added to 6 flasks, each containing 50 mL of 50 ppm reactive green dye at a pH value of 4.0. The flasks were mounted on a shaker (Germany Orbit Shaker, Model: VRN480, Figure 1 and 2) and shaken for different contact time (30, 60, 120, 210, and 270 min).



Figure 1: Preparation of ADS



Figure 2: Germany Orbit Shaker (Model: VRN480)

III. Adsorption method

The dye removal efficiency of the prepared activated carbon was calculated using equation 1 as follows:

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} * 100 \quad (1)$$

Where

C_i = initial solute concentration

C_f = final solute concentration

The adsorption capacity of the activated carbon at time t , q_t (mg/g) was determined using equation 2 as follows:

$$q_t = \frac{(C_i - C_t) \times V}{m} \quad (2)$$

Where

C_i = initial dye concentration

C_t = concentration of green dye at time t

q = amount of adsorbed metal per given adsorbent amount (mg/g).

V = volume of solution

m = mass of the activated carbon (g).

The adsorption rate at equilibrium (q_e) was determined using equation 3 as follows:

$$q_e = \frac{(C_i - C_e) \times V}{m} \quad (3)$$

Where

C_e = concentration of green dye at equilibrium.

3. Results and Discussion

I. XRD analysis of ADS

The XRD patterns of the prepared ADS at different ADS concentrations were shown in Figures (3-5). From the figures, the presence of a broad peak between 25° and 28° in the non-activated and activated ADS confirmed the presence of carbon. However, the absence of extra peaks confirmed the absence of any other compound such as sulfuric acid in the non-activated and activated samples.

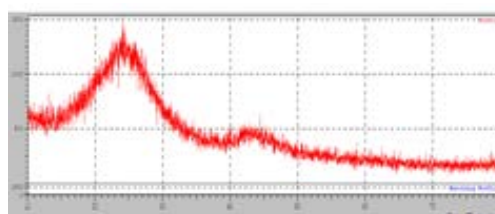


Figure 3: XRD of ADS at a concentration of 0.5 g

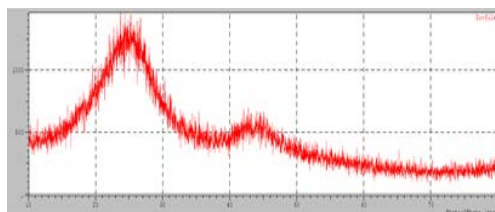


Figure 4: XRD of ADS at a concentration of 1.0 g

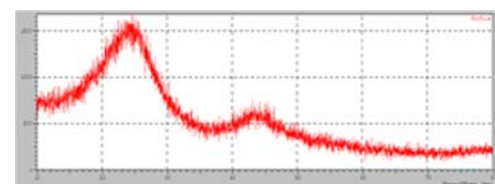


Figure 5: XRD of ADS at a concentration of 1.5 g

II. FTIR analysis of ADS

The FTIR spectrum of ADS was shown in Figure 6. From the figure, the spectrum of the activated date's carbon showed the presence of $C\equiv C$ and $C\equiv N$ groups at the wavelength of 2166 cm^{-1} . The peak in this region can also indicate the presence of moisture. The presence of $C=O$, $C=N$ and $C=C$ groups was confirmed by the peaks at the band between $1765\text{-}1572 \text{ cm}^{-1}$. The stretching of $N-O$ in nitrogen compounds was confirmed by the band at 1354 cm^{-1} while methyl group was identified by the peak around 1383 cm^{-1} . Another peak at the wavelength region of 1111 cm^{-1} confirmed the presence of $-OH$ groups. The

fingerprints which represent the alkyne group are responsible for the peaks at wavelengths of less than 1000 cm^{-1} [21].

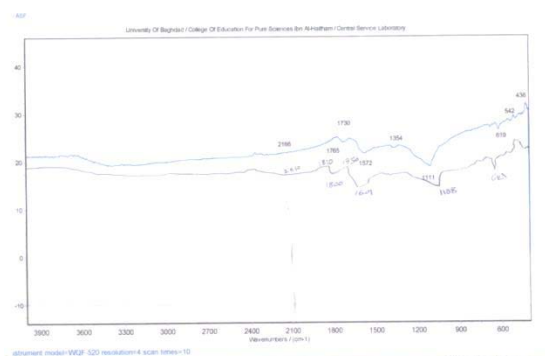


Figure 6: FTIR spectrum of ADS

III. Effect of process parameters

a. Effect of contact time

The effects of contact time on the removal of green dye by the prepared activated carbon was shown in Figure 8. The removal efficiency was observed to increase with the contact time. The first 20 min witnessed a rapid rate of adsorption by the activated carbon, but upon reaching equilibrium, the rate was slowed. The equilibrium was found to be more than 20 min for both and activated and inactivated carbons. A full equilibration was ensured during the process by employing a shaking time of 60 min for all the concentrations of activated carbon.

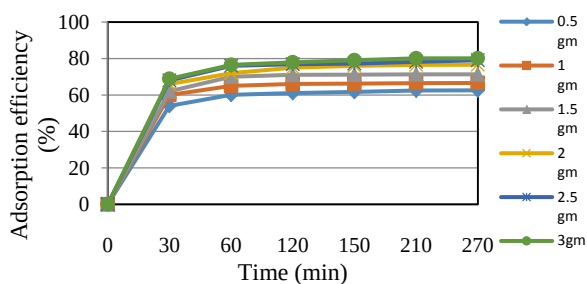


Figure 7: Effect of contact time on dye removal

b. Effect of pH

The solution pH is one of the important factors during the adsorption process. Figure 7 depicted the effect of pH on the rate of reactive green dye adsorption on the prepared activated carbon. From the figure, the rate of blue dye adsorption was found to be unaffected by changes in the pH of the solution over the studied pH range (5 – 9).

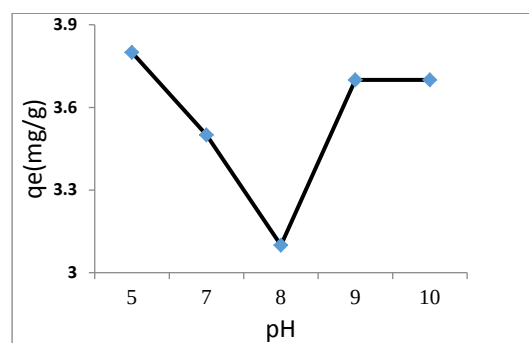


Figure 8: Effect of pH on the adsorption of the green dye by the ADS

c. Effect of activated carbon concentration

The concentration of the activated carbon was varied (0.5 to 5.0 g) and studied for effects on the adsorption efficiency at a temperature of 25°C , pH 5.5, and an initial dye concentration of 20 ppm. As own in Figure 8, the adsorption rate of the dye onto the activated carbon was found to increase with the adsorbent concentration. This was an expected outcome since a larger surface area is expected at a higher adsorbent concentration. However, at a higher adsorbent concentration, there was no significant increase in the dye adsorption rate because there was no appreciable surface area increase due to solvent saturation and the consequent conglomeration of the exchanger particles. Meanwhile, an adsorbent concentration of 2 g/100 mL was found to be the ideal concentration for maximum dye adsorption.

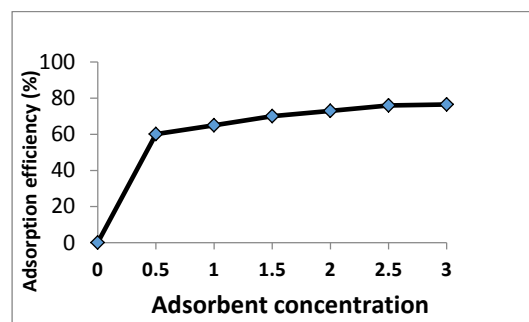


Figure 9: The effect of adsorbent concentration on the removal of green dye

IV. Adsorption isotherms

Various models, including the Langmuir and Freundlich isotherms, were used to study the adsorption isotherms. The Langmuir model (Equation 4) assumes homogeneous monolayer coverage, as well as an identical and energetically equivalent adsorption site on the surface of a molecule.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \quad (4)$$

Where

q_e = amounts of dispersed green dye (mg/g) adsorbed at equilibrium

q_m = monolayer adsorption capacity (mg/g)

K_L = Langmuir adsorption constant (L/mg) which relates to the free adsorption energy

C_e = concentration of the dye (mg/L) in the solution at equilibrium.

The Freundlich model (Equation 5) assumes physicochemical adsorption on heterogeneous surfaces.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

Where

K_F And $(1/n)$ = Freundlich adsorption isotherm constants, indicating the extent of adsorption and the adsorption intensity, respectively.

The maximum adsorption capacity of the prepared activated carbon was determined at a temperature of 25°C, pH 9, the initial dye concentration of 20 ppm, and different adsorbent concentrations (0.5 to 3 g) using the Langmuir isotherm equation. Table 2 provides the values of R^2 and the isotherm constants while the linear plot of $1/q_e$ vs $1/C_e$ was shown in Figure 9. The high correlation coefficient value indicates the suitability of the Freundlich isotherm to fit with the equilibrium data. However, the data was found to fit poorly with the Langmuir isotherm (Figure 10) compared to the Langmuir isotherm. Table 2 also presented the isotherm parameters derived from the intercept and slope of the plots.

Table 2: Langmuir and Freundlich isotherm constants

Isotherm constant	Langmuir			Freundlich		
	R^2	q_m	K_L	R^2	K_F	n
Constants/correlation coefficient						
Value	0.9906	8.06	0.154	0.9932	6.915	0.348

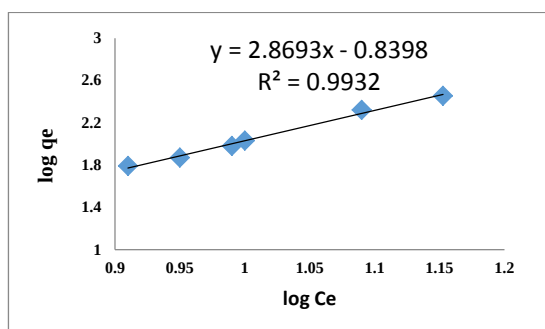


Figure 9: Freundlich adsorption isotherm for reactive green dye

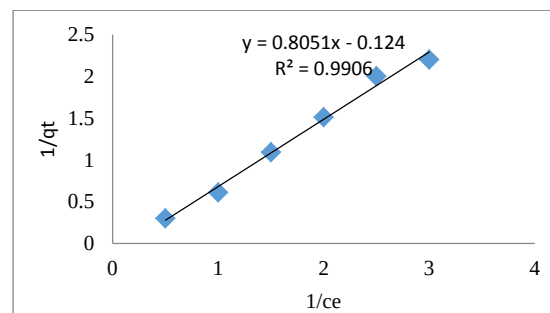


Figure 10: Langmuir adsorption isotherm for reactive green dye

V. Kinetics of reactive green dye adsorption

The adsorption kinetics of the reactive green dye was studied at an initial reactive green concentration of 20 ppm, temperature 25°C, and a pH range of 5-9. The equilibrium time for the activated and inactivated carbon was found to be over 210 min. The obtained experimental data were processed using a pseudo-second-order linearly represented in Equation 6.

$$\frac{1}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (6)$$

Where

q_e and q_t = amounts of disperse green (mg/g) respectively adsorbed at equilibrium and at time t and k_2 = pseudo-second-order adsorption rate constant (g/min.mg).

The pseudo-second-order plots of the experimental data are shown in Figure 11, while Table 3 showed various rate constants derived from the intercepts and slopes of the plot. The determined correlation coefficient (R^2) and the calculated adsorption capacity were found to be close to the experimentally determined value.

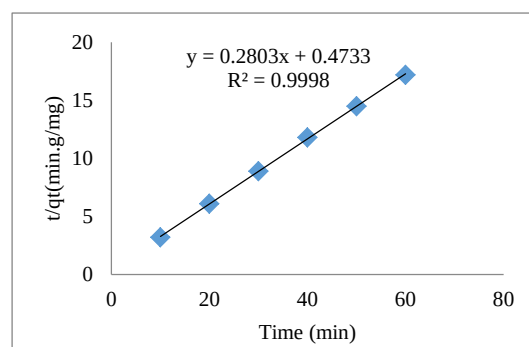


Figure 11: Pseudo-second-order kinetic model for reactive green dye adsorption onto ADS (adsorbent concentration = 1 g).

Table3: Pseudo-second-order kinetic model for dispersing green dye adsorption onto ADS

Adsorbent dose (g/100 mL)	Pseudo-second-order kinetic		
	q_e (mg/g)	K_2 (g/mg.min)	R^2
1	2.113	0.799	0.9998

4. Conclusion

The outcome of this study showed that ADS could be used as an adsorbent for the removal of reactive green dye from solution. The pseudo-second-order kinetic model equation was found to be the best model for the description of dispersing green dye adsorption on ADS. The results also showed that the Freundlich isotherm equation provided the best fit for the experimental data. Finally, the use of ADS for the removal of reactive green dye showed a high removal efficiency of 72.5% and could be considered for industrial wastewater treatment.

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