Comparative Study of Direct Red 81 Sorption using Date Pits Waste

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Abstract: - This study evaluates the ability of recycled date pit waste for dye sorption. The potential of natural date pits waste (NDP) to remove direct red 81 from an aqueous solution was compared with activated date pits (ADP) and commercial activated carbon (CAC). The effect of operating parameters such as initial pH, initial dye concentration, and contact time were investigated in batch system. The maximum capacity of sorption reaches 3.06 mg/g 1.29 mg/g and 19.23 mg/g for (NDP); (ADP) and (CAC), respectively, showing the potential of natural date pits to direct red 81 removal. The pseudo-second-order kinetic model has proved favorable for (RD81) sorption by (NDP), (ADP), and (CAC). The prepared materials were analyzed using FT-IR spectroscopy before and after direct red 81 sorption, to detect the major functional groups related to the sorption process.

Key-Words: - Date pit waste; dye removal; direct red 81; commercial activated carbon; sorption; kinetics; modelling.

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1 Introduction

Date palm, (Phoenix dactylifera) is a tree of the palm family (Arecaceae) cultivated for its sweet edible fruits called dates. The species is widely cultivated in northern Africa, the Middle East, and South Asia, and is naturalized in many tropical and subtropical regions worldwide, [1]. However, from a more industrial point of view, Algeria is one of the world leaders in the field of date production. This emerging sector enhances value to dates and creates value-added products by transforming them into a number of products, such as sugar, alcohol, vinegar, forage, jam, drinks energy, cosmetics, bread yeast, etc. The main by-products in date production are date pits (DP) from date consumption and the processing industry, which represent about 10-15 % of the total mass of fruits, [2]. The processing of date pits biomass has shown its wide use for several applications such as production of animal feed, [3], as activated carbon for energy, [4], and much more in water treatment, [5], [6]. Their use in human food remains very poorly explored, with the single exception of a few traditional applications which have been developed in some countries, [7]. Natural materials based on agricultural wastes have attracted more and more interest for eco-friendly materials and environmental care due to their renewable nature, biodegradability, economic feasibility, and eco-balance benefits. The method of synthesis of these materials and their application as sorbents represent a novelty in this field of science. For the water treatment sector and in comparison to commercial activated carbon for removing various toxic pollutants, including metals and dyes, agricultural waste is a valuable resource with a great potential for reuse, [8]. Based on recent advances, dye removal from wastewater and industrial aqueous effluents is a much-explored area of research. In general, the use of agricultural waste for dye sorption is closely related for its chemical composition and the availability of numerous functional groups including hydroxyl, aldehyde, carbonyl, carboxyl and phenolic, which allow them to interact with pollutants present in wastewaters through a variety of binding mechanisms and interactions, [9]. According to the literature review, azo dyes are commonly characterized by the presence of the azo functional group (N=N) linking two identical or non-identical alkyl groups (symmetrical or dissymmetrical azo). They are toxic, carcinogenic, and recalcitrant to biological treatments. These dyes are the most widespread in terms of application, representing more than 50% of the world's dye production, [10]. They are widely used in the dyeing of textiles and in the printing industry, plastics, surface treatment, and other materials. The effluents from textile industries are extremely concentrated in dyes. In general, coloring waters present problems related to color, temperature, high concentration of biological oxygen demand (BOD5), chemical oxygen demand (COD), and suspended solids (SS), as well as toxicity and high conductivity. Increasing demands for natural resources and environmental protection (discharge standards, taxes, etc.) require manufacturers to adopt appropriate pollution control to reduce the impact of dyes on the environment. The industrials have a choice of three possibilities for treating aqueous effluents. Depending on the case, discharges of azo dyes and their byproducts into the natural environment after treatment by an independent treatment plant (internal to the industrial site). On the other hand, after pretreatment on the industrial site, the wastewater is discharged into a sewage plant via a municipal or urban wastewater treatment plant before being discharged into the natural environment. Therefore, the treatment of industrial dyeing wastewater can be performed by biological, chemical, or physical methods, [11], [12]. Among these methods for textile dyes removal, the one selected method is often related to operating costs and ease of design.

In this study, direct red 81 as a coloring agent, is a most common azo dye in textile industry and was used as one of the case studies to investigate the potential application of date pits (DP) as a dye sorbent. One of the main objectives of this study, date pits were used as a sorbent to remove direct red 81 from an aqueous solution via batch sorption experiments under experimental conditions including pH, initial dye concentration, temperature, and contact time. Kinetic parameters were determined.

2 Experimental

2.1 Materials

2.1.1 Dye

The azo dye direct red 81 (C29 H19 N5 Na_2 O_8 S_2) and M = 676 g mol^{-1} obtained from Sigma-Aldrich company (Figure 1). The stock solution (1000 ppm) of direct red 81 (DR81) was prepared by dissolving the dye in 1000 mL of demineralized water (Milli-Q). Standard solutions of the selected concentrations were prepared by appropriate dilution. Dye concentration was measured using a spectrophotometer (UV–visible Thermo ELECTRON CORPORATION) at a wavelength of 510 nm.

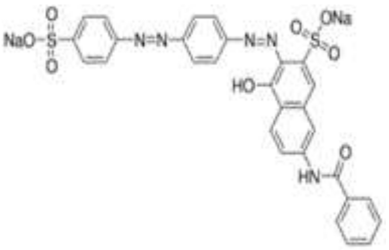

Fig. 1: Chemical structure of Direct red 81

2.1.2 Reagents

All chemicals and reagents used in this work are of analytical grade purity. The solutions were prepared using demineralized water (Milli-Q). The following reagents were used without further purification: Phosphoric acid (H_3PO_4, 85%) from Sigma-Aldrich. The solution pH was adjusted using appropriate amounts of 0.1 M (HCl/NaOH) purchased from Fluka.

2.1.3 Sorbents

2.1.3.1 Date Pits Waste

The date pits waste were collected from Daglet nour of Ouled Djallal region (Southwest of Algeria). The collected material was first washed with tap water to remove particles, before being dried in sunlight for a week. The dried material was then crushed into powder. The date pits (DP) were sieved to form different particle sizes from small to large as : G1 (<125 µm), G2 (125–250 µm), G3 (250–500 µm), G4 (500–710 µm), and G5 (710–1000 µm). In this study, the G2 fraction was used as the reference size material.

2.1.3.2 Preparation of Activated Carbon

Activated carbon was synthesized by chemical activation of date pits. H_3PO_4 (20%) during 90 minutes. The impregnated material (PO/H, H_3PO_4) was carbonized under airflow for 3 h at 600 °C and the final product was filtered after several washings with distilled water and drying at the ambient temperature. The obtained activated date pits are treated with HCl (0.1 N) and placed at room temperature for 90 minutes. The collected material is first washed several times with tap water and then with distilled water until neutral pH. Once washed, the samples are drained and dried in an oven at a temperature of 105°C about 24 h. Activated date pits (ADP) were conserved in closed bottles until use. For comparison, a commercial activated carbon (CAC) was used in this study as granular, (12-20 mesh) purchased from Sigma Aldrich with surface area. of 650 $m^2.g^{-1}$

2.2 Sorption Experiments

The effect of some parameters: pH, contact time, and initial concentration of dye was examined on the prepared sorbent by varying parameters and carried out in batch sorption. The sorption experiment was obtained using experimental set up as previously described, [13], [14].

To investigate the effect of pH on direct red 81 sorption, the pH was ranged from 2.0 to 7.0 with an initial dye concentration of 10 mgL^{-1} and a sorbent concentration of 1 g L^{-1}. The solutions are stirred at 150 rpm for 24 h. The pH solution was measured using the pH-meter OHAUS (STARTER 3100) and adjusted during the experiments to the desired value using a molar solution of HCl or NaOH. The equilibrium time for maximum sorption was studied in conical flasks (250 mL) of dye solutions (5, 10, and 25 $mg.L^{-1}$) at different time intervals by adjusting the pH to a value of 2-3 with either molar solution at a constant speed of 150 rpm at 25 °C. At each time, samples are filtrated and the absorbance data of the filtrates were analyzed using UV–visible spectrophotometer of the Thermo ELECTRON CORPORATION to evaluate residual dye concentration (C_{eq}). For the sorption isotherm experiments, the sorption efficiency of direct red 81 and the sorption capacity of different sorbents (NDP, ADP, and CAC), were studied using 100 mL conical flasks containing 50 mL of dye solutions at the desired initial dye concentration and pH. The sorption capacity (q, mg DR81 g^{-1}) was calculated by using a mass balance with the following equations:

$$q_{eq} = (C_0 - C_{eq}) \times V/m \quad (1)$$

$$\%\text{sorption} = (c_0 - c_e) \times \frac{100}{c_0} \quad (2)$$

C_0: initial dye concentration in mg/L.
C_e: final dye concentration at equilibrium mg/L.
m: mass of biomass in g.
V: volume of dye solution in L.

3 Results and Discussions

Figure 2, shows the UV absorption spectra profile of direct red 81 used in this work. By examining Figure 2, UV–Vis absorption spectroscopy was used to determine the maximum absorbance (maximal wavelength λmax), of direct red 81, represented by λmax = 510 nm.

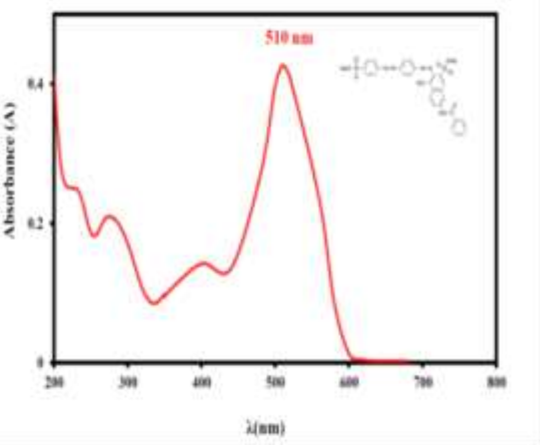

Fig. 2: Sorption spectra of Direct Red 81

3.1 pH Effect on Direct Red 81 Sorption

pH solution is an important parameter in the sorption process as it acts directly on the surface charge, the degree of ionization of dye as well as the dissociation of functional groups of the available active sites on material surfaces. Figure 3 shows the effect of pH on sorption capacity of direct red (DR81) by natural date pits (NDP), activated date pits (ADP) and commercial activated carbon (CAC): the variation of pH on the adsorption of (DR81) (a), adsorption capacity (b) and sorption yield (c), studied under similar operating conditions, temperature T: (25 °C), C_0:10 mg DR81 L^{-1}. As depicted in Figure 3, the removal of direct red (DR81) decreased, with increasing pH solution. It can be seen, that natural date pits (NDP) have approximately the same sorption capacity as the prepared activated date pits (ADP) from pH 2 up to pH 7. In short, comparing the sorption capacity, it was noted that the acidic condition in the range (pH = 2 and 3) was most suitable for (DR81) sorption by (NDP, ADP, and CAC) respectively. However, the removal efficiency of direct red 81 (DR81) at pH 2 is 91.42% for natural date pits (NDP) while for activated date pits (ADP) the efficiency decreases significantly and reaches 17.73% for an optimum pH equal to 3. The removal of (DR81) by (CAC) is optimal at pH 3 with removal efficiency equal to 84.33%. According to the literature research, date pits have an acidic character (the pH zero charge point pHpzc is equal to pH=5.9 and 4.01 for natural date pits and activated carbon, respectively), [15]. Meanwhile, if the pH is higher than pHpzc, the surface of the date pits is negatively charged which favors the attraction of cations and the opposite occurs when the pH value is lower than pHpzc. Therefore, for this study, the optimum adsorbate solution at pH condition was established at pH 2.0 for natural date pits (NDP) and pH 3.0 for (ADP) and (CAC).

3.2 Isotherm

To describe the adsorption process of DR81 dye on the studied materials for our experimental results, the sorption isotherm was analyzed by both empirical Langmuir and Freundlich models respectively, [16], [17]. The batch isothermal data relating to the equilibrium concentrations of the dye adsorbed onto the materials are shown in Figure 4. The relevant fitting parameters and correlation coefficients obtained for the adsorption of DR81 are summarized in Table 1. It is clear that (CAC) had the highest sorption capacity for direct red 81 solution. The maximum adsorption capacity q_m, as obtained by (CAC) was about 19.23 mg g^{-1} and decreased from 3.06 mg g^{-1} in (NDP) to 1.29 mg g^{-1} for (ADP).

The following equation was used for Langmuir isotherm model :

$$q_e = K_f C_e n \tag{3}$$

where q_e (mg/g) and C_e (mg/L) represent solid-phase and liquid-phase concentrations of solute at sorption equilibrium condition, respectively; K_f ((mg/g)/(mg/L)n) is sorption coefficient; n is linearity index. Values where n >1 represent favorable adsorption conditions. In most cases the exponent between $1 < n < 10$ shows beneficial adsorption. A linearized expression of the Langmuir model [14] follows as equation (4) :

$$\frac{1}{q_e} = \frac{1}{k_l q_0} + \frac{1}{c_e} + \frac{1}{q_0} \tag{4}$$

where q_0 is a constant related to the area occupied by a monolayer of sorbate, reflecting the maximum sorption capacity (mg g^{-1}), C_e is the equilibrium liquid-phase concentration (mg L^{-1}), K_L is a direct measure of the intensity of sorption (L mg^{-1}) and q_m is the amount sorbed at equilibrium (mg g^{-1}). A linearized form of the Freundlich model, [15], is represented by equation (4):

$$logq_e = \log K_F + \frac{1}{n}\ logC_e \tag{5}$$

where K_F ((mg/g) (L/mg)1/n) and n are Freundlich constants integrating all factors affecting the adsorption process such as adsorption capacity and intensity, respectively. The dependence of the direct red 81 uptake (q_e) on the equilibrium concentration (C_e) in aqueous solution and the Langmuir and Freundlich isotherm plots of direct red 81 sorption onto natural date pits (NDP), activated date pits (ADP) and commercial activated carbon (CAC) at 25 °C and pH 2-3 are shown in Figure 4 (a, b).

Under our experimental conditions, we conclude that activation of material has no significant impact on the prepared adsorbent. As a result, we can say that the prepared adsorbent is still sufficient for low dye concentrations, particularly if we compare our results with a commercial activated carbon, which has an average q_m. From the values of R^2, it can be seen from the fitting results that the sorption behavior of dye (DR81) on the different date pits samples is highly consistent with a higher R^2 value ($R^2 > 0.99$). In the present work, sorption data is well fitted by Freundlich isotherm equations, suggesting that the surface of the materials is energetically heterogeneous and multi-layer sorption. This model considers that there are different types of adsorption sites with different energies but with the same entropy, distributed according to an exponential distribution as a function of adsorption heat. The adsorption of direct red (DR81) dye using the natural date pits (NDP), activated date pits (ADP), and commercial activated carbon (CAC) is compared with other reported materials in Table 2.

Table 1. Isotherm parameters for direct red 81 sorption

Sorbent	**Langmuir**			**Freundlich**		
	q_m ($mg.g^{-1}$)	**K_L ($L.mg^{-1}$)**	**R^2**	**n_f**	**k_F ($mg.g^{-1}$)**	**R^2**
Natural date pits (NDP)	3,067	2,99	0,745	3,52	1,455	0,952
Activated date pits (ADP)	1.29	0.525	0.890	1.4	0.99	0,898
Commercial Activated Carbon (CAC)	19,23	0,426	0.962	1,845	6,924	0,64

The sorption capacity of direct red 81 found to be 120.48 mg.g^{-1} using soy meal hull, [18]. Besides that, a significant results on the direct red 81 sorption was 23.83 mg.g^{-1} obtained by Cross-linked chitosan bead, [19]. Sorption of direct red 81 on *Xanthuim strumarium* demonstrated a sorption capacity of 14.67 mg.g^{-1} at pH 3, [20]. The maximum sorption capacity under optimal conditions was found to be 13.83 mg.g^{-1} and 6.43 mg.g^{-1} for both treated bamboo dust and natural bamboo dust respectively, [21]. On the other hand, the waste from banana pith were inspected and the maximal direct red 81 sorption capacity was 5.92 mg.g^{-1}, [22]. The lowest sorption capacity of 1.83 mg.g^{-1} at pH 3 was obtained with Pumice stone, [23]. For sorption properties using *Argemone mexicana*, sorption capacity was 16.21 mg.g^{-1}, [24].

3.3 Sorption Kinetics

The effect of contact time on the prepared material compared to commercial activated carbon is shown in Figure 5. The adsorption kinetics profile is marked by the presence of two phases. Red direct 81 sorption by (NDP), (ADP) and (CAC) respectively is rapid in the first 60 min, and the adsorption capacity increase progressively during the next 360 min with a slow rate to equilibrium. The first phase is rapid and due to the presence of several active sites on the surface of adsorbent. A second, slower phase is also observed when the adsorption sites are saturated, which requires diffusion of the adsorbate within the pores of the adsorbent and achieves equilibrium. The values of the rate constants of the pseudo second order model k_2 for the Direct Red 81 dye (DR81), decrease from 0.0065 to 0.0017 mg g^{-1}min^{-1} for activated date pits (ADP), and from 0.006 to 0.00038 mg.g^{-1} min^{-1} for commercial activated carbon (CAC). The activated date pits (ADP) and commercial activated carbon (CAC) show that the pseudo-second-order kinetic model has a better correlation coefficient R^2. As a result, the model, [25], is the most suitable for expressing the order of dye (DR81) adsorption kinetics at various initial concentrations (Table 3).

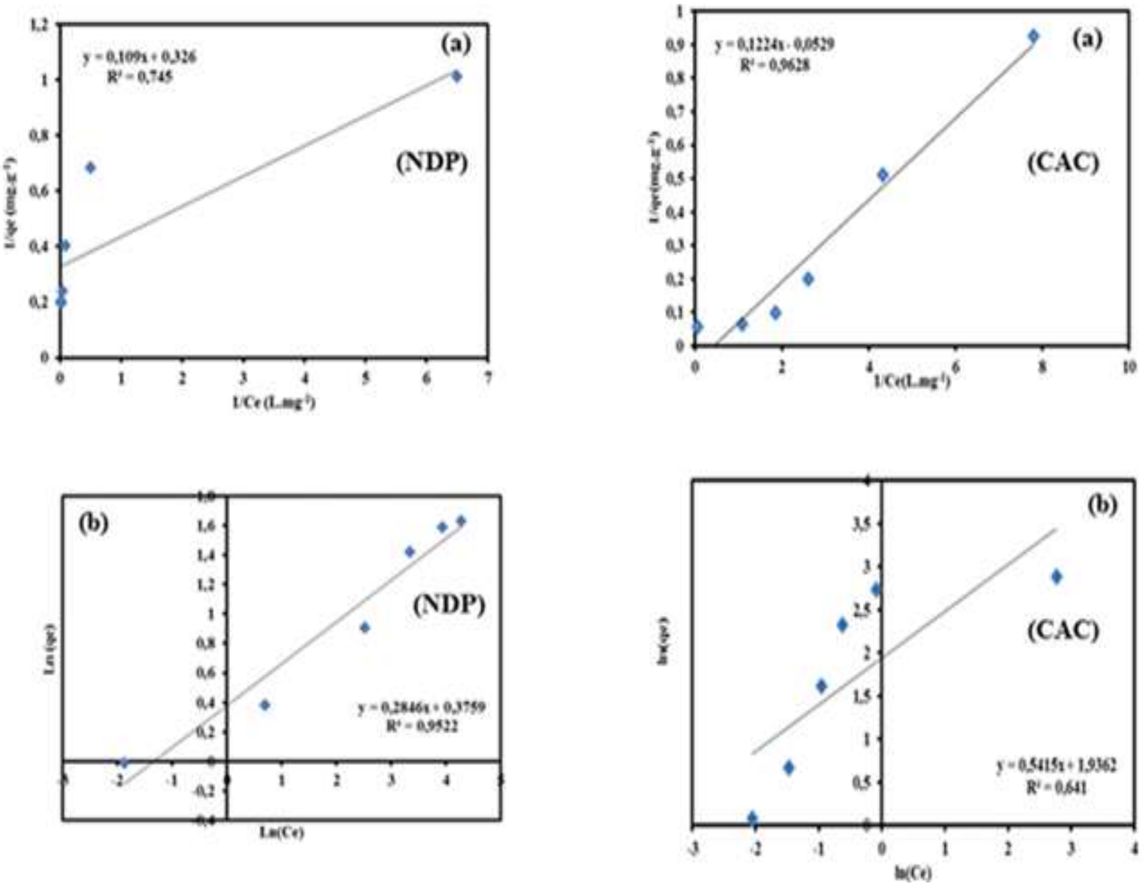

Fig. 4: The plots of the experimental data for direct red 81 sorption onto prepared sorbent using (a) Langmuir, and (b) Freundlich isotherm models

Table 2. Comparison of direct red 81 (DR81) for different sorbents

Sorbent	**Sorption Capacity q ($mg.g^{-1}$)**	**pH**	**References**
Natural date pit	3.06	2	In this study
Activated date pit	1.29	3	
Commercial activated carbon	19.23	3	In this study
Soy meal hull	120.48	3	**[18]**
Cross-linked chitosan bead	23.83	4	**[19]**
Xanthuim strumarium	14.67	3	**[20]**
Treated bamboo dust	13.83	2	**[21]**
Natural Bamboo dust	6.43	2	
Banana pith	5.92	2	**[22]**
Pumice stone	1.83	3	**[23]**
Argemone mexicana	16.21	2	**[24]**

Table. 3 Sorption Kinetic constant parameters at various dye concentrations

Sorbent	**C_0 ($mg.L^{-1}$)**	**Pseudo-Second-Order (PSO)**				
		q_e ($mg.g^{-1}$)	**q_m ($mg.g^{-1}$)**	**k_2 ($mg.g^{-1}min^{-1}$)**	**h ($mg.g^{-1}min^{-1}$)**	**R^2**
Activated date pits	**5**	2,28	2,18	0,0065	0,034	0,96
	10	3,73	3,53	0,003	0,044	0,988
	25	5,376	5,00	0,0017	0,0497	0,921
Commercial Activated Carbon	**5**	5,15	5,26	0,006	0,166	0,995
	10	9,9	9,58	0,002	0,2118	0,991
	25	22,22	20,55	0,00038	0,19	0,935

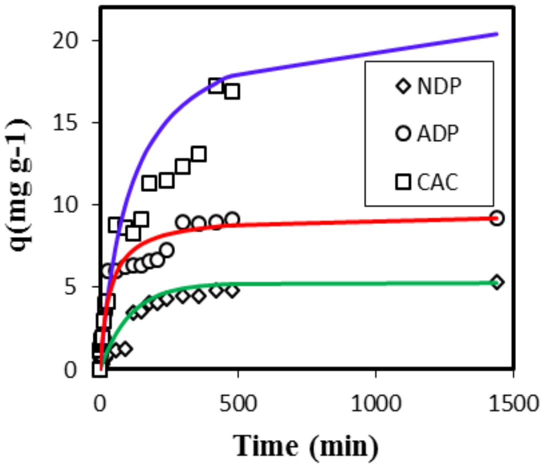

Fig. 5: Effect of contact time on direct red 81 (RD81) removal efficiency by prepared materials at pH 2-3 for an initial concentration of 25 mg/L

3.4 FTIR Studies

Fourier transform infrared spectroscopy (FT-IR) is an analytical method used to determine the amount of light absorbed by the material as a function of wavelength. In this study, FT-IR measurements were performed before and after dye sorption, to identify a number of absorption bands corresponding to different functional groups (Figure 6). The FT-IR spectroscopy of the synthesized materials are shown in Figure 6. The absorption bands show the presence of alkane, aldehyde, aliphatic, ketone, aromatic, alkyle, nitro, and ester groups in the prepared adsorbents. The peak obtained at 2964 cm^{-1} and 2970 cm^{-1} indicates the symmetric and asymmetric C-H stretching vibration with high intensity belonging to the alkane groups (CH_3). In the range 2880 cm^{-1}, we notice the presence of a weak intensity attributed to aliphatic -C-H groups with a C-H bond. On the other hand, we observe an absorption of variable intensity at the region 1696 cm^{-1}, which confirms the existence of the band C=O attributed to aromatic ketone groups. Additionally, we also note the presence of four bands of average intensity located at 1575 cm^{-1} attributed to a C=C band related to aromatic groups. The appearance of a C-O bands with strong intensity located at 1212 cm^{-1}, suggests the existence of an acid group and the presence of primary alcohol groups of variable intensity. Analysis of the spectra of activated date pits (ADP) and commercial activated carbon (CAC) after adsorption of Direct Red 81 (DR81) shows an almost similar profile as it does not show any distinct peaks / absorption changes in the spectrum. According to [26], this type of profile explains that there were no substantial changes on the adsorbent surface before and after dye sorption. Based on the above results, several possibilities can be generated between materials and dye, involving hydrogen bonding and electrostatic interaction.

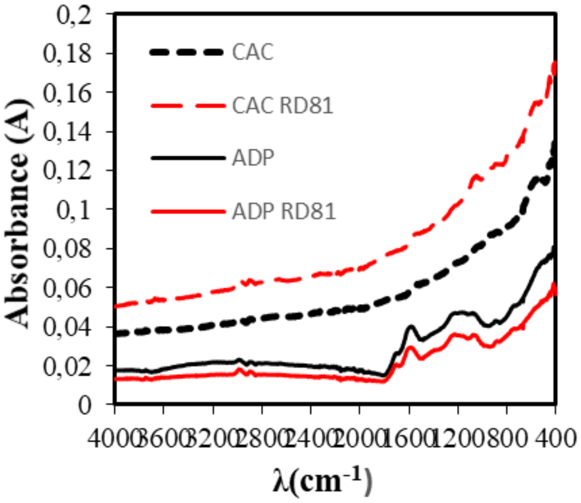

Fig. 6: FT-IR Spectra of the selected material before and after direct red 81 (DR81) sorption

4 Conclusion

Solid waste of date pits from date palm have been tested as a resource to obtain renewable sorbents for the removal of textile dyes from aqueous solutions. The experimental study showed the role of the main parameters controlling the sorption process including pH, contact time, and dye concentration. For direct red 81 sorption, we noted that increasing pH induces a decrease in the sorption capacity by natural date pits (NDA); activated date pits (ADP); and commercial activated carbon (CAC) respectively which indicates that the sorption system involves electrostatic interactions which is the most important mechanism. From the kinetic profiles, we can conclude that the process is relatively fast from the very first instants for the selected material and follows the pseudo second-order reaction. This work opens up several possibilities for research and development of new sorbents from natural and renewable origin. However, a new conditioning and design in perspective should make it possible to treat effluents from the textile industry with low dye concentration compared with a commercial activated carbon (CAC).

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