

The bio-material as sorbent for 2,4-Dichlorophenoxyacetic acid removal from aqueous solution

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ABSTRACT

Abstract: The purpose of this study is to focus on the elimination of organic pollutant 2,4-D pesticide from water by using an activated carbon resulting from date pits was prepared, first, by pyrolysis at 700 °C under 100 cm³ min⁻¹ nitrogen flows for 2h and then, activated under N₂/H₂O at 700 °C for 3h. The activated carbon obtained were characterized using Infrared Spectroscopy (FT-IR), Thermogravimetric analysis (TGA), Scanning electron microscopy (SEM). This activated carbon was realized on adsorption of pesticide acid (2,4-D), the obtained adsorption capacity was 56,03 mg/g at ambient temperature T=20°C and 24 h equilibrium contact time. The Langmuir and Freundlich isotherm models were applied for this study. The isotherm data could be well described by Langmuir equation.

I. Introduction

Water pollution is the contamination of water bodies such as lakes, rivers, oceans, and groundwater by human activities [1]. Water pollution by pesticides results from agriculture activities; The role of pesticides is to kill the insect-pests, and weeds but this property of pesticides makes them a poison to other organisms including different birds, fish species, animals and humans. [2] Pesticides can be eliminated from water in different ways, most frequently by adsorption on granular activated carbon (GAC) and/or by ozonation [3]. However, due to the high cost of commercial activated carbon, its use in the field is sometimes restricted on economic considerations. Moreover, the high cost associated with its regeneration led to exploring new inexpensive materials [6,7]. This has been the thrust of this work aiming at preparing renewable agricultural by-product activated carbon. Most activated carbon are made from raw materials (biomass) and valorization to low-cost adsorbent such as coffee grounds [8], cotton stalk [9], nutshells, peach

stones, olives stones [12], oranges peel, bananas peels ...etc.[4][10], they can be prepared by physical or chemical activation. Activated carbon produced by physical activation is obtained after two steps: the first one is the carbonization so-called pyrolysis of carbonaceous material at high temperature (500–1000°C) in inert atmosphere in order to eliminate the maximum of oxygen and hydrogen elements [4]. The second one is the thermal activation at the similar temperature as for pyrolysis or at a higher temperature in the presence of oxidizing gas such as water, carbon dioxide or both [4][11].

In this study; date pits (DP) was pyrolysed and activated for removal of the pesticide acid (2,4-D) by adsorption. Parameters such as adsorbent masses, pH and contact time, were investigated at room temperature. While the adsorption isotherm data were used to analyze the adsorption process.

II. Materials and methods

II.1. Adsorbate

2,4-D Dichlorophenoxyacetic acid commercial formulation consisting of 600 g/L 2,4-D Ester butyl glycol.

Table 1. Physical property of pesticide acid

Chemical formula	C ₈ H ₆ Cl ₂ O ₃
Formula weight(g/mol)	221.04
Solubility in (water mg/L)	900
UV absorption λ _{max} (nm)	284

II.2. Sorbent

Activated carbons were prepared from biomass of Algerian date pits; they were obtained from the pastry date manufacturing.

First, the pits were washed, and dried at 105°C for about 24 h. Then, they are ground to grind between 1 and 4 mm and sifted; The gotten grains are impregnated in an acid sulfuric solution (H₂SO₄ at 60 %), washed with distilled water until neutral pH, dried at 105 °C during 24 hours; The clean pits were kept in a desiccator to protect them from moisture. The precursor is pyrolyzed and activated out under nitrogen flow in a horizontal tubular furnace. The reactor was a quartz tube which was placed in the furnace [4]. For all the pyrolysis operations, about 20 g of entire date pits were placed in the middle of the reactor for pyrolysis at 700 °C under 100 cm³ min⁻¹ nitrogen flows for 2h and then, activated under N₂/H₂O at 700 °C for 3h. Some initial characteristics of date pits were determined in Table 2; [4].

Table 2. Some characteristics of date pits used in adsorption

Parameter	Value
density (g.cm ⁻³)	0,32
Moisture (%)	9
pH	6,67

II.3. Adsorption characteristics

The adsorption process has many advantages such as: low-cost of adsorbent, easy application, utilization of biomass origin agricultural vegetable waste (bio-material) as adsorbents. The experiments were conducted in the system "Batch": we added to 250 ml of 2,4-D a dose of activated carbon (DPAC) and we stirred for 24 hours at a speed of 200 tours / min. Spectro-photometer (1800 SHIMADZU) was used to measure the concentration of 2,4-D. The amount of organic compounds adsorbed per gram of adsorbent (qt, mg/g) at time (t) and the percent adsorption (R, %) are given by the following relations Eqs. (1) and (2) [13]

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where C₀ is the initial 2,4-D concentration and C_t is the 2,4-D concentration (mg·L⁻¹) at any time t, V is the volume of the solutions (L) and m is the mass (dose) of the used adsorbents (g).

II.4. Adsorption isotherm models

Langmuir and Freundlich are the two frequently used isotherm models to represent the adsorption data. The Langmuir isotherm model is based on the supposition of monolayer adsorption from the homogenous surface while Freundlich isotherm models assume adsorption from heterogeneous surface, with non-uniform heat distribution on the surface [14]. The Langmuir and Freundlich models can be expressed mathematically by Eqs. (3) and (4) respectively

$$\frac{C_e}{q_e} = \frac{q_e}{q_m} + \frac{1}{K_L} \times q_m \quad (3)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

Where C₀ and C_e (mg/l) are the liquid-phase concentrations of adsorbate at initial and equilibrium, respectively. V is the volume of the solutions (L), and m is the mass of the used adsorbent (g); q_m (mg/g) = maximum adsorption capacity. K_L = Langmuir constant. K_f and n are the Freundlich constants.

II.5. Characterizations

Thermogravimetric analysis (TGA/DTG)

allows for the continuous recording of the mass changes of a sample with linearly increasing temperature. The apparatus used was a 2050 TGA V5.4A from TA Instruments. The thermal evolution of the raw Dates pits (DP) was followed by thermogravimetric analysis (TGA) from room temperature up to 600 °C. The sample to be analyzed had a mass of approximately 20 mg.

Identification of surface functional groups of the raw Dates pits (DP) and the prepared activated carbon (DPAC) was carried out by using **Fourier transform infrared (FTIR) spectroscopy**. The infrared transmission spectra were obtained using a spectrometer of Perkin Elmer (Spectrum One FTIR) in the scanning range of 4000-650 cm⁻¹ and using the KBr wafer technique.

Scanning electron microscopy (SEM) was used to visualize the morphology of the raw materials and

the prepared materials; by using High Resolution Quanta FEI200; Crech Republic.

III. Results and discussion

III.1. Characterization

III.1.1. Thermogravimetric analysis

The (TGA/DTG) thermal curve of raw date pits (DPAC) are showing in **(figure.1)**. TGA analyses exhibit that the process of mass loss contained 5 sections. First, the mass loss 6,03 % resulting in moisture removal happen at 65,54 °C, in the second phase, the process of decomposition attains 39.15% load loss at the maximum rate of 278,69 C°. The third stage was found at 328,90 C° with load loss of 12,48%. After that at 365,25 C° there is a loss of 7,71% of mass, the last mass loss was 6,06%, it occurs at 409,35 °C.

At first, hemicelluloses decompose between (200 and 300 °C), next cellulose (300 and 380 °C) and finally lignin at (180–500 °C) [19, 20].

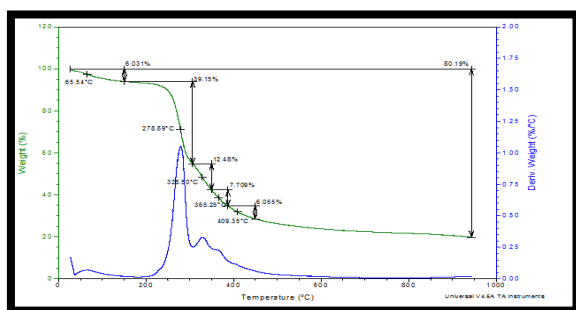


Figure 1. TGA/DTG analysis of raw dates pits

III.1.2. FTIR spectra analysis [21]

The FTIR spectra of raw dates pit (DP) and activated carbon (DPAC) (**figure 2. (a), (b)**)

Spectra of date pits shows many bands characteristic of cellulose, hemicelluloses and lignin, the main compounds of dates pits. Peaks at 3726-3629 and 3400 cm^{-1} are attributed to O-H stretching vibration in hydroxyl groups [4]. The bands observed at 2923, 2852 and 2360 cm^{-1} are assigned to asymmetric and symmetric C-H stretching in alkyl groups and C=C groups respectively [4]-[15]. C=O stretching in aldehydes, ketons groups and esters are observed at 1740 cm^{-1} while the skeletal (C=C) stretching in aromatic rings are observed at 1435 cm^{-1} . The bands at 1365,

1228 and 719 cm^{-1} are assigned to (C-H) deformations in lignin and (C-H) deformation in cellulose [16].

After the thermal activation of dates pits, the peaks between 3726 and 2852 cm^{-1} exhibit an inferior intensity than the raw state because of degradation of water and aliphatic compounds of dates pits. New band assigned to C=C skeletal stretch in condensed aromatic system appeared at 1550 cm^{-1} indicating the increase of aromaticity in the obtained materials.

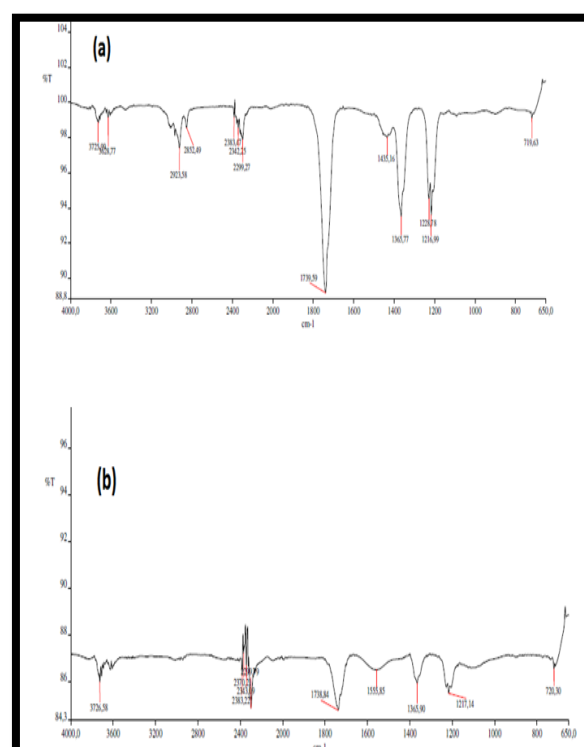


Figure 2. FTIR spectra of DP precursor (a), DPAC (b)

III.1.3. Scanning electron microscopy (SEM)

SEM it have been used to view the surface structure of raw dates pits (DP), activated carbon (DPAC). It can be seen from the **(figure.3 (A))** that the raw date pits have irregular and plugged porous structure but after pyrolysis and activation **(figure.3(B))** a well degaged and regular porous structure is shaped. The development of porosity is attributed to the removal of volatile matters resulting from the decomposition of major compounds of dates pits (cellulose- hemicelluloses and lignin) at high temperature of pyrolysis and activation.

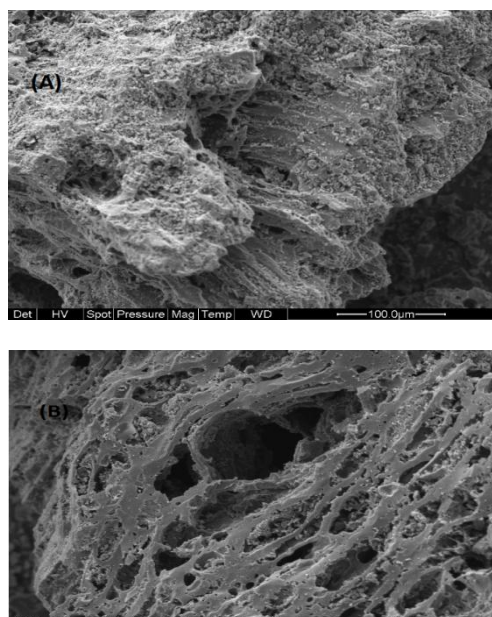


Figure 3. SEM micrographs of: (A) raw DP, (B) DPAC.

III.2. Effect of date pits activated carbon dose

Adsorption process was carried on the dates pits activated carbon (DPAC); according to the tests of 10ppm 2,4-D adsorption on different doses (0,1-0,5-1-1,5-2-2,5) g/250mL of the (DPAC), it was found that the optimal dose was 0.5 g; when the adsorption capacity was remained constant appeared in (figure.4)

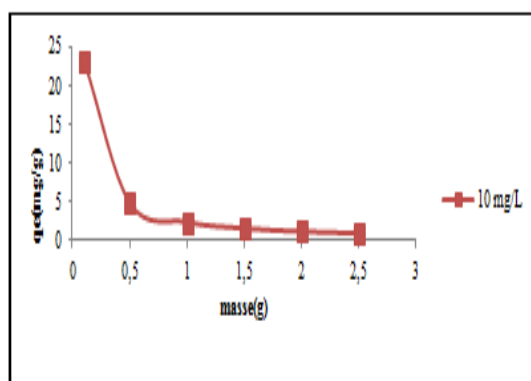


Figure 4. Effect of date pits activated carbon dose ($pH=5.64$, $V=0,25L$, $T=20^{\circ}C$).

III.3. Effect of pH solution

The effect of initial solution pH on the adsorption of 2,4-D is depicted in (Figure.5). It could be observed that there was a decrease in equilibrium adsorption capacity with increasing solution pH. This behavior shows that the adsorption was characterized by some interaction between 2,4-D and DPAC surface. The pK_a of 2,4-D is 2.8 and at pH greater than this, 2,4-D molecule exists

predominantly as the 2,4-D anion. As pH is increased, the degree of dissociation of 2,4-D increased there by making it more negatively charged [5]. Adsorption capacity was best at $pH=2$.

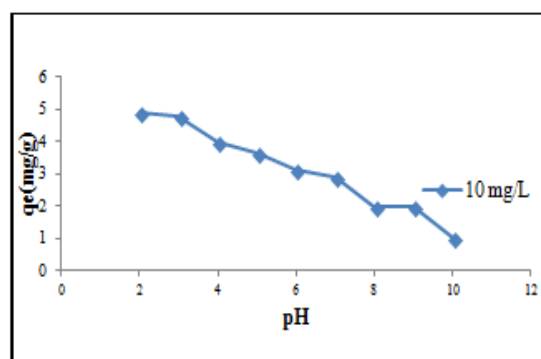


Figure 5. Effect of pH 2,4-D solution ($m=0,5g$, $V=0,25L$, $T=20^{\circ}C$)

III.4. Effects of contact time and 2,4-D concentration

Adsorption was carried on equal mass 0,5 g of DPAC and different concentration (10-30-60-100-150) mg/l at room temperature; the adsorption capacity of 2,4-D increased with increased of initial concentrations (figure.6), after 24h extending the contact time has no effect on the residual concentration of 2,4-D in the solution; this explains the saturation of adsorbent, the maximum adsorption capacity calculated by eq.(1), it was 56,03mg/g .

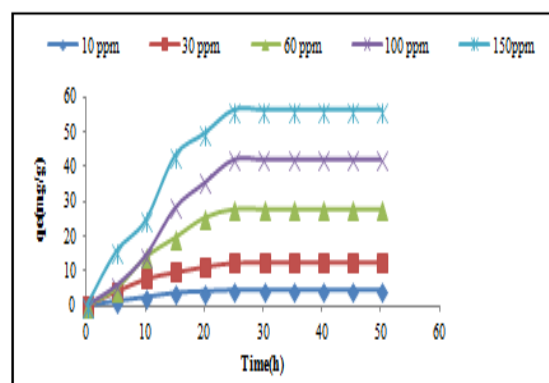


Figure 6. Effect of 2,4-concentration on DPAC adsorption capacity ($pH=2$, $m=0,5g$, $V=0,25L$, $T=20^{\circ}C$).

In (figure.7), the results show that the adsorption removal of (DPAC) from 2,4-D initial concentration (10ppm) was 86.94% calculated by eq. (2) , at contact time 24 h the R% was remained constant .So The equilibrium contact time of 2,4-D adsorption on the activated carbon (DPAC) was 24h .

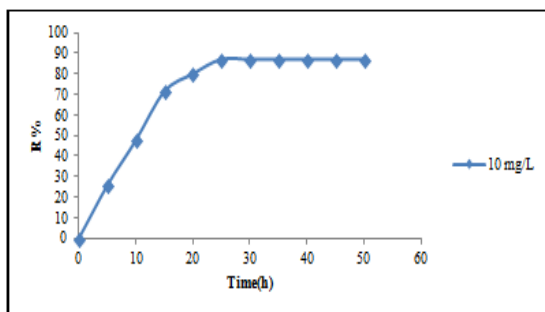


Figure7. Effect of contact time on adsorptive removal ($pH=2$, $m=0,5g$, $V=0,25L$, $T=20^{\circ}C$)

III.5. Adsorption Isotherms

The experimental results obtained on the adsorption of 2,4-D were analyzed by the Langmuir and Freundlich models. Adsorption isotherm of 2,4-D on (DPAC) is reported in (Figure.8); The isotherm in (Figure.8) was of type I, (Figure.8) shows that the fit between experiments and Langmuir model is acceptable. The comparison of correlation coefficients (R^2) of the linearized form of both equations indicates that the Langmuir model yield a better fit for the Experimental equilibrium adsorption data than the Freundlich model. Values of Langmuir and Freundlich parameters are given in **Table 3**.

Table3. Langmuir and Freundlich parameters for the adsorption of 2,4-D in aqueous solution on(DPAC) at room temperature $20^{\circ}C$

Models parameters	DPAC
<u>Langmuir</u>	
q_m (mg/g)	55,5
K_L (L/mg)	0,1961
R^2	0,9611
<u>Freundlich</u>	
K_F (mg/g)	4,4866
n	1,1502
R^2	0,8429

The important characteristics of the Langmuir isotherm can be articulated in terms of a dimensionless equilibrium parameter (R_L) [17, 18]. The parameter is defined by eq. (5)

$$R_L = \frac{1}{(1 + K_L \times C_0)} \quad (5)$$

Where K_L is the Langmuir constant and C_0 (mg/L) is the highest initial 2,4-D.

The parameter R_L indicates the shape of isotherm as follows: $R_L > 1$: Unfavorable; R_L : Linear; $0 < R_L < 1$: favorable; $R_L = 0$: Irreversible [17].

Value of R_L was established to be 0,033 This again confirmed that the Langmuir isotherm was favorable for adsorption of 2,4-D on the (DPAC).

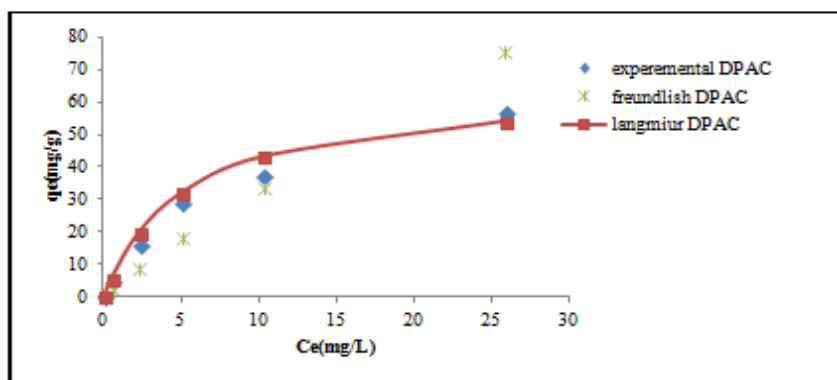


Figure 8. Modeling of adsorption isotherm of 2,4-D on (DPAC) at room temperature = $20^{\circ}C$

IV. Conclusion

From the obtained results, it is evident that the pyrolysis at 700 °C under 100 cm³ min⁻¹ nitrogen flows for 2h and then, physical activation under N₂/H₂O at 700 °C for 3h of date pits is a good process to obtain an activated carbon adsorbent for removal of 2,4-Dichlorophenoxyacetic acid from aqueous solution; the prepared activated carbon was characterized by following methods: ATG showed that 700 °C can be the temperature of pyrolysis and activated carbon for date pits; FTIR spectroscopy has been shown the presence of cellulose, hemicelluloses and lignin in the raw material, after pyrolysis and activation the spectra show clearly the presence of different oxygen groups besides olefin, aliphatic and aromatic carbon structure. SEM examination of raw date pits; date pits activated carbons shows that the porosity increases gradually after pyrolysis and activation. The isotherm study indicates that adsorption data can be adequately modeled by Langmuir. We have demonstrated that agricultural wastes, specifically date pits, may be used as raw materials or bio-material to produce inexpensive and efficient activated carbons or low-cost adsorbent.

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