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ORIGINAL ARTICLE

Adsorption Features Remove a Toxic Dye from an Aqueous Solution by a Cost-effective Palm Leaf Activated Carbon (PLAC)

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KEYWORDS

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Dye;
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ABSTRACT: This research addressed the elimination of the dye Congo red (CR) from an aqueous solution utilizing dried palm leaf activated carbon (PLAC). Therefore, we performed batch experiments for isotherms and sorption kinetics. According to the experimental data, the adsorption method largely depends on the equilibrium time, initial concentration of dye, pH solution, and adsorbent amount. We observed sorption equilibrium for the dye Congo red via PLAC in 60 min and an adsorption capacity of 52.1 mg g^{-1}. A pseudo-first-order kinetic model was followed by sorption kinetics, whereas the Langmuir isotherm has been proposed to be help reache the equilibrium factor. The above data demonstrated that PLAC is an effective, low-cost, and environmentally friendly biomaterial for removing the dye from the aqueous solution.

INTRODUCTION

According to the studies in the field, adsorption has been considered one of the phase transfer processes, with extensive uses for removing the materials from the fluid phase (liquid or gas) and transferring them to the solid phase (adsorbent particle). Moreover, it is possible to observe adsorption in various environmental compartments as one of the natural processes. A solid and a pollutant like pharmaceuticals molecules interact, regarding water or effluents treatments and the pollutant is known as adsorbate but the solid is adsorbent. Researchers have employed the above method to efficiently remove a wide variety of contaminants [1, 2]. As stated in Ho et al., (2000) study, adsorption is performed in the fixed-bed columns or batches consisting of a specific mass of porous adsorbent in practice. Based on the mentioned conditions, the effects of mass transfer cannot be avoided. A detailed adsorption sequence includes 3 steps. Step 1: Film diffusion (external diffusion); that is transporting the adsorbate found in the solution to the external surface of the adsorbent. Step 2: Pores' diffusion (intra-particle diffusion); transporting the adsorbate from the surface of the adsorbent into the pores and Step 3: Surface reaction; that is, the adsorbate fixation on the surfaces of the adsorbent pores. This step would be implemented rapidly and a film or intra-particle diffusion would determine the total adsorption rate. As both steps are implemented in series, the slower process would characterize adsorption [3, 4]. Adsorption is one of the acceptable and attractive techniques because of the multiple benefits like affordability, efficiency,

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environmental benignity, and availability [5-7]. Several possible substances are applied as the adsorbents, including activated carbon of mineral, ion exchange resin, animal or vegetable origin, chitosan, carbon nanotubes (CNTs), and organic resins as well as fly ash . Both efficiency and analysis of the development of the adsorbents, regeneration capacity and, costs of utilization are of high importance. The concept 'low-cost adsorbents' has been presented based on an economic view, which refers to a material with little processing that occurs abundantly in nature, or maybe a waste product or material from industrial activities [4, 8]. In the case of the last materials, the acquisition economy may compensate for the processing costs. Therefore, further research must deal with a cost study. Some instances of low-cost adsorbents have been proposed to be parts of plants, animals, or other materials with higher carbon content like bark, fruit residues, mosses, algae, keratin, and hair, as well as clays [9, 10].

MATERIALS AND METHODS

A stoke solution (1000 mg L^{-1}) of the preparation via Congo red (CR) dye (Aldrich) (≥97.5%) via mixing (1 g) as a specific volume of dye in (1000ml) D.W, then Working and standards (2–50 mg L^{-1}). The absorbance was estimated via utilizing a UV-V Spectrophotometer as shown in Figure 1.

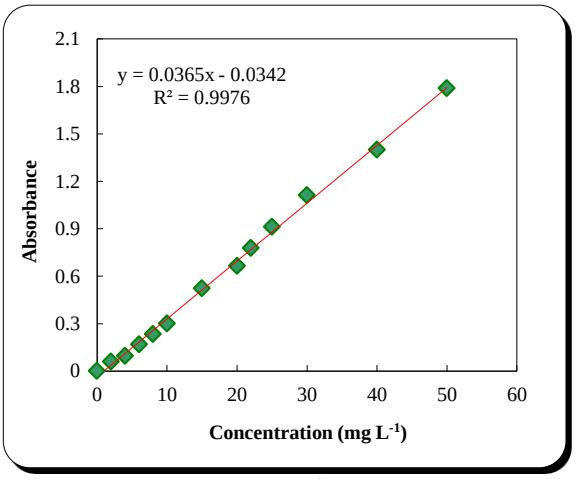

Figure 1. Calibration curve of Congo red (CR) dye.

Preparation of HCl -Activated carbon (palm leaf)

Palm leaf was obtained from Hill city, Iraq, to make a higher degree of microporosity and activation surface areas via Chemical activation of HCl.The materials were mixed (2:1 wt. ratio) on concentrated HCl at 300°C for 2 hr, thus at 25°C the samples cooled after that washed by distilled water until the pH of the AC make pH 7, finally for 24 h dying at 115°C and sieved to gain the required particle size (25 µm).

Batch adsorption studies

The equilibrium isotherm of dye adsorption on PLAC adsorption tests was carried out utilizing 100 ml conical flasks in which 100 ml of CR dye solutions with several primary concentrations (10–100 mg l^{-1}) were placed in each flask. The solution's pH was set to a pH equal to 7 by gradual addition of a 0.1 M HCl and NaOH solution. Then, we poured PLAC (0.05 g) into all flasks and put it in a shaker at 220 rpm, 293 K for 60min to attain equilibrium. The samples were filtered and thus a concentration of the dye residue in the filtrate was analyzed via a UV–Visible Spectro-photometer. Moreover, we employed UV–Vis spectro-photometer to analyze the CR dye's residue concentrations in the filtrate at 492 nm wavelength. Expressions (1) and (2) calculate the adsorbed content of dye at equilibrium, QE (mg g^{-1}).

$$Q_e = \frac{Co-Ce}{W} * V \quad (1)$$

$$E\% = \frac{Co-Ce}{Co} * 100 \quad (2)$$

C_o (mg L^{-1}) refers to the primary concentration of GR dye. C_e (mg L^{-1}) represents the concentration of the GR dye equilibrium at time t (min), W (g) implies the

adsorbent weight and V (L) stands for the solution volume.

RESULTS AND DISCUSSION

FT-IR characterization for Palm Leaf Activated Carbon (PLAC)

According to the research design, we employed FT-IR spectroscopy for characterizing the PLAC. Spectra FTIR was collected in a mid -IR range between 4000 and 400 cm^{-1} with 1 cm^{-1} resolution. Spectra FTIR of PLAC before and following a Congo red (CR) dye. Adsorption is appeared in Figure 2. FTIR pattern looks declined in the intensity of bands next to the adsorption, to we observe a difference real among PLAC, before and following the interactions by Congo red (CR) dye. Therefore, a physic-sorption phenomenon happens as the result of attractive forces among the surface of PLAC and Congo red (CR) dye in the study [11].

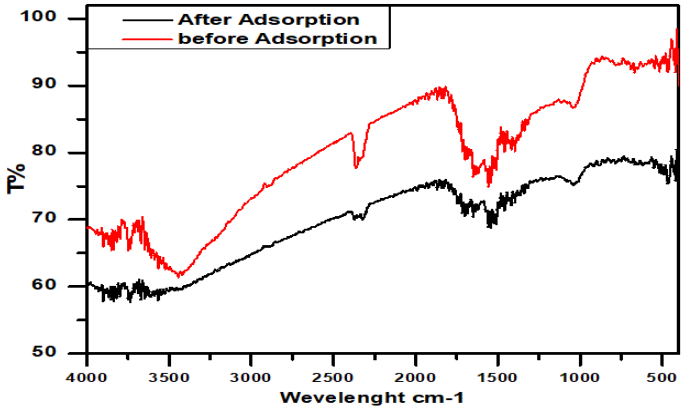

Figure 2. FT-IR spectra of PLAC before and after adsorption of Congo red (CR) dye.

Field Emission Scanning Electron (FESEM)

Scanning electron microscopy (FESEM) is one of the primary tools for the characterization of the adsorbent's surface morphology as well as basic physical features. Therefore, we took FESEM of the adsorbent materials before and after the dye adsorption on AC (Figure 3). Figure (3a) shows an acceptable possibility for trapping the dye and adsorbing it into the pores. In addition, FESEM images of the adsorbed specimens showed very distinct dark spots that may be taken as one of the signs of efficient adsorption of the dye molecules in this adsorbent's pores and cavities. Moreover, micro-graphs are shown in Figure. (3b) and (c) indicate the dye-loaded adsorbent that has been coated by the dye molecules over the entire surface under the natural pH conditions. The molecules of the dye form a void-free film that masks the particles' reliefs as well as the aggregates' porosity[12].

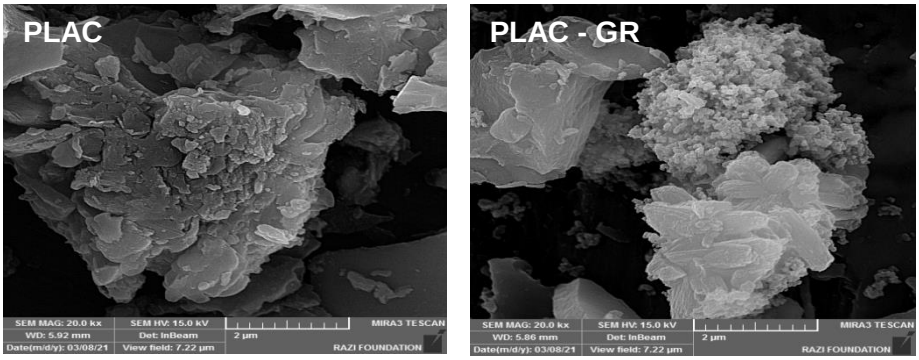

Figure 3. FESEM image of AC before and after and the GR dye adsorption.

Effects of PLAC weight

Effect of the PLAC dosage was needful to predestine the lowest potential amount that displays the highest adsorption stoichiometric. Moreover, the amount of PLAC was several (0.001 – 0.08 gm). Results appear in (Figure 4). The increased percentage removal is due to increased adsorption sites and surface area, but with decreased adsorption efficiency. This might be because of AC aggregation that decreases surface area and binding sites, leading to decreased adsorption capacity [13, 14].

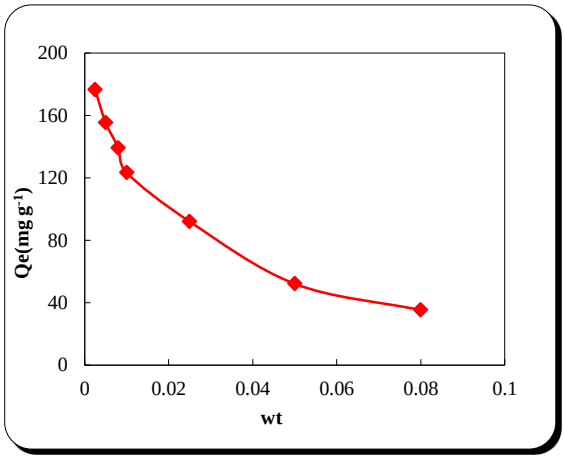

Figure 4. Effects of the weight adsorbent (PLAC) on the amount of adsorbed CR dye (primary concentration of the dye = 30 mg L^{-1}, contact time 1 hr and T = 20°C)

Effects of solution pH

Adsorption capacity of Congo red (CR) dye adsorbed from solutions were as follows: un-buffered, 59.073 mg g^{-1} pH = 3, 55.786 mg g^{-1}, pH 4, 53.353mg g^{-1}, pH = 6, 25.7095 mg g^{-1}, pH 8 and 6.47123 mg g^{-1}, pH = 10 that result appear in Figure 5. Hence it is clear from the data that the adsorption method is solution pH-dependent, the adsorption efficiency of Congo red (CR) dye adsorbed resting through pH and being at a maximum at pH 3. The electrostatic attraction is a result of the columbia forces among the positive Congo red (CR) dye molecules as well as the active sites with the negative charges on the surface of the adsorbent. Whereas at the lower pH lower about 8–10, protonation of the H+ activity dominated that influenced the adsorbents' surface for reaching a positive charge, the active adsorbent surfaces and repulsion reaction among the Congo red (CR) dye molecules[15-18].

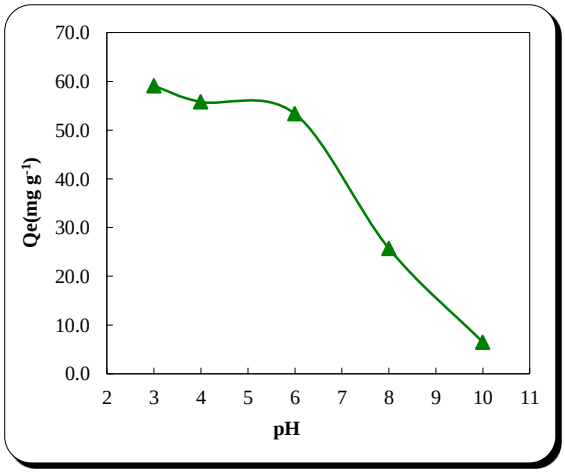

Figure 5. Effects of solution pH on the CR dye adsorption on AC. (optimum Condition: concentration = 30 mg L^{-1}, a mass of AC 0.05 gm and T. = 20°C).

Effects of temperature

Notably, that the percentage removal of GR dye has been studied at a temperature of 10, 15, 20 and, 25°C. the changing temperature has a proportional effect on the adsorption efficiency (Figure 4). In this study, the GR dye adsorption capacity raised as from 58.1723 to 50.1917 as the temperature enhanced from 10°C to 25°C. Figure 6 presents the enhanced adsorption rate by elevating the temperature, which shows the reaction is exothermic (see Table 1) and increases the propagation speed of the adsorbate samples on the outer surface of the adsorbent by reducing the solution speed. Furthermore, the enhanced temperature elevates the mobility of the dye molecules, which enhances the number of the adsorbate molecules interacting with the surface effective sites [12, 19]

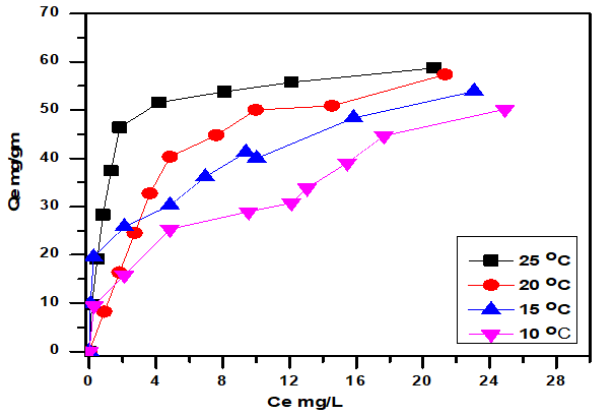

Figure 6. Adsorption isotherms of Congo red (CR) dye on PLAC at several temperatures.

Table 1. Effect of temp. on highest adsorption of Congo red (CR) dye on PLAC.

T (°C)	T(k)	C_e=12	
		X_m	lnX_m
10	283	55	4.007
15	288	50	3.912
20	293	42	3.737
25	298	30	3.401

thermodynamic parameter variables like variations of the (ΔG) free energy, change of enthalpy (ΔH) ,and Change entropy (ΔS) (Table 2)

$$K_d = \frac{q_e}{C_e} \qquad (3)$$

where Kd is equilibrium constant, C_e and QE, concentrations of the equilibrium CR, are the solution (mg L^{-1}) and absorbent (mg g^{-1}) concentrations, in the same order. though, changes in ΔG maybe estimated via equation 4:

$$\Delta G = RT \ln K_{eq} \qquad (4)$$

the (ΔH) change in enthalpy is estimated via the equation 5 :

$$\ln K_e = \frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (5)$$

Table 2. Variations in enthalpy (ΔH), free energy (ΔG), as well as variations in entropy (ΔS) for GR, are absorbed on the AC.

T(K)	ΔG^o/KJ mol^{-1}	ΔH^o/KJ mol^{-1}	ΔS^o/JK^{-1} mol^{-1}	K_{eq}
283	-3.582			
288	-3.417	-27.823	64.514	1750
293	-3.051			
298	-2.270			

Adsorption isotherms

Numerous isotherm equations are existing for investigating the sorption equilibrium factors, and the most public being is the isotherms Langmuir, isotherm Freundlich, and isotherm Temkin. The isotherm Langmuir (Figure 7A) is built on the theory that there is a fixed quantity of active sites, which are regularly dispersed over the surface of the adsorbent; these sites have identical desirability for adsorbing a mono-molecular layer and do not have any interactions among adsorbed molecules. Moreover, isotherm Freundlich (Figure 7B) is applicable for heterogeneous surface adsorption. This isotherm positive relationship between adsorbate concentration and adsorbent quantities on the surface. Similarly, the energy sorption proportionally declines at the end of the sorption centers of the adsorbent. Isotherm Timken (Figure 7C) comprises an element that considers interactions of adsorbent-adsorbate. By disregarding the meager and important value of concentrations, the model supposes the adsorption heat of all molecules in the layer linearly decreases instead of the logarithmic with the coverage. Calculation of (R2) was done by fitting the experimental equilibrium result for the dye- AC system utilizing Langmuir, Freundlich, and Timken isotherms. Figures 7 and Table 3 appear the highest (R^2 = 0.9994) related to the model Langmuir [20-22].

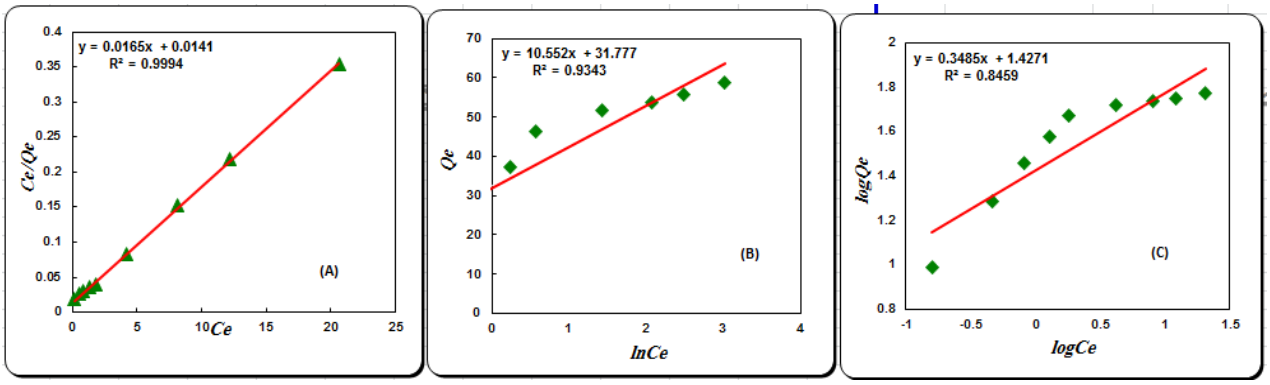

Figure 7. Isotherm Langmuir (A), Isotherm Freundlich (B), and Isotherm Temkin (C) of CR dye adsorption on AC.

Table 3. Correlation coefficient and constant of Langmuir, Freundlich, and Timken of adsorption CR dye adsorbed on PLAC at 20°C.

Langmuir equation			Freundlich equation			Timken equation		
K_L	q_m	R^2	K_F	n	R^2	K_T	B	R^2
60.6060	1.17021	0.9994	5.9831	0.09476	0.9343	60.0380	0.3485	0.8459

Effect of kinetics and equilibrium time

After all other factors' steadiness, the Congo red (CR) adsorption was studied at different times 5 to 220 mint. In Figure 8, the adsorption efficiency of Congo red (CR) was augmented as the time elongated until reaching maximum value (saturation state); after that, the adsorption amount reductions through increasing time due to a desorption method. The kinetics models of the adsorption method, which define the experimental result, elected for adsorbing the CR dye on the PLAC shown in Figure 8. Experimental result investigation was done utilizing the Kinetic first model as well as Kinetic second order. Table 4 results display adsorption of the CR via the AC is an achievable method because the value of (R^2) was shown to be high for the kinetic first order compared to the kinetic second order [23, 24].

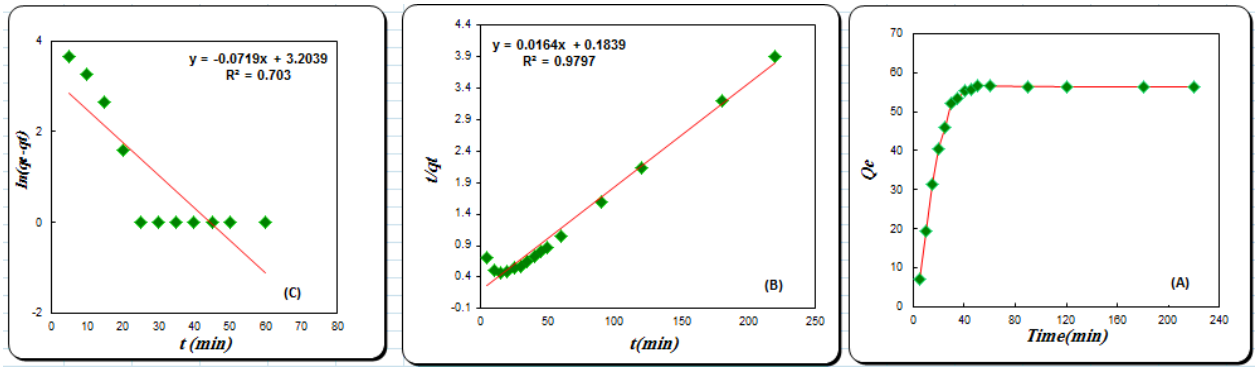

Figure 8. The effects of reaction time (A), first-order (B) and, second-order on Congo red (CR) dye.

Table 4. Adsorption kinetics factors of the adsorption of the CR.

Kinetic First-order					
Slope	**Intercept**	**k_1 $(min)^{-1}$**	**QE (mg g^{-1})**	**R^2**	
0.0164	0.1839	-0.0164	1.20189	0.9797	
Kinetic Second-order					
Slope	**Intercept**	**QE$(min)^{-1}$**	**k_2 (g.mg.min^{-1})**	**H**	**R^2**
0.0719	3.2039	-13.9082	0.001614	0.31212	0.703

CONCLUSIONS

In its broadest sense, active carbon contains various amorphous carbonaceous materials with increased porosity and widened inter particulate surface areas. it is provided by combustion, partial combustion, and thermal decomposition of diverse carbonaceous materials. As mentioned earlier, our research thoroughly reviewed the dye processing industry, the respective basic features, as well as common environmental implications. In addition, we presented a summary of the main advancements in the recommended precursors and activated agents, the impact of the dose of adsorbent, contact time, concentration, pH, isotherms, and kinetic. studies for dye adsorption over AC and, temperature[15].

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Conflict of interest

There are no conflicts to declare.

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