The importance of surface functional groups in the adsorption of copper onto walnut shell derived activated carbon
Ruzhen Xie, Yan Jin, Yao Chen and Wenju Jiang

ABSTRACT
In this study, activated carbon (AC) was prepared from walnut shell using chemical activation. The surface chemistry of the prepared AC was modified by introducing or blocking certain functional groups, and the role of the different functional groups involved in the copper uptake was investigated. The structural and chemical heterogeneity of the produced carbons are characterized by Fourier transform infrared spectrometry, X-ray photoelectron spectroscopy, Boehm titration method and N2/77 K adsorption isotherm analysis. The equilibrium and the kinetics of copper adsorption onto AC were studied. The results demonstrated that the functional groups on AC played an important role in copper uptake. Among various surface functional groups, the oxygen-containing group was found to play a critical role in the copper uptake, and oxidation is the most effective way to improve Cu (II) adsorption onto AC. Ion-exchange was identified to be the dominant mechanism in the copper uptake by AC. Some other types of interactions, like complexation, were also proven to be involved in the adsorption process, while physical force was found to play a small role in the copper uptake. The regeneration of copper-loaded AC and the recovery of copper were also studied to evaluate the reusability of the oxidized AC.

Key words | adsorption, functional group, heavy metals, ion-exchange, kinetics

INTRODUCTION
Heavy metal pollution in water bodies is of worldwide environmental concern. Heavy metals are unbiodegradable, and they tend to accumulate in living organisms. Copper poisoning causes a number of illnesses in humans, such as nausea, diarrhea, liver and kidney failure (Demiral & Güngör 2016). Much effort has been expended on exploring techniques to effectively remove copper from wastewater (Younas et al. 2011; Jellouli Ennigrou et al. 2014; Nazari et al. 2015; Oladipo & Gazi 2015; Ungureanu et al. 2015; Zhou et al. 2017). Among these techniques, adsorption is recognized as a promising way to remove copper from water bodies, due to its easy operation, high efficiency and low initial cost. Adsorption by activated carbon (AC) is a preferred approach because of its porous structure, insensitivity to toxic environments, and copper recoverable from the loaded adsorbent for reuse (Demiral & Güngör 2016; Ihsanullah et al. 2016).

The adsorption capacity of AC is largely dependent on its pore structure and surface chemistry. Up to now, many studies have been carried out to investigate the influence of the pore structures on the carbon’s adsorption capacity (Lu & Sorial 2004; Lillo-Ródenas et al. 2005; Tseng & Tseng 2005). Micropores with sizes less than 7 nm were reported to govern the performance of AC on volatile organic compounds and benzene removal at low concentration (Lillo-Ródenas et al. 2005). Corn cob based ACs with a uniform micropore size (close to 2 nm) showed excellent removal capacity towards many kinds of dyes, chlorophenol and phenol (Tseng & Tseng 2005). Further efforts have also been made to study the carbon’s surface chemical properties in order to enhance their affinity for metal ions (Song et al. 2010; Rivera-Utrilla et al. 2011; Xie et al. 2015). Zhu et al. found that introducing S⁻, Cl⁻ and N⁻ containing ligands to an AC surface would increase its adsorption capacity toward Hg (Zhu et al. 2009). Liu et al.
modified an adsorbent with ethylenediaminetetraacetic acid, leading to an increased number of carboxyl groups on the adsorbent, resulting in a higher affinity for lead. Yantasee et al. (2004) functionalized AC with amine, which resulted in a high and rapid adsorption for copper. Previous research revealed oxygen and nitrogen containing functional groups would improve the uptake capability of AC towards metal ions, such as Cu (II), Cr (VI) (Sun et al. 2010; Xie et al. 2012, 2013). Surface modifications of AC have been recognized as effective approaches to enhance the metal ion uptake from aqueous media by increasing the metal ion binding sites (Yantasee et al. 2004; Liu et al. 2012b; Shen et al. 2013). However, not much information is available on clarifying the contribution of the physical and various functional groups.

The metal ion binding mechanism during adsorption processes involves ion exchange, complexation, electrostatic attraction and microprecipitation processes (Nurchi & Villaescusa 2008; El-Hendawy 2009; Moreno-Castilla et al. 2010; Shen et al. 2013; Majumder et al. 2016). Although metal–functional group interactions are often reported in the literature, large uncertainties still remain on assessing the contribution of physical and chemical adsorption (Chand et al. 2009; Marín et al. 2010; Rivera-Utrilla et al. 2011). Therefore, it is of high importance to identify the adsorption mechanisms, and assess the role of the physical properties and functional groups on adsorption. This is indispensable for identifying adsorption process parameters, and also provides useful information for AC selection in the particular design of a wastewater treatment unit.

Chemical treatment is reported to allow the blockage of certain functional groups on the biomass (Liu et al. 2010; Marín et al. 2010; Nurchi et al. 2010; Yang et al. 2012). The blockage of a given functional group is to prevent its participation in the adsorption process, so the contribution of some certain functional groups in metal ion removal can be evaluated (Marín et al. 2010; Yang et al. 2012). In this study, the functional groups on walnut shell-derived carbon were modified without significantly changing its pore structures, and their contribution to the copper removal was investigated. Adsorption and regeneration experiments, in combination with characterization analysis such as elemental analysis, Fourier transform infrared (FTIR) spectrometry, Boehm titration method and X-ray photoelectron spectroscopy (XPS) studies, were carried out to elucidate the role of functional groups on the carbons participating in the adsorption process. The reusability of carbons and the feasibility of Cu (II) recovery were also investigated.

### MATERIALS AND METHODS

#### Functionalization of AC

**Carbon oxidation (designated as OAC)**

Carbon preparation and oxidation was carried out following the method in a previous study (Xie et al. 2013). Walnut shell was used as a raw material, which was washed with distilled water, dried at 105 °C for 12 h to reduce the moisture content, crushed, and ground to pass through a 60-mesh sieve before use. Walnut shell based-carbon (AC) was prepared by H3PO4 activation at a temperature of 500 °C. After that, 20 g AC was reacted with 200 mL 6 M HNO3 solution and then agitated in a magnetic agitator (ZH7918, Beijing) at 100 rpm under 80 °C until dry. The samples were then washed repeatedly with hot deionized water (DI) until reaching neutral pH, and dried at 105 °C for 12 h.

**Reaction with thionyl chloride and ethylenediamine (designated as TEAC)**

Of note, 15 g of the oxidized carbon (OAC) was refluxed with 45 mL 5% thionyl chloride in toluene for 5 h at 70 °C. After being extensively washed with toluene, the samples were purified by Soxlet extraction for 3 h, and dried at 150 °C for 13 h. Later, the carbon was mixed with 0.05 M ethylenediamine and stirred for 24 h at 90 °C. The filtered carbon was then washed several times with ethanol in an ultrasonicator for 10 min to ensure the removal of all free chemicals from the carbon, and dried overnight. This treatment resulted in amino-rich carbon. The main reaction scheme is (Zhu et al. 2009):

\[
\text{RCOOH} + \text{SOCl}_2 \rightarrow \text{RCOOSOCl} \rightarrow \text{RCOCl} + \text{SO}_2 + \text{HCl} \tag{1}
\]

\[
\text{ROH} + \text{SOCl}_2 \rightarrow \text{ROSOCl} + \text{HCl} \tag{2}
\]

\[
\text{H}_2\text{N} + \text{R} \rightarrow \text{RCONHR} \rightarrow \text{RCONHR} + \text{HCl} \tag{3}
\]

\[
\text{H}_2\text{N} + \text{S} \rightarrow \text{RCONH} + \text{NH}_2 + \text{HCl} + \text{N}_2 \tag{4}
\]
Methylation of amino groups (designated as MAC)

The modification of the amino group was carried out by shaking 5 g amino-rich carbon in 150 mL of formaldehyde (HCHO) and 300 mL of formic acid (HCOOH) for 6 h at 125 rpm. Then the carbon sample was filtered and thoroughly washed with DI water, and dried at 60 °C until reaching a constant weight. This treatment resulted in methylation of the primary and secondary amines. The general reaction scheme is:

\[ R - \text{CH}_2\text{NH}_2 \xrightarrow{\text{HCHO}/\text{HCOOH}} R - \text{CH}_2\text{N(CH}_3\text{)}_2 + \text{CO}_2 + \text{H}_2\text{O} \]  

where R presents the other components of AC except for the functional groups (Panda et al. 2006; Liu et al. 2010).

Characterization

The changes of element content on AC before and after modification were analyzed by elemental analyser (EURO EA3000, Italy). IR analyses of the AC samples were performed to detect the vibration frequency changes after chemical treatment using FTIR spectroscopy (FTIR 6700 NEXUS Nicolet, USA). About 2 mg of the AC sample was mixed with 200 mg of spectroscopic grade KBr, and the FTIR spectral was recorded within the range 4,000–400 cm\(^{-1}\), with all spectra plotted using the same scale on the transmittance axis. The pH point of zero charge (pH\(_{\text{PZC}}\)) of the AC was determined according to the method described by Kikuchi et al. (2006). The quantitative estimation of the oxygenated surface groups was measured in accordance with the method described by Boehm (2002) and Kikuchi et al. (2006). The Brunauer-Emmett-Teller (BET) surface area and pore volumes were analyzed using the nitrogen adsorption–desorption method (SSA-4200, China). XPS was employed to determine the functional groups on the AC using an XSAM-800 spectrometer (KRATOS, UK). High-resolution spectra of C1s, O1s, and N1s were collected.

Adsorption experiments

The impacts of pH on Cu (II) adsorption by the AC were evaluated under different pH ranges at an initial concentration of 25 mg/L. The pH of each test was adjusted with dilute HNO\(_3\) and NaOH. Adsorption equilibrium isotherms were studied to evaluate the efficiency of the modified AC in the Cu (II) uptake. Stock solutions (1 g/L) of Cu (II) were prepared by dissolving analytical grade Cu(NO\(_3\))\(_2\)·3H\(_2\)O in DI water. The desired concentration was prepared by dilution of the stock solution. In the kinetics study, 0.8 g of the AC was added to a 1,000 mL glass flask containing 800 mL of Cu (II) solution, without adjusting the solution pH. The suspensions were shaken at 150 rpm at 20 ± 1 °C for 5 h. Ten milliliters of solution was continuously sampled by a plastic syringe at certain time intervals, and after filtration, the residual Cu (II) was analyzed by atomic absorption spectrometer. The equilibrium isotherm studies were performed by adding a fixed dosage of 1 g/L AC to a series of 150 mL Erlenmeyer flasks in an isothermal shaker for 5 h. The initial copper concentration varied from 10 to 100 mg/L. The suspensions were shaken at 150 rpm under 20 ± 1 °C for 5 h, and the solutions were then sampled and analyzed for Cu (II) concentrations. All experiments were conducted in duplicate, and mean values are reported.

Desorption studies

The adsorption/regeneration experiments were used to investigate the reusability of the AC and the recovery of adsorbed Cu (II). 0.05 g OAC was added into a 200 mL conical flask containing 50 mL of 25 mg/L Cu (II). After being shaken for 6 h, the mixture was filtered and the supernatant was analyzed for Cu (II). The exhausted OAC was rinsed with DI water, dried and transferred to a 1,000 mL glass flask containing 50 mL 0.1 M HNO\(_3\) and rotated for 1 h, and then the solution was sampled and analyzed for Cu (II). After elution, the regenerated OAC was rinsed with DI water, dried, and tested in the subsequent five consecutive adsorption/desorption experiments.

Data analyses

The amount of copper adsorbed on the AC was calculated using Equation (6):

\[ q (\text{mg/g}) = \frac{(C_0 - C_e)V}{m} \]  

where \(C_0\) is the initial Cu (II) concentration (mg/L), \(C_e\) is the equilibrium Cu (II) concentration (mg/L), \(V\) is solution volume (L) and \(m\) is the AC dosage (g).

The pseudo-first-order model (Equation (7)), and pseudo-second-order model (Equation (8)) were applied to fit the experimental data in order to study the adsorption rate and the mechanism of copper adsorbed onto AC (Liu et al. 2006).
where \( q_e \) and \( q_t \) are the amounts of Cu (II) (mg/g) adsorbed at equilibrium and time \( t \) (h), respectively, and \( k_1 \) (1/h) and \( k_2 \) (g/mg h) are the rate constants of the pseudo-first-order model and second-order model, respectively.

Three adsorption isotherms, the Langmuir model (Equation (9)), Freundlich model (Equation (10)), and Dubinin-Radushkevich (D-R) model (Equation (11)) have been used to investigate the mechanism of copper adsorption on AC (Freundlich 1906; Langmuir 1916; Luo et al. 2016).

\[
\log \left( \frac{q_e - q_t}{q_t} \right) = \log q_e - \frac{k_1 t}{2.303}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}
\]

\[
\ln q_e = \ln k_F + \frac{1}{n} \ln C_e
\]

\[
\ln q_e = \ln q_m - \beta \epsilon^2
\]

where \( q_m \) is the monolayer adsorption saturation capacity for AC, (mg/g), \( C_e \) is the equilibrium Cu (II) concentration in the solution (mg/L), \( q_e \) is the amount of Cu (II) adsorbed at specified equilibrium (mg/g), \( n \) is the constant representing the adsorption intensity of the AC, \( q_m \) is theoretical saturation capacity for AC (mmol/g), \( E \) is the mean free energy of adsorption per mole of the AC (kJ/mol), \( K_L \) (L/mg), \( K_F \) (mg/g) (L/mg) \( 1/n \) and \( \beta \) (mol²/kJ²) are the constants for the Langmuir, Freundlich and D-R models, respectively, and \( \epsilon \) is Polanyi potential, which equals RT \ln (1 + 1/C_e).

**RESULTS AND DISCUSSION**

**Characterization**

The element content of the raw AC, oxidized carbon (OAC), amino enriched carbon (TEAC), and amino methylation carbon (MAC) is shown in Table 1. As can be seen from Table 1, the introduction of nitric acid onto AC led to a significant increase of oxygen content. The O content increased from 22.11% to 37.74% on OAC. The nitrogen content in TEAC after ethylenediammine modification is 2.47 times as high as that of OAC (3.21%), which represents the successful introduction of the nitrogen functional groups. The methylation of the amino group led to a decrease of the nitrogen contents in MAC.

FTIR spectra were used to analyze the change of functional groups on the AC during the modification process. As can be seen from Figure 1(a), the most characteristic change by oxidation was the appearance of bands observed at 1,709 cm⁻¹ on OAC, which can be referred to the C = O stretch of the carboxylic acid groups (Xie et al. 2015). In addition, an increase of bands at 1,590 cm⁻¹ on OAC was observed, which can be attributed to the quinone structure, indicating an increase of oxygen content in OAC (Shim et al. 2001; Xiao & Thomas 2005; Liu et al. 2010). After being treated with thionyl chloride and ethylenediamnine, as shown in Figure 1(b), the wavenumber at 1,709 cm⁻¹ representing the carboxylic acid groups disappeared, and the quinone related peak at 1,590 cm⁻¹ decreased, which confirms the blocking of oxygen-containing functional groups on TEAC. However, as also can be seen from Figure 1(b), the peak associated with pyridine-like functionalities and NH stretching at 1,330 cm⁻¹ and 2,350 cm⁻¹ increased (Kuo 2009; Shafeeyan et al. 2011), indicating that TEAC had become amino-enriched carbon. After further methylation of amino groups in MAC, as shown in Figure 1(c), the peak at 2,350 cm⁻¹, associated with NH stretching, disappeared, and bands at 1,350 cm⁻¹ related to pyridine-like functionalities were reduced, indicating the blocking of nitrogen-containing functional groups in MAC.

The zeta potential of all carbon samples (pH_PZC) and their total surface acidity obtained from Boehm titration experiments are listed in Table 2. The pH_PZC was determined to be around 6.41, 1.5, 2.75 and 2.55 for AC, OAC, TEAC and MAC, respectively. The lower pH_PZC in OAC indicated that nitric acid modification would introduce some acidic functional groups on OAC, this phenomenon is also observed in the Boehm titration result, which shows an increment of surface acidity on OAC, as shown

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**Table 1 | Analysis of element content**

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>72.93</td>
<td>4.46</td>
<td>0.5</td>
<td>22.11</td>
</tr>
<tr>
<td>OAC</td>
<td>55.4</td>
<td>3.65</td>
<td>5.21</td>
<td>37.74</td>
</tr>
<tr>
<td>TEAC</td>
<td>59.88</td>
<td>4.45</td>
<td>7.94</td>
<td>28.03</td>
</tr>
<tr>
<td>MAC</td>
<td>60.25</td>
<td>4.21</td>
<td>6.36</td>
<td>29.18</td>
</tr>
</tbody>
</table>

*Calculated by difference.

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**Table 2 | Characteristics of the carbon samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH_PZC</th>
<th>Total surface acidity (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>6.41</td>
<td>3.16</td>
</tr>
<tr>
<td>OAC</td>
<td>1.5</td>
<td>1.9</td>
</tr>
<tr>
<td>TEAC</td>
<td>2.75</td>
<td>1.5</td>
</tr>
<tr>
<td>MAC</td>
<td>2.55</td>
<td>1.3</td>
</tr>
</tbody>
</table>
From Table 2, it can be seen that OAC possesses the number of largest total acidic groups among AC, with a value of 2.300 meq./g; the increment in carboxylic groups by oxidation was obvious. After being oxidized, some oxygenated anchoring sites were developed on the AC surface, which then acted as an intermediate to introduce nitrogen functional groups to the carbons’ surface. Thus, by modifying OAC with ethylenediamine, basic amino groups were formed on TEAC, with TEAC showing higher pH_PZC than OAC. Accordingly, the methylation of the amino group resulted in a slight decrement of pH_PZC in MAC. The atomic ratios (determined by XPS) of C:O:N on the AC, OAC, TEAC and MAC surface were 95.0:4.5:0.5, 80.2:18.7:1.1, 80.3:13.4:6.3 and 82.0:14.5:3.5, respectively. A significant increase of oxygen atoms was observed on OAC after nitric acid modification, indicating that nitric acid treatment introduced oxygen functional groups on OAC. Further treatment of OAC with ethylenediamine resulted in more nitrogen atoms and fewer oxygen atoms on TEAC. This demonstrates that the reaction with thionyl chloride and subsequently ethylenediamine could block oxygen functional groups and increase the nitrogen content.

Table 2 | Physicochemical properties of the produced ACs obtained from point of zero charge, Boehm method, and N2 adsorption isotherms at 77 K

<table>
<thead>
<tr>
<th>Sample</th>
<th>AC</th>
<th>OAC</th>
<th>TEAC</th>
<th>MAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH_PZC</td>
<td>6.41</td>
<td>1.5</td>
<td>2.75</td>
<td>2.55</td>
</tr>
<tr>
<td>Total acidic groups (meq./g)</td>
<td>1.301</td>
<td>2.300</td>
<td>0.770</td>
<td>0.934</td>
</tr>
<tr>
<td>Carboxylic group (meq./g)</td>
<td>0.813</td>
<td>1.750</td>
<td>0.350</td>
<td>0.448</td>
</tr>
<tr>
<td>Lactonic group (meq./g)</td>
<td>0.313</td>
<td>0.315</td>
<td>0.275</td>
<td>0.328</td>
</tr>
<tr>
<td>Phenolic group (meq./g)</td>
<td>0.175</td>
<td>0.235</td>
<td>0.145</td>
<td>0.158</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>936</td>
<td>25</td>
<td>28</td>
<td>26</td>
</tr>
<tr>
<td>Pore volume (cm³/g)</td>
<td>0.91</td>
<td>0.15</td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td>Pore width (nm)</td>
<td>1.95</td>
<td>12.2</td>
<td>11.0</td>
<td>10.8</td>
</tr>
</tbody>
</table>

Figure 1 | FTIR spectra of AC, TEAC, OAC and MAC.
on TEAC. Methylation of the amino groups led to the decrement of nitrogen atoms on MAC. Besides, as we can see from Table 2, the surface physical parameters for OAC, TEAC and MAC are similar, which suggests both amination and methylation of amino groups did not cause significant changes to the surface area and pore volumes on AC, that is, the introduction or blockage of the amino groups did not block or enlarge the pores’ mouth on the AC surface.

As can be seen from Table 3 and Figure 2, the area ratio for the peak at 288.5 ± 0.5 eV attributed to the carboxyl group increased significantly from 9.5% to 15.4%. After modification with nitric acid, the area ratios for C-O at a peak of 285.0 ± 0.2 eV increased from 18.0% to 39.0%. After adsorbing Cu (II), the area ratios for O−C-O at a peak of 288.5 ± 0.5 eV decreased from 15.4% to 6.8%. The decrement of O−C-O may be due to the formation of carboxyl-metal complexes between oxygen groups on OAC and Cu (II), and led to the increment of electron density at the adjacent carbon atoms, thus reducing the binding energy (BE) of the carbon (Yu et al. 2008). Thus, it can be concluded that carboxyl groups are involved in Cu (II) adsorption. The XPS spectra of Cu (II) is shown in Figure 3, and a peak with BE of 934.4 eV was observed in the Cu (2p3/2) spectrum. It is known that Cu (II) located in ionic bonding shows a peak at around 935 eV, while Cu (II) located in a coordination bonding shows a peak at a

### Table 3 | Area ratios of C1s spectra for AC, OAC, TEAC and MAC before and after copper adsorption

<table>
<thead>
<tr>
<th>Carbons</th>
<th>peak area ratio (%)</th>
<th>C-C 284.3 ± 0.2(eV)</th>
<th>C-O 285.0 ± 0.2(eV)</th>
<th>O−C-O 288.5 ± 0.5(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>72.5</td>
<td>18.0</td>
<td>9.5</td>
<td></td>
</tr>
<tr>
<td>OAC</td>
<td>45.6</td>
<td>39.0</td>
<td>15.4</td>
<td></td>
</tr>
<tr>
<td>OAC-Cu (II) loaded</td>
<td>64.9</td>
<td>28.3</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>TEAC</td>
<td>61.1</td>
<td>32.2</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>TEAC-Cu (II) loaded</td>
<td>63.6</td>
<td>30.4</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>MAC</td>
<td>57.9</td>
<td>34.6</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>MAC-Cu (II) loaded</td>
<td>61.5</td>
<td>31.9</td>
<td>6.6</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 2** | XPS spectra of C 1s, N 1s, and O 1s of (a) AC, OAC, TEAC and MAC, (b) copper-loaded OAC, TEAC and MAC, and (c) OAC and TEAC before and after copper-loading.
relatively lower BE (Deng & Ting 2005). Therefore, the peak with BE of 934.4 eV in Figure 3 can be assigned to the copper ions interacting with carbon through ionic bonding, i.e. ion-exchanged Cu (II) (Vieira et al. 2014).

The results from the OAC deconvoluted O 1s spectra in Figure 2(c) shows three peaks with BEs of 530.09, 531.49 and 533.49 eV. The peak at 530.09 eV may be assigned to the C=O bond representing carboxyl and/or ether groups, the peak at 531.49 eV results from the C-O bond related to the alcohol and/or carbonyl groups, while the peak at 533.49 eV can be attributed to the adsorbed H$_2$O in AC (H$_2$O) (Zhu et al. 2009; Li et al. 2010). After copper adsorption, the BE values of the C = O groups and C-O groups in OAC increase from 530.09 eV and 531.49 eV to 531.66 eV and 532.87 eV, respectively, which is likely due to the decrease of the electron cloud density of the oxygen (O) atoms after the copper ion binding to the O atoms. The area ratio for these two peaks decreased from 33.4% and 50.0% to 28.5% and 45.8%, respectively, indicating that the C = O and C-O groups act as adsorption sites (Zuo 2014). On the basis of the XPS analysis for O1s spectra, both C = O and C-O are involved in the adsorption of copper, which could be an ion exchange reaction in the manner shown in Equations (12) and (13). This phenomenon is in line with the Boehm titration results and the observations in the C 1s analysis.

![Figure 3](https://iwaponline.com/wst/article-pdf/76/11/3022/210074/wst076113022.pdf)

\[ 2R - COOH + Cu^{2+} \rightarrow R - COOCu + 2H^+ \] (12)

\[ R - OH + Cu^{2+} \rightarrow R - OCu^+ + H^+ \] (13)

Similarly, as shown in Figure 2(c), the N 1s spectra in TEAC can also be deconvoluted into two peaks with BEs of 398.8 and 400.2 eV, which can be assigned to nitrogen (N) atoms in the R-NH$_2$ group and R – NH$_3^+$ complexes. After copper adsorption, the BEs of the two N 1s peaks shift to 399.14 and 400.58 eV, respectively, which can be related to the formation of R-NH$_3$Cu$^{2+}$ complexes as shown in Equations (14) and (15). The covalent bond between N and Cu$^{2+}$ can be formed due to a pair of lone electrons in the N atoms, which causes the decrease of the electron cloud density of the N atom (Liu et al. 2011a). Studies on Cu (II) adsorption onto chitosan coated perlite beads and chitosan-cellulose hydrogel beads also revealed the complexion of N in amine with Cu (II) through XPS spectral analysis (Kannamba et al. 2010).

\[ R - NH_2 + Cu^{2+} \rightarrow R - NH_2Cu^{2+} \] (14)

\[ R - NH_3^+ + Cu^{2+} \rightarrow R - NH_2Cu^{2+} + H^+ \] (15)

**Effect of solution pH**

pH affects both the solubility of metal ions and the ionization states of functional groups on the adsorbents. Figure 4 shows that within a pH range of 1–6, free Cu$^{2+}$ ions formed the predominant species as calculated by MINTEQA2. To avoid the precipitation of copper, adsorption experiments were conducted with the initial pH ranging from 1 to 6. From Figure 5, we can see that the adsorption of copper was highly pH dependent for all four

![Figure 4](https://iwaponline.com/wst/article-pdf/76/11/3022/210074/wst076113022.pdf)

\[ \text{Species (\%)} \]

<table>
<thead>
<tr>
<th>pH</th>
<th>Cu$^{2+}$</th>
<th>Cu(OH)$_2$ (aq)</th>
<th>Cu(OH)$_3^+$</th>
<th>Cu(OH)$_4^{2-}$</th>
<th>Cu$_2$O$_3$H$_2$</th>
<th>Cu$_2$O$_3$</th>
<th>Cu$_8$(OH)$_4$$^{3+}$</th>
<th>CuOH$^+$</th>
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<tbody>
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<td>1</td>
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Effect of solution pH
AC, and the removal efficiency increased sharply as pH increased. The lower metal removal efficiency at pH 1 may be due to the protonation of active sites on the AC, thus H$_3$O$^+$ ions competed with Cu$^{2+}$ for the binding sites on the AC. The points of zero charge (pH$_{PZC}$) of AC, OAC, TEAC and MAC are 6.41, 1.5, 2.75 and 2.55, respectively. At pH < pH$_{PZC}$, the surfaces of the AC are positively charged, thus restricting the approach of copper ions due to repulsion at lower pH values. A sharply continuous increasing removal rate occurred in the pH range of 2.5 to 6 on all four AC, with OAC showing the highest removal efficiency. In the pH range of 2.5–6, the OAC surface is negatively charged, which favors the binding of cations. In addition, with increasing pH values, the oxygen-containing functional groups on OAC became deprotonated, thus enhancing the electrostatic attraction between OAC and Cu (II). This further increases the amount of Cu (II) adsorption onto OAC, as OAC possesses the highest amount of oxygen-containing functional groups among the four AC. After the oxygen functional groups were blocked, the adsorption of copper on TEAC was reduced. The dramatic decrease in copper binding after blocking the oxygen functional groups on TEAC suggests that the carboxyl groups and hydroxyl groups on OAC are largely responsible for the uptake of copper on AC. As can be seen from Figure 4, after methylation of the nitrogen groups, MAC shows a lower copper ion uptake capacity compared with TEAC, indicating the amino group present on AC also partially contributes to the copper uptake. This can be explained by the long pairs of electrons on the nitrogen available on TEAC to interact with the copper ions. To sum up, the blockage of oxygen-containing functional groups on AC greatly reduced the copper uptake, and methylation of the amino groups slightly decreases the amount of copper being adsorbed. Therefore, it can be concluded that the carboxyl groups and hydroxyl groups are more important functional groups involved in the adsorption of copper, and ion-exchange is the dominant mechanism, as shown in Equations (14) and (15).

**Adsorption kinetics**

The kinetic data are shown and summarized in Figure 6 and Table 4. It can be seen from Figure 6, for all AC, that the uptake of copper was rapid in the first 10 min and then gradually slowed down and finally reached equilibrium after 3 h. The fast removal rate in the first few minutes has significant practical importance, as a short reaction time requires a smaller reactor volume to achieve high efficiency. The results in Table 4 reveal that the adsorption process can

**Table 4** | Kinetic parameters of the pseudo-first-order and pseudo-second-order models for the adsorption of Cu (II) onto four adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$q_e, \text{exp}$ (mg/g)</th>
<th>$q_e, \text{cal}$ (mg/g)</th>
<th>$k_1$ (1/h)</th>
<th>$R^2$</th>
<th>$q_e, \text{cal}$ (mg/g)</th>
<th>$k_2$ (g/mg h)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>12.82</td>
<td>0.91</td>
<td>1.270</td>
<td>0.7967</td>
<td>12.97</td>
<td>3.497</td>
<td>1</td>
</tr>
<tr>
<td>OAC</td>
<td>23.13</td>
<td>0.46</td>
<td>1.950</td>
<td>0.6865</td>
<td>23.15</td>
<td>9.331</td>
<td>1</td>
</tr>
<tr>
<td>TEAC</td>
<td>15.16</td>
<td>1.33</td>
<td>1.730</td>
<td>0.8967</td>
<td>15.20</td>
<td>4.811</td>
<td>1</td>
</tr>
<tr>
<td>MAC</td>
<td>13.95</td>
<td>2.17</td>
<td>1.143</td>
<td>0.9756</td>
<td>14.05</td>
<td>1.877</td>
<td>1</td>
</tr>
</tbody>
</table>
be best described by a pseudo-second order model with correlation coefficients ($R^2$) observed to be 1, for four AC. The theoretical $q_e$ values for the four AC were also very close to the experimental $q_e$ values. These observations suggested that copper adsorption by AC follow the pseudo-second order reaction. Thus the adsorption process is controlled by a chemical adsorption process involving valence forces through sharing or exchanging of electrons between AC and Cu (II) (Iqbal et al. 2009; Shen et al. 2013).

It should also be noted that the copper uptake amounts $q_e$ were 12.97, 23.15, 15.20 and 14.05 mg/g for AC, OAC, TEAC and MAC, respectively, varying in the order OAC > TEAC > MAC > AC. Since the surface area and pore volumes of OAC, TEAC and MAC are similar, the higher adsorption capacity for OAC can be ascribed to oxygen related adsorption sites on the OAC surface, which react with copper ions. Amino-enriched TEAC exhibited a slightly higher adsorption capacity than MAC and AC, suggesting nitrogen functional groups could also be involved in the copper uptake.

**Adsorption isotherms**

The theoretical parameters of the adsorption isotherms for copper adsorption onto AC at 20 ± 1 °C are given in Table 5. The comparison of the calculated adsorption isotherms and the experimental data are presented in Figure 7. It can be seen from Table 5 that the Langmuir model yields the highest $R^2$ values, which represent a better fit than the Freundlich and D-R isotherm models. According to the Langmuir isotherm hypothesis, copper adsorption onto AC occurs on a homogeneous surface through monolayer adsorption, and the maximum monolayer copper adsorption capacity was in the order of OAC > TEAC > MAC > AC. OAC exhibited the highest adsorption amount of 89.29 mg/g, which was much higher than other three types of AC, since OAC, TEAC and MAC have closely developed surface areas. It can be inferred that the oxygen functional group-enriched OAC has a greater affinity than amino-enriched TEAC towards the adsorption of copper, and amino-enriched TEAC was favored for copper adsorption compared with functional group-blocked MAC.

In the Freundlich equation, the constant $1/n$ stands for the interaction between exchange sites in the adsorbent and adsorbate, and $K_f$ (mg/g (L/mg)1/n) reveals the adsorption capacity of the adsorbent. From Table 5, we can see the value of $1/n$ for all four AC was less than 1, which indicates that the adsorption of copper onto AC is favorable. The $K_f$ value for OAC was the highest, and confirms that oxygen-containing functional groups are prone to bind copper. The magnitude of $E$ in the D-R constant can be used to estimate the adsorption process type. Usually, with $E$ values in the range of 8–16 kJ/mol, the adsorption type can be explained as chemical adsorption. The $E$ values for the four AC adsorbing Cu (II) were between 3.38–4.81 kJ/mol, indicating physical adsorption also partly contributes to the adsorption process (Köse & Kivanc 2011).

**Regeneration and reuse of OAC**

In this study, 0.1 M HNO3 was used as an elution agent for Cu (II) recovery. The desorption efficiency for copper-loading OAC was higher than 85.65%, as seen in Table 6. The adsorption capacity of OAC can be well maintained over five adsorption/desorption cycles, and the five sequences' desorption efficiencies were in the range of 91.23%–93.12%. These data reveal that OAC has a good reuse potential and a high possibility of recovery Cu (II) from aqueous solution. The high efficiency of HNO3 desorption efficiency indicates the dominant ion-exchange mechanism in Cu (II) adsorption onto OAC (Wang et al. 2010).

**Adsorption mechanism**

From adsorption isotherm studies, physical adsorption contributes to a certain extent in the copper uptake. Assuming the dominant mechanism of adsorption is physical adsorption, the adsorption isotherm of copper onto OAC was much higher than other three types of AC. oxygen functional group-blocked MAC.

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**Table 5 | Langmuir, Freundlich, and D-R adsorption isotherm parameters for AC adsorbing copper at 20 °C, respectively**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
<th>D-R isotherm</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$Q_m$ (mg/g)</td>
<td>$K_L$ (L/mg)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>AC</td>
<td>50.25</td>
<td>0.043</td>
<td>0.9907</td>
</tr>
<tr>
<td>OAC</td>
<td>89.29</td>
<td>0.096</td>
<td>0.9909</td>
</tr>
<tr>
<td>TEAC</td>
<td>55.56</td>
<td>0.045</td>
<td>0.9917</td>
</tr>
<tr>
<td>MAC</td>
<td>53.48</td>
<td>0.043</td>
<td>0.9936</td>
</tr>
</tbody>
</table>
adsorption, the adsorption capacity should then be directly proportional to the AC’s surface area. However, from the BET results and the adsorption experiments, although OAC, TEAC and MAC exhibited similar surface areas and pore volumes, their adsorptive capacities towards copper were quite different. Besides, we evaluate the maximum adsorptive surface on the AC responsible for physical adsorption on the basis of ionic radii (the molecular weight, cross-section area and radius of copper are 63.5 g/mol, 1.58 Å², and 0.71 Å (Ho et al. 2002)), so the calculated maximum adsorptive surface area for copper uptake (with assumption of monolayer) are 7.53 m²/g for AC, 13.37 m²/g for OAC, 8.32 m²/g for TEAC and 8.01 m²/g for MAC, respectively. As raw AC has highest surface area of 936 m²/g, only 0.8% of the surface area of the AC was effective in the physical adsorption process, according to the calculation. On this basis, we can deduce that physical adsorption is not dominant in the copper adsorption process.

In order to assess the contribution of the functional groups in the chemical adsorption process, AC was chemically modified to introduce/block certain functional groups on AC and was used for the adsorption of copper ions to interpret the binding mechanism. From equilibrium adsorption studies (results are shown in Table 5), it can be seen that the adsorption capacity of OAC towards copper was enhanced 77.68% by introducing oxygen functional groups onto the AC, while the blockage of oxygen functional groups and the introduction of nitrogen groups resulted in TEAC with lower copper uptake capacity (reduced from 89.29 mg/g to 55.56 mg/g). Further methylation of amines by reaction with formaldehyde and formic acid resulted in a 3.7% reduction in copper uptake by MAC. The increased adsorption capacity due to the introduction of the oxygen functional group and the decreased adsorption capacity resulting from replacing the oxygen functional groups into nitrogen groups, indicates that carboxyl and/or hydroxyl groups are largely responsible for the adsorption of copper.
onto AC in the ion exchange, as shown in Equations (12) and (15). Blocking of primary and secondary amines by reacting with formaldehyde-formic acid led to a 3.7\% reduction of copper uptake amount. This phenomenon indicates that amines might also be involved in the copper removal process. Copper can undergo chelation through dative bonds with the lone pair of electrons on nitrogen present in the –NH₂ groups on TEAC, as shown in Equations (14) and (15), even if they are not the major binding sites.

In summary, this study showed that nitric acid treatment introduces oxygen functional groups onto AC, and improves its adsorption capacity towards copper uptake mainly by ion exchange. The thionyl chloride-ethylenediamine reaction offers a valuable method for blocking oxygen functional groups on AC and introduces amino groups onto AC. Further, formaldehyde-formic acid treatment induces blockage of the primary and secondary amines by methylation, without significantly changing its physical properties (Panda et al. 2007). The adsorption of copper ions on the AC’s surface may be regarded as the dominant ion-exchange mechanism, as well as some other lesser types of interactions like physical force and complexation. This study provides an insight into identifying the importance of surface role functional groups in binding copper onto AC, which is also helpful in AC selection for a particular design of wastewater treatment units.

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NOTES

The authors declare no competing financial interest.

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