

Possibility of Removing Phosphates from Activated Charcoal Made from Date Kernels

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ABSTRACT: Phosphates in natural waters and whatever their origin, promote the formation of algae, reduce dissolved oxygen and reduce biodiversity in aquatic ecosystems. At high doses, phosphate salts can cause health problems. The objective of our study was to develop a simple, efficient and environmentally friendly sorption depollution technique on available and inexpensive media. We have studied the adsorption of phosphate on activated carbons prepared from date kernels. Batch tests were carried out in order to study different operating parameters such as the effect of contact time, pH, initial phosphate concentration and adsorbent dosage and adsorption kinetic. The sorption equilibrium was analyzed by Langmuir, Freundlich isotherms model. Results show that the phosphate adsorption was reversible and the quantity adsorbed reached its maximum value (14.49 mg/g) after 40 minutes. It was also found that phosphate uptake was affected by variation of pH, initial concentration of phosphate and activated carbon dosage. The adsorption improved with an acidic pH (pH = 6), initial concentration and adsorbent dosage. The results of kinetic studies revealed that adsorption phosphate on activated carbon based on date kernels (Biocar) and the intra-particle diffusion involved in the adsorption mechanism. Also, isotherm study showed that Langmuir isotherm best fit the data and the adsorption was a physical type.

1. INTRODUCTION

Phosphates are part of anions that can be assimilated by the body of a human being [1]. Whatever their origin (domestic, industrial or agricultural), their presence in waters with high concentrations (concentrations greater than 0.2 mg / l) promotes the massive development of algae, which lead to the eutrophication of lakes and rivers. of water [2]. There are several conventional processes for the removal of phosphates from contaminated waters such as biological treatments [3,4] and physicochemical processes which are based on precipitation phenomena of calcium salts, iron or aluminum [5] or on coagulation flocculation of aluminum sulphate [6] or by adsorption on clay; [7, 8].

Nowadays, the increasing demand for adsorbent materials for environmental protection processes calls for further research into the production of activated carbon from non-conventional materials, specifically from vegetable waste [9]. Activated carbon is one of the most used adsorbent materials for the filtration of water and liquids. It is a material with an extremely complex porous structure and a very large surface area that can absorb a wide variety of substances. Among the various plant source materials for

the production of activated charcoal are: coconut husks, hazelnut and nut almond hulls, apple pulp as well as olive kernels and date kernels [10].

A significant amount of date kernels are generated each year and constitute a significant source of agricultural waste. Such byproducts corresponding to this loss are nevertheless likely to be of significant economic interest. It turns out, therefore, important to value such waste. The dates kernels have been the subject of various studies for various applications such as adsorption. The aim of our work is to develop a simple, efficient and environmentally friendly sorption depollution technique on available and inexpensive media. We have studied the adsorption of phosphates on raw and active coals prepared by date kernels.

The influence of some relevant factors, including contact time, pH value, initial phosphate content, concentration and adsorbent dosage, are investigated. In addition, the kinetics and sorption of equilibrium studies were performed.

2. MATERIALS AND METHODS

The preparation of the activated carbon from the date nuclei was carried out by chemical activation using phosphoric

acid H_3PO_4 as an activating agent. Nut processing involved the following operations:

2.1. The preparation of activated carbons necessarily passes through preliminary stages (collection, carbonization, grinding, sieving, ...).

a) Collecting the dates kernels (variety Deglet-Nour).

In order to valorize local materials in activated charcoal, we used as precursor dates kernels coming from a region of the southwest Algerian (Biskra) which is an oasis known by its dates of very good quality. The wilaya of Biskra, capital of the Ziban located about 470km south-east of Algiers limited to the north by the wilaya of Batna, to the east by wilaya of Khenchela, the west by wilaya of Msila and Djelfa, south by wilaya of El-Oued and Ouargla. It is part of the arid region of the country whose climate is of the Saharan type (hot summer and mild winter). The collection was carried out during the months of November and December 2018.

b) Pretreatment of date kernels.

- After separating the date cores from the pulp, we washed the nuclei thoroughly with distilled water to remove the dust and then dried in an oven at 130 °C for 24 hours.
- After 24 hours of drying, the date cores were crushed using a grinder (IKA Werk MF10) Basic and sieved to obtain a fraction with a particle size of between 0.5 and 1 mm. The ground material is retained and stored in airtight containers sealed.

c) Chemical activation.

Chemical activation is activation in the liquid phase: the previously treated material was impregnated in the

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activating agent and then pyrolyzed under an inert atmosphere. The agent used is: H_3PO_4 . The carbonization and the actual activation are combined in a single step, it requires only a single heat treatment of temperatures between 400 and 800 °C, values below the usual physical activation temperatures. The activating agent, the impregnation rate, the temperature and the duration of the activation are the main parameters of the chemical activation, they condition the properties of the carbons obtained in terms of pore volume, pore size distribution and chemical composition of the surface.

The choice of the activating agent is very often dictated by the nature of the precursor materials (for a given precursor, certain activating agents are better adapted) and by the properties required by the final product [10, 11].

In our work, we have opted for phosphoric acid as an activating agent and is widely used for the activation of coals. The stages of preparation and activation of activated charcoal by date kernels are presented in (Fig.1):

- 10 g of each raw sample was mixed with 20 g of the H_3PO_4 solution (40% by weight) and kept stirring for 10 h, the mixtures are put in an oven for 24 h at 110 °C.
- The products are then placed in a calcination furnace with a heating rate of 10 °C./min and maintained at a temperature of 450 °C. for one hour (1 h).
- The products obtained were washed several times with distilled water until the pH of the supernatant became 6.5.
- The products were then dried at 110 °C for 24 h.



Fig.1.The stages of the preparation and activation of activated carbon from date kernels

2.2. Preparation of solutions.

Phosphate stock solution at 1g/l P was prepared by dissolving an accurate quantity of Na_2HPO_4 . All experimental solutions of phosphate are prepared by proper dilution of the stock solution.

2.3. Description of adsorption tests

The adsorption tests are carried out in a static reactor. Adsorption is accomplished by contacting aqueous phosphate solutions with increasing amounts of activated carbon in 1 liter beakers. All the experiments were carried out without adjusting the pH (except for the study of pH

effect).the kinetic study (between 0 and 120 min), the influence of pH (pH values ranging from 2 to 12), the effect of the amount of adsorbent (m between 0.1 to 2.5 g/l) and the initial phosphate concentration (C_0 ranging from 5 to 20 mg /l).

2.4. Kinetic study. Adsorption kinetic experiments were conducted by following the residual phosphate content during a contact time of 0 to 120 minutes. The mineralized water was doped with 10 mg/l of phosphate. Tests of the kinetics were carried out in beakers of one liter by adding 1 g/l of adsorbent to the phosphate solutions.

2.5. Adsorption isotherm models

Several models have been proposed to describe the isothermal adsorption curves in aqueous or gaseous media. The Langmuir and Freundlich equations have the advantage of being simple and often appropriate for the modeling of adsorption kinetics in an aqueous medium.

3. RESULTS AND DISCUSSION

3.1. The kinetics of adsorption of phosphate

Fig.2 illustrates the efficiency of phosphate adsorption at different contact times. As seen, the uptake of phosphate ions on biochar is a rapid phenomenon, and two steps can be distinguished by tracing the phosphate removal

efficiencies against the stirring time. The kinetics shows that the equilibrium is reached after a time close to 40 min and a plateau is observed from 80 up to 120 minutes. Or the effect of contact time has no effect on the adsorption capacity of phosphate. In the first stage, an increase in the percentage of phosphate removal with increasing contact time was observed. The maximum removal, which is reached after 40 minutes, corresponds to the maximum of phosphate ions fixed on the surface of activated charcoal made from date kernels compared to raw coal. In the second stage, a decrease in the adsorption efficiency indicates the desorption of phosphate ions by this coal. This can be correlated to the nature of adsorbate-adsorbent interactions

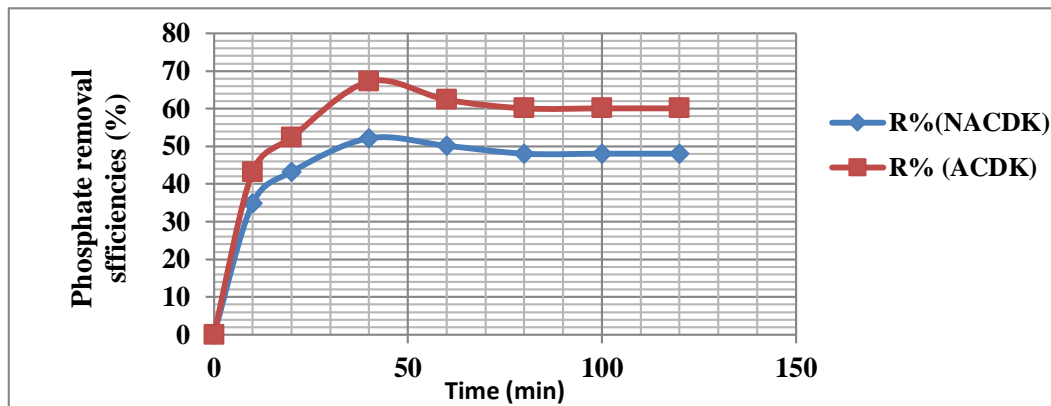


Fig.2. Percentage of phosphate removal as a function of contact time on both coals tested (Non-activated carbon dates kernels (NACDK) and Activated carbon dates kernels ACDK) (C0= 10mg/l, adsorbent dose = 0.5g).

3.2. The effect of the adsorbent dose on the elimination of phosphate

In our tests, we set the initial concentration of phosphate at 10 mg / l, and the adsorbent masses are from 0.1 to 2.5 g. From Fig 3 which shows the results obtained for each sample and the variation of the phosphate removal

efficiency as a function of the adsorbent mass. The best removal efficiencies of phosphates are obtained with a dose of 1 g and which are of 71.20% and 62.45 % respectively for activated charcoal prepared from date kernels and non-activated charcoal.

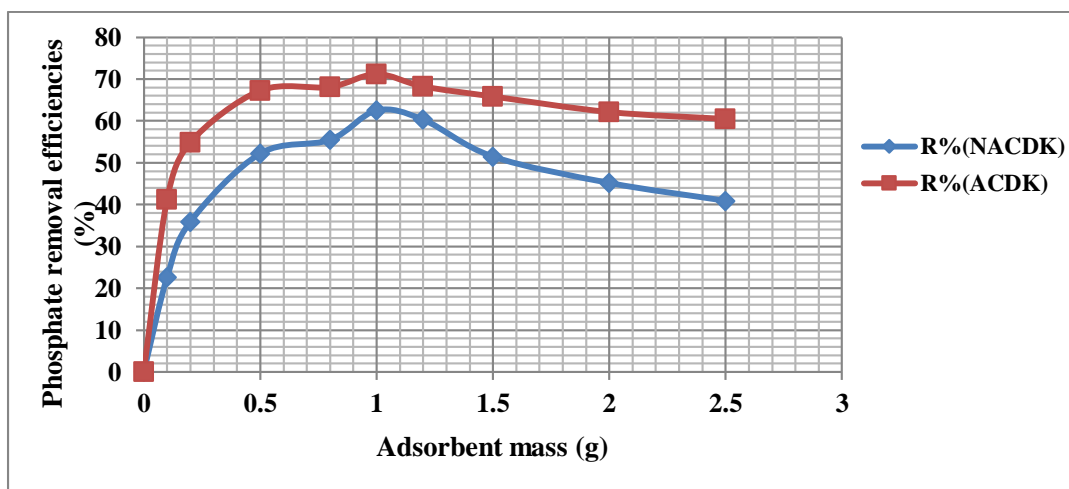


Fig.3. Phosphate elimination efficiency at various dosage of carbon.

(C0= 10mg/l, t = 40 minutes)

3.3. Effect of solution pH and phosphate removal mechanism

The results obtained in Fig. 4 show that the activated carbon prepared from the date kernels has led to better adsorption results of the phosphates at an acidic pH. The removal of phosphates decreases rapidly when the pH goes from 2 to 6. At acid pH, the adsorption sites are positively charged, and therefore the attachment of the phosphate anions to the

adsorbent by electrostatic traction forces is favored. Our results are consistent with work on the effect of pH on the adsorption of phosphates on coals [12]. These same authors have found that the maximum of phosphorus removal is reached at pH between 2 and 6. The work of [13], which relates to the retention of phosphates by two types of activated carbon, has shown that the maximum adsorption is recorded at pH 4 to 7.

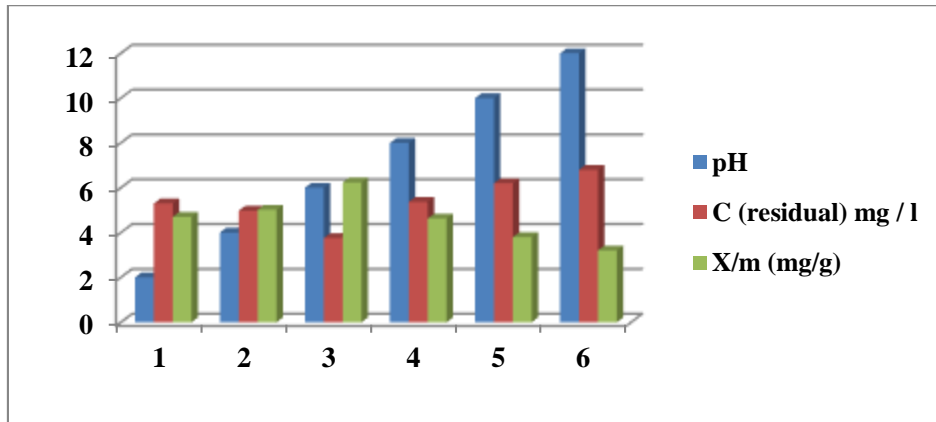


Fig. 4. Effect of pH on the amount of adsorbed phosphate using using activated charcoal made from date kernels: C₀ = 10 mg/l, t = 40 minutes, adsorbent dose = 1 g/l

3.4. Adsorption isotherm models.

Phosphate adsorption isotherm is obtained by varying initial phosphate concentration (from 5 to 20mg/l) with a constant dose of active charcoal (1 g/l). We followed the elimination of phosphate according to the initial concentration of phosphate. The results obtained showed that the dephosphatation is effective for low levels of phosphates (in

our study C₀ < 20mg /l. Similar results were found by [14]. We were able to trace the corresponding isotherms, those of Freundlich and Langmuir. The plot of the phosphate adsorption capacity q_e against the phosphate equilibrium concentration C_e is shown in Fig.5. The constants of these two laws are presented in Table 1.

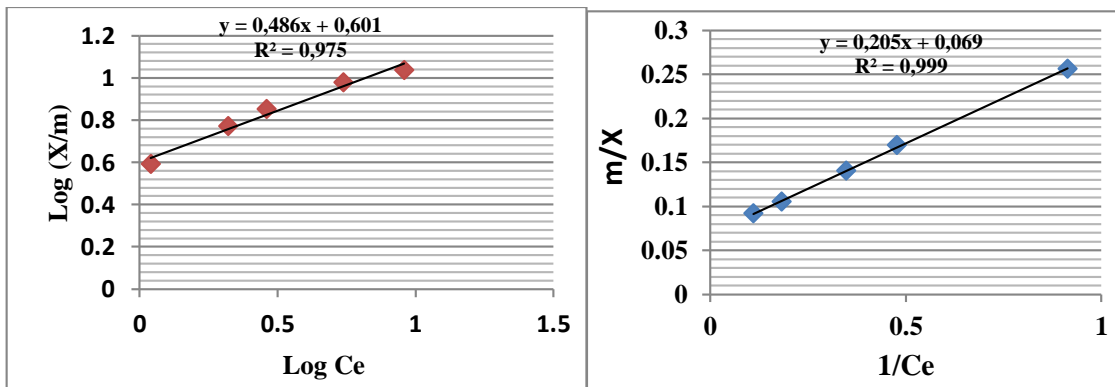


Fig. 5. Langmuir and Freundlich isotherms for phosphate ion adsorption using activated charcoal made from date kernels: t = 40 minutes, adsorbent dose = 1 g/l

Table II.1: Freundlich and Langmuir constants obtained for activated carbon prepared by date kernels

Adsorbent	Freundlich			Langmuir			
	n	K(mg/g)	R ²	Q _m (mg/g)	b(l/mg)	R ₁	R ²
Activated carbon	2.058	3.99	0.975	14.493	0.336	0.229	0.999

The maximum adsorption capacity according to the Langmuir model is equal to 14.49 mg / g. The same results

were obtained using activated fruit juice residue with a maximum adsorption capacity of 13.89mg/g [15].

4. CONCLUSION

The aim of this work was to assess the phosphate removal by adsorption using activated carbon prepared from date kernels.

- Removal of phosphate ions is a reversible phenomenon and reaches its maximum value after 40 minutes.
- Powdered activated carbon gives better yields and reaches 71.20%. This can be attributed to an important surface area, a macroporosity and surface functions allowing the retention of phosphates.
- The adsorption of phosphate on these adsorbents obeys the Freundlich and Langmuir laws with a maximum capacity of 14.49mg / g for activated carbon prepared by date kernels. This value shows that the active carbon has a good adsorption capacity because it contains a higher percentage of porous fraction.
- The results obtained show that the activated carbon used has led to better adsorption results of phosphates at an acidic pH (pH = 6).

Results show that the granular activated carbon has an important capacity of phosphate ion removal from waters which gives a promising prospect of practical use.

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