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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

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H I G H L I G H T S

- ▶ H₂O₂ modification increases oxygen-containing functional groups on hydrochar.
- ▶ H₂O₂ modified hydrochar effectively removes aqueous heavy metals.
- ▶ H₂O₂ modified hydrochar can be used as an effective sorption media in filters.

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Biochar converted from agricultural residues can be used as an alternative adsorbent for removal of aqueous heavy metals. In this work, experimental and modeling investigations were conducted to examine the effect of H₂O₂ treatment on hydrothermally produced biochar (hydrochar) from peanut hull to remove aqueous heavy metals. Characterization measurements showed that H₂O₂ modification increased the oxygen-containing functional groups, particularly carboxyl groups, on the hydrochar surfaces. As a result, the modified hydrochar showed enhanced lead sorption ability with a sorption capacity of 22.82 mg g⁻¹, which was comparable to that of commercial activated carbon and was more than 20 times of that of untreated hydrochar (0.88 mg g⁻¹). When used as filter media in a packed column, the modified hydrochar was also much more effective in filtering lead than the unmodified one. The lead removal capacity of the modified hydrochar packed column was about 20 times of that containing untreated hydrochar. In a multi-metal system, the modified hydrochar column still effectively removed lead, as well as other heavy metals (i.e., Cu²⁺, Ni²⁺, and Cd²⁺) from water flow. Model results indicated that the heavy metal removal ability of the modified hydrochar follows the order of Pb²⁺ > Cu²⁺ > Cd²⁺ > Ni²⁺. Findings from this work suggest that H₂O₂-modified hydrochar may be an effective, less costly, and environmentally sustainable adsorbent for many environmental applications, particularly with respect to metal immobilization.

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1. Introduction

Biochar, an emerging carbon material produced mainly from low-cost biomass residuals, has received much attention recently in the science community because of its promising potentials in many environmental applications, including carbon sequestration, soil improvement, water treatment, and environmental remedia-

tion [1-3]. Although biochar can be produced using various thermal conversion methods, most of current research has been focused on biochar converted from slow or fast pyrolysis (i.e., dry pyrolysis) [4]. Only few studies have been conducted examining the potential environmental applications of biochars produced by alternative thermal conversion technologies such as hydrothermally produced biochar (hydrochar) [4-6].

Hydrochar refers to the solid char product from hydrothermal carbonization (HTC) of carbon-rich biomass in the presence of subcritical liquid water, which is also called hydrous pyrolysis or wet pyrolysis [7-9]. The HTC process usually employs relatively low

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temperatures (150–350 °C) and can be applied directly to wet feedstocks, such as wet animal manures, algae, and biomass with pore moisture. As a result, it is more energetically advantageous than dry pyrolysis processes, which require a greater initial investment of energy and the energy-intensive drying of feedstock [10]. In addition, HTC has been reported to have a higher yield (30–60 wt%) than fast or slow pyrolysis [8,11]. HTC was originally designed to simulate natural coalification, but at accelerated rates using water as the sole reaction medium under pressure and heat to produce artificial coal from biomass. It is environmentally friendly in that the process does not generate any hazardous chemical waste or by-products as dry pyrolysis can [7].

Like other types of biochars, hydrochar is porous and has reactive, functionalized/aromatic surfaces [12]. Those properties make hydrochar a potential alternative lower-cost adsorbent to remove contaminants from water. For example, Sun et al. [5] compared the sorption of organic contaminants on hydrothermally- and on thermally-produced biochars. They found that biochars made by HTC had stronger affinities to both polar and nonpolar organic contaminants than thermally-produced biochars. Only a few studies, however, have examined the characteristics of sorption of aqueous contaminants onto hydrochars.

The sorption of heavy metals (Pb (II) and U (VI)) on hydrochars was examined by laboratory experiments [6,12]. In a laboratory batch experiment, Liu and Zhang [6] measured the sorption capacity of Pb (II) on hydrochars prepared from pinewood (P300) and rice husk (R300). They found that the maximum lead adsorption capacity was about 4.25 (P300) and 2.40 (R300) mg g⁻¹, which was lower than that of most other biomass-based adsorbents, including thermally produced biochar [13,14]. Both batch and column experiments were used in a recent study to assess the removal of U (VI) from aqueous solution by switch grass hydrochar [12]. Although it was found that the switch grass hydrochar could be used as a reactive barrier medium to remove uranium from groundwater, its maximum uranium sorption capacity was only around 2–4 mg g⁻¹ under acid or neutral pH conditions.

The removal of heavy metals by hydrochar has been suggested to be mainly controlled by interactions between metal ions in solution and oxygen-containing functional groups on hydrochar's surface [6]. Several studies suggested that hydrochar may contain some heavy metal reactive surface functional groups, such as hydroxyl and carboxylic groups [6,15,16], however, the adsorption capacity of the hydrochar to heavy metals seems to be much lower than that of thermally produced biochars or other common adsorbents [17–20]. This is probably because hydrochar may contain fewer oxygen-containing surface functional groups than the thermally produced biochars [21]. In order to increase the effectiveness of hydrochar as an alternative adsorbent for water purification or soil remediation, it may be necessary to modify/activate the hydrochar surface to enhance its ability to remove heavy metal contaminants.

In this work, hydrochar was hydrothermally-produced from peanut hull and then treated with hydrodioxide (H₂O₂). We hypothesized that H₂O₂ treatment of the hydrochar could increase oxygen-containing functional groups on its surface and thus enhance its ability to remove heavy metals from water. Laboratory batch sorption and column filtration experiments, as well as mathematical models were used to quantify the effect of hydrogen peroxide treatment of hydrochar on the removal of heavy metals, particularly Pb (II). Our overarching goal was to develop a new technology to modify hydrochar and to develop value-added, hydrochar-based sorbents for the removal of heavy metal contaminants. The specific objectives of this work were to: (1) compare physical and chemical properties of H₂O₂-modified and unmodified hydrochars; (2) compare sorption characteristics of lead on H₂O₂-modified and unmodified hydrochars; (3) compare filtration

and transport of lead in laboratory columns packed with H₂O₂-modified and unmodified hydrochars; and (4) determine the ability of H₂O₂-modified hydrochar as a filter medium to remove multiple heavy metals from water.

2. Materials and methods

2.1. Hydrochar production

Peanut hull, one of the most abundant agricultural residues, was collected in Gainesville, FL as the feedstock for hydrochar production. About 60 g of naturally dried peanut hull was mixed with 400 mL deionized (DI) water and the mixture was added into a 500 mL stainless steel autoclave. The reactor was heated and held at 300 °C for 5 h at a pressure of about 1000 psi measured by a pressure gauge. The reactor was then cooled to room temperature and the solid product (hydrochar) was collected. The peanut hull hydrochar (PHHC) was rinsed several times with DI water and dried at 80 °C in an oven. The dried PHHC sample was then ground and sieved to a uniform size fraction of 0.5–1.0 mm. After further rinsing with DI water several times to remove impurities (e.g., ash) and drying at 80 °C, the final PHHC sample was stored for later experiments.

To make the modified PHHC (mPHHC), about 3 g of the final PHHC sample was placed into 20 mL 10% H₂O₂ solution for 2 h at room temperature (22 ± 0.5 °C). After rinsing with DI water and drying at 80 °C, the mPHHC sample was stored for later experiments.

2.2. Characterizations

Physical and chemical properties of the PHHC and mPHHC were determined using method reported previously [3,22]. Briefly, carbon, hydrogen, and nitrogen contents of the samples were determined using a CHN Elemental Analyzer (Carlo-Erba NA-1500). Major inorganic elemental constituents were determined using inductively coupled plasma with an optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 2100 DV). To measure the pH, the sample was added into DI water at a mass ratio of 1:20. The mixture was then shaken and allowed to stand for 5 min before measurement with a pH meter (Fisher Scientific Accumet Basic AB15). Specific surface areas of the samples were measured with a Quantachrome Autosorb-1 surface area analyzer using both N₂ (BET) and CO₂ adsorption methods to determine macro- and micropore surface area [23,24].

Fourier transform infra-red (FTIR) analysis was used to verify the presence of surface functional groups on the samples. The hydrochars (PHHC or mPHHC) were first ground into powder and then directly mounted on the diamond base of a Nicolet 6700 FTIR (Thermo Scientific) and a transparent polyethylene film was used to cover the samples for the FTIR analysis. In addition, X-ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI 5100 series ESCA spectrometer (Perkin Elmer) to determine the elemental composition on the sample surface. X-ray diffraction (XRD) analysis was used to detect crystalline minerals on either pre- or post-sorption hydrochar samples using a computer-controlled X-ray diffractometer (Philips Electronic Instruments). This approach has proved to be effective in showing the removal of lead by thermally-produced biochars through a precipitation mechanism [13].

2.3. Batch sorption of lead

Laboratory batch sorption experiments were conducted to compare the kinetics and isotherms of lead sorption on the PHHC and

the mPHHC. For each experiment, about 0.1 g of the adsorbent was mixed with 50 mL Pb (II) aqueous solution ($\text{Pb}(\text{NO}_3)_2$) in a 68 mL digestion vessel (Environmental Express). The mixture was then shaken in a mechanical shaker at room temperature. To test the kinetics of lead on the adsorbents at different reaction times 50 ppm lead solutions were used and subsamples were taken at different time intervals. To obtain the sorption isotherms, solutions of various lead concentrations (1, 5, 10, 30, 70, 100, 200 ppm) were shaken with the adsorbent for 24 h. At the end of each experiment, the mixtures were immediately filtered and lead concentrations in the filtrate were determined.

In another sorption experiment, the mPHHC was pre-saturated with Na^+ by repeatedly (three times) shaking in a 50 mL sodium chloride (1 mol L^{-1}) solution in the digestion vessel for 24 h. The ion exchange process of lead on the mPHHC was examined by reacting 0.1 g of the Na-saturated adsorbent with 50 mL lead (50 ppm) solution in the digestion vessel. Both lead and sodium concentrations in the filtrate were determined at the end of the experiment.

Solutions without either the sorbent or the sorbate (i.e., blanks) were included in all sorption experiments as controls. Lead and sodium concentrations in the filtrates were determined with the ICP-OES (Perkin Elmer Optima 2100 DV). Lead concentrations on the sorbents were calculated based on the differences between initial and final aqueous solution concentrations. All sorption experiments were performed in triplicate and the average values are reported here. Additional analyses were conducted whenever two measurements showed a difference larger than 5%. All chemical reagents used in the experiments were of high purity grade from Fisher Scientific. Stock lead solution of lead nitrate was prepared by dissolving appropriate amount of lead nitrate in DI water. All the experimental solutions were prepared with DI water without any pH or ionic strength adjustments.

2.4. Removal of lead in hydrochar columns

About 1 g of the hydrochar sorbent (PHHC or mPHHC) was wet-packed as an interlayer in an acrylic column measuring 15.6 mm in diameter and 51 mm in height. About 9.4 g of acid-cleaned quartz sand (0.5–0.6 mm average size) was used at each end of the column to help distribute the flow. The final heights of the top sand, hydrochar, and bottom sand layers were about 12 mm, 21 mm, and 18 mm, respectively. Detailed information about sand cleaning and column packing procedures can be found in Tian et al. [25]. The column was initially flushed with DI water for about 6 h. A peristaltic pump (Masterflex L/S, Cole Parmer Instrument, Vernon Hills, IL) was used at the influent (top) of the column to maintain a downward flow rate in the column of 1 mL/min. The column experiment was initiated by switching the influent to a 50 ppm Pb (II) solution for about 20 h. Effluent samples from the column were collected with a fraction collector (IS-95 Interval Sampler, Spectrum Chromatography, Houston, TX) during the experiment to analyze lead concentrations.

2.5. Removal of heavy metals in a mPHHC-packed column

A fresh column packed with mPHHC was used in the experiment. A mixture solution of four heavy metals was prepared with nickel nitrate, cadmium nitrate, copper nitrate and lead nitrate. The molar concentrations (ionic strengths) of Ni (II), Cd (II), Cu (II), Pb (II) in the solution were made to be the same (0.25 mmol/L). The same column experimental procedures as above were used to test the filtration and transport of the four heavy metals in the mPHHC column. Heavy metal concentrations in the effluents were determined with the ICP-OES.

2.6. Mathematical models

Pseudo-first-order, pseudo-second-order, and Elovich models were used to simulate the sorption kinetics data. Governing equations for these models can be written as [26]:

$$\text{First-order: } q_t = q_e(1 - e^{-k_1 t}), \quad (1.1)$$

$$\text{Second-order: } q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e^2 t}, \quad (1.2)$$

$$\text{Elovich: } q_t = \frac{1}{\beta} \ln(\alpha \beta t + 1), \quad (1.3)$$

where q_t and q_e are the amount of sorbate removed at time t and at equilibrium, respectively (mg g^{-1}), and k_1 and k_2 are the first-order and second-order sorption rate constants (h^{-1}), respectively, α is the initial sorption rate (mg g^{-1}) and β is the desorption constant (g mg^{-1}). The first- and second-order models are semi-empirical equations, while the Elovich model is an empirical fitting equation.

The Langmuir and Freundlich models were used to simulate the sorption isotherms. Their governing equations can be written as [26]:

$$\text{Langmuir: } q_e = \frac{K S_{\max} C_e}{1 + K C_e}, \quad (2.1)$$

$$\text{Freundlich: } q_e = K_f C_e^n, \quad (2.2)$$

where K and K_f are the Langmuir bonding term related to interaction energies (L mg^{-1}) and the Freundlich affinity coefficient ($\text{mg}^{(1-n)} \text{L}^n \text{g}^{-1}$), respectively, S_{\max} is the Langmuir maximum capacity (mg kg^{-1}), C_e is the equilibrium solution concentration (mg L^{-1}) of the sorbate, and n is the Freundlich linearity constant. The Langmuir model assumes monolayer adsorption onto a homogeneous surface with no interactions between the adsorbed molecules. The Freundlich model is an empirical equation commonly used for heterogeneous surfaces.

Filtration and transport of heavy metals in the hydrochar columns were described by the advection–dispersion equation (ADE) coupled with a modified Elovich equation to describe removal. The governing equations can be written as [27]:

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial q}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} \quad (3.1)$$

$$\frac{\rho_b}{\theta} \frac{\partial q}{\partial t} = k_c C \exp\left(-\lambda \frac{q}{q_{\max}}\right) \quad (3.2)$$

where C is the sorbate concentration in pore water (mg L^{-1}), t is time (min), ρ_b is the medium bulk density (g L^{-1}), θ is the dimensionless volumetric moisture content, q is the concentration of heavy metal adsorbed on the sorbent (mg g^{-1}), z is the distance traveled in the direction of flow (cm), D is the dispersion coefficient ($\text{cm}^2 \text{min}^{-1}$), and v is the average linear pore-water velocity (cm min^{-1}), k_c is the removal rate constant (min^{-1}), λ is a dimensionless constant controlling the decline of heavy metal removal with the increase in q , and q_{\max} is the maximum removal capacity of the sorbent in column/bed (mg g^{-1}), which is the same as the Langmuir maximum capacity (S_{\max}) for some adsorbents. Eqs. (3.1) and (3.2) were solved numerically with a zero initial concentration, a pulse-input and a zero-concentration-gradient boundary conditions for the hydrochar layer. The Levenberg–Marquardt algorithm was used to estimate the value of the model parameters by minimizing the sum-of-the-squared differences between model-calculated and measured effluent concentrations over multiple calculation iterations.

3. Results and discussion

3.1. Hydrochar properties

Weight-based production yields of PHHC were around 38%, which is similar to previously reported values for hydrothermal conversion of peanut hull [8]. There was almost no weight loss from the H₂O₂ treatment and the weight of the mPHHC was almost the same as the PHHC. As a result, the two hydrochars have similar bulk density (Table 1). In addition, elemental analysis indicated that H₂O₂ treatment had little impact on the mineral compositions of the two hydrochars (Table 1). The CHN analysis also showed similar hydrogen and nitrogen contents of the two hydrochars. The carbon content of mPHHC (48%), however, was lower than that of PHHC (56%), suggesting part of the carbon in PHHC was oxidized by the H₂O₂ resulting in the calculated higher oxygen content of the mPHHC (44%) versus that of PHHC (37%). XPS analysis confirmed that, after H₂O₂ modification, the oxygen content on the hydrochar surface increased from 16.4% to 22.3% (Fig. 1). This result is consistent with findings of previous studies that H₂O₂ treatment can oxidize carbonized surfaces and increase oxygen-containing surface function groups, particularly carboxyl group [28].

The FTIR spectra of the PHHC and mPHHC were similar for the most of the wavenumbers except at around 1700 cm⁻¹, corresponding to carbonyl group, where mPHHC had a much stronger absorbance peak than PHHC (Fig. 2). In addition, XPS analysis of C_{1s} binding energies on the two hydrochar surfaces showed that the -COOH (289.1/289.6 eV) content of the mPHHC (8.2%) was almost four times of that of PHHC (2.1%), further confirming H₂O₂ modification increased carboxyl surface functional group (Fig. S1, Supporting Information).

The measured N₂ and CO₂ surface areas of the mPHHC were slightly higher than that of the PHHC (Table 1), perhaps due to the increase of surface carboxyl groups after H₂O₂ treatment. This result suggests that H₂O₂ oxidization could not create or change the pore structure of biochar to dramatically enhance its surface area. The surface area, particularly the N₂-BET surface area, of the hydrochars was low, which is common for biochars produced at low temperature [29]. Previous studies have suggested that temperature plays an important role in affecting biochar surface area through controlling the creation of pores and creaking in the biochars basal-structural sheets [29,30]. The PHHC was slightly acidic, with pH of around 6.2, common for hydrothermally produce biochars [4]. The pH of the mPHHC was lower (4.4), which could be attributed to the weak acidic nature of the created carboxyl surface functional groups.

3.2. Batch experiment lead sorption on PHHC and mPHHC

Lead sorption on the mPHHC occurred much faster and to a greater extent than on the PHHC (Fig. 3), suggesting H₂O₂ treatment could facilitate the sorption of lead on the hydrochar. It took less than 12 h for lead sorption on the mPHHC to reach apparent equilibrium whereas sorption equilibrium on the PHHC

was reached even after 24 h. In addition, the sorption kinetic curve of the mPHHC was smoother than that of the PHHC, reflecting less surface heterogeneities of the mPHHC after H₂O₂ modification. The kinetic models described the experimental data fairly well with all R² greater than 0.86 (Table S1, Supporting Information). The Elovich model had the best fits for both the PHHC (R² = 0.89) and the mPHHC (R² = 0.99), but these were not much better than the second order model (R² = 0.89 and 0.96, respectively). The first-order model performed the worst for both the PHHC (R² = 0.86) and the mPHHC (R² = 0.90), suggesting that lead sorption on the two sorbents may not follow the mononuclear (single site) mechanism [26,31]. The best-fit kinetic model parameters are listed in the Supporting Information (Table S1).

Lead sorption isotherms demonstrated that the H₂O₂ treatment increased the sorption capacity of the hydrochar dramatically (Fig. 4). The plateau of the mPHHC isotherm reached about 20 mg g⁻¹, which was more than 20 times higher than that of the PHHC isotherm. Although both models reproduced the isotherm data very well, the Langmuir model (R² = 0.99) fitted the mPHHC sorption isotherm better than the Freundlich model (R² = 0.92). For the PHHC isotherm, however, the Freundlich model (R² = 0.99) showed a better fit than the Langmuir model (R² = 0.97). Usually, the Langmuir model better describes adsorption on homogeneous surfaces, while the Freundlich model is better for heterogeneous surfaces. Thus, the modeling results of lead sorption isotherms suggested that H₂O₂ modification reduced the surface heterogeneities of the hydrochar. The best-fit isotherm model parameters can also be found in the supporting information (Table S1).

The Langmuir maximum lead sorption capacity of the PHHC was about 0.88 mg g⁻¹, lower than that of hydrochars prepared from pinewood (4.25 mg g⁻¹) or rice husk (2.4 mg g⁻¹) [6]. After modification, however, the Langmuir maximum lead sorption capacity of the mPHHC increased almost 25 times to about 22.82 mg g⁻¹, which is comparable to that of commercial activated carbons (15–80 mg g⁻¹) and other biochar sorbents (2–150 mg g⁻¹) [13,17–20,32–35]. This indicates that H₂O₂ can be used as an oxidation reagent to modify/activate hydrochar to produce an effective sorbent to removal lead from water.

Our previous studies have suggested that thermally produced biochars remove aqueous lead through a surface precipitation mechanism and the immobilized lead on the biochar surfaces are often in mineral form with crystalline structures [13,36]. In this work, XRD analysis did not detect any crystalline structures in either the pre- or post-sorption hydrochars (XRD scans of all samples only showed the baselines). This suggested that surface precipitation may not be the governing mechanism of lead removal by the peanut hull hydrochars.

Other studies have showed that the removal of heavy metals by biochars, including hydrochar, is directly correlated with the amount of oxygen-containing functional groups [6,21,37]. In this work, the enhanced lead removal by the H₂O₂-modified hydrochar could be attributed mainly to the increase of carboxyl surface functional groups. It has been reported in the literature that carboxyl groups on carbonized surfaces can react with Pb (II) to form bound complexes [38], such as:

Table 1
Bulk properties and composition of hydrochars used in this study.

| | Surface area (m ² g ⁻¹) | | Bulk density (g cm ⁻³) | pH | Elemental composition (% mass based) | | | | | | | | | | | |
|-------|--|-----------------|------------------------------------|-----|--------------------------------------|-----|----------------|------|------|----------------|------|------|----------------|----------------|------|------|
| | N ₂ | CO ₂ | | | C | H | O ^a | N | P | K | Ca | Mg | Zn | Cu | Fe | Al |
| PHHC | 1.3 | 96.9 | 0.24 | 6.2 | 56.3 | 5.6 | 36.6 | 0.89 | 0.08 | – ^b | 0.20 | 0.02 | – ^b | – ^b | 0.07 | 0.07 |
| mPHHC | 1.4 | 114.4 | 0.25 | 4.4 | 48.3 | 5.8 | 43.8 | 0.79 | 0.09 | 0.01 | 0.23 | 0.03 | – ^b | – ^b | 0.01 | 0.03 |

^a Determined by weight difference assuming that the total weight of the samples was made up of the tested elements only.

^b <0.01%.

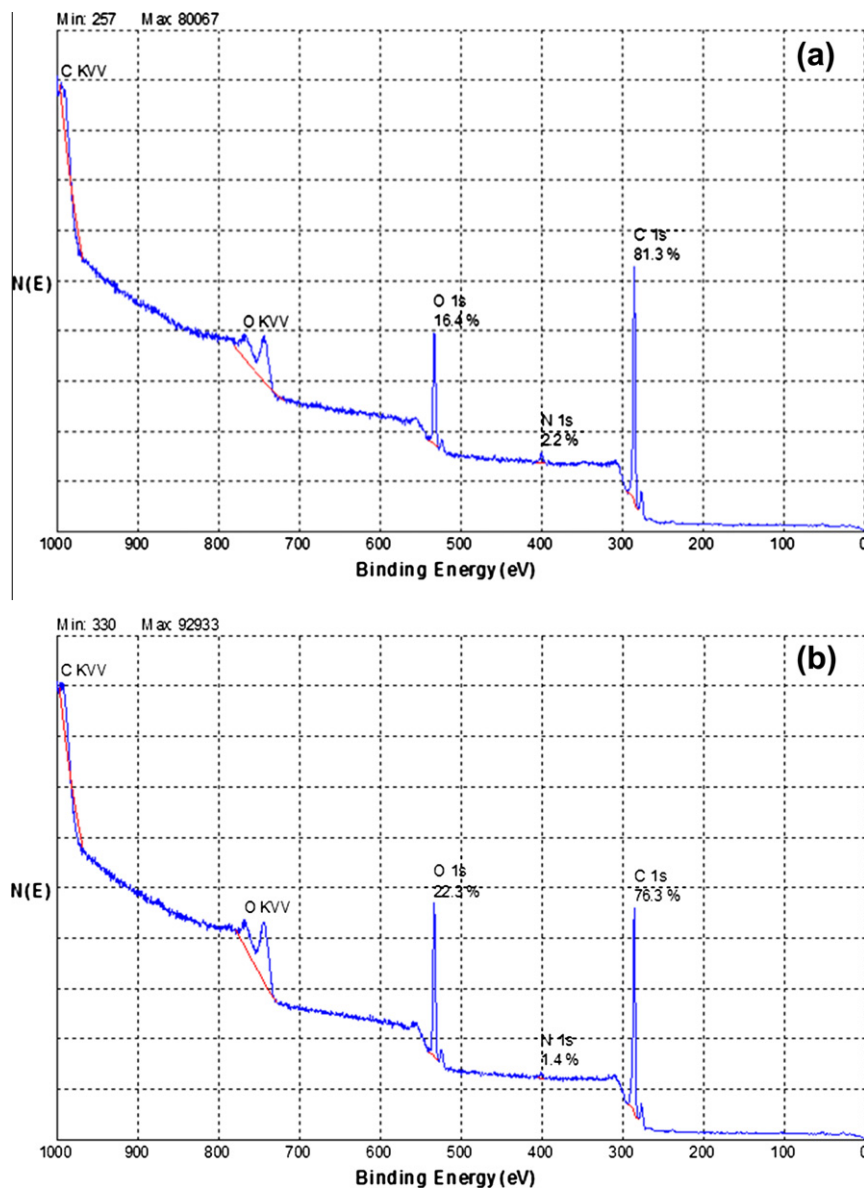


Fig. 1. XPS analysis of C_{1s}, O_{1s}, and N_{1s} contents on PHHC (a) and mPHHC (b) surfaces. Each of the peaks shows the surface element contents.

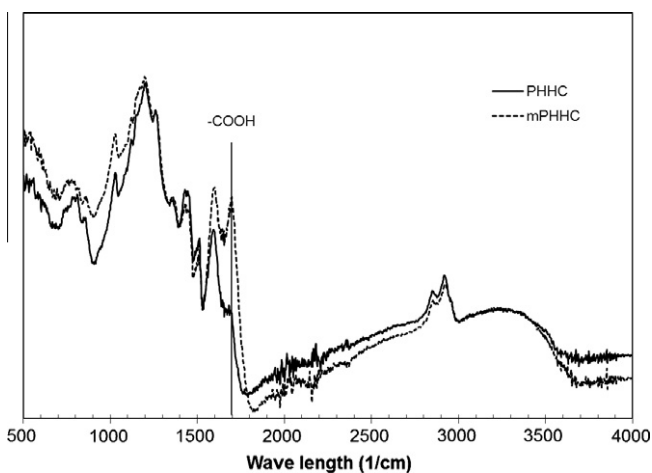
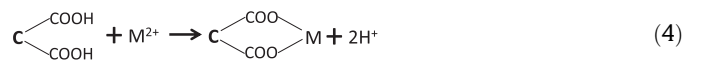


Fig. 2. FTIR spectra of PHHC (solid line) and mPHHC (dash line).



where M²⁺ represents divalent metal ions, such as Pb (II).

This mechanism was further confirmed by the lead sorption experiment with Na-saturated mPHHC. At the end of the experiment, about 2.5 mg/L of extra Na⁺ (compared with the blank) was released into the solution, suggesting that more than 67% of the lead sorption on the hydrochar occurred through a surface exchange reaction such as the proposed complexation mechanism with carboxyl groups.

3.3. Lead removal in column experiment

The breakthrough of lead in the mPHHC column occurred much later and eluted much lower concentrations of lead than that in the PHHC column (Fig. 5). The PHHC and mPHHC columns eluted lead after about 3 and 150 bed volumes (BV), respectively. At the end of the experiment (400 BV), the final effluent lead concentration in

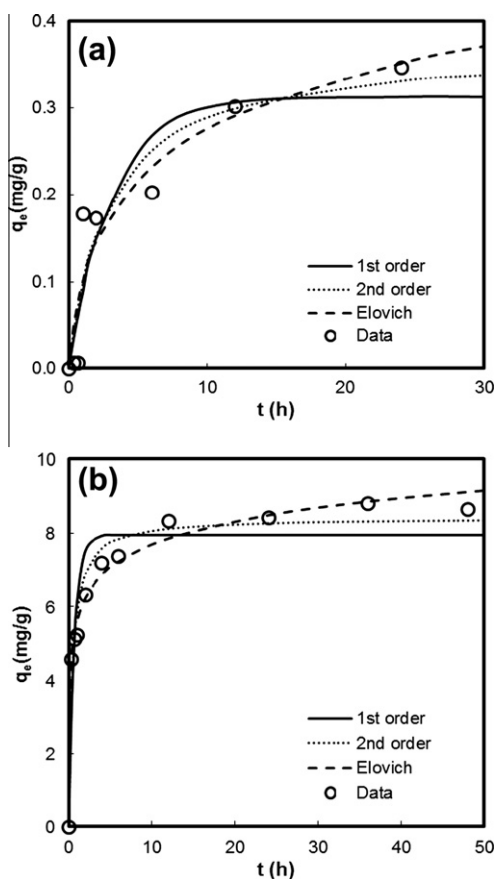


Fig. 3. Kinetics of lead adsorption onto PHHC (a) and mPHHC (b).

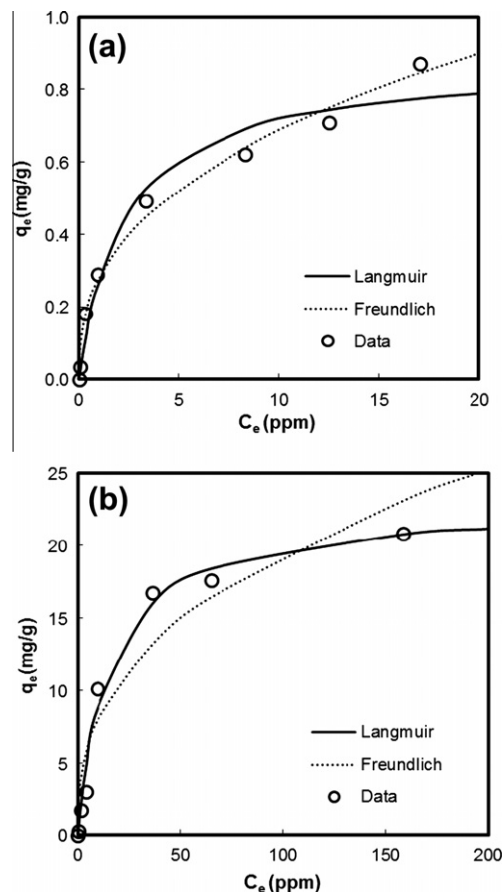


Fig. 4. Isotherms of lead adsorption onto PHHC (a) and mPHHC (b).

the PHHC was close to the input concentration (i.e., $C/C_0 \sim 1$), while the mPHHC column still effectively removed about half of the lead in the influent (i.e., $C/C_0 \sim 0.5$).

The ADE model simulated the lead breakthrough curve data well (Fig. 5). The model was first applied to the mPHHC column to obtain the best-fit values of k and λ by setting the maximum lead removal capacity in the column (q_{max}) to be the same as S_{max} as determined in batch experiments (Table 2). This is justified because the Langmuir model fitted the mPHHC isotherm very well. The best-fit λ was then used in the model to estimate the lead removal rate (k) and capacity (q_{max}) in the PHHC column. The best-fit q_{max} of PHHC column was around 1.04 mg g^{-1} , slightly larger than its Langmuir maximum capacity (S_{max}), but still much smaller than that of the mPHHC column. This result further quantifies the extent that H_2O_2 enhanced the peanut-hull hydrochar's ability to remove lead from water. In addition, it also suggests that the maximum sorption capacity (e.g., Langmuir capacity) obtained from batch sorption experiment could be a good representation of the maximum contaminant removal capacity of the same adsorbents in reactive barriers or packed bed filters.

The model estimated k values for the PHHC and the mPHHC columns were around 1.29 and 3.68 min^{-1} , respectively, indicating that the initial lead removal (i.e., under 'clean-bed' conditions) by the mPHHC was much faster than that of the PHHC. This is consistent with the results obtained from the sorption kinetic experiment. The Damkohler numbers ($Da = \frac{kL}{v}$, where L is the length of the hydrochar layer) for lead removal were 3.76 and 10.68 for the PHHC and the mPHHC columns, respectively. The magnitude of the Da indicated that, for both cases, the time scale was much shorter for lead removal in the 'clean bed' than for leaching through the columns even though only a small amount of sorbent

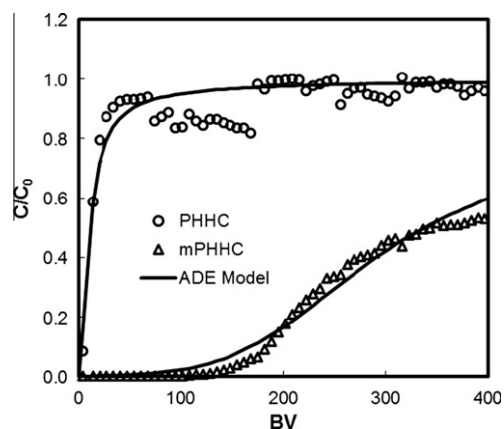


Fig. 5. Removal and transport of lead in hydrochar columns. BV and C/C_0 represent bed volume and relative concentration (i.e., effluent concentration divided by original concentration), respectively.

was used ($L = 21 \text{ mm}$). As a result, the effectiveness of the two sorbents in the columns was mainly controlled by their removal capacity (q_{max}). Due to its greater removal capacity, mPHHC should be a much better lead sorbent than PHHC and can be used as an effective adsorption media in filters and reactive barriers to remove lead from water flow.

3.4. Heavy metal removal by mPHHC in column experiment

The mPHHC column was also effective in treating water containing multiple heavy metals (Fig. 6). After the heavy metal solution was applied to the column, Cd^{2+} and Ni^{2+} were first detected

Table 2

Summary of model results of heavy metal removal and transport in the hydrochar columns.

| | D ($\text{cm}^2 \text{min}^{-1}$) ^a | k (min^{-1}) | λ | q_{max} (mg g^{-1}) | Da | R^2 |
|------------------------------------|---|------------------------------|-----------|--|-------|-------|
| <i>Single-metal system (Pb):</i> | | | | | | |
| PHHC | 0.047 | 1.29 | 11.13 | 1.04 | 3.76 | 0.78 |
| mPHHC | 0.047 | 3.68 | 11.13 | 22.82 | 10.67 | 0.98 |
| <i>Multi-metal system (mPHHC):</i> | | | | | | |
| Cd ²⁺ | 0.047 | 4.26 | 11.13 | 0.21 | 12.37 | 0.99 |
| Cu ²⁺ | 0.047 | 106 | 11.13 | 1.22 | 3.09 | 0.95 |
| Ni ²⁺ | 0.047 | 8.17 | 11.13 | 0.07 | 23.73 | 0.99 |
| Pb ²⁺ | 0.047 | 0.75 | 11.13 | 16.45 | 2.18 | 0.95 |

^a Model simulations were not sensitive to the dispersion process under the experimental conditions, therefore, D of heavy metals in the hydrochar columns were set to be the same as that reported for lead in sand columns [40].

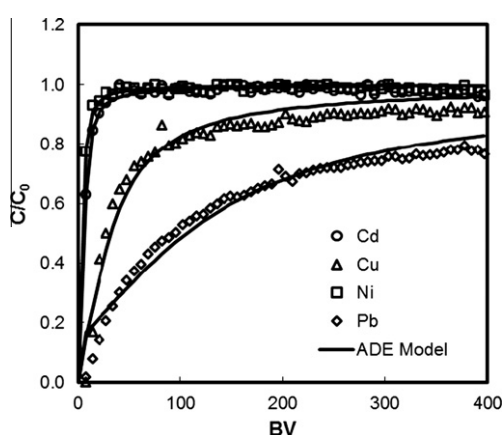


Fig. 6. Removal and transport of heavy metals in mPHHC column. BV and C/C_0 represent bed volume and relative concentration (i.e., effluent concentration divided by original concentration), respectively.

in the effluent. After around 40 BV, the column lost its ability to remove Cd²⁺ or Ni²⁺, and the two breakthrough curves stabilized at $C/C_0 = 1$. Although the Pb²⁺ and Cu²⁺ in the solution had the same molar concentration as Cd²⁺ or Ni²⁺, their removal by the mPHHC column was much greater. After 400 BV, the mPHHC column could still remove about 10% of Cu²⁺ and more than 20% of Pb²⁺ from the solution. Based on the breakthrough curves, the ability of the mPHHC to remove aqueous heavy metals followed a trend of Pb²⁺ > Cu²⁺ > Cd²⁺ ≈ Ni²⁺.

Lead removal in the multi-metal experiment, however, was lower than that in the single-metal system, indicating that competition for surface adsorption sites from other heavy metals in solution. Because the sorption of lead on the mPHHC is mainly through complexation with surface functional groups, particularly carboxyl groups, other heavy metals must also react with the same groups to form complexes (Eq. (4)). Based on the Langmuir maximum capacity of lead (i.e., 22.82 mg g⁻¹), the total available sites for adsorption of divalent metals on the mPHHC were about 0.11 mmol g⁻¹, equivalent to a single-metal removal capacity of 12.38, 6.47, or 7.00 mg g⁻¹ for Cd²⁺, Ni²⁺, and Cu²⁺, respectively.

The ADE model also described all the breakthrough data in the multi-metal experiment well (Fig. 6). The best-fit q_{max} of the mPHHC column was 0.21, 0.07, 1.22, and 16.45 mg g⁻¹ for Cd²⁺, Ni²⁺, Cu²⁺, and Pb²⁺, respectively (Table 2). This result suggested that Pb²⁺ competitively occupied most of the adsorption sites (72.1%) on the mPHHC. The second most competitive metal was Cu²⁺, which occupied about 17.1% of the site. Only small amount of the adsorption sites on mPHHC were available for Cd²⁺ (1.7%) and Ni²⁺ (1.1%). The model result indicated that about 8% of the

adsorption sites on the mPHHC were unavailable in the multi-metal system. These findings are in-line with Corami et al. [39], who also found that the removal capacity of a sorbent in a multi-metal system could be much lower than that in the single-metal system due to the competition effect.

The model-estimated k values of the four metals ranged 0.75–8.17 min⁻¹, and the corresponding Damkohler numbers ranged 2.18–23.73, indicating fast initial removal of all heavy metals by the mPHHC in the column. Therefore, filtration and transport of the four heavy metals in the multi-metal system were also ultimately controlled by their removal capacity (q_{max}) in the column. Under the tested experimental conditions, model results indicated that the heavy metal removal ability of the mPHHC followed the order of Pb²⁺ > Cu²⁺ > Cd²⁺ > Ni²⁺ and the modified hydrochar was especially effective in removing aqueous lead in both single- and multi-metal systems.

4. Conclusions

It was found that H₂O₂ modification can activate hydrochar produced from peanut hull and greatly enhance its ability to remove heavy metals, particularly lead, from water. Lead removal was effective in both batch and column modes. Thus, H₂O₂-treated hydrochar can be used as an effective sorption media in filters and reactive barriers to remove lead from water flow. The lead removal capacity of the modified hydrochar is comparable to that of many commercial water treatment agents, including activated carbon. Because biochar/hydrochar can be produced from various biomass residues (e.g., agricultural residues, wood by-products) at a relatively low cost, it is expected that this simple modification/activation method can also be applied to other hydrothermally and thermally produced biochars to create alternative and value-added sorbent for many environmental applications, such as wastewater treatment and groundwater remediation. Further experiment should be focused on the optimization of treated hydrochar for specific needs, as well as examination of the regeneration ability of this sorbent.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2012.06.116>.

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