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Treatment of Wastewater by Material Based on Dates Rods

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Abstract

With the growth and development of the industry, the problem of pollution remains the most important subject of many scientists, since it affects several vital sectors. In this work, we focus on the treatment of water polluted with chemicals that can cause various health problems. For example, phenols and heavy metals are a major source of pollution, and are mainly the result of industrial wastes such as plastics, polymers, insecticides, etc.

In this context, the adsorption is a very effective industrial technique for eliminating these unwanted compounds. The objective of this study is to improve the adsorption capacity of a plant material, i.e. dates rods by using the activation process which contributes significantly in the increase of surface area and therefore the creation of active sites and the improvement of adsorption. The results show that the adsorbent derived from dates rods and activated by various acids (nitric, phosphoric, hydrochloric and sulfuric acid) at different concentrations does not behave in the same way towards the solutes. The best activation was obtained from concentrated acid giving a maximum adsorption rate (97.99%) for copper ions with a burn-off equal to 77% for an adsorbent mass of 2g and a volume of bulk solution of 25mL. On the other hand, it has been proved that the adsorbent is more selective for copper ions than phenol molecules; contained both in solutions whatever the activating agent.

Keywords: Dates Rods; Adsorption; Phenol; Copper Ions; Adsorption Rate; Burn-Off

Introduction

Many methods are available for the elimination of pollutants from wastewaters including physico chemical and biological treatment techniques (solvent extraction, chemical oxidation by ozone, ion exchange by resins, photocatalytic, electrodialysis filtration and adsorption. However, these methods are not preferable due to their high cost of investing, operating and equipping [1-3]. Over the last few years, the use of adsorption to remove pollutants from aqueous solutions is a powerful technology especially using locally available adsorbents [4]. Agricultural waste materials are cost effective and eco-friendly materials due to their unique chemical composition, availability, low cost, being renewable, and other many factors that attract many researchers toward such studies. This work concerns the use of date rods as an agricultural waste material in wastewater treatment. The date rods waste can be an alternative and favorable adsorbent material for pollutants since it is abundantly available in Algeria and can be considered as cost effective sorbent. To our knowledge, minor works were carried on date rods to remove pollutants from contaminated solutions [5-7].

The authors indicated that date rods have the average composition of most of lignocellulosic precursors [6]. A proximate analysis of this material has shown the following composition (Ash 5%, Moisture 3%, Volatile matter 67.24% and fixed carbon 24.76%). For other characteristics of date rods, the X-Ray diffraction of the raw material sample i.e. the date rods, a broad peak appearing at $2\theta = 21.786°$ is a typical silica characteristic, which can be attributed to the presence of disordered cristobalite [6,8]. On the other hand, analysis of nitrogen adsorption isotherm of the raw date rods results a specific surface area and a pore volume of 5.9 m^2 /g and 0.07 cm^3 /g respectively [9].

In the literature several works have shown that thermal and/or chemical activation process changes irreversibly the surface condition of the raw material to thereby allow adsorption retention of different organic substances and inorganic [10-12]. In this context, our contribution is focused on removal of heavy metals i.e. copper ions in single salt solutions and in mixed solutions with phenol. The enhancement of the adsorption capacity of the material prepared from date rods has been carried by using the activation process. The effect of the nature and the concentration of activating agent have been investigated.

Experimental

Preparation of Adsorbent

The adsorbent material used in this study was prepared from dates rods which were washed thoroughly with distilled water and dried at 105 °C for 15 hours. Then they were crushed and sieved. The obtained material was treated chemically with different acids: nitric acid, sulfuric acid, phosphoric acid and hydrochloric acid at different concentrations: 3N, 7N, 10N and concentrated acid for 21 hours. At the end, it was washed with distilled water until neutral pH and dried at 105 °C for 48 hours. The following figure gives an idea about appearance of the product resulting from this activation.

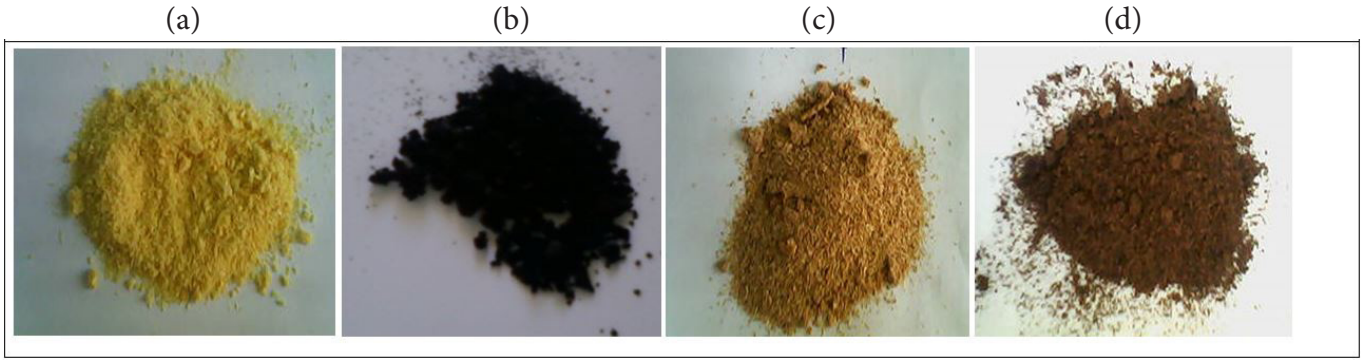


Figure 1: Photos of different adsorbents resulting of dates rods activated by **(a)** nitric acid; **(b)** sulfuric acid; **(c)** phosphoric acid; **(d)** hydrochloric acid

After activation process a decrease in the mass of adsorbent has been observed. This phenomenon can be expressed by the degree of activation or activation rate whose is called "Burn-off". Indeed, the activation reaction produces a porous material of a lower mass than to its initial mass. The degree of activation depends upon the nature of the activating agent and the duration of activation. It was calculated using the following equation:

$$\text{Burn-off (\%)} = [(\text{initial mass} - \text{final mass}).\ 100] / \text{initial mass} \quad (1)$$

Experiment Adsorption

The activated material derived from date rods used in this study was tested of viewpoint its retention capacity of metal ions and organic molecules dissolved in water. Therefore adsorption solutions were prepared from single salt $CuSO_4.5H_2O$ and from a mixture containing $CuSO_4.5H_2O$ and phenol molecules. The concentration of each solute was fixed at 100 mg L^{-1} in both single salt solutions and in the mixtures. 2g of solid material was mixed with 25 mL of solution and stirred at a temperature of 18 ± 2 °C with a speed of 300 rpm for a contact time equal to six hours. No adjustment of pH has been realized. At the end of the adsorption, solution was filtered by centrifugation at speed of 5000 rpm for 30 minutes to ensure the separation of fine solid particles. Analysis of copper ions contained in the filtrates was made by complexing with EDTA at pH 10 in the presence of Murexide while that of phenol molecules was made by UV-Visible spectrophotometer (Jenway) at wave length of 270 nm. All reagents were supplied by Fisher Scientific and all solutions were prepared from analytical grade products and distilled water. The adsorption rate was calculated in percentage (R %) by following formula :

$$R\ (\%) = [(C_0\ V_0 - C_e\ V_e).100] / C_0\ V_0 \quad (2)$$

Where C_0 and C_e represent respectively the initial and equilibrium concentration while V_0 denotes the initial volume of solution before adsorption and V_f after adsorption. In this study the uncertainty analyzes have reached 5% in all trials adsorption and each assay were repeated at least three times.

Results and Discussions

Effect of the Concentration of Activating Agent on the Adsorbent Mass

The Burn-off percentage generally increases with increasing the concentration of the activating agent and appears also very affected by the nature of the acid (Table 1). The best rate of activation is obtained by impregnation of the adsorbent in the concentrated sulfuric acid (Burn-off = 77%). This result can be explained by the fact that H_2SO_4 is the stronger acid in all acids used. Indeed, it also proves the role of acid in the elimination of contents tarred inside the pores of adsorbent material and therefore causes the loss of its mass as it is shown in Figure 2:

	HNO_3	H_3PO_4	H_2SO_4	HCl
Acid concentration	**Burn-off (%)**			
3N	52	49.8	44.5	11
7N	61	49.5	53	45
10N	64	50	52	51.5
Concentrated acid	69.3	49.4	77	60

Table 1: Burn-off of activated adsorbent based on date rods: initial mass of Adsorbent =10g, activation time = 21 hours

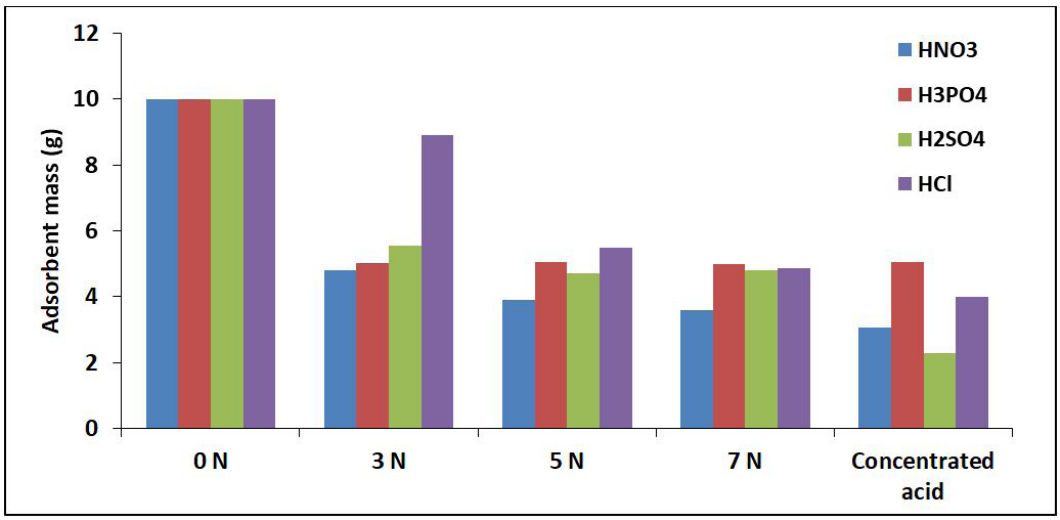


Figure 2: Variation of adsorbent mass versus concentration of activating agent

Effect of the concentration of activating agent on the adsorption rate of copper ions in single salt solutions

The results obtained in Figure 3 show that the rate adsorption of copper ions on raw material is 17.45% and it is improved when the concentration of the acid increases. The best efficiency is about of 97.99 % corresponding to a high Burn-off value (77% see Table 1) deduced from activation of date rods with concentrated sulfuric acid. This result can be explained by the increase in specific surface area of adsorbent and the creation of micro-pores which strongly contribute to the adsorption of copper ions. The specific surface area of date stems increased until a 682 m^2/g when they were activated by phosphoric acid [6].

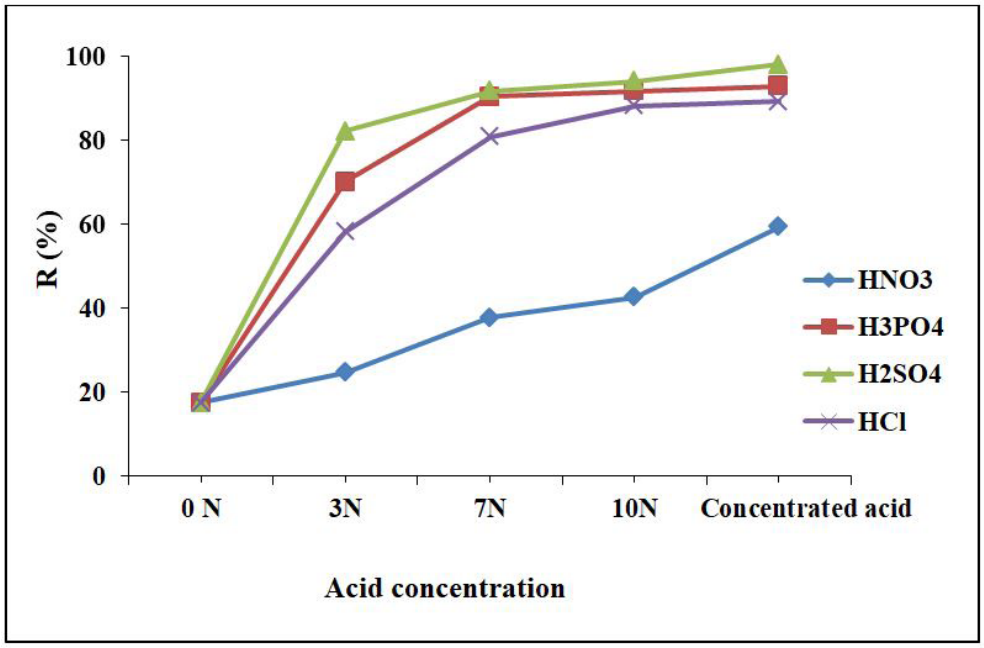
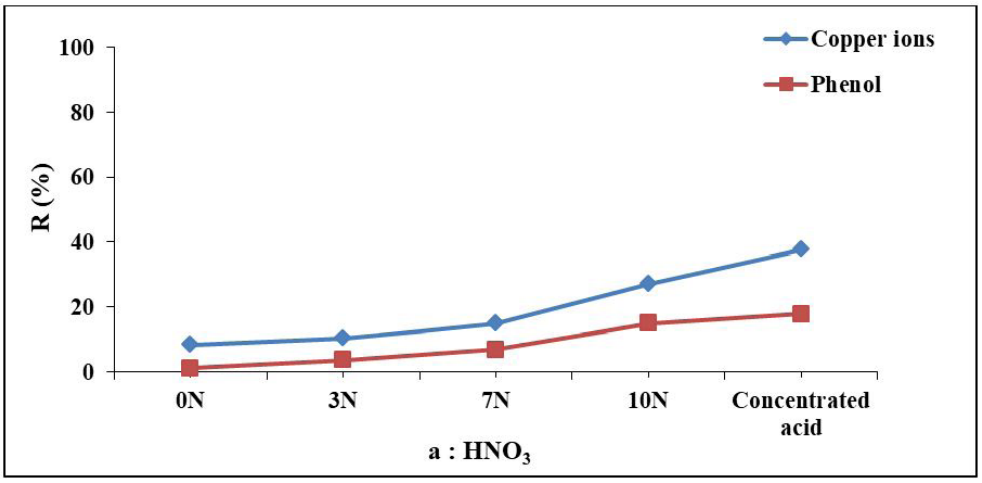


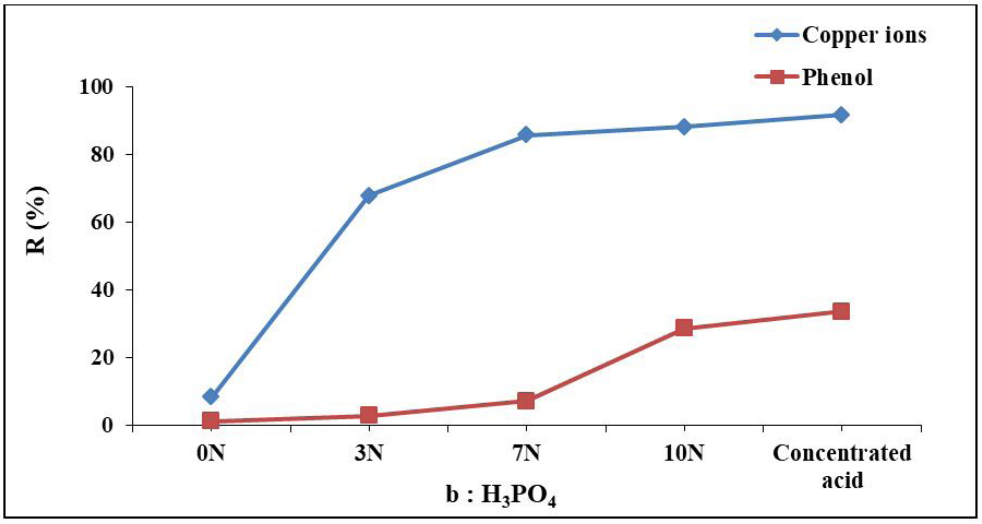
Figure 3: Adsorption rate of copper ions versus concentration of activating agent. $[Cu^{2+}]_0$ = 100 mg.L^{-1}. Adsorbent mass = 2 g. $V_{CuSO4.\,5H2O}$ = 25 mL. Stirring speed = 300 rpm. Contact time = 6 hours. Temperature = 18 ± 2 °C.
pH = 5.6 ± 0.1 (natural pH).

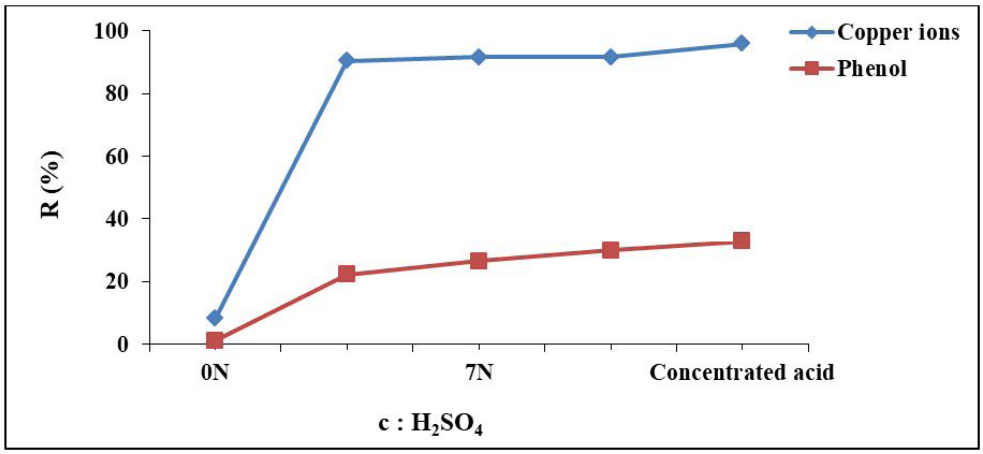
On the other hand, the adsorption rate of copper ions obtained after adsorption on date rods treated with phosphoric acid at 7N, 10N and concentrated acid are almost identical i.e. 90.42%, 91.62% and 92.82% respectively. This finding can be explained by the similar values of Burn-off found previously (49.5%. 50% and 49.4% see Table 1).

Adsorption rate of copper ions and phenol on date rods in mixed solutions

The adsorption rate of copper ions and phenol molecules present simultaneously at equal mass concentrations in solutions i. e. 100 mg.L^{-1} for each solute are illustrated in Figure 4 (a-d).







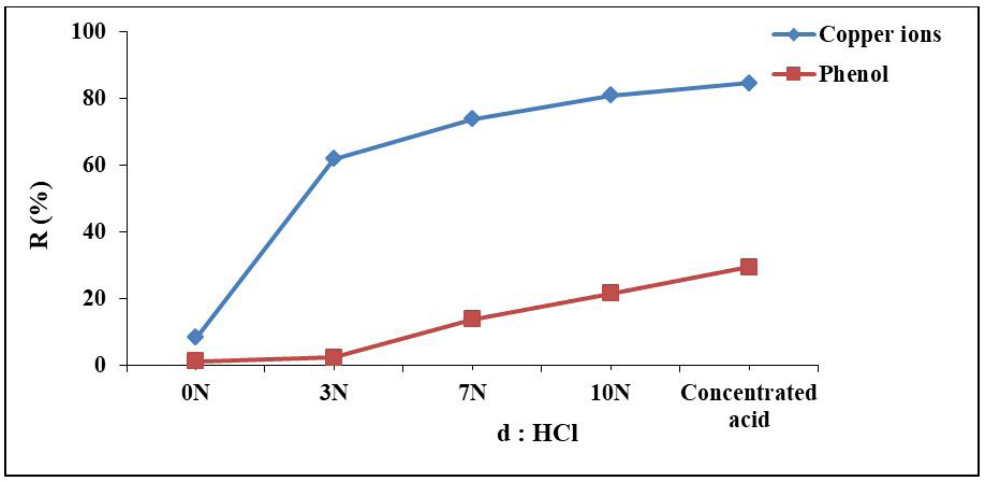


Figure 4 (a-d): Adsorption rate of copper ions and phenol versus concentration of activating agents. $[Cu^{2+}]_0 = [C_6H_6O]_0$=100 mg.L^{-1}, adsorbent mass = 2 g. $V_{(solution)}$= 25 mL, stirring speed = 300 rpm, contact time = 6 hours, temperature = 18 ± 2 °C, pH = 5.6 ± 0.1 (natural pH).

The results indicate that the retention of the adsorbent towards copper ions and phenol was enhanced by increasing the concentration of the activating agent. This seems very logical view that the activation process improves the surface area of adsorbent and gives it more active sites for the adsorption. The adsorption of the two components depends also on the nature of the activating agent, e.g.:

- The best rates adsorption for both copper ions and phenol are obtained from date stems activated by concentrated acids.
- Adsorption rates of copper ions are 37.79% (nitric acid), 84.44% (hydrochloric acid), 91.62% (phosphoric acid) and 95.91% (sulfuric acid).
- Adsorption rates of phenol are 17.85% (nitric acid), 29.28 % (hydrochloric acid), 33.57% phosphoric acid) and 32.85% (sulfuric acid).

Table 2 summarizes the average adsorption rates calculated using formula (3) and this in simple solutions containing only copper ions and in mixed solutions containing copper ions and phenol molecules at the same time.

		HNO3	H3PO4	H2SO4	HCl
Single solution	Raverage(%) Cu2+	36.35	72.48	76.62	66.75
Mixed solution	Raverage (%) Cu2+	19.67	68.24	75.56	61.78
	Raverage (%) C6H6O	8.86	14.64	22.5	13.50

Table 2: Results of mean adsorption rates of copper ions contained in single salt solutions and in mixed solutions with phenol

$$Raverage(\%)=[R(0N)+R(3N)+R(7N)+R(10N)+R(concentrated\ acid)]/5 \quad (3)$$

It is found that the best results are obtained by activating the adsorbent with sulfuric acid. Comparing the adsorption of copper ions in simple and mixed solutions, it is clear that this later is not affected by the presence of phenol molecules except in the case of adsorbent activated by nitric acid which caused a decrease of about 50% (Table 2). This finding may be explained by the fact that the activation caused by nitric acid makes the adsorbent less attractive to these ions.

The adsorbent is more selective to copper ions than phenol whatever the activating agent; this results can be attributed to the presence of carboxylic (-COOH), hydroxyl (-OH) and carbonyl (-C=O) groups on surface of date rods [6], which can make the material negatively charged and therefore enhances the adsorption of positively charged copper ions through electrostatic forces of attraction [13]. Other studies have also shown that the carboxyl and hydroxyl groups inhibit the adsorption of phenol by increasing the adsorbent affinity for water. These groups have a tendency to form hydrogen bonds with the molecules water promoting their competitive adsorption and leading to the formation of true aggregates that block access of molecules pollutants to micro pores [14]. The phenomenon can be explained by the steric effect and also the difference between diffusivities of copper ions and phenol which makes copper ions more adsorbed than phenol [15].

Conclusion

The material prepared from date rods and activated by different acids: nitric, phosphoric, hydrochloric and sulfuric acid; is a good candidate for the treatment of wastewater contaminated by heavy metal. The nature and the concentration of the activating agent affect clearly the mass of the adsorbent and also the retention of pollutant. The adsorption of copper ions in single salt solutions has reached 97.99 % in the case of date rods activated by a concentrated sulfuric acid. In mixed solution, the material based on date rods become more selective towards copper ions than phenol molecules for example in the case of adsorbent activated by concentrated sulfuric acid the adsorption rate is about of 95.91% for copper and 32.85% for phenol.

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