Research Article

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**Calcium oxide addition and ultrasonic pretreatment-assisted hydrothermal carbonization of granatum for adsorption of lead**

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Abstract: Hydrochar is a promising adsorbent for the removal of heavy metals, but the low surface area limits the removal efficiency and practical application. Therefore, improving the surface area of the hydrochar is critical to increasing the adsorbent removal. In this study, the ultrasonic pretreatment of biomass (10–30 min) and CaO addition (5–15%) were adopted to assist the hydrothermal carbonization (HTC) of granatum at 220°C. The properties of the modified hydrochar and the removal efficiency for Pb²⁺ in the aqueous solution were investigated. Results showed that the porosity of hydrochar was obviously improved by the CaO addition, and the largest surface area of 21.86 m²·g⁻¹ was obtained during HTC with 15% CaO addition. Meanwhile, the functional groups of −OH and C=O increased and the pH of the hydrochar increased from weakly acidic to alkaline by CaO addition. The Pb²⁺ adsorption capacity of raw hydrochar was 10.03 mg·g⁻¹, and it was enhanced by 80.76–171.58% after CaO addition. The ultrasonic pretreatment of granatum had little effect on the characteristics of hydrochar except to improve the surface area from 8.27 to 9.06 m²·g⁻¹, resulting in a 1.30–6.78% increase in the adsorption capacity.

Keywords: hydrothermal carbonization, hydrochar modification, ultrasonic pretreatment, CaO addition, Pb²⁺ adsorption

1 Introduction

With the rapid pace of global industrialization and urbanization, large quantities of heavy metals were disposed into the environment, causing them to accumulate in water bodies to levels that exceed the environmental quality standards [1]. Water quality in China continues to deteriorate, and the heavy metal that accumulates along the food chain threatens public health and the ecological environment. For example, due to the multitude of sources and the possibility of serious harm to human health, especially to the nervous and reproductive systems, lead (Pb²⁺) is ranked as a precedent-controlled contaminant. Adsorbent removal is a common method to remove heavy metals from wastewater, but most adsorbents are expensive and not very environment-friendly [2]. Biochar has gained much attention as it can remove toxins from contaminated water [3]. However, the pyrolysis of biomass results in the production of exhaust gas and tar, which may potentially result in environmental damage [4,5]. Consequently, there remains an urgent need for greener and more eco-friendly adsorbents to remove heavy metals from contaminated water.

Hydrochar is the solid carbonaceous adsorbent produced by hydrothermal carbonization (HTC) of biomass. Hydrochar can retain higher contents of H and O than biochar, resulting in a higher density of surface functional groups [6,7]. Additionally, less exhaust gas is produced during HTC, and the wastewater can be treated by anaerobic digestion [8]. Surface functional groups of the carbon-based adsorbents play an important role in the removal of heavy metals from wastewater. Hydrochar has shown considerable promise in heavy metal removal owing to several advantages [9]. However, the low surface area of hydrochar weakens the removal effect and precludes further application of hydrochar. Some methods have been developed for hydrochar activation, such as microwave assistance and alkali modification, but these...
are limited by high energy consumption and complexity of operation [10–12].

It was reported that the porosity of the hydrochar could be considerably enhanced by the addition of CaO during HTC [13,14]. However, not much is known about the heavy metal removal capacity of hydrochar modified by CaO and the effect of CaO addition on the functional groups of hydrochar. In addition, the porous structure of the biomass may be improved by ultrasonic pretreatment [15], a combination of ultrasonic and H$_2$O$_2$ synergistic treatment is adopted for hydrochar activation [16], and the application of ultrasonic pretreatment-assisted HTC is also performed for hydrochar modification in this study.

The objectives of this study are as follows: (1) to assess the effects of HTC assisted by CaO addition and ultrasonic pretreatment of biomass on the characteristics of hydrochar; (2) to explore the Pb$^{2+}$ removal efficiency of such hydrochar; and (3) to investigate the optimal CaO additive content for hydrochar modification.

2 Materials and methods

2.1 Materials and reagents

Dry granatum (pomegranate husk) was used as the material for hydrochar preparation, which was obtained from the Pomegranate Research Center at Zaozhuang University. The granatum was ground using a blender (CPEL-23, China) until the powder passed through a 100-mesh sieve. Analytical-grade chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). The Pb$^{2+}$ standard solution (1 mg·mL$^{-1}$, in 1% HNO$_3$) was purchased from Guobiao Testing and Certification Co., Ltd (Beijing, China).

2.2 Hydrochar preparation and modification

Stainless-steel cylindrical reactors (MMJ-200, OM Labtech, Japan) of 100 mL capacity were used to perform the HTC experiment. Five grams of granatum and 40 mL of distilled water were loaded into each reactor. Ultrasonic pretreatment of the granatum and CaO addition during HTC were used to prepare the modified hydrochar, respectively. An ultrasonic cleaner (QK-500E, Kunshan Ultrasonic Instruments Co. LTD, China) was used to carry out the ultrasonic pretreatment of granatum, and the pretreatment durations were 10, 20, and 30 min, respectively. The weight of the added CaO was 0.25, 0.5, and 0.75 g, respectively, corresponding to the granatum content of 5%, 10%, and 15%. The HTC of untreated granatum without CaO addition was designed as the control group.

The reactors were heated to 220°C and maintained at the same temperature for 4 h using an electric heating oven (DHG-9023A, Yiheng, Shanghai, China). After being cooled to room temperature, the solid product was separated from the liquid using vacuum filtration (FY-1H-N, VALUE, Zhejiang, China) through a 0.22-μm membrane. The hydrochar was washed with distilled water and dried at 105°C for 24 h. The dried hydrochar was stored in enclosed plastic bags for further use. Hydrochar produced from the control group, ultrasonic pretreatment (10, 20, and 30 min), and CaO addition (5%, 10%, and 15%) at 220°C were denoted as H220, H220-U10 (U20 and U30), and H220-Ca5 (Ca10 and Ca15), respectively.

2.3 Adsorption experiments

The adsorption experiments were carried out on a shaking table with constant stirring of 150 rpm at 25°C for 4 h, using 50 mL conical flasks in which 0.1 g hydrochar and 25 mL of Pb$^{2+}$ adsorption solution (200 mg·L$^{-1}$, pH = 6.05) are placed. The adsorption solution was prepared with 5 mL of Pb$^{2+}$ standard solution (1 g·L$^{-1}$) and 20 mL of ultrapure water. Each group of adsorption experiments was repeated thrice. After that, the mixtures were filtered and the equilibrium concentration of Pb$^{2+}$ in the aqueous solutions was determined using an atomic adsorption spectrometry (Z-2000, Japan). The final pH of the solution was measured after adsorption, and no pH adjustment was adopted during the adsorption. The adsorption capacity of hydrochar ($Q_e$, mg·g$^{-1}$) was calculated as follows:

$$Q_e = \left(C_0 - C_e\right) \times \frac{V}{M} \quad (1)$$

where $C_0$ (mg·mL$^{-1}$) and $C_e$ (mg·mL$^{-1}$) represent the initial solution concentration and equilibrium solution concentration, $V$ (mL) represents the volume of adsorption solution, and $M$ (g) represents the hydrochar content.

2.4 Characterization methods

The Brunauer–Emmett–Teller (BET) surface area and pore diameter were measured using an automatic nitrogen adsorption analyzer (JW-BK, JWGB SCI. & TECH., Beijing, China). The hydrochar morphology was analyzed using a scanning electron microscope (SEM, JSM-7800F, Japan). The pH value of hydrochar was measured using a pH meter.
(PHS-3D, INESA, Shanghai, China) in deionized water at a 1:10 ratio of hydrochar to water. The crystal structure of the hydrochar was examined by X-ray powder diffractometer (XRD) with XRD-6000 (Shimadzu, Japan). The functional groups of the hydrochar were determined using Fourier transform infrared (FTIR) spectroscopy (Nicolet IS50, Thermo, USA) with KBr.

3 Results and discussion

3.1 BET surface area and SEM analysis

The pore properties and pH value of the hydrochar after HTC under different conditions are shown in Table 1. The BET surface area of the hydrochar was 8.27 m²·g⁻¹ in the control group; it was enlarged to 8.43–9.06 m²·g⁻¹ after ultrasonic pretreatment and to 14.15–21.86 m²·g⁻¹ after CaO addition. The low surface area of the hydrochar was because HTC was a mild and inadequate carbonization reaction during HTC, while the peak at 29–30°C was consistent with the trace amount of elemental Ca in granatum [20,21]. The stronger peaks of aromatic carbon and weaker peaks of Ca²⁺ were observed for the hydrochar from HTC with ultrasonic pretreatment, and the peak intensity of aromatic carbon was basically reinforced with the increase in the duration of ultrasonic treatment. It may be because C, H, and O were major elements while Ca was a trace element in granatum, and the element distribution in granatum became more uniform after ultrasonic pretreatment [22]. The hydrochar modified by CaO addition exhibited a crystal structure dominated by Ca²⁺, and there was no distinct difference in the peak intensity of Ca²⁺ with increasing CaO content. It was suggested that the structure of CaO was much stronger than that of aromatic carbon, and the crystal structure of Ca²⁺ was free from the influence of CaO dosage.

3.2 XRD pattern

The XRD patterns of different hydrochar are shown in Figure 2. The hydrochar showed four weak diffraction peaks in the control group. Three of these peaks (44°, 65°, and 78°) were ascribed to the amorphous structure of aromatic carbon because of the inadequate carbonization reaction during HTC, while the peak at 29–30°C was consistent with the trace amount of elemental Ca in granatum [20,21]. The stronger peaks of aromatic carbon and weaker peaks of Ca²⁺ were observed for the hydrochar from HTC with ultrasonic pretreatment, and the peak intensity of aromatic carbon was basically reinforced with the increase in the duration of ultrasonic treatment. It may be because C, H, and O were major elements while Ca was a trace element in granatum, and the element distribution in granatum became more uniform after ultrasonic pretreatment [22]. The hydrochar modified by CaO addition exhibited a crystal structure dominated by Ca²⁺, and there was no distinct difference in the peak intensity of Ca²⁺ with increasing CaO content. It was suggested that the structure of CaO was much stronger than that of aromatic carbon, and the crystal structure of Ca²⁺ was free from the influence of CaO dosage.

3.3 FTIR analysis

The FTIR spectra of hydrochar for different HTC conditions are shown in Figure 3. Four peaks related to the stretching vibration were found on the surface of the hydrochar because of the dehydration and aromatization during HTC, which were ascribed to the –OH (3,440 cm⁻¹),

|               | BET surface area (m²·g⁻¹) | Total pore volume (cm³·g⁻¹) | Average pore size (nm) | pH         |
|---------------|--------------------------|-----------------------------|------------------------|------------|
| H20           | 8.27 ± 0.46              | 0.024 ± 0.003               | 27.59 ± 0.38           | 6.37 ± 0.06|
| H220-U10      | 8.87 ± 0.56              | 0.026 ± 0.005               | 27.72 ± 0.39           | 6.38 ± 0.07|
| H220-U20      | 8.43 ± 0.53              | 0.024 ± 0.004               | 26.03 ± 0.37           | 6.36 ± 0.06|
| H220-U30      | 9.06 ± 0.64              | 0.027 ± 0.007               | 27.28 ± 0.44           | 6.39 ± 0.07|
| H220-Ca5      | 14.15 ± 0.63             | 0.043 ± 0.007               | 27.95 ± 0.46           | 6.95 ± 0.11|
| H220-Ca10     | 18.20 ± 0.72             | 0.055 ± 0.011               | 28.76 ± 0.51           | 7.46 ± 0.14|
| H220-Ca15     | 21.86 ± 0.86             | 0.064 ± 0.010               | 27.74 ± 0.41           | 7.94 ± 0.17|
C=O (1,590 cm\(^{-1}\)), C–H (1,430–1,290 cm\(^{-1}\)), and C–O (1,090 cm\(^{-1}\)) functional groups [23,24]. The functional groups in the hydrochar showed no difference after ultrasonic pretreatment, while the peaks of –OH and

Figure 1: SEM image of different hydrochar: (a) H220, (b) H220-U30, and (c) H220-Ca15.

C=O became more intense after CaO addition. This may be because the functional groups were formed under the catalysis of H\(^+\), and the H\(^+\) yield was improved by CaO addition during HTC because of the alkaline pH of CaO [19]. It has also been reported that the formation of ketone organics (C=O) was promoted under alkaline environments during HTC [25]. However, the intensity of the functional groups showed a non-obvious reinforcement with the CaO content increasing from 5% to 15%, which was similar to the previous results [13]. This was possible because the decomposition of biomass reached dynamic equilibrium under low alkaline conditions at a certain temperature.

Figure 2: XRD patterns for hydrochar resulting from HTC under different conditions.

Figure 3: FTIR spectra of hydrochar resulting from HTC under different conditions.
3.4 Adsorption capacity of \( \text{Pb}^{2+} \)

\( \text{Pb}^{2+} \) adsorption by hydrochar is considered to be the result of multiple mechanisms, including physical adsorption by porous structures, metal interaction with aromatic \( \text{C} = \text{C} \) bonds, and metal complexation with oxygen-containing functional groups \([31]\). In addition, the solution pH has important effects on the \( \text{Pb}^{2+} \) adsorption. The adsorption of \( \text{Pb}^{2+} \) was improved with the increase in pH values, since it favors the competition with \( \text{H}^+ \) and the complexation with functional groups \([32]\). However, it was also reported that a high pH (>7.0) was unfavorable for the adsorption because of the reduction of \( \text{Pb}^{2+} \) mobility and the formation of \( \text{Pb} \) precipitates \([33]\). Hence, the optimum pH value for \( \text{Pb}^{2+} \) adsorption is in the range of 4.0–7.0 \([34]\).

Table 2: Adsorption capacity of reported hydrochar for \( \text{Pb}^{2+} \) in aqueous solutions

| Adsorbent                              | Surface area (m\(^2\)·g\(^{-1}\)) | \( Q_e \) (mg·g\(^{-1}\)) | Reference |
|----------------------------------------|-------------------------------------|-----------------------------|-----------|
| Raw hydrochar                          | 1.4                                 | 0.9                         | [26]      |
| \( \text{H}_2\text{O}_2 \)-modified hydrochar | 114.4                               | 22.8                        | [26]      |
| Raw hydrochar                          | 18.0                                | 11.3                        | [27]      |
| Microwave-assisted hydrochar           | 6.1                                 | 45.3                        | [10]      |
| Raw hydrochar                          | –                                   | 27.8                        | [11]      |
| Alkali-modified hydrochar              | –                                   | 137.0                       | [11]      |
| \( \text{CO}_2 \)-treated hydrochar    | 85.0                                | 47.0                        | [28]      |
| Raw hydrochar                          | 7.0                                 | 36.0                        | [29]      |
| \( \text{CO}_2 \)-treated hydrochar    | 1308.0                              | 225.4                       | [29]      |
| Raw hydrochar                          | –                                   | 2.2                         | [16]      |
| \( \text{H}_2\text{O}_2 \) ultrasonic-modified hydrochar | –                                      | 92.8                        | [16]      |
| Raw hydrochar                          | –                                   | 11.0                        | [12]      |
| Hydrochar/MgAl-LDH                     | –                                   | 62.4                        | [12]      |
| Oxone-modified hydrochar               | 7.7                                 | 46.7                        | [30]      |

LDH – layered double hydroxides.

Figure 4 shows the adsorption capacity of different hydrochar for \( \text{Pb}^{2+} \). The \( \text{Pb}^{2+} \) adsorption capacity of hydrochar was 10.03 mg·g\(^{-1}\) in the control group, which was improved to 10.16–10.71 mg·g\(^{-1}\) after ultrasonic pretreatment and to 18.13–27.24 mg·g\(^{-1}\) after CaO addition. The adsorption capacity of different hydrochar for \( \text{Pb}^{2+} \) in aqueous solutions reported by other studies is shown in Table 2, and the adsorption performance of modified hydrochar in this study was lower than the results of other studies because of the difference in the modification conditions. The FTIR spectra of the hydrochar after adsorption are shown in Figure 5. The characteristics of \( \text{–OH} \) reinforced after adsorption, proving the contribution of functional.
groups to Pb²⁺ adsorption. Only the surface area of the hydrochar was slightly improved after ultrasonic pretreatment, and hence, the enhancement of the Pb²⁺ adsorption capacity could be attributed to providing points for extra adsorption on the surface of the hydrochar. An overt linear relationship between the surface area and the adsorption capacity of the hydrochar is presented in Figure 6. The surface area and the adsorption capacity of hydrochar were increased by 1.93–9.55% and 1.30–6.78%, respectively, after ultrasonic pretreatment. It suggested that the adsorption capacity of Pb²⁺ was increased by 0.71 mg·g⁻¹ for each increase of 1 m²·g⁻¹ in the surface area of the hydrochar. On the other hand, although the pH value of hydrochar was not conducive to improving the capacity of Pb²⁺ adsorption after the CaO addition, the increment in the surface area (71.10–164.33%) and the intensified functional groups achieved an increase of 80.76–171.58% for the Pb²⁺ adsorption capacity.

4 Conclusion

Granatum hydrochar prepared by CaO addition and ultrasonic pretreatment-assisted HTC were characterized and investigated for the adsorption of Pb²⁺ from water. The properties of the hydrochar are little affected by the ultrasonic pretreatment of biomass, while it is obviously improved by CaO addition. The surface area of the hydrochar was enlarged with the CaO content increasing from 5% to 15%, and the functional groups of the hydrochar were also reinforced. As a result of the performance enhancement, the Pb²⁺ adsorption capacity of hydrochar was enhanced more than twice. The results suggested that CaO addition is a promising method for improving the properties of hydrochar, which will be beneficial for the application of hydrochar in environmental restoration.

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References

[1] Wang XL, Zhang L, Zhao ZH, Cai YJ. Heavy metal pollution in reservoirs in the hilly area of southern China: Distribution, source apportionment and health risk assessment. Sci Total Env. 2018;634:58–169.
[2] Qin HQ, Hu TJ, Zhai YB, Lu NQ, Aliyeva J. The improved methods of heavy metals removal by biosorbenons: A review. Env Pollut. 2020;258:113777.

[3] Peng ZY, Liu XM, Chen HK, Liu QL, Tang JC. Characterization of ultraviolet-modified biochar from different feedstocks for enhanced removal of hexavalent chromium from water. Water Sci Technol. 2019;79:1705–16.

[4] Gelardi DL, Li CY, Parikh SJ. An emerging environmental concern: Biochar-induced dust emissions and their potentially toxic properties. Sci Total Env. 2019;678:813–20.

[5] He LZ, Zhong H, Liu GX, Dai ZM, Xu JM. Remediation of heavy metal contaminated soils by biochar: Mechanisms., potential risks and applications in China. Env Pollut. 2019;252:846–55.

[6] Gasco G, Paz-Ferreiro J, Álvarez ML, Saa A, Méndez A. Biochars and hydrochars prepared by pyrolysis and hydrothermal carbonisation of pig manure. Waste Manage. 2018;79:395–403.

[7] Lin Y, Ma X, Peng X, Yu Z. Forecasting the byproducts generated by hydrothermal carbonisation of municipal solid wastes. Waste Manage Res. 2017;35:92–100.

[8] Zhao K, Li YQ, Zhou Y, Guo WY, Jiang H, Xu Q. Characterization of hydrothermal carbonization products (hydrochars and spent liquor) and their biomethane production performance. Bioresour Technol. 2018;267:9–16.

[9] Yang XD, Wan YS, Zheng YL, He F, Gao B. Surface functional groups of carbon-based adsorbents and their roles in the removal of heavy metals from aqueous solutions: A critical review. Chem Eng J. 2019;366:608–21.

[10] Elaigw SE, Rocher V, Kyriaou G, Greenway GM. Removal of Pb\textsuperscript{2+} and Cd\textsuperscript{2+} from aqueous solution using chars from pyrolysis and microwave-assisted hydrothermal carbonization of Prospis africana shell. J Ind Eng Chem. 2014;20:3467–73.

[11] Petrović JT, Stojanović MD, Milojković JV, Petrović MS, Šoštarić TD, Laušević MD, et al. Alkali modified hydrochar of grape pomace as a perspective adsorbent of Pb\textsuperscript{2+} from aqueous solution. J Env Manage. 2016;162:292–300.

[12] Luo XW, Huang ZJ, Lin JY, Li XY, Qiu JL, Liu JH, et al. Hydrothermal carbonization of sewage sludge and in-situ preparation of hydrochar/MgAl-layered double hydroxides composites for adsorption of Pb\textsuperscript{2+}. J Clean Prod. 2020;258:120991.

[13] Lang QQ, Zhang B, Liu ZG, Jiao WT, Xia Y, Chen ZL, et al. Properties of hydrochars derived from swine manure by CaO assisted hydrothermal carbonization. J Env Manage. 2019;233:440–6.

[14] Zhang JQ, Hu XL, Zhang KJ, Xue YW. Desorption of calcium-rich crayfish shell biochar for the removal of lead from aqueous solutions. J Colloid Interf Sci. 2019;554:417–23.

[15] Zhao F, Cheng DL. Changes in pore size distribution inside sludge under various ultrasonic conditions. Ultrason Sonochem. 2017;38:390–401.

[16] Xia Y, Yang TX, Zhu NM, Li D, Chen ZL, Lang QQ, et al. Enhanced adsorption of Pb\textsuperscript{2+} onto modified hydrochar: modeling and mechanism analysis. Bioresour Technol. 2019;288:121593.

[17] Ghanim BM, Pandey DS, Kwapisinski W, Leahy J. Hydrothermal carbonisation of poultry litter: Effects of treatment temperature and residence time on yields and chemical properties of hydrochars. Bioresour Technol. 2016;216:373–80.

[18] Capobianco L, Caprio FD, Attiprari P, Astolfi ML, Pagnanelli F. Production of an iron-coated adsorbent for arsenic removal by hydrothermal carbonization of olive pomace: Effect of the feedwater pH. J Env Manage. 2020;273:111164.

[19] He C, Zhao J, Yang YH, Wang JY. Multiscale characteristics dynamics of hydrochar from hydrothermal conversion of sewage sludge under sub- and near-critical water. Bioresour Technol. 2016;211:486–93.

[20] Liu Q, Fang Z, Liu Y, Liu YY, Xu YF, Ruan XX, et al. Phosphorus speciation and bioavailability of sewage sludge derived biochar amended with CaO. Waste Manage. 2019;87:71–7.

[21] Yan W, Zhang HH, Sheng KC, Mustafa AM, Yu YF. Evaluation of engineered hydrochar from KMnO\textsubscript{4} treated bamboo residues: Physicochemical properties, hygroscopic dynamics, and morphology. Bioresour Technol. 2018;250:806–11.

[22] Zhao X, Li W, Kong FG, Chen HL, Wang QZ, Liu SX, et al. Carbon spheres derived from biomass residue via ultrasonic spray pyrolysis for supercapacitors. Mater Chem Phys. 2018;219:461–7.

[23] Tekin K, Karagöz S, Bektas S. A review of hydrothermal biomass processing. Renew Sustain Energ Rev. 2014;40:673–87.

[24] Zhang XJ, Zhang L, Li AM. Hydrothermal co-carbonization of sewage sludge and pine wood sawdust for nutrient-rich hydrochar production: Synergistic effects and products characterization. J Env Manage. 2017;201:52–62.

[25] Liu XM, Zhai YB, Li SL, Wang B, Wang TF, Liu YL, et al. Hydrothermal carbonization of sewage sludge: Effect of feedwater pH on hydrochar's physicochemical properties, organic component and thermal behavior. J Hazard Mater. 2020;388:122084.

[26] Xue YW, Gao B, Yao Y, Inyang M, Zhang M, Zimmerman AR, et al. Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: Batch and column tests. Chem Eng J. 2012;200:202–202:673–80.

[27] Alatalo SM, Repo E, Mikiliä E, Salonen J, Vakkilainen E, Sillanpää M. Adsorption behavior of hydrothermally treated municipal sludge & pulp and paper industry sludge. Bioresour Technol. 2013;147:71–6.

[28] Sun Y, Zhang JP, Guo F, Zhang L. Hydrochar preparation from black liquor by CO\textsubscript{2} assisted hydrothermal treatment: optimization of its performance for Pb\textsuperscript{2+} removal. Korean J Chem Eng. 2016;33:2703–10.

[29] Fang J, Gao B, Zimmerman AR, Ro KS, Chen JJ. Physically (CO\textsubscript{2})\textsubscript{4} activated hydrochars from hickory and peanut hull: preparation, characterization, and sorption of methylene blue, lead, copper, and cadmium. RSC Adv. 2016;6:24906–11.

[30] Madduri S, Elsayed I, Hassan EB. Novel oxone treated hydrochar for the removal of Pb\textsuperscript{2+} and methylene blue (MB) dye from aqueous solutions. Chemosphere. 2020;260:127683.

[31] Wang L, Wang YJ, Ma F, Tankpa V, Bai SS, Guo XM, et al. Mechanisms and reutilization of modified biochar used for removal of heavy metals from wastewater: A review. Sci Total Env. 2019;668:1298–309.

[32] Li SS, Yang F, Li JS, Cheng K. Porous biochar-nanoscale zero-valent iron composites: synthesis, characterization and application for lead ion removal. Sci Total Env. 2020;746:143037.

[33] Liu JW, Mwamulima T, Wang YM, Fang Y, Song SX, Peng CS. Removal of Pb\textsuperscript{II} and Cr\textsuperscript{VI} from aqueous solutions using the fly ash-based adsorbent material-supported zero-valent iron. J Mol Liq. 2017;243:205–11.

[34] Park MH, Jeong S, Lee G, Park H, Kim JY. Removal of aqueous-phase Pb\textsuperscript{II}, Cd\textsuperscript{II}, As\textsuperscript{III}, and As\textsuperscript{V} by nanoscale zero-valent iron supported on exhausted coffee grounds. Waste Manage. 2019;92:49–58.