

ELIMINATION OF NICKEL (II) IN WATER WITH DIFFERENT ACTIVATED CARBONS(DATES NUT, PEACH NUTS AND APRICOT KERNELS)

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Adsorption Phenomenon the growing demand for adsorbents used in environmental protection processes has made their price more and more expensive, which sparks additional research for the manufacture of new, less expensive adsorbent materials from materials that do not are not classic, Concretely from vegetable waste. This study focuses on the removal of nickel in aqueous solution by different carbon prepared with natural citric acid (0.1N) activated carbon was prepared at carbonization temperatures of 600 ° C. Factors, contact time, mass of coal and initial nickel concentration, have a significant influence on the rate of removal of this metal. The adsorption isotherm for Ni (II) was studied over the concentration range considered where the experimental data are well represented by the Freundlich model. The kinetics is pseudo second order for the adsorption of nickel (II) by activated carbons (date nuts, peach nuts and apricot nuts).

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1. Introduction

Currently, throughout the planet, efforts relating to the preservation of the environment, namely flora and fauna, are taking on great importance over time. This field therefore attracts the attention of all green chemists, especially with regard to water pollution and its contamination by dyes.

Dyes are invariably released in industrial residues which affect the aquatic environment, soils and therefore plants. The presence of various organic molecules, in particular with aromatic nuclei, as well as the high stability of modern dyes, leads to the ineffectiveness of conventional treatments, both physicochemical and biological, in the elimination [1].

Activated carbons are very well known and widely used in the industrial world. These are porous carbonaceous materials by pyrolysis of biomass, which then undergo an activation which gives them a highly developed internal porous structure. The study of the pyrolysis conditions (nature of biomass, temperature, heating rate) and the activation (physical and chemical) make it possible to optimize the porosity [1].

Adsorption is a much more conventional process, widely used for a long time and in other fields, the main advantages of which are the simplicity of implementation and the very high efficiency, even at low concentration, when using high-performance adsorbents. The two major drawbacks of adsorption result from the non-destruction of the pollution (only retained on the adsorbent) and above all from its accumulation on the adsorbent which ends up making it ineffective when it is saturated. The elimination of pollutants, allowing this adsorbent to be regenerated, is the biggest challenge to be taken up in order to establish the competitiveness of absorption processes outside the domain of extremely dilute pollutants (micro pollutants). Among high-performance adsorbents, activated carbon (AC) is by far the most widely used material, given its performance / price ratio. Many regeneration techniques exist, with varying performances depending on the adsorbent and the adsorbate, but for the moment, in water treatment on an industrial scale, only a high temperature treatment (900 ° C) is validated. Without this expensive ex situ treatment, spent activated carbon is classified as waste to be incinerated [2].

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2. Experimental

2.1. Materials

- UV-Visible 1800 spectrophotometer (SHIMADZO) controlled by a computer.
- A BINDER type oven (maximum 400 ° C).
- CONSERT type pH meter (multi-parameter analyzed).
- Tamiseur à effet 3-D type AS200 basic.
- Broyeur mixeur waring Blended.
- Quatre à mouffles type LM 312.06.

2.2. Products used

1. Nickelsulphate hex hydrate ($\text{NiSO}_4 + 6\text{H}_2\text{O}$): $M = 262.85\text{g / mole}$
2. Natural citric acid ($\text{C}_6\text{H}_8\text{O}_7$): $M = 192.124\text{g / mole}$ concentration (0. 1M)

2.3. Preparation of the adsorbent

The steps followed during the manufacture of activated various carbon[4,13- 17] from the nuts of dates and the shells of peach stones and apricot nuts shells are detailed in the diagram below (Fig. 1).

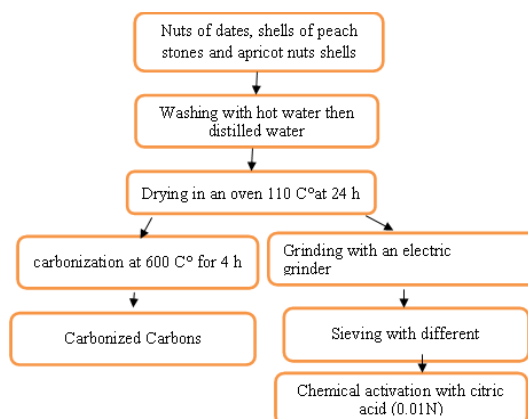


Fig. 1. Steps of Synthesizing Charcoal from Different carbons

3. Results and discussion

3.1. Physico-chemical analysis of the various coals and activated carbon

3.1.1. Percentage of humidity

The humidity level is a ratio expressed as a percentage; it is determined by drying the adsorbent in an oven [1]. 5 g of activated carbons are placed in a ceramic crucible and weighed. Then it is dried in an oven at 110 ° C until its weight remains constant. On leaving the oven, it is cooled to room temperature and then it is re-weighed.

The humidity rate (% H) can be calculated by the following formula:

$$\% H = ((M3-M2)) / M1 \times 10 \quad (1)$$

Or :

M1: the initial mass of activated carbon (AC) used in (g).

M2: The mass of the crucible filled after drying in (g).

M3: The mass of the crucible filled before drying in (g).

3.1.2. Ash content

For incineration, 5 g of sample powder are placed in a porcelain dish and then incinerated in a muffle furnace at approximately 250 ± 5 ° C for 4 hours until a gray, light or gray color is obtained Whitish. The ash content is expressed as a percentage of the dry matter. [1]

$$\% \text{ MO} = ((\text{M2}-\text{M4})) / \text{M1} \times 100 \quad (2)$$

The ash content expressed as a percentage is calculated after determining the organic matter content according to the following formula:

$$\text{Cd} = 100 - \text{MO}\% \quad (3)$$

Is :

OM%: Organic matter.

M2: Mass of capsules + test sample (g)

M4: Mass of capsules + ash (g).

M1: Mass of the test portion (g)

The results obtained are given in the following table (1):

Table 1. Determination of the moisture content H (%) and ash content Cd of raw carbon..

raw carbon (nut dates)				raw carbon (apricot nut shells)				raw charbon(peach nuts shells)			
%H	%Cd	%Ms	%MO	%H	%Cd	%MS	%MO	%H	%Cd	%Ms	%MO
2.68	86.67	97.32	14.33	6.1	87.7	93.9	95.9	2,32%	83.08%	97.68	97.68

From Table 1 above, it can be seen that the raw charcoal of date nuts has a relatively low moisture content of no more than 7%; this value corresponds to water free of hydration which evaporates from 100 °C. On the other hand, it is observed that the humidity is inversely proportional to the size of the grains (diameter of the smallest grains with the highest humidity), this can be explained by the fact that the finest carbons has more contact surface which allows it to attract more water molecules. the ash content is high, and the waste of the raw coal(apricot nut shells) a high ash content and therefore a majority of organic compounds, which promotes their use as raw material for the production of activated carbon.

3.2. Analysis of activated and raw carbon

In 15ml of distilled water, is introduced 5g of the support of activated carbon and raw carbon. After stirring, the mixture is left to stand for 30 min, and then the pH of the supernatant solution is measured at room temperature using a CONSERT type pH meter (multi-parameter analyzed).The results are presented in the following table (2):

Table 2. Determination of solution characterization.

	raw carbon (nut dates)		raw carbon (apricot nut shells)		raw charbon(peach nut shells)	
	Raw carbon(250°C)	Activated carbon (600°C)	Raw carbon	Activated carbon (600°C)	Raw carbon	Activated carbon (600°C)
Conductivities ((μs))	2.17-2.18	2.63-2.72	903 - 905	856 – 860	350-356	741-751
PH	4.80-4.82	9.95-10.08	5.98 - 6.1	8.4 - 8.6	6.93	7.42
Salinities (ppm)	1.05-1.07	1.61-1.63	403 - 404	428 – 433	138-140	391-395
TDS mineral solution rate (ppm)	1320-1332	1260-1284	530 - 535	554 – 560	100-103	508-516

According to the pH results presented in the previous table, it can be seen that the raw charcoal (nut of dates) is acidic in nature because the value obtained between (4.82) and other raw charcoals, the pH values obtained between (6.1-6.93) is very close to that of the distilled water used. The pH of activated charcoals is a little high (pH >7) this can be explained by the fact that the degradation of date stones during carbonization leads to products of a basic nature. For activated charcoal, its pH is very close to that distilled water (pH = 7.00) following the washings carried out at the end of activation.

3.3. Main study of the adsorption of nickel on activated carbon

3.3.1. Effect of contact time

effect of contact time on the adsorption of nickel on the adsorbent, we put in contact during different time intervals (15, 30, 45, 60, 90 min) solutions of 150ml of nickel solution to different concentrations of adsorbate (6000 mg / l) at the pH = 7 of the solution, the solution has a temperature of 20.7 ° C, at a stirring speed of 120tr / min depicted in Fig. 2.

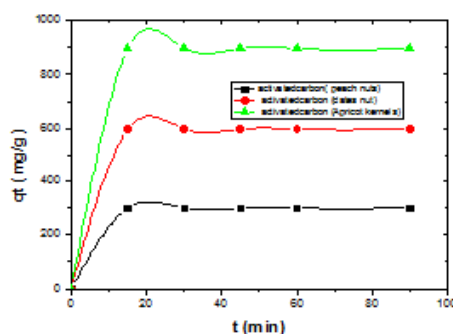


Fig.2. Effect of contact time on the adsorption performance of nickel on activated various carbons.

The figure indicated the adsorption of nickel is rapid during the first minutes of the reaction; this can be interpreted by the fact that at the start of adsorption, the numbers of active sites available on the surface of the adsorbent are much greater than that of the sites remaining after some time [4,7,9]. For high contact times(90min) , the molecule needs time to diffuse inside the adsorbent pore [4,5], for the rest of the non-adsorbed quantity is interpreted by the saturation of the adsorbent surface (all adsorption sites are occupied).

3.3.2. Effect of the initial nickel concentration:

The effect of the initial concentration of nickel in a sulphate solution medium by activated carbons were studied at various initial concentrations of nickel from 0 to 6000mg / L, in the presence of 1g of the adsorbent in the solutions, and a contact time of 1.5 hours, the pH = 7.02, V = 120 rpm and T = 20. ° C. Fig. 2 shows the increase in the quantity of adsorbed with the increase in nickel concentration up to 6000 mg / l and with maximum quantities for the activated carbon (apricot nuts). The quantity of nickel adsorbent rise in the original concentration of this metal adds to the impelling cause to over com the mass transfer position of nickel molecules between the adsorbent and adsorbate. Moreover number of collision between this metal and the adsorbent (apricot kernels) also increase with result and increase of the adsorption[6, 13-17].

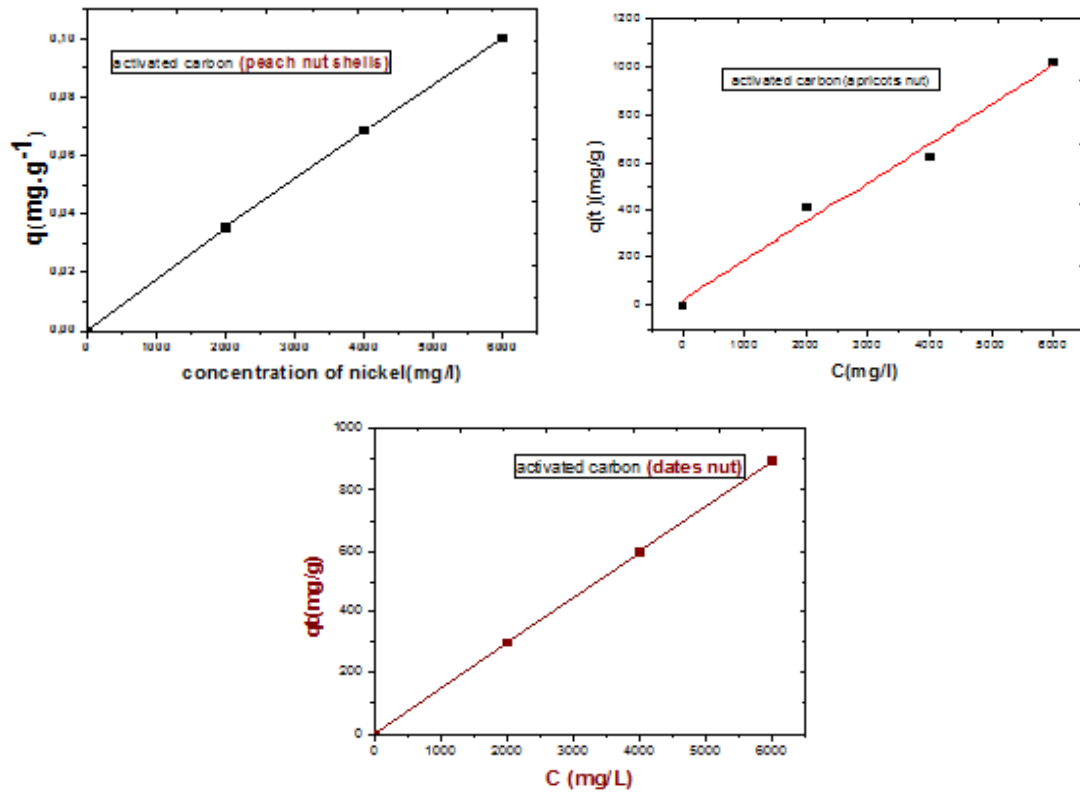


Fig. 3. Effect of nickel concentration on adsorption performance on activated various carbons.

3.4. Adsorption isotherm

Plotting an adsorption isotherm of a liquid on a solid requires the determination of the amount of solute adsorbed as a function of the concentration of the solute in the solution at equilibrium at a given temperature. Several methods for obtaining the adsorption isotherm have been updated. The exploitation of adsorption isotherms of activated carbon are written by the laws of Freundlich and Langmuir.

3.4.1. Freundlich's law

The linearization of the Freundlich relation gives [10]:

$$\ln Q_e = \ln \frac{X}{m} \ln(KC_e^{1/n}) = \ln K + \left(\frac{1}{n}\right) \ln C_e \quad (4)$$

C_e : Residual adsorbate concentration at equilibrium (mg / l)

K, n : Freundlich constants characteristic of adsorbate and carbon concerned

X : Amount of adsorbat (mg)

m : Mass of activated carbon (g).

By plotting $\left(\ln \frac{X}{m}\right) e$ as a function of $(\ln C_e)$, we obtain a line with slope of $(1 / n)$ and y-intercept $(\ln K)$. The linear regression of the experimental data at equilibrium [11] according to the Freundlich isotherm is presented in Fig. 4.

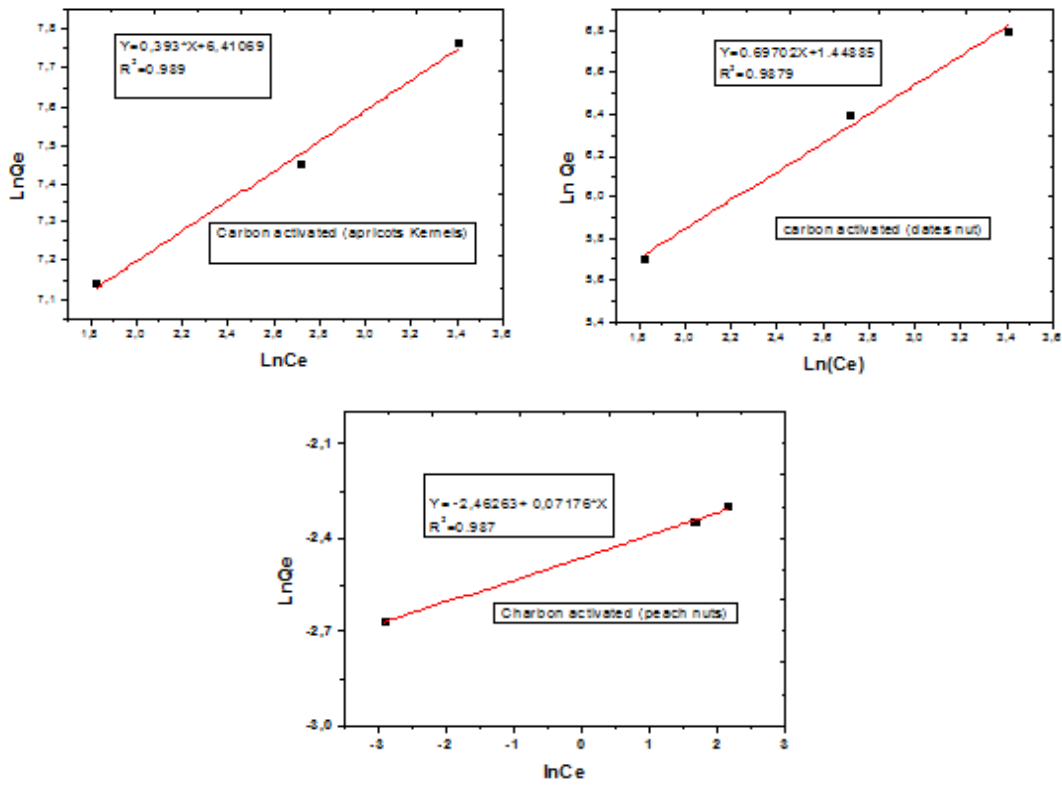


Fig. 4. Freundlich isotherm of various carbon activate.

3.4.2. Langmuir's law

The linearization of the Langmuir relation gives [12]:

$$\frac{1}{Q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \quad (5)$$

Q_e : Amount of solute adsorbed per unit mass of carbon (mg / g)

b : Thermodynamic equilibrium constant in relation to the adsorption energy

$Q_0 = Q_{max}$: Maximum quantity adsorbed per unit mass of adsorbent and forming a monomolecular layer on the surface (mg / g). By plotting $\left(\frac{1}{Q_e}\right)$ as a function of $\left(\frac{1}{C_e}\right)$, we obtain a line with

slope $\left(\frac{1}{Q_0 \cdot b}\right)$ and ordinate at the origin $\left(\frac{1}{Q_0}\right)$ [13]. The linear regression of the experimental data to the following equilibrium the Langmuir isotherm is listed in Fig. 5.

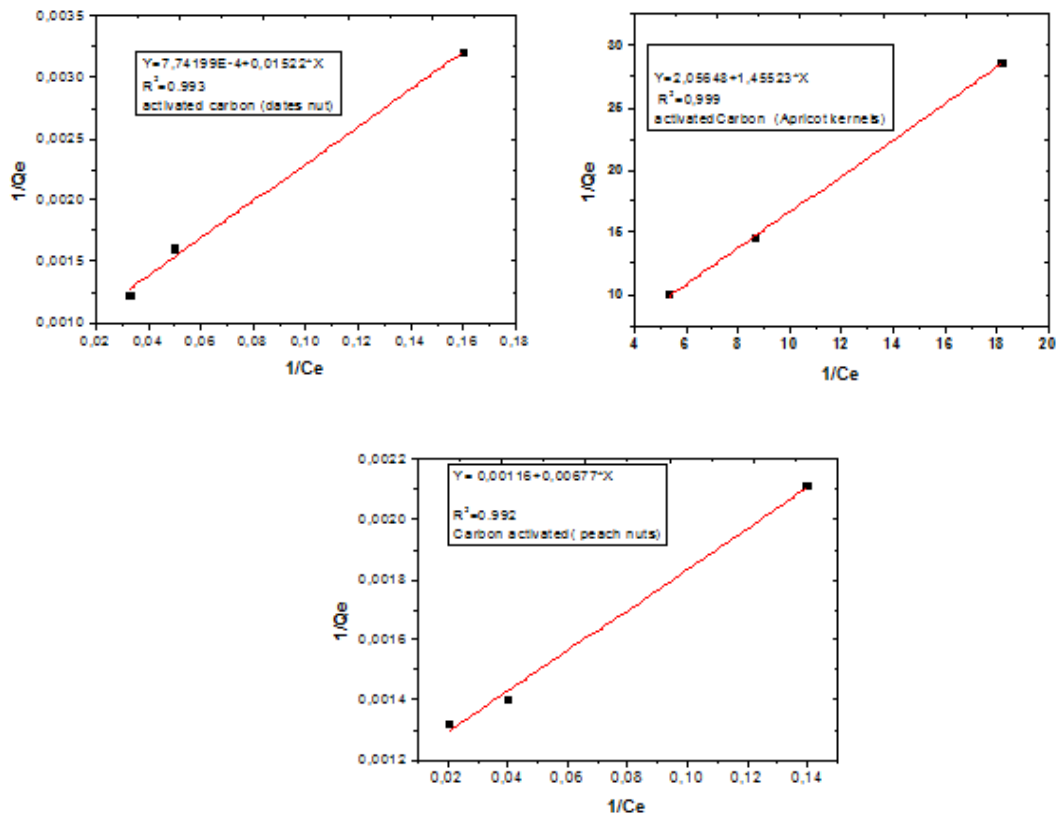


Fig. 5 Presentation of the Langmuir model on the adsorption of nickel by activated carbon (peach nuts)

Table 3. Langmuir and Freundlich. Constants for adsorption of nickel.

	Constants Freundlich			Constants Langmuir		
	1/n	lnK	R ²	Q _{MAX} (mg/l)	b (l/mg)	R ²
Carbon activated (apricot kernels)	0.597	6,41069	0.989	1291.65	3.34	0.999
Carbon activated (dates nut)	0.393	1,448	0.987	0.4862	0.70	0.993
Carbon activated(peach nuts)	0.071	-2, 462	0.987	862.09	0.173	0.992

Experimental data for adsorption studies was applied to the Langmuir and Freundlich isotherms indicated strong adsorption capacity of nickel with activated carbon (apricot kernels) From the constant of at equilibrium RL defined as follows [11,12]

$$RL = \frac{1}{1 + bC_0} \quad (6)$$

We find $0 \leq RL \leq 1$ so we can say that the Langmuir isotherm is favorable for nickel adsorption.

3.5. Modeling of adsorption results

Knowledge of adsorption kinetics is of considerable practical interest for the optimal implementation of an adsorbent in an operation based on adsorption phenomena. To describe the experimental data of this adsorption over time, the literature reports several kinetic models but a

large majority is traditionally based on first-order or second-order reaction schemes with respect to the amount of solute fixed.

3.5.1. Pseudo-first-order kinetic model

This model was proposed by Lagergren in 1898, it is based on a linear relationship between the amount of solute (adsorbate) as a function of time.

$$dq_t / dt = k_1 (q_e - q_t) \quad (7)$$

k_1 : speed constant (min^{-1})

Q_e : amount of adsorbate at equilibrium (mg / g).

Q_t : amount of adsorbate at time t (mg / g).

t : contact time (min).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

The value of k_1 is obtained from the slope of the linear plot of $\ln(q_e - q_t) = f(t)$.

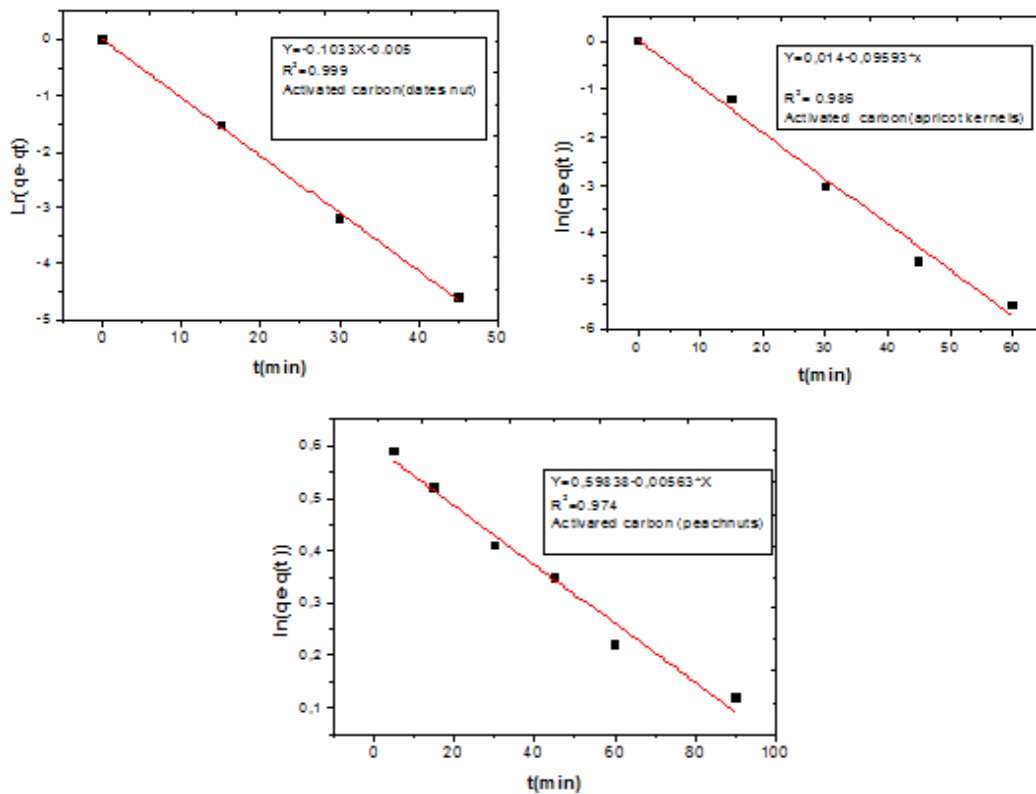


Fig.6 The pseudo first order model for the adsorption of nickel on activated various carbons

3.5.2. Pseudo-second-order kinetic model

The pseudo-second-order model allows to correctly describing the binding of solute molecules to the solid surface of the material. Analysis of the kinetic data reveals a lower order model [2].

This model is given by the following expression:

$$dq_t / dt = k_1 (q_e - q_t)^2 \quad (9)$$

q_e : amount adsorbed at equilibrium (mg / g).
 q_t : amount adsorbed at time t (mg / g).
 t : Contact time (min).
 K_2 : pseudo-second-order rate constant (g / mg.min).
 linearization of the previous equation gives:

$$t / q_t = 1 / (K_2 \times q_e^2) + 1 / q_e t \quad (10)$$

When we plot $t / q_t = f(t)$

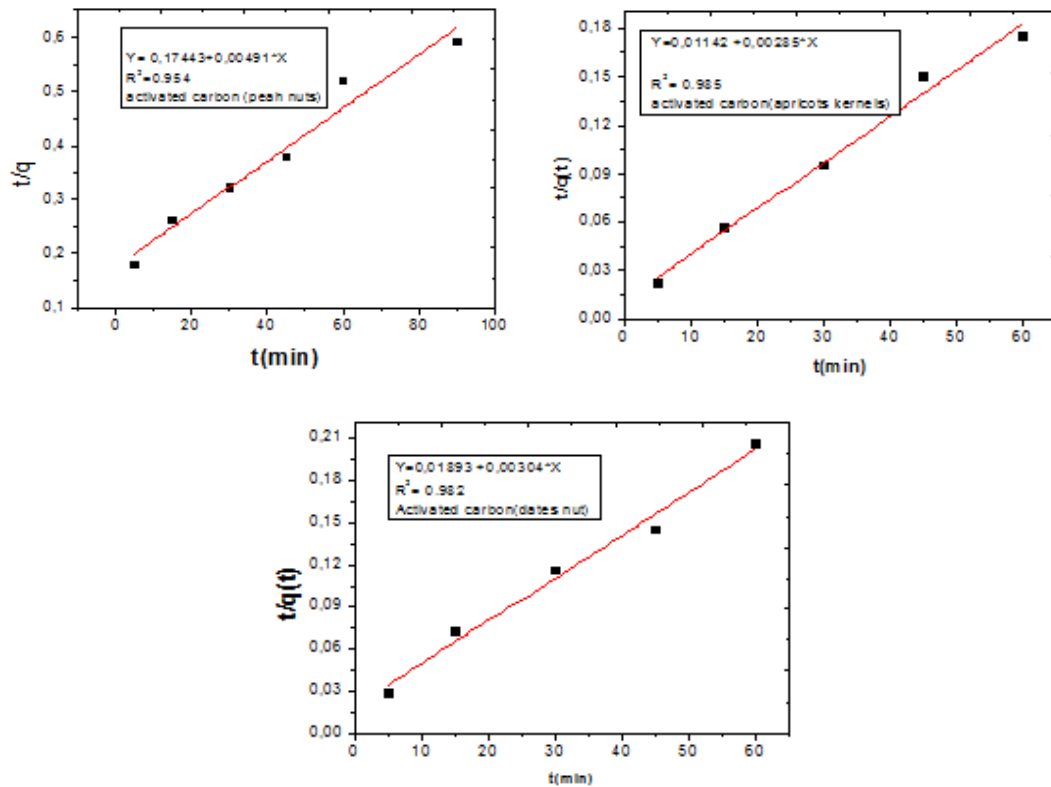


Fig. 7. Application of the pseudo second order model for the adsorption of nickel on activated various carbons.

Table 4. The values of the pseudo-first and second order nickel adsorption rate constants and correlation coefficients.

	pseudo-first - order			pseudo- second -order		
	$\ln q_e$	K_1	R^2	q_e (mg/g)	K_2	R^2
Carbon Activated(peach nuts)	-0.1033	0.00563	0.974	203.66	3.29×10^3	0.964
Carbon Activated(dates nut)	0.014	0.0054	0.981	328.95	2.048×10^3	0.982
Carbon Activated(apricots kernels)	0.018	0.095	0.986	350.88	1.406×10^3	0.985

The results of table (4) show that the pseudo second order model is better suited to the experimental results compared to the pseudo first order model, this is reflected by the large values

of the correlation coefficients R^2 for the pseudo second order model (0.985) from activated carbon (apricot kernels) and the adsorption capacity of nickel is equal (350.88mg / g).

4. Conclusion

In this study, dates nut, pean nuts and apricots kernels were used as a biosorbent for the removal of nickel in batch mode. The optimal experimental parameters for nickel adsorption are: initial pH (7), contact time (90 min), initial concentration (0-6000 mg L⁻¹) and temperature (20 ° C). The experimental adsorption isotherm results are in good agreement with the Freundlich model as well as the Langmuir model. The maximum adsorption capacity of the monolayer, Q_{max} , calculated from the Langmuir model is 350.88 mg g⁻¹ at 20 ° C. The adsorption kinetic studies showed that the pseudo-second-order kinetic model yields the best fit for the kinetic data with a regression constant, R^2 , of (0.964 to 0.985). Based on the results obtained by the present study, we can conclude that the best results obtained from the adsorption of nickel in a sulphate medium with an activated carbon (apricot kernels), this carbon is a biosorbent readily available locally and at low cost; they can be considered as a cost effective means and a potential biosorbent for the removal of nickel from aqueous solutions.

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