Effect of H$_{2}$O$_{2}$ concentrations on copper removal using the modified hydrothermal biochar

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HIGHLIGHTS

- Sorption behaviors of the modified biochar were varying under different H$_{2}$O$_{2}$ levels.
- Sorption property of the modified HLG by 20% H$_{2}$O$_{2}$ (mHLG2) was the most desirable.
- H$_{2}$O$_{2}$ modification availably advanced sorption capacity of hydrothermal biochars.
- The functional groups changed non-uniformly with the increase of H$_{2}$O$_{2}$ levels.
- Carboxylic group had a significant relationship with H$_{2}$O$_{2}$ modification.

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ABSTRACT

This study investigated effect of H$_{2}$O$_{2}$ concentrations on copper removal using H$_{2}$O$_{2}$ modified hydrothermal carbonization Cymbopogon schoenanthus L. Spreng (HLG). Sorption behaviors of Cu (II) on the modified HLG by 20% H$_{2}$O$_{2}$ (mHLG2) could be the most desirable. Based on Langmuir isotherm, the maximum amount of Cu (II) uptake was in the sequence of mHLG2 (53.8 mg g$^{-1}$) > mHLG1 (44.2 mg g$^{-1}$) > mHLG3 (42.0 mg g$^{-1}$) > mHLG0 (35.8 mg g$^{-1}$), which was higher than the results from majority of previous studies, suggesting that H$_{2}$O$_{2}$ modification advanced sorption capacity of hydrothermal biochars evidently. Effect mechanisms exploration indicated that the difference of Cu (II) removal by biochars before and after the modification was mainly related to functional groups. Carboxylic group was responsible for the best sorption property of Cu (II) by mHLG2, which was attributed to its significant relationships with H$_{2}$O$_{2}$ modification and Cu (II) removal.

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1. Introduction

Sorption was found to be an effective method for the removal of metals in water-bodies (Singha and Das, 2013). Many types of sorbents have been effectively developed and applied for metal removal so far, such as activated carbon (Song et al., 2011) and biochars (Yang and Jiang, 2014). Especially, biochar can be created from varying low-cost materials, which has been proved to be one of the promising sorbents (Tan et al., 2015).

The preparation of biochar is comprised of two methods – pyrolytic and hydrothermal carbonization (HTC). This type of sorbent can be produced from a variety of sources, such as plants. Leboda et al. (2003) studied sorption properties of four types of activated carbons prepared by the carbonization of commercial resins. Mizuta et al. (2004) used the carbonization of bamboo to prepare carbonized materials. On the one hand, previous studies were partial to the application of pyrolytic biochar to remove metals from aqueous solutions, where pyrolytic biochar were commonly used as carbon-based materials linking with functional materials (Ma et al., 2014) or magnetic materials (Wang et al., 2015) to obtain desirable results. However, Kumar et al. (2011) reported metal removal efficiency by pyrolytic biochar was significantly lower than that by the corresponding hydrothermal biochar. It should be due to much more oxygen-containing functional groups on hydrothermal biochar surface (Liu et al., 2010).

Recently, Xue et al. (2012) studied the advanced ability of hydrogen peroxide (H$_{2}$O$_{2}$) modified biochar from peanut hull by the HTC, which provides a better channel for the increase of oxygen-containing functional groups on biochar surface. However, it is a pity that no discussions are found on the effects of H$_{2}$O$_{2}$ concentrations on sorption properties and the responsible oxygen-containing groups in the mentioned study. Although there was a literature about the effects of H$_{2}$O$_{2}$ treatment on pyrolytic biochar
with respect to cation exchange capacity, field water-retention capacity, and dye adsorption (Huff and Lee, 2016), the available information about the mentioned shortage is still limited. More importantly, there is less systemic report on the relationship between oxygen-containing functional group and metal removal, although carboxyl group was reported in the previous study (Nata and Lee, 2010). Meanwhile, the mentioned relationship was very important for the analysis of the effect mechanisms of H₂O₂ concentrations on metal removal. On the other hand, *Cymbopogon schoenanthus* L. Spreng (Lemon grass, LG) is widely indigenous in tropical and semi-tropical areas and has been found to be commercially biological resources (Dagar et al., 2004). However, there were no literatures on the use of LG as the source of hydrothermally carbonized sorbents until now.

Therefore, LG was chosen as the model source of biochar, and hydrothermal carbonization was used to transform LG into the hydrothermal carbonization LG (HLG) in this study. H₂O₂ in varying concentrations was finally applied to modify HLG surface. The sorption behaviors of the initial and modified HLG were investigated as a function of pH, sorbent dosage and contact time to explore the effects of H₂O₂ concentrations on metal removal with Cu (II) as model metal. Sorption isotherms of the initial and modified HLG were also compared to make sure the optimal H₂O₂ concentration. The emphasis was placed on the discussion of effect mechanisms of H₂O₂ concentrations on metal removal by chemical and surface analyses.

2. Methods

2.1. Reagents and sorbent preparation

Copper and its stock solutions were prepared from copper chloride dihydrate (CuCl₂ 2H₂O, Merck). Fresh *Cymbopogon schoenanthus* L. Spreng was purchased from the supermarket in Singapore. A laboratory scale semi-batch 500-ml Parr autoclave reactor (USA) was used for the production of HLG. The HTC of LG (10 g) was carried out at a heating rate of 10 °C min⁻¹ up to 200 °C with DI-water (weight ratio 1:1). Meanwhile, the temperature (200 °C) was kept for 3 h to obtain HLG. And then, the obtained HLG was washed five times with DI-water (500 mL) to remove potentially leachable materials. The rinsed HLG was subsequently dried at an air oven temperature of 60 °C overnight. The dried HLG was ground into appropriate particle sizes by placing a portion of HLG into a blender, after that sieved with #10 meshes (2 mm). 30% hydrogen peroxide (Sigma-Aldrich, Singapore) was added to prepare the H₂O₂ solutions with different concentrations. The final HLG (6 g) was equally added into the same volume (50 mL) H₂O₂ solutions with different concentrations (v/v = 10%, 20%, 30%) for 3 h at room temperature to respectively obtain the modified HLG (mHLG1, mHLG2, mHLG3) after the filtration, washing and drying (60 °C, 2 h).

2.2. Sorption experiments

Batch sorption experiments were conducted as a function of pH, sorbent dosage and contact time using 250 mL Erlenmeyer flasks as reaction vessels. A known quantity of the initial HLG (mHLG0) and modified HLG were added into aqueous solutions (100 mL) consisting of Cu (II) at 10 mg L⁻¹, respectively. Solution pH was adjusted to the desired values at the range of 2–8 using 0.1 M HCl and 0.1 M NaOH. The reaction vessels were placed on a rotary shaker at 200 rpm at 25 °C. After the completion, the mixture was filtered through a 0.45 μm PTFE membrane filter. ICP-OES was used to determine metal concentrations in the filtrates. The amount of metal adsorbed by adsorbent could be calculated using the Eq. (1):

\[ q_e = \frac{V(C_0 - C_e)}{M} \]  

(1)  

where \( q_e \) is the equilibrium metal uptake (mg g⁻¹); \( C_0 \) and \( C_e \) are the initial and equilibrium metal concentrations in the solution (mg L⁻¹), respectively; \( V \) is the solution volume (L); and \( M \) is the mass of adsorbent (g). All experiments were done in triplicate, and then the mean values of three replicated experiments were used for the reported data.

2.3. Chemical analysis

Oxygen-containing functional groups (carboxylic —COOH, lactone —C=O and hydroxyl —OH) were determined by Boehm titration method with different alkali solutions (NaOH, Na₂CO₃ and NaHCO₃). Briefly, a given amount of hydrothermal biochars were respectively added to the alkali solutions (1 M) and the mixture was agitated at agitating bed for 24 h. The supernatant was drawn and back titrated with 1 M HCl (Boehm, 1966).

2.4. Surface analysis

Surface characteristics for the used sorbents were obtained using ASAP (Micromeritics ASAP 2000) by means of the sorption of ultra-pure nitrogen at 77 K. Surface morphologies of sorbents were characterized by SEM (JEOL JSM-6700F). The initial sorbents were analyzed with a Nicolet 5700 FTIR spectrophotometer to examine the characteristics of the used sorbents. All the spectra were recorded and plotted on the same scale for comparison of their absorbance. The element analyses on the initial and Cu (II) – loaded sorbents were conducted by X-ray photoelectron spectroscopy (Kratos AXIS Ultra, UK). The XPS spectra were obtained by applying the monochromatic Al Ka X-ray energy source (1486.7 eV) operated at 15 kV and 5 mA. The wide scans were conducted from −5 to 1100 eV with pass energy of 80 eV and step size of 1 eV. The high resolution scans were conducted according to the peak being examined with pass energy of 40 eV and step size of 0.05 eV. To compensate for the charging effect, all spectra were calibrated with graphitic carbon as the reference at a binding energy of 284.6 eV. The software package Vision (XPSPEAK 41 Software) was used to fit the XPS spectra peaks.

3. Results and discussion

3.1. The change of sorption behaviors

There are slight changes among pH values at the peaks of Cu (II) sorption efficiencies on HLG modified by H₂O₂ with different concentrations (Fig. 1a). At pH 6, Cu (II) uptake on the initial HLG got to the equilibrium, while the one on the modified HLG arrived at the peak before pH 6. And, the optimum pH value of Cu (II) uptake was the sequence of mHLG2 (about 5) < mHLG1 (about 5.5) < mHLG3 (about 5.7). Sounthararajah et al. (2015) claimed that the competition between protons and metal ions for the same binding sites was responsible for the sorption behavior at low pH values. But, the competition effect of protons could be equivalent for the initial and modified HLG, because Cu mainly existed as free Cu (II) ion at pH values less than 6.0, and as Cu₂(OH)₂⁺ (aq) or CuOH⁺ (aq) at pH values above 6.0 (Sylva, 1976). The difference of the above sorption behaviors among mHLG0, mHLG1, mHLG2 and mHLG3 should be due to the variation between their surface characteristics caused by H₂O₂, such as the number of binding sites and the type of functional groups available (Vijayaraghavan and Yun, 2008).
In this study, sorbent dosage was varied from 0.1 to 5.0 g L\(^{-1}\) to study the influence of H\(_2\)O\(_2\) concentrations on the optimal sorbent dosage of Cu (II) uptake by HLG (Fig. 1b). The profiles for both \(q\) and removal efficiencies of Cu (II) changing with sorbent dosage were different for mHLG0, mHLG1, mHLG2 and mHLG3. Based on \(q\) and removal efficiencies, the optimal dosage was about 1.2 g L\(^{-1}\) for mHLG2, 1.5 g L\(^{-1}\) for mHLG1, 1.5 g L\(^{-1}\) for mHLG3, and 2.0 g L\(^{-1}\) for mHLG0. It implied that the modification of H\(_2\)O\(_2\) played a positive role in developing the sorption property of HLG. Under the same conditions, the relationship of contact time with Cu (II) removal by the used sorbents was also investigated. It was found from Fig. 1(c) that all removal efficiencies of Cu (II) by the initial and modified HLG increased at faster rates during the initial 30 min, but the sorption equilibrium for mHLG2 arrived first at around 90 min with 91.7% of removal efficiency, while that for both mHLG1 and mHLG3 were found after 100 min of sorption process. Based on the mentioned investigation, it could be found that sorption behaviors of Cu (II) by the modified HLG were varying with the difference of H\(_2\)O\(_2\) concentrations, and the sorption behavior of mHLG2 could be the most desirable.

### 3.2. The comparison of sorption isotherms

Langmuir isotherm (2) and Freundlich isotherm (3) were both applied to model the sorption behavior in this study.

**Langmuir equation**:

\[
q_e = \frac{Q_{\text{max}} b_i C_e}{1 + b_i C_e} \tag{2}
\]

**Freundlich equation**:

\[
q_e = K_F C_e^{1/n} \tag{3}
\]
where $Q_{\text{max}}$ is the maximum metal uptake (mg g$^{-1}$), $b_i$ the Langmuir equilibrium constant (L mg$^{-1}$), $K_F$ and $n$ are the Freundlich constant.

Fig. 2 shows the relationship between metal uptake ($q$) and metal equilibrium concentrations ($C_e$). Results from Fig. 2 indicated that the amounts of Cu (II) adsorbed by all of the sorbents increased with the increase of equilibrium concentration ($C_e$) of Cu (II). However, the profiles of $q$ with $C_e$ were obviously varying for the used sorbents. The sorption data were fitted by the Langmuir and Freundlich equations, and correlation coefficients ($R^2$) are given in Table 1.

Langmuir isotherm could imply monolayer sorption and constant sorption energy, while Freundlich isotherm could explain physicochemical sorption on heterogeneous surfaces. The agreement of the experimental data for Cu (II) sorption on the initial and modified HLG with both models implied that both monolayer sorption and heterogeneous surface conditions existed at experiments. However, the emphasis was varying for the different mHLG. Based on the correlation coefficients ($R^2$) in Table 1, sorption isotherms of mHLG for Cu (II) could be better described by Freundlich equation and Langmuir equation. This indicated that the modification of H$_2$O$_2$ caused the change of sorption patterns on HLG surfaces, which should be related to the change of oxygen-containing functional groups through H$_2$O$_2$ treatment (Xue et al., 2012). The maximum amount of Cu (II) uptake ($Q_{\text{max}}$) was in the sequence of mHLG2 > mHLG1 > mHLG0 > mHLG3. It implied that the modified HLG by 20% H$_2$O$_2$ could perform best for Cu (II) removal. For favorable sorption, high $Q_{\text{max}}$ and a steep initial isotherm slope (i.e., high $b_1$) are desirable. The sorption order of Cu (II) on mHLG0, mHLG1, mHLG2 and mHLG3 were consistent with the order of the affinity constants ($b_i$) listed in Table 1. The highest value of $K_F$ was observed for Cu (II) with the highest value of $n$. It implied that the binding capacity had a significantly positive correlation with the affinity between metal ions and the used sorbents, but not lineal relationship with H$_2$O$_2$ concentrations.

Sorption capacity of the sorbent can be reflected through the maximum uptake amount ($Q_{\text{max}}$). In this study, sorption capacities of the modified HLG were evidently larger than that of the initial HLG. The highest sorption capacity was found on mHLG2 surface, which implied that the modification of 20% H$_2$O$_2$ had the largest improvement to the sorption capacity of HLG. Many literatures have reported the Cu (II) removal by biochars from different materials. Meng et al. (2014) reported that the maximum Cu (II) sorption capacity of biochar derived from fresh swine manure was 17.71 mg g$^{-1}$. Similarly, Yang and Jiang (2014) found 17.01 mg g$^{-1}$ of the maximum Cu (II) sorption capacity by amino-modified biochar from saw dust char obtained by Tong et al. (2011). As a chemical activation, Regmi et al. (2012) claimed that the maximum Cu (II) sorption capacity (31 mg g$^{-1}$) of 2 M KOH activated biochar from switchgrass (Panicum virgatum species) was nearly three times more than the result (10.26 mg g$^{-1}$) of 2 M KOH activated biochar from brewers draft (Trakal et al., 2014). But, the mentioned results were lower than the obtained in this study. In addition, Li et al. (2013) reported 48.49 mg g$^{-1}$ of the maximum Cu (II) sorption capacity using biochar prepared from Spartina alterniflora. In contrast, only 20% H$_2$O$_2$ modified HLG in this study was more desirable than the biochar prepared from S. alterniflora for Cu (II) uptake. Thus, HLG modified by H$_2$O$_2$ have a greater potential as alternative sorbents for metal removal in aqueous solutions.

### Table 1

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>$Q_{\text{max}}$ (mg g$^{-1}$)</th>
<th>$b_1$ (L mg$^{-1}$)</th>
<th>$K_F$ (L g$^{-1}$)</th>
<th>$R^2$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mHLG0</td>
<td>35.8</td>
<td>44.2</td>
<td>53.8</td>
<td>42.0</td>
<td>0.9356</td>
</tr>
<tr>
<td>mHLG1</td>
<td>0.09</td>
<td>0.122</td>
<td>0.165</td>
<td>0.096</td>
<td>1.28</td>
</tr>
<tr>
<td>mHLG2</td>
<td>0.9738</td>
<td>0.9469</td>
<td>0.9142</td>
<td>0.9571</td>
<td></td>
</tr>
<tr>
<td>mHLG3</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

### 3.3. The effect mechanisms of H$_2$O$_2$ concentrations on copper removal

Surface analyses (ASAP, SEM, FTIR and XPS) are commonly used to explore sorption mechanisms through finding out the surface characteristics and responsible functional groups. But, there is little information available on the amount of each responsible functional group on sorbent surfaces. The amount of responsible functional groups is critical to evaluate the modification degree of sorbents by H$_2$O$_2$, while previous studies reported the amount change of responsible functional groups before and after H$_2$O$_2$ modification seldom. Furthermore, no literatures have reported that the relationship between the amount of responsible functional groups and the level of H$_2$O$_2$ modification and the relationship of each responsible functional group with metal removal. However, two mentioned relationships are very important to make sure the effect mechanisms of H$_2$O$_2$ concentrations on Cu (II) removal by hydrothermal biochar. Therefore, both chemical and surface analyses were applied to explore effect mechanisms of H$_2$O$_2$ concentrations on Cu (II) removal in this study.

The measurement of specific surface area for the used sorbents was obtained based on nitrogen sorption/desorption data, as well as pore volume and average pore diameter. It was found that the specific surface area, pore volume and average pore diameter were 27.2 m$^2$ g$^{-1}$, 0.533 cm$^3$ g$^{-1}$ and 2.0 nm for mHLG0, 26.9 m$^2$ g$^{-1}$, 0.537 cm$^3$ g$^{-1}$ and 2.0 nm for mHLG1, 27.3 m$^2$ g$^{-1}$, 0.541 cm$^3$ g$^{-1}$ and 2.1 nm for mHLG2, 27.1 m$^2$ g$^{-1}$, 0.548 cm$^3$ g$^{-1}$ and 2.1 nm for mHLG3, respectively. The surface morphology of characterized by SEM indicated the structure of the initial HLG was significantly rough and folded (S1), while the modification of H$_2$O$_2$ with different concentrations resulted in little change of surface structure of HLG. Thus, the difference of Cu (II) removal by HLG before and after the modification resulted hardly from the specific surface area and surface structure.

FTIR analysis was also used to explore the surface characteristics of HLG before and after H$_2$O$_2$ modification. There were numerous and multifarious functional groups on the surface of the initial and modified HLG (S2). The broad and strong band ranging from 3200 to 3600 cm$^{-1}$ could be due to the overlapping of O–H and N–H stretching bands in spectrums of the used sorbents (Shriner et al., 2004), and it had different changes before and after the modification. The peak at 3417.9 cm$^{-1}$ in mHLG0 significantly changed in the modified HLG. The peak at 1631.8 cm$^{-1}$ attributed to C=O and/or C=O stretching changed into 1629.8 cm$^{-1}$ for mHLG1, 1627.9 cm$^{-1}$ for mHLG2, and 1626.0 cm$^{-1}$ for mHLG3. The peak at 2360.9 cm$^{-1}$ assigned to lactone C=O stretching in mHLG0 changed into 2364.7 cm$^{-1}$ for mHLG2, 1633.7 and 2362.8 cm$^{-1}$ for both mHLG1 and mHLG3, respectively. Similarly, the peaks at 1161.1 and 1205.5 cm$^{-1}$ attributed to carboxylic acids C=O–OR stretching in mHLG0 changed respectively into 1163.0 and 1209.3 cm$^{-1}$ for mHLG1, 1163.0 and 1211.2 cm$^{-1}$ for mHLG2, 1163.0 and 1207.4 cm$^{-1}$ for mHLG3. The peak at 1371.4 cm$^{-1}$ assigned to hydroxyl O–H stretching in mHLG0 changed into 1373.3 cm$^{-1}$ for mHLG1, 1375.2 cm$^{-1}$ for mHLG2, 1377.2 cm$^{-1}$ for mHLG3, respectively. In addition, the C–H and C–O–C stretching could also be well-reflected by peaks (1427.3 and 1058.9 cm$^{-1}$) in the initial and modified HLG. On the basis of the above chemical bonds,
there should be carboxylic, lactone and hydroxyl groups on the initial HLG, and these functional groups changed with different degrees after the modification of H$_2$O$_2$.

XPS analysis was further applied to find out the responsible functional groups for Cu (II) uptake (S3). The deconvoluted C 1s spectra of the used sorbents before and after Cu (II) uptake were comprised of four peaks with differentiated binding energy (BE). In contrast with the initial HLG, these peaks for the modified HLG attributed to C—C, C—O, C=O, and O—C=O bonds had changed obviously with different BE, respectively. It indicated that H$_2$O$_2$ modification played a well role in the amount of carboxylic, lactone and hydroxyl groups on HLG surface. After Cu (II) uptake, the BEs of C—O, C=O, and O—C=O bonds can respectively originate from hydroxyl, lactone, and carboxylic groups, based on the literature (Moulder et al., 1992). This implied that hydroxyl, lactone, and carboxylic groups on the use sorbents were responsible for Cu (II) uptake.

Based on FTIR and XPS analyses, three oxygen-containing functional groups (Carboxylic, Lactone and Hydroxyl) were responsible for metal removal on surface of the used sorbents. The following was the discussion of the relationship between H$_2$O$_2$ concentrations and the amount of the mentioned functional groups. The definition of ratio ($k$) is given as the Eq.(4) to reflect the change of each functional group with H$_2$O$_2$ concentrations. The definition of ratio ($f$) is given as the Eq. (5) to show the amount ratio of hydroxyl groups to carboxylic groups under different modified HLG.

$$\begin{align*}
k & = \frac{a}{b} \\
f & = \frac{c}{d}
\end{align*}$$

where $a$ is the amount of functional group on the modified HLG by H$_2$O$_2$, $b$ is the amount of the corresponding functional group on the initial HLG. $c$ and $d$ are respectively the amount of hydroxyl group and carboxylic group on mHLG modified by the same H$_2$O$_2$ concentrations.

The previous study demonstrated that the processes of hydrolysis, dehydration and decarboxylation on sorbent surface were found during HTC (Funke and Ziegler, 2010), which can explain the abundant C=C bonds on the initial HLG. After the modification of H$_2$O$_2$, the C=C bond likely broke due to the oxidation reaction, and could change into ortho alcoholic hydroxyx groups, which was testified by the varying peaks assigned to C=C bonds on the modified HLG (S3). The profiles of $k$ in Fig. 3 implied that the hydroxyl group on HLG was close to increase linearly with the increase of H$_2$O$_2$ concentrations. On the other hand, Fang et al. (2014) claimed that persistent free radicals (PFRs) were contained on biochar surface and could produce carboxylic groups when H$_2$O$_2$ was added. However, carbon loss was also very obvious with the increase of H$_2$O$_2$ concentrations (Guo and Chen, 2014), which could mainly be due to aromatic carbons decomposed by H$_2$O$_2$ (Heard and Senftle, 1984). Kumar (2011) reported that the decomposition of aromatic carbons by H$_2$O$_2$ was comprised of two different products: (i) aliphatic carboxylic acids; (ii) CO$_2$ and H$_2$O. The carboxylic and lactone groups increased at first and then decreased (S4), which indicated that the aliphatic carboxylic acid was the dominant decomposition product when H$_2$O$_2$ level lower than 20%. In addition, the profile of lactone group was not in line with that of carboxylic group, which should be due to that C=O bonds on the initial HLG (S3) cut down the effect of H$_2$O$_2$ on the produced C=O bonds.

Although the amount of hydroxyl groups on HLG had a positive correlation with H$_2$O$_2$ concentrations, the sorption behavior was not the most desirable for the mHLG3 (Fig. 1). The relationship between metal removal and the responsible functional groups was also investigated. In practice, experiments on metal removal using single functional groups are hardly operated, which indicates that the quantitative relationship between metal removal and single functional group could be obtained with difficulty. On the other hand, the affinity of metal with the responsible functional groups is less related to sorbent species. In this study, twenty copies of the used sorbents with different concentrations (dosage from 0.1 g L$^{-1}$ to 2.5 g L$^{-1}$) were applied to the same condition experiments of determining the amount of oxygen-containing functional groups and Cu (II) removal efficiency. Data statistical analysis and graph were done by MINITAB (version 15). The relationship of functional groups with Cu (II) removal was evaluated by cluster analysis (Fig. 3). Cluster analysis could determine the correlation among different factors. And correlation degree was obtained by identifying the distance across variables using a tree-shape figure (Pitt et al., 2004). Based on Fig. 3, the correlation of Cu (II) removal with carboxylic groups on the used sorbents was the most significant, and the following is the one between Cu (II) removal and hydroxyl groups. Carboxylic groups were good for Cu (II) binding as they were bidentate ligands including (SCO$_3$)$_2$Cu$_2^+$ and (SCO$_3$)$_2$-Cu(OH)$^-$ (Corapcioglu and Huang, 1987). Majority of researchers reported the optimum pH for metal sorption by biochars was less than 7.0 (Tan et al., 2015), while the data varied with the different of sorbent species (Meng et al., 2014; Yang and Jiang, 2014; Han et al., 2015). This was in line with the results of sorption behavior of the modified HLG in this study. The role of carboxylic group should be responsible for this point. But, hydroxyl group was also the important functional group. Based on the profile of $f$, the amount of hydroxyl group was twice as much as that of carboxylic group on the modified HLG by 30% H$_2$O$_2$, while the corresponding Cu (II) removal was not the highest. It indicated that the growing rate of Cu (II) removal had not linear relation with the one of hydroxyl group. Therefore, effect mechanism of H$_2$O$_2$ modification on copper removal by biochars was achieved through the improvement of carboxylic groups on biochars, and the critical was the control of H$_2$O$_2$ concentration. However, the formation of carboxylic acids on biochars through the H$_2$O$_2$ modification needs further investigation mechanistically. In addition, the previous study claimed that components in natural environments were known to influence transport and fate of heavy metals between aqueous solutions and solid surfaces (Chen et al., 2011). Although the emphases in this study were sorption behaviors, sorption isotherms and effect mechanisms of H$_2$O$_2$ concentrations on metal removal, there might be the effect of water matrix on removal efficiency of heavy metals by H$_2$O$_2$ modified hydrochar in natural water environments, based on the recent literature.

**Fig. 3.** The dendrogram of functional groups with Cu (II) removal.
(Park et al., 2016). Therefore, the application of mHLG in natural water environments needs also further exploration systematically.

4. Conclusions

Sorption behaviors of Cu (II) by mHLG2 could be the most desirable. Langmuir isotherms suggested that the modification of H₂O₂ advanced sorption capacity of hydrothermal biochars evidently. The functional groups changed non-uniformly with the increase of H₂O₂ concentrations. Carboxylic group was responsible for the best sorption property of Cu (II) by mHLG2, which was attributed to its significant relationships with H₂O₂ modification and Cu (II) removal. However, the formation of carboxylic acids on biochars through the H₂O₂ modification needs further investigation mechanistically.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.biortech.2016.02.032.

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