Characterization of biochar prepared from slow pyrolysis of Jordanian olive oil processing solid waste and adsorption efficiency of Hg\textsuperscript{2+} ions in aqueous solutions

Ali El Hanandeh, Rund A. Abu-Zurayk, Imad Hamadneh and Ammar H. Al-Dujaili

ABSTRACT

Solid waste from Jordanian olive oil processing (OOSW) was used to prepare biochar samples by slow pyrolysis at terminal temperatures of 350, 450, 550 and 630 °C; henceforth known as BC-350, BC-450, BC-550 and BC-630, respectively. These samples were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy and X-ray diffraction, ash content, moisture content and surface area. The ability of the biochar to remove Hg\textsuperscript{2+} ions from aqueous solutions was investigated in laboratory scale batch experiments. The kinetics, effect of pH and temperature were studied. The optimum pH value for Hg\textsuperscript{2+} adsorption was 5. Dubinin-Radushkevich (D-R) isotherm model was the best fit for the experimental results. Based on the D-R model, the maximum adsorption capacities at 25 °C were 84.93, 94.48, 96.11 and 104.59 mg.g\textsuperscript{-1}, for BC-350, BC-450, BC-550 and BC-630, respectively. The pseudo-second-order kinetic model was a good fit for the experimental data. The calculated change in free energy ΔG and enthalpy ΔH indicated that the adsorption process was spontaneous and exothermic in nature. The positive value of ΔS showed increased randomness of the solid/solution interface during the adsorption. The results indicated that biochar derived from OOSW can be a good adsorbent for treatment of water contaminated with Hg\textsuperscript{2+}.

Key words | adsorption, biochar, Hg\textsuperscript{2+}, mercury (II), olive husk, slow pyrolysis

INTRODUCTION

Mercury (Hg) is a highly toxic chemical that can cause serious health and environmental impacts. It can vaporize at low temperatures and can enter the human system through ingestion, inhalation and dermal contact. It can also bio-accumulate in living tissues (De et al. 2013). Therefore, Hg contamination of water bodies, even in low concentrations, can be a serious health and environmental risk.

Biochar is a promising material for heavy metal adsorption. Biochar can be produced from a variety of organic materials, such as waste and agricultural residue (Mohan et al. 2014). Olive oil production, worldwide, has been growing at a remarkable rate over the past two decades (International Olive Council 2015). However, olive oil processing generates large quantities of solid waste and wastewater (El Hanandeh 2015). On average, around 4–5 kg of olive fruit are required to produce 1 kg of olive oil. In addition to the olive oil, around 2.35 kg of solid waste (also known as olive husk and olive cake) and 4.5 L of wastewater are produced (Tsagaraki et al. 2007). Both waste streams are highly polluting and have been associated with adverse environmental effects such as soil hydrophobicity and phytotoxicity. In Jordan, olive oil production has doubled between 1991 and 2014 to reach 22,835 Mg (National Center for Agricultural research (NCARE) 2015); therefore, it is estimated that around 53,662 Mg of olive cake is produced in Jordan annually. Olive cake is a lignocellulosic material that can be processed to generate useful products such as biochar (El Hanandeh 2015). Interest in biochar production as a method for carbon-soil sequestration as well as soil amender has been growing (Lehmann et al. 2011). Biochar has also been suggested as a potential...
Adsorptions of heavy metals on biochars prepared from a variety of agricultural wastes have been previously studied. Tan et al. (2015) and Mohan et al. (2014) published extensive literature reviews on the application of biochars for heavy metal adsorption and water treatment. Both reviews showed that most researchers focused on Cu$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Cr$^{2+}$ and Cr$^{6+}$. On the other hand, very few studies were found about Hg adsorption using biochar.

De et al. (2013) reported that activated carbon prepared from biochar and impregnated with halides were effective for removing Hg$^{2+}$ from aqueous solutions. Biochars with and without iron oxide impregnation were compared for their efficiency to adsorb Hg$^{2+}$ from aqueous solutions. Iron oxide impregnated biochars showed improved capacity for heavy metal adsorption (Ramola et al. 2014). The removal of elemental Hg by adsorption on biochar was also investigated. Li et al. (2015) compared biochars prepared from agricultural, medical and municipal solid waste for their ability to remove elemental mercury from flue gas. They found that biochar prepared from agricultural waste and impregnated with NH$_4$Cl was more efficient than activated carbon for the removal of Hg. However, activation and impregnation are expensive processes and may pose a challenge to reactivate.

Klasson et al. (2014) experimented with the effect of pyrolysis temperature on the adsorption capacity of biochar for Hg from simulated flue gas. They reported that washed biochar made from poultry manure at 650 and 800 °C were able to remove 95% of Hg$^{2+}$ ions from flue gas. Biochar produced from malt spent rootlets at 850 °C was also investigated for its potential to sorb Hg$^{2+}$ ions from aqueous solutions. Based on batch experiments, biochar was able to remove 71–100% of Hg$^{2+}$ ions from aqueous solution (50 mg L$^{-1}$) with biochar dose ranging from 0.3–1.0 g L$^{-1}$ (Boutsika et al. 2014).

The literature suggested that the removal efficiency depended on initial concentration, dose rate, pH, pyrolysis temperature and parent biomass. Although different biochars were investigated for their potential as low cost adsorbents to treat Hg$^{2+}$ contaminated waters, no attempt was done to study the potential use of biochar prepared from the olive oil processing industry. This study aims to characterize the biochar produced at different pyrolysis temperatures from Jordanian olive oil processing waste and to investigate the effect of pyrolysis temperature on the Hg$^{2+}$ removal efficiency of the product.

### MATERIALS AND METHODS

Four samples of biochar were prepared in the laboratory from olive husk obtained from a modern olive press in northern Jordan. The samples were prepared using slow pyrolysis at terminal temperatures 350, 450, 550 and 630 °C. The product biochar was then used in all of the characterization and adsorption experiments.

### Biochar preparation

Olive husk was ground into fine powder (particle size < 0.5 mm). Four samples of 40 g each were measured. Each sample was wrapped tightly in aluminum foil. A small hole was made in the wrapping using a needle to allow the evolved gases (when placed in the furnace) to escape. The sample was placed inside a tube furnace (Protherm PC 402). The furnace was programmed to reach the terminal pyrolysis temperature (350, 450, 550 or 630 °C) at a heating rate of 20 °C per minute and stay at the terminal temperature for 1 h before cooling down gradually to room temperature. Samples were then removed and placed in the desiccator for 15 min before the biochar yield was weighed. Samples were finally labelled according to their terminal pyrolysis temperature as: BC-350; BC-450; BC-550 and BC-630 and stored in air tight containers for further use.

### Biomass and biochar characterization

To gain a better understanding of the biomass and biochar characteristics the following analyses were conducted: pH; electric conductivity (EC); moisture content; ash content; specific surface area; scanning electron microscopy (SEM); X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR).

### pH measurement

The pH was determined following the method described by Ahmedna et al. (2000) where the biomass or biochar was mixed with distilled water at a ratio of 1 g: 20 mL distilled water. The slurry was continuously stirred and heated to 90 °C for 20 min and then allowed to cool to room temperature before the pH reading was taken.

### Moisture content

Moisture content (mc) of biomass was determined by drying samples in the oven at 105 °C for 24 h and recording the
weight loss after allowing the samples to cool down in the desiccator for 15 min. Mc was calculated using Equation (1).

\[
mc = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \times 100
\] (1)

**Ash content**

Ash content was determined according to ASTM D1762-84 standards (ASTM International 2013). Oven dry samples were placed in open crucibles and weighed. The samples were combusted in the tube furnace for 3 h at 650 °C. Samples were allowed to cool down gradually to room temperature in the furnace then moved to the desiccator before finally weighing them.

**Surface area estimation using iodine number**

The total surface area of the biochar was estimated using the Iodine Number following the ASTM D4607-94 method (ASTM International 2011).

**Surface functional groups (FTIR)**

The FTIR spectra of the biochar samples were obtained using a Perkin Elmer 1600 FTIR spectrophotometer over the range 4,000–400 cm\(^{-1}\) after embedding the samples in KBr discs, to determine the surface functional groups.

**Scanning electron microscopy (SEM) and XRD**

The surface morphology of the biochar was scanned using the electron microscope (FEI inspect F50 scanning electron microscope) operated at accelerating voltages of 2 kV with magnification of \(\times 15,000\). The mineralogical compositions of the samples were determined from the XRD patterns of the samples using XRD (7000 Shimadzu 2 kW model X-ray spectrophotometer with a nickel filtered copper X-ray radiation (Cu Kα 1.5418 Å).

**Hg\(^{2+}\) adsorption studies**

A series of batch experiments were carried out by shaking adsorbent with 50 mL aqueous solution of Hg\(^{2+}\) to determine the effects of various process parameters as described in the following subsections.

### The calibration curve and Hg\(^{2+}\) concentration measurement

Concentration of Hg\(^{2+}\) ions in solution were measured using inductively coupled plasma (ICP) analysis (GBC Scientific Equipment). Standard Hg\(^{2+}\) solutions with concentrations that varied from 10 to 100 mg.L\(^{-1}\) were prepared to generate the calibration curve; Yttrium salt was used as interference reagent.

### The effect of pH

A solution with initial Hg\(^{2+}\) concentration of 70 mg.L\(^{-1}\) was prepared. Then, 0.05 g biochar was added to a series of 50 mL samples of the solution at a pH range from 2 to 7 and set for overnight agitation; the pH of the solution was monitored and adjusted by adding 0.1 M HCl and 0.1 M NaOH solution as required.

### Isotherm study

The adsorption isotherms for the adsorbent were obtained by varying the Hg\(^{2+}\) solution initial concentration over the range 40–100 mg.L\(^{-1}\) at pH = 5 and biochar dosage of 0.05 g per 50 mL solution at 25 °C temperature. Experimental data were fitted to Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) models.

The metals uptake capacity, \(q_e\) (mg metal adsorbed per g adsorbent), was calculated from the mass balance equation as follows:

\[
q_e = \frac{(C_i - C_{eq})V}{m}
\] (2)

where \(C_i\) is the initial concentration (mg.L\(^{-1}\)); \(C_{eq}\) is the equilibrium concentration (mg.L\(^{-1}\)) of the Hg\(^{2+}\) ion in the aqueous phase; \(V\) is the volume of solution (L) and \(m\) is the mass of the adsorbent (g).

The percentage removal (%R) of Hg\(^{2+}\) ions was calculated as follows:

\[
%R = \frac{(C_i - C_{eq})}{C_i} \times 100
\] (3)

All experiments were performed in triplicate and the mean values reported. Blank tests were performed as well.

### Equilibrium time

A constant amount (0.05 g) of adsorbent was added to 50 mL of 70 mg.L\(^{-1}\) Hg\(^{2+}\) solution. The content in the
flask was shaken for the desired contact time (260 min) in an electrically thermostated reciprocating shaker at 350 rpm. The time required for reaching equilibrium condition was estimated by drawing samples at prescribed time intervals (5, 10, 15, 30, 45, 60, 90, 120, 150, 180, 210, 240 and 260 min). The content of each flask was separated from the adsorbent by centrifuging at 3,500 rpm and the supernatant liquid was analyzed for the remaining Hg²⁺ concentration in the sample.

Temperature effect

The thermodynamic effect was studied by agitating 70 mg L⁻¹ solution of Hg²⁺ ions solution with 0.05 g of adsorbents at temperatures 25, 35, and 45 °C for a time period of 210 min.

RESULTS AND DISCUSSION

The results showed that pyrolysis temperature affected the product biochar characteristics and the adsorption capacity of Hg²⁺. The following sections present the experimental results in further detail.

Biochar characteristics

The original biomass (dried olive oil processing solid waste) had 8.9% moisture content; it was slightly acidic (pH = 5.81) and had moderate electric conductivity (EC = 5.46 μS/cm). The characteristics of the four biochar (BC-350, BC-450, BC-550 and BC-630) are presented in Table 1. As expected, the highest yield (35.5%) was obtained at the lowest pyrolysis temperature (350 °C) and the yield decreased with increasing temperature as shown in Table 1. All biochars were alkaline with pH ranging from 9.94 to 10.20; although, there was no clear trend for the pH. The pH range found in this study is consistent with the findings of other researchers who reported alkaline pH for biochar (Som et al. 2012; Yargicoglu et al. 2015). Furthermore, Hmid et al. (2014) reported that the pH for biochar derived from three-phase olive waste was in the range of 8.9–9.7. EC showed an increasing trend with temperature. The increase in EC can be explained by the increased concentration of metals and inorganic salts in the biochar. Similarly, the alkaline nature of the biochar can be attributed to the presence of alkaline metallic elements such as K⁺, Ca²⁺. As the temperature increased, the carbonization process was more complete and, due to the loss of volatile and other organic compounds, the inorganic elements such as salts and metals become more concentrated in the biochar which made it more conductive and alkaline (Chen et al. 2011; Ramola et al. 2014).

Table 1 | Biochar basic characteristics

<table>
<thead>
<tr>
<th>Biochar</th>
<th>Yield (%)</th>
<th>pH</th>
<th>EC (mS/cm)</th>
<th>Ash content (%)</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC-350</td>
<td>35.5</td>
<td>9.94</td>
<td>1.28</td>
<td>67.69</td>
<td>17</td>
</tr>
<tr>
<td>BC-450</td>
<td>29.0</td>
<td>10.20</td>
<td>2.71</td>
<td>80.35</td>
<td>21</td>
</tr>
<tr>
<td>BC-550</td>
<td>26.3</td>
<td>9.68</td>
<td>2.99</td>
<td>84.95</td>
<td>24</td>
</tr>
<tr>
<td>BC-630</td>
<td>22.5</td>
<td>10.19</td>
<td>4.39</td>
<td>91.27</td>
<td>49</td>
</tr>
</tbody>
</table>

Figure 1 shows the FTIR analysis of the biochars prepared at different temperatures. As can be seen, biochars prepared at higher temperature had lower transmittance which indicates better carbonization and the formation of compounds with stronger bonds. It can also be seen that a new band has formed around wave number 2,330 cm⁻¹ in the BC-450, BC-550 and BC-630. This wave length is associated with triple bonds such as nitriles and carbene groups. It is also observed that the band around 1,430 cm⁻¹ has progressed with pyrolysis temperature and became prominent in the BC-630. This band may be associated with the formation of alkanes of C-H bend. Furthermore, the development of a new band around 1,020 cm⁻¹ in BC-550 and BC-630 indicates the presence of aliphatic amines (C-N stretch). Moreover, as pyrolysis temperature increased, it can be seen that a new band which may be caused by the presence

Figure 1 | FTIR spectra of biochar prepared at different pyrolysis temperatures (temperature in °C).
of carboxylic acid or alkyl halides, started to develop around 860 cm\(^{-1}\). Another interesting observation is the gradual disappearance of the band around 2,900 cm\(^{-1}\) as the pyrolysis temperature increased. This may have been caused by the valorization of alkanes of C-H stretch.

**XRD and SEM analysis**

The XRD diffraction pattern of the different biochars are shown in Figure 2. Figure 3 shows the SEM images of the biochars prepared at different pyrolysis temperatures. A more porous structure can be observed developing as the pyrolysis temperature increased, thus confirming our findings regarding the surface area shown in Table 1. Nevertheless, both scans show that there was little difference between the biochars. XRD results suggested increased crystallization as pyrolysis temperature increased. Even so, the overall structure did not change significantly with the peaks occurring at the same diffraction angle.

**Effect of initial pH**

The effect of pH on the adsorption capacity of Hg\(^{2+}\) from aqueous solutions was investigated. The results presented
in Figure 4 show that maximum adsorption was achieved in the 4 to 5 pH range for all biochars. At pH values higher than 6.0 precipitation of mercury started taking place, which makes adsorption studies difficult (Anagnostopoulos et al. 2012). The speciation of a mercury solution, shows that HgCl₂, Hg(OH)Cl, and Hg(OH)₂ are present in the solution. HgCl₂ was the main form in the solution at pH values lower than 6, while above pH 6 Hg(OH)₂ is the predominant form due to extensive hydrolysis. Efficient removal of mercury at lower pH values is attributed to a higher degree of ionization of metal ions due to the reduced competition of H⁺ ions with the mercury ions for adsorption sites. This range is in agreement with other researchers who reported that the highest adsorption of Hg²⁺ was achieved within the pH range 4 to 6 (Kushwaha et al. 2009; Dewangan et al. 2010; Wang & Wang 2010; Boutsika et al. 2014). Therefore, all subsequent experiments were run at pH = 5.

Adsorption isotherms

In the present study, Langmuir, Freundlich, Temkin and D-R models were used to fit the experimental data. The Langmuir isotherm model (Equation (4)) assumes a monolayer adsorption onto a homogeneous surface, where the binding sites have equal affinity and energy (Langmuir 1918).

\[ q_e = \frac{q_{\text{max}} K_L C_{\text{eq}}}{1 + K_L C_{\text{eq}}} \]  

(4)

where \( q_e \) is the uptake of metal ions per unit weight of the adsorbent (mg·g⁻¹), \( q_{\text{max}} \) is the maximum metal uptake (mg·g⁻¹), \( K_L \) is the Langmuir constant (mg·g⁻¹) and is related to the energy of adsorption. \( C_{\text{eq}} \) is the equilibrium (residual) concentration of metal ions (mg·L⁻¹). The maximum adsorption capacity \( q_{\text{max}} \) and \( K_L \) can be calculated from the slope and intercept of the linear plot, \( C_{\text{eq}}/q_e \) versus \( C_{\text{eq}} \).

The Freundlich isotherm (Equation (5)) assumes that the adsorption occurs on a heterogeneous surface and that the amount of adsorbed adsorbate infinitely increases with an increase in the concentration (Freundlich 1906).

\[ q_e = K_F C_{\text{eq}}^{1/n} \]  

(5)

where \( K_F \) is the Freundlich constant denoting adsorption capacity (mg·g⁻¹) and \( n \) is an empirical constant, which is indicative of the adsorption intensity. The Freundlich constants \( K_F \) and \( n \) can be calculated from the intercept and slope of the linear plot of \( \log q_e \) versus \( \log C_{\text{eq}} \).

The Temkin isotherm model explicitly takes into account the adsorbent–adsorbate interactions and is not applicable to extremely low and high concentrations. The Temkin isotherm is expressed as (Temkin & Pyzhev 1940):

\[ q_e = B_T \ln(K_T C_{\text{eq}}) \]  

(6)

where \( (RT/b_T) = B_T \) (J·mol⁻¹) is the Temkin constant related to the heat of adsorption. \( K_T \) (L·g⁻¹) is the equilibrium binding constant related to the maximum binding energy.

The D-R isotherm is generally used to describe the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface and can be expressed as (Dubinin & Radushkevich 1947):

\[ q_e = q_{\text{max}} \exp(-\beta e^2) \]  

(7)

where \( q_{\text{max}} \) (mg·g⁻¹) is the theoretical sorption capacity at saturation state, \( \beta \) (kJ²·mol⁻²) is a constant related to adsorption energy and \( e \) is the Polanyi potential calculated by the following equation:

\[ e = RT \ln \left(1 + \frac{1}{C_{\text{eq}}}ight) \]  

(8)

where \( R \) (kJ·mol⁻¹·K⁻¹) is the universal gas constant (8.314 J·mol⁻¹·K⁻¹) and \( T \) (K) is the solution temperature. \( q_{\text{max}} \) and \( \beta \) are the result from the intercept and the slope of plotting \( \ln q_e \) versus \( e^2 \) in Equation (7), respectively. \( E \) (kJ·mol⁻¹), the average adsorption energy, is determined through Equation (9) (Krisha et al. 2000):

\[ E = \frac{1}{\sqrt{2\beta}} \]  

(9)
Figure 5 shows the adsorption isotherms of Hg$^{2+}$ onto BC-350, BC-450, BC-550 and BC-630. As evident from Figure 5, the adsorption isotherms presented an initial curvature followed by a plateau. The initial curvature confirms the high affinity between BC-350, BC-450, BC-550 and BC-630 adsorbent and the Hg$^{2+}$ ions. The plateau represents the maximum adsorption capacity (Georgin et al. 2016). The experimental results were fitted using Langmuir, Freundlich, Temkin and D-R models. The results of the fitting are shown in Table 2. The $R^2$ values shown in Table 2 indicate strong correlation between Langmuir, Freundlich, Temkin and D-R isotherm models and the experimental results which implies that the adsorption of Hg$^{2+}$ ions on the BC-350, BC-450, BC-550 and BC-630 surfaces is complex, involving more than one mechanism. According to the Freundlich model an $n$ value of greater than 1.0 indicates a favorable adsorption (Mohapatra et al. 2009). Accordingly, Hg$^{2+}$ adsorption is favorable on all the biochar samples investigated in this study because $n$, as shown in Table 2, is greater than 1.0 in all cases. Nevertheless, the D-R presents the best fit because it had the highest $R^2$ value and smallest deviation from experimental data as evident from Figure 5.

The Temkin isotherm values, $B_T$ and $K_T$, suggest that the heat of adsorption of all the molecules in the layer decreased linearly with coverage due to adsorbent–adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to a maximum binding energy (Kim et al. 2004). The free energies of transfer ($E$) of one mole of solute from solution to the BC-350, BC-450, BC-550 and BC-630, surfaces were evaluated from the slopes ($\beta$) of the D-R curves using Equation (7) and presented in Table 2. These $E$ values for all biochars

![Figure 5](attachment:image.png)
are < 16 kJ.mol⁻¹ indicating a physisorption mechanism (Onyang et al. 2006).

Dong et al. (2013) reported that carboxylic acids and graphite like structure groups played a major role in the adsorption of mercury on biochar derived from Brazilian peppers. As discussed earlier, Figure 1 shows the development of carboxylic groups as pyrolysis temperature increased. This may explain the increased adsorption capacity as the pyrolysis temperature increased.

The biochar derived from the olive oil processing solid waste showed good potential for the removal of Hg²⁺ from aqueous solutions. Table 3 shows reported values in the literature of different biochar capacities for Hg²⁺ adsorption. In comparison to other biochar derived from different agricultural waste (e.g. Kong et al. 2011; Dong et al. 2013; Boutsika et al. 2014), olive oil processing waste derived biochars have a high adsorption capacity. It is also noted that, in this study, biochar prepared at higher temperatures (BC-550 and BC-630) compares favorably to activated carbon prepared from pistachio-nut shells and licorice residues and impregnation with ZnCl₂ as reported by Asasian et al. (2012). Therefore, biochar derived from olive oil processing waste is a promising material for treatment of mercury contaminated water and wastewater.

### Kinetics of adsorption

The effect of contact time was obtained using BC-350, BC-450, BC-550 and BC-630 adsorbents at pH of 5.0, with constant initial Hg²⁺ concentration (70 mg.L⁻¹), as shown in Figure 6. It was found that more than 90% of saturation was attained within the first 90 min of reaction for all biochars. After this time, the adsorption rate decreased considerably.

Adsorption kinetics of Hg²⁺ onto BC-350, BC-450, BC-550 and BC-630 experimental results were fitted using two kinetic models: pseudo-first-order and pseudo-second-order models.

The pseudo-first-order kinetics is derived by using the simple Lagergren equation (Qiu et al. 2013):

\[
dq/dt = k_1(q_e - q_t)
\]

### Table 2 | Parameters of Langmuir, Freundlich, D-R and Temkin isotherms for Hg²⁺ adsorption onto BC-350, BC-450, BC-550 and BC-630 at 25 °C

<table>
<thead>
<tr>
<th>Model</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BC-350</td>
</tr>
<tr>
<td>Langmuir</td>
<td></td>
</tr>
<tr>
<td>q max (mg/g)</td>
<td>120.482</td>
</tr>
<tr>
<td>K L (L/mg)</td>
<td>0.084</td>
</tr>
<tr>
<td>R²</td>
<td>0.9701</td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
</tr>
<tr>
<td>K f (mg/g)</td>
<td>10.593</td>
</tr>
<tr>
<td>n (g/L)</td>
<td>1.484</td>
</tr>
<tr>
<td>R²</td>
<td>0.8901</td>
</tr>
<tr>
<td>D-R</td>
<td></td>
</tr>
<tr>
<td>q max (mg/g)</td>
<td>84.928</td>
</tr>
<tr>
<td>E (kJ/mol)</td>
<td>2.585</td>
</tr>
<tr>
<td>R²</td>
<td>0.9925</td>
</tr>
<tr>
<td>Temkin</td>
<td></td>
</tr>
<tr>
<td>B T (kJ/mol)</td>
<td>35.062</td>
</tr>
<tr>
<td>K T (L/mg)</td>
<td>0.448</td>
</tr>
<tr>
<td>R²</td>
<td>0.9333</td>
</tr>
</tbody>
</table>

### Table 3 | Comparison of reported Hg²⁺ adsorption capacity of biochar and activated carbon derived from agricultural waste

<table>
<thead>
<tr>
<th>Material Description</th>
<th>q max (mg/g)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biochar derived from soybean stalk 700 °C</td>
<td>0.675</td>
<td>Kong et al. (2011)</td>
</tr>
<tr>
<td>Biochar derived from spent rootlets malt 850 °C</td>
<td>103.0</td>
<td>Boutsika et al. (2014)</td>
</tr>
<tr>
<td>Biochar prepared from Brazilian peppers 350 °C</td>
<td>24.2</td>
<td>Dong et al. (2013)</td>
</tr>
<tr>
<td></td>
<td>450 °C</td>
<td>18.8</td>
</tr>
<tr>
<td></td>
<td>600 °C</td>
<td>15.1</td>
</tr>
<tr>
<td>Activated carbon derived from pistachio-nut shells and licorice residue</td>
<td>147.1</td>
<td>Asasian et al. (2012)</td>
</tr>
<tr>
<td>Olive oil processing solid waste* 350 °C</td>
<td>84.93³</td>
<td>This study³</td>
</tr>
<tr>
<td></td>
<td>450 °C</td>
<td>94.48³</td>
</tr>
<tr>
<td></td>
<td>550 °C</td>
<td>96.11³</td>
</tr>
<tr>
<td></td>
<td>630 °C</td>
<td>104.59³</td>
</tr>
</tbody>
</table>

*q max for olive oil processing solid waste (this study) reported in this table are based on the D-R model.
where $q_t$ (mg/g) are the amounts adsorbed per unit mass at equilibrium and at time $t$ (minute), $q_e$ (mg/g) is the theoretical value for the adsorption capacity and $k_1$ (min$^{-1}$) is the pseudo-first-order adsorption rate constant. The values of $q_e$ and $k_1$ can be obtained from the slope and intercept of the linear plot of $\ln(q_e - q_t)$ versus $t$.

A pseudo-second-order equation is based on adsorption equilibrium capacity and may be expressed in the form (Qiu et al. 2009):

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$  \hspace{1cm} (11)

where $k_2$ (g.mg$^{-1}$.min$^{-1}$) is the rate constants of pseudo-second-order model. The values of $q_e$ and $k_2$ can be obtained from the intercept and slope of linear plotting $t/qt$ versus $t$.

Figure 6 also shows the results of fitting the experimental data to the pseudo-first-order and pseudo-second-order models. The values of calculated $q_e$ ($q_{e,\text{Calcd}}$), $k_1$, $k_2$ and the correlation coefficient $R^2$ are presented in Table 4. The $q_{e,\text{Calcd}}$ determined from the pseudo-first-order model is not in good agreement with the experimental values ($q_{e,\text{Exp}}$). Therefore, we conclude that the pseudo-second-order model more adequately represents the adsorption kinetics of $\text{Hg}^{2+}$ on BC-350, BC-450, BC-550 and BC-630 adsorbents than the pseudo-first-order model.

**Thermodynamic study**

The free energy change of the specific adsorption $\Delta G$ is linked to the distribution coefficient $K_d$, through the following equation:

$$\Delta G = -RT\ln K_d$$  \hspace{1cm} (12)

The distribution coefficient ($K_d$) (L.g$^{-1}$) of $\text{Hg}^{2+}$ ions between the aqueous phase and the solid phase can be directly obtained using (Kütahyalı & Eral 2010):

$$K_d = \frac{q_{e}}{C_{eq}}$$  \hspace{1cm} (13)

$K_d$ values were obtained from the intercept of the plot of $\ln(q_e/C_{eq})$ versus $q_e$ (Günay et al. 2007).
The relationship between lnKd and temperature (T) is expressed using the following equations (Tahir & Rauf 2003):

\[ \Delta G^0 = \Delta H^0 - T\Delta S^0 \]  

(14)

\[ \ln K_d = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \]  

(15)

where \( \Delta H^0 \) (J.mol\(^{-1}\)) is the change in enthalpy (J.mol\(^{-1}\)), \( \Delta S^0 \) is the change in entropy (J.mol\(^{-1}\).K\(^{-1}\)). From Equation (15) the values of \( \Delta H^0 \) and \( \Delta S^0 \) can be calculated from the slope and intercept of the linear variation of lnKd with reciprocal temperature (figures are not shown). The values of \( \Delta G \), \( \Delta H \) and \( \Delta S \) for adsorption of Hg\(^{2+}\) ions onto BC-350, BC-450, BC-550 and BC-630 are given in Table 5.

The negative value of the Gibbs free energy change (\( \Delta G \)) indicated that the reaction was spontaneous. The decrease in \( \Delta G \) values as the reaction temperature increased indicated that the reaction was less favorable at higher temperatures. The negative value of enthalpy change \( \Delta H \) showed that adsorption of Hg\(^{2+}\) ions onto BC-350, BC-450, BC-550 and BC-630 were exothermic. Positive values of \( \Delta S \) suggested good affinity of the Hg\(^{2+}\) ions toward the adsorbent and increased randomness at the solid-solution interface during the fixation of the Hg\(^{2+}\) ions on the active site of the adsorbent.

### CONCLUSIONS

Biochar was prepared from the solid waste of Jordanian olive oil processing using a slow pyrolysis method at four temperatures: 350; 450; 550 and 630 °C. The product biochar was characterized and evaluated for its ability to remove Hg\(^{2+}\) from aqueous solutions in laboratory scale batch experiments. Although, the biochar had a relatively small surface area compared to activated carbon, it showed high potential for Hg\(^{2+}\) adsorption from aqueous solutions. The capacity of the biochar to adsorb Hg\(^{2+}\) increased with the pyrolysis temperature. The highest adsorption capacity was displayed by the biochar prepared at 650 °C which had a maximum adsorption capacity of 104.95 mg.g\(^{-1}\) at the ambient temperature of 25 °C and
pH = 5. The D-R isotherm adequately modeled the adsorption of Hg$^{2+}$ onto the biochar. The results of the D-R model suggest that the reaction was dominated by physisorption mechanisms. The reaction was spontaneous and exothermic with equilibrium attained within the first 90 min. The pseudo-second-order kinetic model best fit the experimental data. The thermodynamic study showed that the reaction was less favorable at higher temperatures.

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