Synthesis of hydrochar supported zero-valent iron composites through hydrothermal carbonization of granatum and zero-valent iron: potential applications for Pb\textsuperscript{2+} removal

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ABSTRACT

In the present investigation, a one-step synthesis of hydrochar (HC) supported zero-valent iron (ZVI) was performed through hydrothermal carbonization (HTC) of granatum and ZVI. According to XRD, XPS, and FTIR data, ZVI was evenly distributed on the surface of the hydrochar. In addition, the external ZVI oxide layer and the functional groups present in the hydrochar remained on the surface of the HC/ZVI composites after HTC treatment. The surface area of the HC/ZVI composites was between 31.11 and 44.16 m\textsuperscript{2}/g. These numbers were higher than those obtained for hydrochar (20.36 m\textsuperscript{2}/g) and ZVI (12.14 m\textsuperscript{2}/g) separately. The Pb\textsuperscript{2+} adsorption capacity of hydrochar and ZVI was 28.64 and 192.44 mg/g, respectively (25 °C, pH = 6.05, Pb\textsuperscript{2+} concentration of 200 mg/L with 0.05 g HC and 0.01 g ZVI). In addition, the adsorption capacity of the composites was between 49.63 and 88.09 mg/g. The data obtained for Pb\textsuperscript{2+} removal by the samples used in this experiments fitted well the pseudo-second-order kinetics and Langmuir isotherm models. Therefore, hydrochar may represent a promising supporting material for the synthesis of ZVI composites.

Key words: composites, hydrochar, Pb\textsuperscript{2+} adsorption, surface area, zero valent iron

HIGHLIGHTS

• The composites was prepared via hydrothermal carbonization of granatum and ZVI.
• The ZVI was evenly distributed on the surface of the hydrochar.
• The functional groups on the surface of hydrochar were retained in the composites.
• The strong reducibility of ZVI was preserved for the composites.
• The Pb\textsuperscript{2+} adsorption capacity of the composites was between 49.63 and 88.09 mg/g.

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INTRODUCTION

With rapid industrialization, large numbers of rivers and groundwater bodies have been polluted with heavy metals. This process has resulted from inappropriate discharge of wastewater from different industries including fuels, mining, painting, electronics, electroplating, and metal processing, among others (Li et al. 2020). Heavy metals, which accumulate in living organisms, are highly toxic. For this reason, heavy metal pollution is a great threat to the environment and public health. For example, lead (Pb²⁺) is considered a priority contaminant since it can cause anemia, diarrhea, chronic headaches, and irreversible damages to the nervous and reproductive systems (Zhang et al. 2020a). The permissible limit for lead in drinking water is below 0.01 mg/L (WHO 2011). Many methods including membrane filtration, ion exchange, redox reaction, precipitation, and adsorption have been developed for heavy metal elimination from industrial wastewater and contaminated groundwater. Among these methods, adsorption is widely used because of its convenience and high efficiency (Zhang et al. 2021).

In recent years, zero-valent iron (ZVI), especially nanoscale ZVI (nZVI), has been studied for its potential use in environmental remediation, including the removal of heavy metals from water (Li et al. 2017; Yoshino et al. 2018). This material presents abundant active sites, a strong reductive capability, and high surface area. However, the practical application of ZVI is limited because of its strong tendency towards aggregation and surface passivation (Sun et al. 2018). In order to simultaneously reduce the poor stability and aggregation of ZVI, as well as to maintain high removal capacities, ZVI composites produced using porous materials as support carriers have been used. Various carbon-based materials and minerals, such as activated carbon (Zhang et al. 2020b), biochar (Li et al. 2020), attapulgite (Zhang et al. 2019) and zeolite (Arancibia-Miranda et al. 2016), have been selected for the synthesis of ZVI composites. Although with enhanced adsorption capacity, the utilization of ZVI composites has been limited by its complex synthesis and low ZVI content. Thus, it is important to develop new methods to optimize the synthesis of ZVI composites.

Hydrochar (HC), which presents simple and easily controlled operating conditions for hydrothermal carbonization (HTC), is famous for its porous structure and variety of functional groups (Azzaz et al. 2020). For these reasons, HC can be a promising candidate for ZVI immobilization. Some researchers investigated the removal capacity of Pb²⁺ and Hg²⁺ using HC/ZVI composites that were prepared through Fe²⁺ reduction during the HTC process (Tang et al. 2016; Wang et al. 2020). However, the synthetic route was still limited because of the need of biomass pretreatment or hydrochar modification.

Little information exists about loading ZVI directly on the surface of hydrochar during HTC. In the present study, HC/ZVI composites were prepared through HTC of dry granatum biomass and nZVI. In this process, the production of hydrochar and ZVI loading on the HC surface simultaneously occurred. Also, in order to determine the potential use of HC/ZVI composites...
as adsorbents for the removal of Pb$^{2+}$ from wastewater, we investigated the characteristics of Pb$^{2+}$ adsorption and the corresponding removal mechanisms.

**MATERIALS AND METHODS**

**Materials and reagents**

Dry granatum (pomegranate husk) was used as the starting material for hydrochar preparation, which was obtained from the Pomegranate Research Center in Zaozhuang University. The granatum was ground using a blender (CPEL-23, China) until particles passed through a 100 mesh screen. Lead nitrate (Pb(NO$_3$)$_2$, 80073616) with a purity of 99% was purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). nZVI powder (100 nm, 3.0 g/cm$^3$) was purchased from Youyan alloy materials, Hebei, China. The surface area and the structure of the ZVI are presented in Table 1 and supplemental figure, respectively. All chemicals were of analytical reagent grade and used without further purification.

**Synthesis of HC/ZVI composite**

100 mL stainless-steel cylindrical reactors were used to carry out the HTC experiment (Xu 2020). Each reactor contained 2 g granatum, 40 mL distilled water, and varying amounts of ZVI (0.5, 1.0, 1.5, and 2.0 g). Thus, the ZVI accounted for 25, 50, 75, and 100% of the granatum content, respectively. Mono-HTC of granatum or ZVI were assigned as the control groups. The reactors were heated to 220 °C and maintained for 2 h in an electric oven (DHG-9023A, China). The pressure (2.4 MPa) in the HTC process was self-generated in closed chamber reactors (Kumar *et al.* 2020). After being cooled to ambient temperature, the solid product was separated from the liquid using vacuum filtration (FY-1H-N, China) through a 0.22 μm membrane. The solid product was washed with distilled water, dried at 105 °C for 24 h, and stored in sealed plastic bags for further use. Hydrochar and ZVI produced from HTC control groups were labeled as HC and ZVI-220, respectively. In addition, HC/ZVI composites were labeled as HC-25, HC-50, HC-75, and HC-100, according to the corresponding ZVI content.

**Adsorption experiments**

A Pb$^{2+}$ stock solution (1,000 mg/L) was prepared by dissolving 0.7995 g of Pb(NO$_3$)$_2$ with ultrapure water into a 500-mL volumetric flask. The test Pb$^{2+}$ solutions were prepared by diluting the stock solution. All batch experiments were performed using 50-mL centrifuge tubes, where the adsorbent and 25 mL of Pb$^{2+}$ solution were mixed and stirred for 24 h using a shaking table (SHY-2A, Jintan Instrument, Jiangsu, China) at a constant stirring velocity of 150 rpm and temperature of 25 °C.

**Adsorption capacity**

In order to determine the adsorption capacity, 0.05 g hydrochar (HC-25, HC-50, HC-75, HC-100, and HC) were reacted with the Pb$^{2+}$ solution (200 mg/L, pH = 6.05) for 24 h. After that, the mixtures were filtered and Pb$^{2+}$ concentrations in aqueous solutions were determined using atomic absorption spectrometry (Z-2000, Japan). The adsorption capacity of the hydrochar (Qe, mg/g) was calculated using Equation (1):

$$Q_e = (C_0 - C_t) \times V/M$$

(1)

**Table 1** | Surface area, porosity, pore size, and pH value of the samples

<table>
<thead>
<tr>
<th></th>
<th>BET surface area (m$^2$/g)</th>
<th>Total pore volume (cm$^3$/g)</th>
<th>Average pore size (nm)</th>
<th>pH value</th>
<th>HSP yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>20.36 ± 2.32</td>
<td>0.035 ± 0.004</td>
<td>6.874 ± 0.152</td>
<td>4.12 ± 0.24</td>
<td>58.75 ± 0.94</td>
</tr>
<tr>
<td>HC-25</td>
<td>31.11 ± 3.42</td>
<td>0.061 ± 0.006</td>
<td>7.978 ± 0.234</td>
<td>4.36 ± 0.22</td>
<td>66.39 ± 0.86</td>
</tr>
<tr>
<td>HC-50</td>
<td>43.20 ± 4.65</td>
<td>0.082 ± 0.008</td>
<td>7.473 ± 0.203</td>
<td>4.61 ± 0.26</td>
<td>68.67 ± 0.75</td>
</tr>
<tr>
<td>HC-75</td>
<td>33.26 ± 3.75</td>
<td>0.059 ± 0.006</td>
<td>6.983 ± 0.156</td>
<td>4.85 ± 0.24</td>
<td>73.11 ± 0.68</td>
</tr>
<tr>
<td>HC-100</td>
<td>44.16 ± 4.84</td>
<td>0.093 ± 0.009</td>
<td>8.415 ± 0.334</td>
<td>5.16 ± 0.22</td>
<td>76.94 ± 0.53</td>
</tr>
<tr>
<td>ZVI</td>
<td>12.14 ± 1.12</td>
<td>0.018 ± 0.002</td>
<td>5.706 ± 0.126</td>
<td>5.96 ± 0.14</td>
<td>—</td>
</tr>
<tr>
<td>ZVI-220</td>
<td>14.31 ± 1.56</td>
<td>0.024 ± 0.003</td>
<td>6.815 ± 0.148</td>
<td>5.85 ± 0.21</td>
<td>96.64 ± 0.42</td>
</tr>
</tbody>
</table>

HSP: HTC solid products.
where \( C_0 \) (mg/L) represents the initial solution concentration; \( C_t \) (mg/L) is the concentration at the adsorption time \( t \); \( V \) (L) stands for the volume of the adsorption solution; and \( M \) (g) corresponds to the hydrochar content (Al-Ananzeh 2021a).

**Adsorption kinetics**

In these experiments, 0.05 g hydrochar (HC-25, HC-75 and HC) and 0.01 g ZVI were reacted with a Pb\(^{2+}\) solution (200 mg/L, pH = 6.05) at different times (10 min, 20 min, 30 min, 1 h, 2 h, 4 h, 8 h, 12 h, and 24 h). The non-linear equations (Eq) of the pseudo-first-order (2) and pseudo-second-order kinetic rate expressions (3) were used for the analysis of the experimental data (Tran et al. 2017; Al-Ananzeh 2021b):

\[
Q_t = Q_e (1 - e^{-K_1 t}) \quad (2)
\]

\[
Q_t = \frac{Q_e t}{1 + K_2 Q_e t} \quad (3)
\]

where \( Q_e \) (mg/g) is the adsorption capacity, \( Q_t \) (mg/g) is the adsorption capacity at time \( t \) (h); \( K_1 \) and \( K_2 \) are the rate constants for the pseudo-first-order and pseudo-second-order adsorption kinetic models, respectively.

**Isotherms adsorption (298.15 K)**

0.05 g hydrochar (HC-25, HC-75 and HC) and 0.01 g ZVI were loaded into tubes containing a Pb\(^{2+}\) solution at initial concentrations of 10, 20, 40, 80, 100, 150 and 200 mg/L. Mixtures were allowed to react for 24 h. The non-linear forms of Langmuir (4) and Freundlich (5) isotherm models were used to fit the experimental data (Tran et al. 2017; Abdelhay et al. 2018):

\[
Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (4)
\]

\[
Q_e = K_F C_e^{1/n} \quad (5)
\]

where \( Q_m \) (mg/g) indicates the maximum adsorption capacity; \( C_e \) (mg/L) is the metal concentration at equilibrium; and \( Q_e \) (mg/g) is the amount of metal adsorbed at equilibrium; \( K_L \) is the Langmuir constant; \( K_F \) and \( 1/n \) are the Freundlich constant.

Each group of adsorption experiments was repeated in triplicate. After reaction time, the mixtures were filtered through a 0.22-\( \mu \)m membrane filter and Pb\(^{2+}\) concentration at equilibrium was determined by atomic adsorption spectrometry (Z-2000, Japan).

The root mean squared error (RMSE) for the adsorption kinetics and isotherms adsorption model was also calculated using Equation (6):

\[
RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (Y_{obs,i} - Y_{mod,i})^2} \quad (6)
\]

where \( Y_{obs} \) and \( Y_{mod} \) (mg/g) correspond to the observed value and the value calculated with the model; \( n \) represents the sample size; and \( i \) is the sample number.

**Analytical methods**

The Brunauer-Emmett-Teller (BET) surface area and pore diameter were measured with an automatic nitrogen adsorption analyzer (JW-BK, China). The morphology of the samples was analyzed using scanning electron microscope (SEM, JSM-7800F, Japan). The pH value of hydrochar and ZVI were measured at a 1:10 ratio of solid to deionized water using a pH meter (PHS-3D, China). The initial pH and the final pH after adsorption of the solution were also determined, and no pH adjustment was adopted during the adsorption.

Elemental information (Fe, C) was obtained using X-ray photoelectron spectroscopy (XPS) (AXIS SUPRA, Ktatos, England). All the spectra were calibrated to the C1s peak at 284.8 eV. The crystal structure of the samples was obtained...
through X-ray powder diffractometry (XRD) with an XRD-6000 (Shimadzu, Japan). The functional groups of the samples were determined by Fourier transform infrared (FTIR) spectroscopy (Nicolet IS50, USA). For this purpose, samples were prepared with KBr.

RESULTS AND DISCUSSION

FTIR and XPS analysis

The functional groups and oxidation state of the elements present on the surface of the materials can be determined using FTIR and XPS, respectively. The FTIR spectra and Fe 2p for the hydrochar and ZVI are shown in Figures 1 and 2, respectively. Three stretching vibration peaks were determined on the spectra of the hydrochar surface, which were assigned to the functional group of \(-\text{OH (3,440 cm}^{-1}\), C = O (1,590–1,680 cm\(^{-1}\)) and C-O (1,090 cm\(^{-1}\)) (Liu et al. 2017a). In contrast, only the weak peak of \(-\text{OH and C = O were found on the ZVI surface (Zhang et al. 2011; Al-Ananzeh 2021b). Conversely, two energy bands were present in the ZVI curve. The peaks located at 711.9 eV and 725.4 eV corresponded to Fe 2p3/2 and Fe 2p1/2 of Fe\(^{3+}\), and may be assigned to iron oxides like FeOOH and Fe\(_2\)O\(_3\), respectively (Meng et al. 2016). This is in good agreement with the results provided by the FTIR spectra and the core-shell structure of ZVI. Thus, because of the strong reducibility, the ZVI surface was enclosed by a 2–4 nm layer of iron oxide (Yan et al. 2010). Data shown in Figure 2 indicated a

![Figure 1](http://iwaponline.com/wst/article-pdf/84/8/1873/952316/wst084081873.pdf)

**Figure 1** FTIR spectra of the samples.

![Figure 2](http://iwaponline.com/wst/article-pdf/84/8/1873/952316/wst084081873.pdf)

**Figure 2** XPS spectra of Fe 2p in the samples.
high resistance to HTC reaction of the passivation layer outside ZVI. Only a slight change on the C = O was observed after ZVI addition during HTC. This result was similar to that obtained in another study reported by Wang et al. (2020), probably indicating that the presence of ZVI had little effect on the formation of functional groups during HTC. With respect to the composites samples, changes in intensity of the iron oxide peak in the XPS spectra indicated a uniform distribution of ZVI particles on the hydrochar surface.

**XRD pattern and hydrochar yield**

The XRD analysis is able to identify various crystalline phases and describe the phase transformations. The XRD patterns of different samples obtained in the present experiments are shown in Figure 3. Hydrochar exhibited a broad peak at 21.96°, which corresponded to the amorphous structure of aromatic carbon. This signal indicates inadequate a carbonization reaction during HTC (Petrović et al. 2016). In the case of ZVI and ZVI-220, the diffraction peak at 44.74° and 65.12° was consistent with (110) and (200) planes of α-Fe⁰, respectively (Zhu et al. 2016). These data also demonstrated the high purity of the used ZVI. Furthermore, no peaks corresponding to iron oxide were identified in the ZVI-220 sample, indicating that ZVI was not oxidized during HTC, probably due to the existence of surface oxide layer. The characteristic peaks of Fe⁰ were observed in the composites samples after ZVI addition during HTC. In addition, it was observed that peak intensity increased with the increasing dosage of ZVI, which demonstrated the successful embedding of Fe⁰ on the surface of the hydrochar. Also, the peak intensity of aromatic carbon decreased after ZVI addition during HTC, probably because the crystal degree of Fe⁰ was much higher than that of aromatic carbon.

**BET surface area and SEM analysis**

Surface area is commonly considered as one of the most important parameters for adsorbents. BET surface area, total pore volume and average pore size of the samples are summarized in Table 1. In the present experiments, the surface area of hydrochar and ZVI were 20.36 and 12.14 m²/g, respectively. In addition, the value for HC/ZVI composites was between 31.11 m²/g and 44.16 m²/g. The increase in surface area of the composites was probably due to the embedding of ZVI on the surface of hydrochar, and the corresponding mechanisms may be explained as follows. First, the hydrochar porosity was produced during HTC after disintegration of organic matter present in the biomass. Moreover, the processes of dehydration and aromatization were not favored as indicated by changes in the nature of the functional groups of the composites. This result suggested that the increase in porosity was caused by some other factor. Second, as shown in SEM images (supplemental figures), hydrochar was flocculent with some carbon spheres in appearance and ZVI presented the typical lamellar structure (Guo et al. 2016; Jiang et al. 2019). In addition, irregular flocs developed on the surface of the composite materials as effect of ZVI and hydrochar particle combination. This resulted in a slight increase on the pore size. Similarly, Wang et al. (2020) reported that surface area of hydrochar increased from 4.78 m²/g to 40.38 m²/g because of the presence of ZVI on hydrochar surface. However, it was observed that surface area of composites did not always increased as ZVI ratio increased, because...
the surface area of hydrochar was free from influence of HTC conditions (Kabakc & Bara 2019), and extra ZVI particles may have blocked the active sites and reduced the effective contact area in the hydrochar (Li et al. 2020).

Table 1 also displays the pH of the samples and HTC yield. Because of the acid pH of the hydrochar (4.12) and ZVI (5.96), the pH value of the composites was between 4.36 and 5.16. Data indicated that pH value increased with increasing ZVI content. According to the results, after HTC the hydrochar yield was 58.75% and the ZVI recovery rate was 96.64%. During HTC, with increasing ZVI content, the HC/ZVI composites yield increased between 66.39% and 76.94%. This indicated that more Fe⁰ was loaded on the hydrochar surface.

Adsorption capacity

Figure 4 presents the Pb²⁺ adsorption capacity of different samples. The adsorption capacity of hydrochar was 28.64 mg/g, value that was higher than those obtained in other studies using raw hydrochar (Xia et al. 2019; Luo et al. 2020). The adsorption of Pb²⁺ on hydrochar involves multiple mechanisms, including physical adsorption by porous structures, metal-π interaction with aromatic C = C bonds, and metal complexation with functional groups containing oxygen (Tan et al. 2019; Nadarajah et al. 2021). As shown in Figure 5, the characteristics of C = O and C–O weaken after adsorption, proving that the functional groups had taken part in the elimination of heavy metal (Zhang et al. 2021). Taking into account the properties of the hydrochar materials used in the present study, it is likely that the porous structure with carbon spheres also played a critical role in Pb²⁺ adsorption.

Given the abundant adsorption sites and reduction present on ZVI, this material exhibited an excellent Pb²⁺ adsorption capacity (192.44 mg/g). It has been proven that ZVI is able to react with water to form OH⁻, which reacts with Fe²⁺ or Fe³⁺ to form the corresponding hydroxide precipitates (Tosco et al. 2014). For example, Fe(OH)₃ is unstable and easily forms FeOOH and Fe₂O₃, providing new adsorption sites for Pb²⁺ (Al-Ananzeh et al. 2007; Bae et al. 2018). The reaction could be described with Equations (7)–(11). Conversely, since the standard reduction potential of Pb²⁺/Pb⁰ (0.1263 V) was slighter positive than that of Fe²⁺/Fe⁰ (0.4402 V), Pb²⁺ could be reduced to Pb⁰ (Equation (12); Zhang et al. 2011). In addition, the corresponding value for ZVI-220 was 184.71 mg/g, indicating a weak effect of HTC on the Pb²⁺ adsorption capacity of ZVI:

\[
\begin{align*}
\text{Fe}^{0} + 2\text{H}_2\text{O} & \rightarrow \text{Fe}^{2+} + 2\text{OH}^{-} + \text{H}_2(\uparrow) \quad (7) \\
\text{Fe}^{2+} + \text{O}_2 + 2\text{H}_2\text{O} + 5\text{e}^- & \rightarrow \text{Fe}^{3+} + 4\text{OH}^{-} \\
\text{Fe(OH)}_3 & \rightarrow \text{FeOOH} + \text{H}_2\text{O} \quad (9) \\
2\text{FeOOH} & \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \quad (10) \\
& = \text{FeOO}^- + \text{Pb}^{2+} \rightarrow \text{FeOOPb}^+ \quad (11) \\
\text{Fe}^{0} + \text{Pb}^{2+} & \rightarrow \text{Fe}^{2+} + \text{Pb}^{0} \quad (12)
\end{align*}
\]

Figure 4 | Pb²⁺ adsorption capacities of different materials used in the present research.
As the ratio of biomass to ZVI increased from 4:1 to 1:1, the Pb$^{2+}$ adsorption capacity of the composites increased from 49.63 mg/g to 88.09 mg/g; however, the increment gradually decreased. This occurred because excess ZVI particles accumulated on the surface of hydrochar, reduced the contact area of the solution with the active sites. In addition, the adsorbed Pb$^{2+}$ or reduced Pb$^0$ by the adsorbent prevented the further removal of the remaining Pb$^{2+}$ in the solution (Luo et al. 2014). Li et al. (2020) observed that the Pb$^{2+}$ removal rate of ZVI composites increased at the beginning and later decreased.

Table 2 displays the comparison of Pb$^{2+}$ adsorption capacities of HC/ZVI composites with other ZVI composites. As shown in this table, Pb$^{2+}$ adsorption capacities of ZVI composites greatly varied, which was due to the difference in the type of support material and ZVI properties. In addition, HC/ZVI composites exhibited an acceptable performance for Pb$^{2+}$ removal. These data suggested that HTC of biomass and ZVI might be a promising method for the synthesis of ZVI composites with proper Pb$^{2+}$ adsorption capacities. Observing the effects of ZVI dosage on Pb$^{2+}$ adsorption capacities and considering the relatively high price of ZVI, it can be concluded that a 2:1 biomass to ZVI ratio during HTC could be a good option.

Solution pH has significant effects on Pb$^{2+}$ adsorption. Higher pH values favor the competition with H$^+$ and the complexation with oxygen-containing functional groups. For example, the saturated adsorption of Pb$^{2+}$ increased when pH increased from 3 to 6 (Li et al. 2020). However, it was also reported that Pb$^{2+}$ removal efficiency showed a slight decrease as the pH increased from 4 to 6. Additionally, a high pH (>7.0) reduces Pb$^{2+}$ mobility and causes the formation of Pb precipitates including Pb(OH)$_2$ (Park et al. 2019). Hence, the optimum pH value for Pb$^{2+}$ adsorption is between 4.0 and 7.0 (Liu et al. 2017b). As shown in Table 1, the pH value of the HC and ZVI was 4.12 and 5.96, respectively. The pH value

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Qe (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite-nZVI</td>
<td>105.50</td>
<td>Arancibia-Miranda et al. (2016)</td>
</tr>
<tr>
<td>Porous carbons-nZVI</td>
<td>128.90</td>
<td>Su et al. (2015)</td>
</tr>
<tr>
<td>Sepiolite-nZVI</td>
<td>44.05</td>
<td>Pu et al. (2015)</td>
</tr>
<tr>
<td>Zeolite-nZVI</td>
<td>85.37</td>
<td>Li et al. (2018)</td>
</tr>
<tr>
<td>Biochar- nZVI</td>
<td>135.40</td>
<td>Li et al. (2020)</td>
</tr>
<tr>
<td>Activated carbon-nZVI</td>
<td>59.35</td>
<td>Liu et al. (2019)</td>
</tr>
<tr>
<td>Coffee ground-nZVI</td>
<td>164.10</td>
<td>Park et al. (2019)</td>
</tr>
<tr>
<td>Kaolin -nZVI</td>
<td>48.00</td>
<td>Zhang et al. (2011)</td>
</tr>
<tr>
<td>Hydrochar-ZVI</td>
<td>88.09</td>
<td>This study</td>
</tr>
</tbody>
</table>
of the composites increased from 4.36 to 5.16 with increasing ZVI ratio. In this study, the initial pH of the solution was 6.05, and after adsorbent addition, it was between 4.25 and 5.54. This pH range favored Pb$^{2+}$ adsorption.

**Adsorption kinetics and isotherm adsorption model**

The effect of contact time and initial concentration on Pb$^{2+}$ removal by the samples is presented in Figures 6 and 7, respectively. Additionally, the fitting values for the kinetic parameters and isotherm adsorption models are also listed in Tables 3 and 4, respectively.

According to the fitting results, kinetics of Pb$^{2+}$ adsorption using HC, ZVI, and ZVI-220 was better fitted to the pseudo-second-order model as compared to the pseudo-first-order model. This indicated that Pb$^{2+}$ removal mainly occurred through a chemical interaction. The $R^2$ value of pseudo-second-order model could up to 0.995, these results were consistent with those obtained in other studies (Arancibia-Miranda et al. 2016; Jiang et al. 2019), where researchers reported that the pseudo-second-order kinetics displayed a higher correlation coefficient for Pb$^{2+}$ adsorption by hydrochar and ZVI. In the case of HC/ZVI composites, the fitting data for both models were very alike because of the increasing surface area. These results were similar to those obtained for Pb$^{2+}$ adsorption by ZVI supported on exhausted coffee grounds (Park et al. 2019). In addition, Pb$^{2+}$ adsorption by the composites reached equilibrium within 6 h, which was comparable to that reported by

**Figure 6** | Effect of contact time on Pb$^{2+}$ adsorption capacity of the samples. Conditions: Pb$^{2+}$ initial concentration 200 mg/L, pH 6.5, at 25 °C.

**Figure 7** | Effect of initial Pb$^{2+}$ concentration on the adsorption capacity of the samples. Conditions: pH 6.5, 24 h, at 25 °C.
Li et al. (2020). However, other studies have indicated that equilibrium can be achieved within 1 h of reaction (Tang et al. 2016; Park et al. 2019).

According to the $R^2$ values, the data fitted Langmuir (0.964–0.970) better than the Freundlich model (0.804–0.815). The results were consistent with those obtained in other studies and may indicate that Pb$^{2+}$ adsorption occurred through the monolayer (Jiang et al. 2019; Liu et al. 2019). In relation to Pb$^{2+}$ adsorption by the HC/ZVI composites, the $R^2$ values of Freundlich fitting increased with increasing ZVI ratios, demonstrating the successful support of ZVI on the hydrochar surface. In addition, the RMSE results indicated that the pseudo-second-order kinetics and Langmuir equation were the best fitting models.

**CONCLUSION**

In the present study, HC/ZVI composite was successfully prepared via HTC of dry granatum biomass and ZVI. The strong reducibility of ZVI and the functional groups present in the hydrochar were retained in the composites. The Pb$^{2+}$ removal capacity of HC/ZVI composites was as high as 88.09 mg/g, value that resulted 3.08 times higher than that obtained with raw hydrochar. Pseudo-second-order kinetics and Langmuir isotherm demonstrated the chemisorption was dominant for the composites in Pb$^{2+}$ capture. Since excess ZVI may reduce the contact of active sites with the solution, the optimal biomass to ZVI ratio was 2:1. The results provide a new perspective for the synthesis of ZVI composites.

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**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.
REFERENCES


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