Kinetic Study of the Adsorption of Zinc and Copper Ions on to Activated Carbon Prepared from Date Pits

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Received: 2020-12-23   Accepted: 2021-10-20   Published: 2021-11-08

ABSTRACT

In the present work, an activated carbon material has been prepared from date pits to remove zinc (Zn²⁺) and copper (Cu²⁺) from a wastewater. The effect of some parameters on adsorption performance has been investigated. The optimization of operational conditions allowed increasing the adsorption of Zn²⁺ ions from 33% to 85% and the adsorption of Cu²⁺ from 23% to 70%. The optimum conditions found are a mass of adsorbent of 4g, a stirring speed of 500 rpm and a ratio of 15 for volume of liquid / mass of solid. It has been shown that the adsorbent has more affinity to the copper ions than zinc ions and the modeling results gave adsorption isotherms type “C”. The results also showed that the kinetics of zinc and copper ions adsorption were described by a pseudo second-order rate model and controlled by the internal diffusion which can be considered as limiting step that controls the rate transfer of these ions to the solid surface.

Keywords: Activation, Adsorption, Modeling, Date pits, Heavy metals, Kinetics
Introduction

The awareness of the problem of inorganic pollutants in wastewater has led the government to implement laws more stringent towards releases from various sources (industrial, urban and agricultural). The presence of heavy metals in aqueous solution beyond certain limit creates serious threat to the environment due to their non-degradability and toxicity [1]. Heavy metals possess the ability to concentrate along the chain and to accumulate in some organs of the human body. It is therefore essential to completely remove these ions present in various industrial effluents or reduce their amount below permissible limits defined by the standards.

Many methods and decontamination techniques developed over recent years, among these techniques, it can be noted chemical precipitation processes [2], ion exchange [3], membrane processes [4] and adsorption on solids [5, 6]. Several studies have shown that a variety of materials of plant origin had the ability to fix heavy metals [7-9]. Date pits have been used as a potential sorbent for the removal of heavy metals [10-12]. Significant amounts of date pits are generated each year and are an important source of agricultural waste. Such as products correspond to this loss are nevertheless likely to have a significant economic interest. Therefore, it appears important to recover such as waste by transforming it into coal capable to fix the pollutants contained in wastewater which allows reducing pollution and protect environment.

The main objective of this contribution is to improve the adsorption of vegetable waste, namely the date pits, to decontaminate aqueous solutions containing zinc and copper ions in similar concentrations of Algerian wastewater. To this end, certain treatment operations have been carried out on the raw adsorbent, which do not require significant investment in energy or in materials, and also some parametric factors have been optimized during the adsorption.

Experimental

Preparation of adsorbent

The date pits were washed thoroughly with distilled water, dried at 105 °C for 24 hours then crushed and sieved. The ground material obtained in the previous step is stored for one hour in absence of air in sealed capsules of porcelain and carbonized in a muffle furnace at 800 °C. The carbonized coal has been chemically activated by nitric acid. A mass of coal was placed in a
beaker containing nitric acid concentration of 10N. The mixture was stirred for 24 hours then filtered through a filter paper. The filtrate is washed for two days with distilled water until a neutral pH. The weight of activated carbon was dried in an oven at 105 °C for 48 hours.

**Reagents and solutions**
During the adsorption tests, salt solutions were prepared from (ZnSO₄, 7H₂O) and (CuSO₄, 5H₂O) supplied by Fisher Scientific. The concentration of each metal was fixed at 100 mgL⁻¹. All solutions were prepared from analytical grade products and distilled water. No adjustment of pH has been realized.

**Instruments**
An electronic balance (type KernABS) was used to measure the weights. The solutions were stirred by a Wise Stir MS-MP8 magnetic stirring platform. The measurements of pH were performed with a pH-meter by Ionolab (level 1 WTW). The adsorption solutions were centrifuged using a centrifuge of Hettich EBA 200 type.

**Adsorption of metal ions**
An amount of activated carbon derived from date pits was mixed with the solution of heavy metals (Zn SO₄· 7H₂O or CuSO₄· 5H₂O) at a concentration of 100 mgL⁻¹ for each metal and stirred on a magnetic stirrer under a well-defined speed and at ambient temperature (20 ± 2 °C) from 15 minutes to 6 hours. At the end of adsorption, the coal particles were separated from the study solution by centrifugation speed at 5000 rpm for 30 minutes. The filtrate obtained was analyzed by adding of EDTA as complexing agent at pH 10 in the presence of colored indicator (murexide) to determine the residual concentration of metal ions.

To improve the adsorption capacity of activated carbon derived from date pits towards metal ions of copper and zinc power, some conditions parameters have been optimized such us contact time, ratio volume of liquid / mass of solid and stirring speed.

**Results and discussion**
The efficiency adsorption of metal ions was expressed in terms of an adsorption rate (Tx %) calculated by the ratio of the adsorbed amount to the initial amount:
\[ T_x (\%) = \frac{(c_0 - c_e) \times 100}{c_0} \]  

(1)

Where:

\( C_0 \) and \( C_e \) represent respectively the initial and equilibrium ions concentration.

It should be noted that during the adsorption experiments the volume of solution has not been changed.

**Kinetics and mass transfer study**

**Equilibrium time**

The results show that the adsorption capacity increases with the contact time to reach a maximum level that starts from 3 hours for \( \text{Zn}^{2+} \) ions and from 2 hours for \( \text{Cu}^{2+} \) ions. This time is considered the equilibrium time for these ions (Figure 1). This phenomenon can be explained by diffusion of zinc and copper ions to adsorption sites to reach a steady state where all the sites become occupied.

![Figure 1. Adsorption kinetics of zinc and copper ions onto activated carbon prepared from date pits. \([\text{Zn}^{2+}]_0 = [\text{Cu}^{2+}]_0 = 100 \text{ mgL}^{-1}\), adsorbent mass = 2g, stirring speed = 300 rpm, \( V_{\text{Liquid}}/m_{\text{Solid}} \) =10, temperature = 20 ± 2 °C.](image)

**Kinetic modeling**

The kinetics adsorption of zinc and copper on activated carbon prepared from date pits can be modeled using the first-order rate equation of Lagergren [13], the pseudo second-order rate
equation [14] and the second order rate equation shown below in Eqs. (2) - (4), respectively:

\begin{equation}
\log (q_e - q_t) = \log q_e - \frac{k_L}{2.3} t
\end{equation}

\begin{equation}
\frac{t}{q_t} = \frac{1}{k' q_e^2} + \frac{1}{q_e} t
\end{equation}

\begin{equation}
\frac{1}{(q_e - q_t)} = k t + \frac{1}{q_e}
\end{equation}

Where \( k_L \) is the Lagergren rate constant of sorption (min\(^{-1}\)), \( k' \) the pseudo-second-order rate constant of sorption (g mg\(^{-1}\) min\(^{-1}\)), \( k \) the rate constant (g mg\(^{-1}\) min\(^{-1}\)), \( q_e \) and \( q_t \) are the amounts of metal adsorbed (mg g\(^{-1}\)) at equilibrium and \( t \) time, respectively. \( q_e \) is determined as follow:

\begin{equation}
q_e = \frac{X}{m}
\end{equation}

\( m \) represents the weight of the solid sample and \( X \) is defined as follows: [15]

\begin{equation}
X = (C_0 - C_e) V
\end{equation}

With \( V \) denotes the volume of solution.

For initial zinc and copper ions concentrations of 100 mgL\(^{-1}\), the different values of constants from the slopes and intercepts of linear plots of \( \log (q_e - q_t) \) versus \( t \), \( t/q_t \) versus \( t \) and \( 1/(q_e - q_t) \) versus \( t \) (figures not shown here) are summarized in Table 1. Only, the pseudo-second-order reaction rate model adequately describes the kinetics of both zinc and copper ions adsorption with a relatively high correlation coefficient.

Table 1. Rate constants for zinc and copper ions adsorption kinetics onto activated carbon prepared from date pits.
### Diffusion process

The transfer of a solute from an aqueous phase to a solid phase typically follows four steps, which may be either independent of each other, or simultaneously. The first step represents the migration of the solute from the aqueous phase to the solid surface. The second step is the diffusion through the interparticle spaces (external diffusion). The third step concerns the intraparticle diffusion (internal diffusion), and finally, the last step concerns the chemical reaction surface between the adsorbent surface functions and active groups of solute. It should be noted that the first step can be controlled from a good stirring, while the latter is rather fast, suggesting that the diffusion process are more likely to be the limiting step controlling adsorption.

Modeling the transfer of a solute from a liquid phase to a solid phase, to express the external diffusion is often given by the expression: [16]

\[
\ln \frac{C_0 - C_e}{C_t - C_e} = k_{ex} \cdot t \tag{7}
\]

Where \(C_t\) is the ions concentration at time \(t\) and \(k_{ex}\) is the constant of external diffusion. The plot of \(\ln(C_0-C_e/C_t-C_e)\) as function of time should shows if the external diffusion constitute the limiting step in the adsorption phenomenon.

From figure 2, it is easy to see that the external diffusion of both zinc and copper ions between the adsorbent particles is not a critical step in the adsorption process. The experimental points do not fit on the equation of this model (\(R^2\) values are not high); in addition the lines do not pass through the origin. The values of the constant of external diffusion \(k_{ex}\), as well as those of \(R^2\), do not reflect a good correlation (table 2). The surface reaction of pseudo-second order, faster,
should outweigh the external diffusion around the particles of the adsorbent.

According to [17], the intraparticle diffusion kinetics expression is often presented by the equation:

$$q_t = k_{in} \cdot t^{1/2} + C$$  \hspace{1cm} (8)$$

Figure 3 presents the plot of this model for both zinc and copper ions contained in simple solutions at 100 mg L$^{-1}$. The values of the constant $k_{in}$ of intraparticle diffusion and those of $R^2$ are given in Table 2. From this figure, it can be seen that the intraparticle diffusion is a significant step in the adsorption process. The experimental points aligned with a considerable regression coefficients, indicate that the step the most influential in the adsorption of zinc and copper ions on the activated carbon prepared from dates of nuclei remains the intraparticle diffusion process, since it can be considered as limiting step that controls the rate transfer of these ions at each time $t$. 
Figure 3. Application of internal diffusion model for zinc and copper onto activated carbon prepared from date pits. 

\[
[Zn^{2+}]_0 = [Cu^{2+}]_0 = 100 \text{mgL}^{-1}, \text{ adsorbent mass} = 2\text{g}, \text{stirring speed} = 300 \text{ rpm}, \\
V_{\text{Liquid}}/m_{\text{Solid}} = 10, \text{temperature} = 20 \pm 2 \, ^\circ\text{C}.
\]

Table 2. Diffusion parameters of zinc and copper ions adsorption onto activated carbon prepared from date pits.

<table>
<thead>
<tr>
<th></th>
<th>([Zn^{2+}]_0 = 100 \text{mgL}^{-1})</th>
<th>([Cu^{2+}]_0 = 100 \text{mgL}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>External diffusion</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k_{\text{ex}})</td>
<td>0.0206</td>
<td>0.0210</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.8615</td>
<td>0.7924</td>
</tr>
<tr>
<td><strong>Internal diffusion</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(K_{\text{in}}) (m. L^{-1}.min^{-0.5})</td>
<td>0.0185</td>
<td>0.0247</td>
</tr>
<tr>
<td>(C)</td>
<td>0.1544</td>
<td>0.0481</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.9556</td>
<td>0.8485</td>
</tr>
</tbody>
</table>

**Effect of operational conditions**
Mass of adsorbent

Figure 4 shows that for a constant initial concentration of zinc ions (100mgL⁻¹) and an equilibrium time of 3h, an increase of the adsorbent mass from 1 to 6g results fairly significant rise in the adsorption rate. Indeed, the adsorption rate of the studied element pass from about 15% for a mass of 1g to a rate of about 33% for 4g Similarly for copper ions, for equilibrium time of 2h, the adsorption rate pass from about 13% for 1g of adsorbent to 23% for 4g. The increase in absorption rate is due to the increase in specific surface area of the adsorbent. However, beyond 4g of adsorbent, the adsorption becomes stable and no improvement in adsorption efficiency was noticed. This finding is in good agreement with some works reported by several authors [18-20]. Therefore a mass of 4 g was designated as the optimal mass of adsorbent.

![Graph showing the influence of adsorbent mass on the adsorption of zinc and copper ions.](image)

**Figure 4.** Influence of activated carbon mass derived from date pits on the adsorption of zinc and copper ions. [Zn²⁺]₀ = [Cu²⁺]₀ =100 mgL⁻¹, stirring speed = 300 rpm, contact time (Zn²⁺) = 3 hours, contact time (Cu²⁺) = 2 hours, V_Liquid/m_Solid =10, temperature =20 ± 2 °C.

**Ratio volume of liquid / mass of solid**

The effect of the ratio; volume of liquid / mass of solid; on the adsorption capacity of activated
carbon has been examined (Figure 5). The chosen ratios are 5, 10, 15 and 20. Both adsorption histograms pass through an optimum (Tx=70% for Zn$^{2+}$ and Tx=55% for Cu$^{2+}$) for a ratio equal to 15, which is equivalent to a volume of 60 mL of aqueous phase. In these experiments the mass of adsorbent used being constant (4g), by against the amount of metallic ions increases by increasing the volume solution for the same metal concentration (100 mgL$^{-1}$). In fact, the optimum obtained reflects a complete saturation of active sites of the activated carbon by the metal ions.

![Figure 5](image.png)

**Figure 5.** Effect of the ratio ($V_{\text{Liquid}}/m_{\text{Solid}}$) on the adsorption of zinc and copper ions onto activated carbon prepared from date pits, $[\text{Zn}^{2+}]_0 = [\text{Cu}^{2+}]_0 = 100 \text{ mgL}^{-1}$, adsorbent mass = 4g, stirring speed = 300 rpm, contact time (Zn$^{2+}$) = 3 hours, contact time (Cu$^{2+}$) = 2 hours, temperature =20 ± 2 °C.

**Stirring speed**

The results presented in figure (6) show that the highest capacity adsorption take place at speed of 500 rpm/ min (Tx=85% for Zn$^{2+}$ and Tx=70% for Cu$^{2+}$). At this value of speed, probably a good diffusion of ions towards the support is ensured; unlike the case of low speeds, where diffusion is insufficient and cannot provide the necessary energy for metal ions to be adsorbed. For a high speed stirring, the adsorbent particles will agglomerate and ions will not have enough of contact surface promoting their adsorption, furthermore the metal ions will not have enough contact time to be linked at adsorbent surface. Several works have reported similar results concerning the effect of the speed on the adsorption of metal ions on biomaterials [21, 22].
Figure 6. Effect of stirring speed on the adsorption of zinc and copper ions onto activated carbon prepared from date pits. \([\text{Zn}^{2+}]_0 = [\text{Cu}^{2+}]_0 = 100 \text{ mgL}^{-1}, \text{ adsorbent mass} = 4g, \text{ contact time (Zn}^{2+}) = 3\text{ hours}, \text{ contact time (Cu}^{2+}) = 2\text{ hours}, V_{\text{Liquid}}/m_{\text{Solid}} = 15, \text{ temperature} = 20 \pm 2 ^\circ\text{C.}

**Adsorption isotherms**

The isotherm is usually represented graphically. It reports the relationship between the amount of the adsorbed solute \((q_e)\) and solute concentration in the fluid phase \(C_e\) at the equilibrium. The adsorption results of zinc ions; contained at 100 mgL\(^{-1}\) in solution; on different mass of activated carbon derived from date pits and for a contact time of 3 hours showed a linear distribution of \(q_e\) as a function of the equilibrium concentration \(C_e\) (Figure 7). The observed curve is consistent with the isotherm "type C". This isotherm is characterized by a constant slope whatever the concentration of the species considered up to the maximum of adsorption. It corresponds to a linear isotherm, which means that the numbers of new adsorption sites are created during adsorption, and implies that isotherms of this class are obtained when the adsorbates are able to modify the texture of the material by opening pores which had not been opened previously by the solvent [22]. Modeling results adsorption (Figure 8) gives also a curve compatible with the isotherm "type C" for copper ions on different masses of activated carbon derived from date pits; with initial concentration equal to 100 mgL\(^{-1}\) and a contact time of 2 hours.
Comparison between the adsorption of zinc and copper ions

All adsorption experiments carried on salt solutions of zinc and copper sulfate showed that the material prepared from date pits and activated by the nitric acid has a greater affinity to copper than zinc. This affinity has been quantified in terms of a gap "E" which is expressed according to the following relation:

\[ E = \frac{1}{2} \left( \frac{C_{eq}^{Cu^2+}}{C_{eq}^{Zn^{2+}}} - 1 \right) \]
Table 3 summarizes all the percentage differences for each parameter studied i.e. contact time, mass of adsorbent, ratio volume of liquid / mass of solid and stirring speed. Values of «E» show a significant difference between the adsorption zinc and copper ions reaches up about 56 %. Since all the studied metal ions are divalent, these results can be ascribed to the size difference; zinc ions are smaller than the copper ions; which allows them to access easily to the active sites of the adsorbent and to be better adsorbed.

**Table 3.** Gap in percentage between the absorption rate of zinc and copper ions; calculated for different studied parameters.

<table>
<thead>
<tr>
<th>E₁ (%)</th>
<th>E₂ (%)</th>
<th>E₃ (%)</th>
<th>E₄ (%)</th>
</tr>
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<tbody>
<tr>
<td>26.57</td>
<td>18.12</td>
<td>55.31</td>
<td>55.31</td>
</tr>
<tr>
<td>(t=1h)</td>
<td>(m=1g)</td>
<td>(Vₗiquid/mSolid =5 mL/g)</td>
<td>(Speed=100 rpm)</td>
</tr>
<tr>
<td>2.10</td>
<td>15.52</td>
<td>31.24</td>
<td>20.33</td>
</tr>
<tr>
<td>(t=2h)</td>
<td>(m=2g)</td>
<td>(Vₗiquid/mSolid =10 mL/g)</td>
<td>(Speed=300 rpm)</td>
</tr>
<tr>
<td>15.51</td>
<td>29.91</td>
<td>20.33</td>
<td>17.15</td>
</tr>
<tr>
<td>(t=3h)</td>
<td>(m=3g)</td>
<td>(Vₗiquid/mSolid =15 mL/g)</td>
<td>(Speed=500 rpm)</td>
</tr>
<tr>
<td>15.51</td>
<td>31.24</td>
<td>4.66</td>
<td>-2.5</td>
</tr>
<tr>
<td>(t=4h)</td>
<td>(m=4g)</td>
<td>(Vₗiquid/mSolid =20 mL/g)</td>
<td>(Speed=700 rpm)</td>
</tr>
<tr>
<td>15.51</td>
<td>32.91</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(t=5h)</td>
<td>(m=5g)</td>
<td></td>
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<tr>
<td>15.51</td>
<td>32.91</td>
<td>-</td>
<td>-</td>
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<tr>
<td>(t=6h)</td>
<td>(m=6g)</td>
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**Conclusion**

This study concerns the activation of a hard plant material i.e. date pits and its use for the adsorption of heavy metals such as zinc and copper. The kinetics study shows that equilibrium time is reached after 3 hours for Zn²⁺ and 2 hours for Cu²⁺. The results also proved that the adsorption followed the pseudo-second-order kinetics and pointed out that the intraparticle
diffusion seems to be a significant step controlling the process. Optimization of operational conditions allowed increasing the adsorption rates of Zn\(^{2+}\) ions from 33\% to 85\% and of Cu\(^{2+}\) from 23\% to 70\%. These yields were obtained for 4g of coal, a ratio of 15 of volume of liquid / mass of solid and a stirring speed equal to 500 rpm. Indeed, the parametric study seems very effective to improve the absorbability of activated carbon prepared from date pits. Modeling results of adsorption of both ions gave curves compatible with the isotherm type C. The absorption of metal ions of copper and zinc showed that the affinity of the activated carbon is greater for the zinc than the copper ions; the difference found is about 56\%. Finally, a further study taking account other parameters such as the influence of pH and temperature would also be useful to improve the adsorption efficiency of the used coal.

**Acknowledgements**

The authors acknowledge the research grant provided by the Algerian Ministry of Higher Education and Scientific Research (project A16N01UN410120180002).

**References**


HOW TO CITE THIS ARTICLE