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Adsorption of cadmium (II) from aqueous solutions by activated carbon produced from Algerian dates stones of *Phoenix dactylifera* by H_3PO_4 activation

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ABSTRACT

Low-cost-activated carbon derived from dates stones of *Phoenix dactylifera* L. has been used to replace the current high-cost methods of cadmium removal from aqueous solutions and waste waters. Effect of some operating parameters such as pH, contact time, initial metal concentration, and solution temperature was examined. Adsorption of cadmium ions was found to increase with increasing pH to reach a maximum removal rate of 4.29 mg/g at pH = 8 ($C_0 = 50$ mg/l). Adsorption data are found to follow the Freundlich model.

Keywords: Adsorption; Activated carbon; Cadmium removal; Langmuir and Freundlich models

1. Introduction

Toxic metals such as Cd(II), Hg(II), Pb(II) have become an ecotoxicological hazard of prime interest and increasing significance owing to their tendency to accumulate in vital organs in man and animals [1]. These heavy metals cannot be degraded into harmless products but they are rather amassed in the food chain, where they may cause a real danger to living organisms if their concentration exceeds the accepted limits [2,3].

Cadmium and their salts are used in electroplating, paint pigments, plastics, silver cadmium batteries, smelting, cadmium-nickel batteries, stabilizers, phosphate fertilizers, and mining and alloy industries [4].

The liver and the kidneys are the main organs being affected by cadmium even at low concentrations, whereas organs such as the bones, the heart, the pancreas and the testes are only affected after chronic exposure. As a result, the organs function is impaired and anemia is frequently observed [5,6]. Cadmium can also cause diarrhea, pulmonary problems, skeletal deformity, and yellow strain appears gradually on the teeth joints [7]. The harmful effects of Cd(II) are hypertension, proteinuria, kidney stone formation, and testicular atrophy. Cd(II) may replace Zn(II) in some enzymes and hence affecting the enzyme activity [3]. Therefore, it is an absolute necessity to remove Cd(II) from wastewaters and drinking waters. Various techniques have been used to treat heavy metals, such as adsorption, chemical precipitation, coagulation, flocculation, extraction, and reverse osmosis [8–12]. Most of these processes need high capital cost [13]. They have the weakness to operate in multiple-step heterogeneous reactions, or distribution of substances between different phases, which usually requires a long operating time. Moreover, the final metal

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recovery requires additional treatments, which may complicate the process [14]. Adsorption technique, among others, using a number of organic, inorganic, natural, synthetic, activated or modified model adsorbents, is the most widely used procedure in the wastewater treatment studies [15]. They are considered as efficient and economic methods to remove the heavy metal pollutants at low concentrations [16–18].

Activated carbons were used as adsorbent materials because of their relatively extended surface area, microporous structure, high adsorption capacity, and high degree of surface reactivity [19–22].

Any low-cost material with a high carbon content, low inorganics can be used as a raw material for the production of activated carbon.

Literature background reported many attempts to obtain low-cost-activated carbon or adsorbents from agricultural wastes, such as coconut shells [23], almond shells [16], peach stones [24], rice shell [3], apricot stones [25], cherry stones [26], olive stones [27], peanut hull [12], palm shells [28], pistachio nut [29], coir pith [30], pecan shells [31], banana pith [32], and sugar can bagasse [33].

There are two different processes for the preparation of the activated carbon namely physical activation and chemical activation. Physical activation involves the carbonization of a carbonaceous material followed by the activation of the resulting char at a temperature between 1073 and 1373 K in the presence of suitable oxidizing gases such as carbon dioxide or steam. In chemical activation, the precursor is mixed with a chemical agent and then pyrolyzed between 673 and 873 K in the absence of air. Chemical activation presents two advantages over physical activation. The first is the lower temperature and the second is the high global yield since burn-off of the char is not required and hence the mass is not affected [3].

Among the numerous dehydrating agents, phosphoric acid in particular is the widely used chemical agent in the preparation of activated carbons [34].

In this study, the Algerian dates stones of *Phoenix dactylifera* cultivated in Ouargla region have been used for preparing the activated carbon. Cd(II) were used to highlight the adsorption capacity of the prepared activated carbon. The effects of the pH, the contact time, the solution temperature, and the heavy metal concentration on the adsorption efficiency were examined.

2. Experimental studies

The tests stock solutions were prepared by dissolving cadmium nitrate $Cd(NO_3)_2$ in distilled water. The pH of the test solutions was adjusted using hydrochloric acid (0.1 M) or sodium hydroxide (0.1 M).

2.1. Instruments

The cadmium concentrations in the water were determined using atomic adsorption spectrophotometer (Thermoelectron Corporation). The pH measurements were taken using a pH-meter (Hanna 4221). During adsorption tests, a shaker (flask) was used. A furnace (Select-Horn) was utilized in the preparation of activated carbon.

2.2. Preparation and characterization of the adsorbent

The starting material for the preparation of activated carbon was the dates stones of *P. dactylifera* (Ouargla, Algeria), a waste agricultural product. Phosphoric acid was used for chemical activation. A ratio of (1:1.5) (w/w) powdered raw material and acid was prepared before distilled water was added in order to remove the impurities. Then, the precursor was dried at 105°C and heated to 450°C. It was washed with distilled water, dried, and sieved to desired particle size.

The surface area and pore size of the adsorbent were measured by means of a nova surface area analyzer using a Brunauer–Emmett–Teller (BET) nitrogen adsorption technique. The average pore size and total pore volume were also determined in the same way. Table 1 displays the characteristics of adsorbent.

2.3. Adsorption experiments

The stock divalent cation solution (Cd^{++}) was prepared by dissolving cadmium nitrate in bi-distilled water at 1,000 mg/l. Working solutions were prepared by diluting different volumes of stock solution to achieve the desired concentration.

In the batch studies, 0.1 g of the adsorbent was placed in a flask containing 20 ml of a cadmium solution with the desired concentration. The flask was continuously shaken (300 rpm) at a desired pH range (2–10). At the end of each step, the supernatant liquids were filtered and the Cd(II) concentrations

Table 1
Characteristics of activated carbon

Surface and physical properties	Activated carbon
Surface area (m^2/g)	54.934
Average pore radius (nm)	1.1286
Total pore volume (cm^3/g)	1.55×10^{-2}
Porosity (%)	70

were determined using an atomic adsorption spectrophotometer. The contact time was determined as the time required for the concentration of the cadmium in the solution to reach equilibrium (24 h). The amount of metal adsorbed by the solid (Q) and the percent of metal removal were calculated using the following equations:

$$q = (C_0 - C_e)\ V/m$$

$$\text{Metal removal rate }(\%) = (C_0 - C_e)100/C_0$$

where C_0 is the initial concentration of Cd(II) (mg/l), C_e is the concentration of Cd(II) at equilibrium adsorption (mg/l), V is the volume of solution (L), and m is the mass of adsorbent (g).

The effect of temperature ranging from 25 to 60°C was also studied. During the tests, the pH was adjusted to 8 and the contact time was set at 1 h. The effect of the initial concentration of metal (5–50 mg/l) was also examined in order to determine its influence on the adsorption rate and also to obtain the adsorption isotherm. The shaking speed (300 rpm), the amount of adsorbent (0.1 g), the contact time (1 h), the pH = 8, and the temperature of 25°C were kept constant.

3. Results and discussion

3.1. pH effect

The removal of metal ions from aqueous solution by adsorption is highly dependent on the pH of the solution, which affects the surface charge on the adsorbent and the degree of ionization. Most research reports that have been conducted on heavy metal sorption indicated that the decrease in ion sorption at acidic pH might be due to the increase in competition with protons on active sites. At alkaline pH, however, different effects may arise due to other processes such as the predominant presence of hydrated species of heavy metals, changes on the surface and precipitation of the appropriate salts [3].

To check the effect of pH on Cd(II) adsorption using activated carbon prepared from dates stones as adsorbent, experiments were conducted by varying pH from 2 to 10 with an initial concentration of 50 mg/l. The results obtained for adsorbent are shown in Fig. 1.

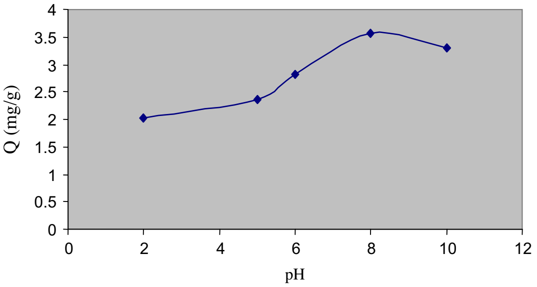

Fig. 1. Effect of pH on the removal of Cd(II).

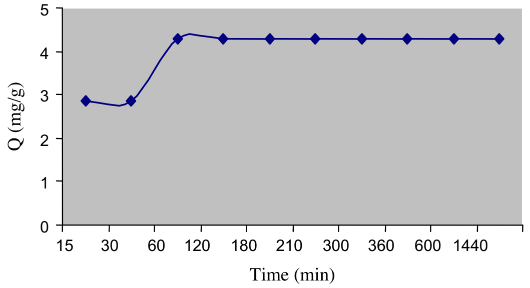

Fig. 2. Effect of the contact time.

Fig. 1 shows that, when the pH of solution is increased from 2 to 8, the adsorbed Cd(II) increases from 2.03 to 3.56. The fact that the amount of Cd(II) removal at low pH is considerably small may be attributed to the competition between Cd^{2+} and H^+ ions on the active sites of the sorbent surface. The decrease in the amount of adsorbed Cd(II) above pH = 8 may be due to the formation of soluble hydroxyl complexes. It is assumed that OH^- in the alkaline medium leads firstly to hydrolysis products of $Cd(OH)^+$, then $Cd(OH)_2$ hydrolysis complexes, which in turn decreases the adsorption rate. We can note that the optimal pH = 8.

3.2. Effect of contact time

The effect of the contact time on the adsorption of Cd(II) by activated carbon is shown in Fig. 2. These data have been obtained from the starting adsorbent and working solution without any pH adjustment (pH = 8). The results showed that increasing the contact time increased the adsorption and then levelled up after 1 h. Consequently, the contact time was set to 1 h in each experiment. The amount of adsorbed cadmium by activated carbon from an initial concentration of 50 mg/l after 1 h was 4.29 mg/g.

3.3. Effect of temperature

To investigate the effect of the temperature (25, 35, 45, and 60°C) on the Cd(II) adsorption, the experiments were conducted with constant concentration of

Cd(II) (50 mg/l), pH = 8, the amount of activated carbon (0.1 g), and contact time (1 h). The results are given in Fig. 3.

As can be seen from this figure, the adsorbed amount of Cd(II) decreases when increasing temperature from 25 to 60°C. The observed decrease in the adsorption capacity with the increase in temperature indicated that the adsorption is preferred at low temperature. This effect suggested that the adsorption mechanism associated with the removal of Cd(II) onto activated carbon involves a physical process, which is usually associated with low adsorption heat. This means that the adsorption process has an exothermic character.

3.4. Effect of initial metal concentration

Dependency of Cd(II) removal on different initial concentrations (5–50 mg/l) is illustrated in Table 2. The examination of the data reveals that the amount of absorbed cadmium increases with the concentration from 0.25 to 4.29 mg/g. The adsorption rate increases also from 24.60 to 42.86%. This means that the removal of Cd(II) is highly concentration dependent. pH is a critical parameter in the process so before carrying out the essays, the Cd(II) stock solutions pH was fixed at the optimum value (pH = 8).

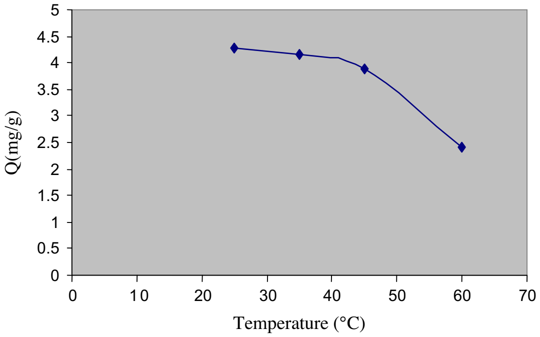

Fig. 3. Effect of the temperature on the removal of Cd(II).

Table 2
Effect of the initial concentration on Cd(II)

Initial concentration (mg/l)	Q	%
5	0.25	24.60
10	0.53	26.50
20	1.22	30.60
30	1.90	31.70
40	2.67	33.42
50	4.29	42.86

3.5. Adsorption isotherms

The equilibrium adsorption isotherms are of fundamental importance in the study and design of adsorption systems. According to the slop of the initial portion of the curves, they are classified into various groups. In this work, the isotherm curve corresponds to S-type in Gile's classification (Fig. 4).

Several methods have been published describing experimental data of adsorption isotherms. The Langmuir and Freundlich models are the most frequently used. In this work, both models were used to describe the relationship between the adsorbed amount of Cd (II) and its equilibrium concentration at 25°C, pH = 8, for initial concentrations of 5, 10, 20, 30, 40, and 50 mg/l during 1 h.

The linear form of the Langmuir isotherm model can be represented by using the equation below:

$$C_e/\ Q_e = 1/Q_0\ b + (1/Q_0)C_e$$

where Q_e is the amount of adsorbed solute per unit weight of adsorbent (mg/g), C_e is the equilibrium of solute concentration in the bulk solution (mg/l), Q_0 is the monolayer adsorption capacity (mg/g), and b is the constant related to the free energy of adsorption. The constants of Langmuir isotherm are obtained by plotting C_e/Q_e vs. C_e (Fig. 5). They are given in Table 3.

The essential characteristics of the Langmuir isotherms can be expressed in term of a dimensionless constant separation factor or equilibrium parameter R that is defined as:

$$R = 1/1 + bC_0$$

where b is the Langmuir constant and C_0 is the initial concentration of Cd (II). The R value indicates the type of the isotherm as follows:

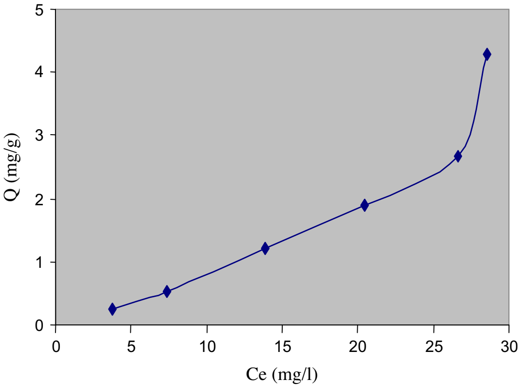

Fig. 4. Adsorption of Cd(II) onto activated carbon.

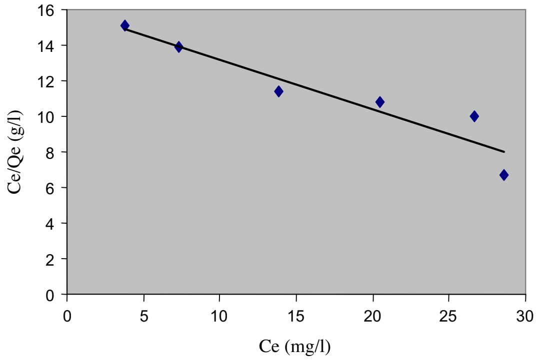

Fig. 5. Langmuir isotherm.

Table 3
Freundlich and Langmuir constants in the adsorption of Cd(II) onto activated carbon

Langmuir				Freundlich		
Q_0	b	R^2	R	K	n	R^2
−3.5997	−0.0174	0.8948	7.6923	25.0207	0.7567	0.9814

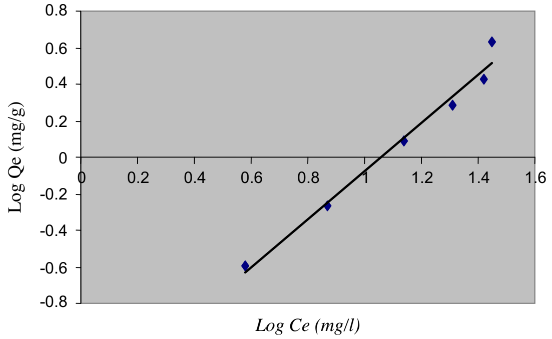

Fig. 6. Freundlich isotherm.

R value	Type of isotherm
$R > 1$	Unfavorable
$R = 1$	Linear
$0 < R < 1$	Favorable
$R = 0$	Irreversible

The value of R (7.6923) indicates unfavorable adsorption.

The linear form of the Freundlich isotherm model is given by the following equation:

$$\text{Log } Q_e = \text{Log } K + 1/n \text{ Log } C_e$$

where K is the constant relevant to the relative adsorption capacity of the adsorbent (mg/g) and $1/n$ is the constant relevant to the intensity of the adsorption. The constants of Freundlich isotherm are obtained by plotting Log Q_e vs. Log C_e (Fig. 6). They are given in the Table 3.

The correlation coefficients reveal that the Freundlich model can be used to fit the data and estimate model parameters.

4. Conclusion

The present investigation shows that activated carbon prepared from Algerian dates stones by phosphoric acid activation can be used as adsorbent for the removal of Cd(II) from aqueous solutions. The removal of this heavy metal followed the Freundlich equation and was found to be dependent on pH, contact time, temperature, and initial concentration.

The obtained data may be helpful to environmental sanitary engineers for designing and establishing a continuous treatment plant for water and wastewaters.

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