

Conversion of Cu(II)-polluted biomass into an environmentally benign Cu nanoparticles-embedded biochar composite and its potential use on cyanobacteria inhibition

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ABSTRACT

Disposal of heavy metal-polluted biomass obtained from bioremediation through harmless approaches is a big challenge. In this work, we investigated the effects of pyrolysis temperatures on the conversion of exhausted Cu(II)-laden biomass into Cu nanoparticles (NPs) embedded biochar composite (CBC), Cu(II) chemical form and behavior variation, and associated ecotoxicity evolution. The potential of the resulted biochar products on the growth inhibition of harmful cyanobacterium species *Microcystis aeruginosa* was also evaluated. At the present study, the increase of pyrolysis temperature from 350 °C to 750 °C increased the pH value, surface area, total pore volume, and Cu concentration of CBC. Ecotoxicity test based on germination and root growth of Chinese cabbage showed that pyrolysis temperature >550 °C relived the ecotoxicity of biomass waste. The further analysis revealed that the Cu in the CBC existed in CuO, CuO/Cu₂O/Cu⁰ mixture, and Cu⁰ crystal forms when they were produced at pyrolysis temperatures of 350, 550 and 750 °C, respectively. The embedded Cu NPs in the CBC decreased from nanosize 28.7 nm –5.8 nm with the temperature increase. Compared with the biochar without Cu, CBC-550 and CBC-750 significantly inhibited the growth of *Microcystis aeruginosa* algae. Overall, this study demonstrated that the pyrolysis of Cu(II) laden biomass at ≥ 550 °C produces Cu NPs *in-situ* embedded biochar nanocomposite, which had the potential to be used as blue-green algae inhibitor with low ecotoxicity.

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1. Introduction

Copper (Cu) is one of the most important metals in modern life. With its wide application, Cu containing substances will be inevitably released into the environment and pose a serious threat to ecosystem (Fernández-Calviño and Băăth, 2016). Bioremediation with biomass, biomass residue or bio-based material is an effective low-cost technology for the remediation of Cu-contaminated water or soil (Suzakia et al., 2017). During the remediation process, Cu(II) was absorbed and transferred to the tissues or structure of biomass, resulting in detoxification of polluted soil and water (Liu et al., 2018). However, after bioremediation, the harvested biomass waste cannot be freely disposed due to the metal pollution (Sas-Nowosielska et al., 2004; Huang et al., 2018a). Developing a

harmless disposal and recycle method with aim to manage polluted biomass wastes will help thrive the bioremediation development (Yousaf et al., 2018; Zabbey et al., 2017).

Thermal treatment of organic biomass has been considered to be an effective method in waste volume reduction and harm mitigation (Liu et al., 2014; Li et al., 2018a). However, biomass treatment due to open burning often contributes large quantities of gaseous pollutants and aerosol particulate matter to the atmosphere, which would have a significant impact on air quality, human health, and climate (Jeong et al., 2016; Zhao et al., 2017). Consequently, controllable pyrolysis is believed to be one of the promising methods for disposal of biomass waste, which not only reduces organic waste volume but also converts biomass waste into valuable products (bio-oil, biosyngas and biochar) in addition to minimized pollutant emission (Chen et al., 2014). During the pyrolysis process, the biomass is decomposed with metals enriched in solid carbon residue (biochar) (Liu et al., 2012; Li et al., 2018b). More importantly, the resulted biochar materials derived from the

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pyrolysis of some heavy metals-loaded biomass could have great potentials for diverse environmental applications (Li et al., 2017; Zhou et al., 2018).

Various human activities have led to the enrichment of nutrients, particularly nitrogen and phosphorus, in soil and water (Wang and Gaston, 2014; Li et al., 2017). The eutrophication in surface waterbody has stimulated growth of algae and especially, of cyanobacteria (also known as blue-green algae) in lakes and reservoirs, posing a great threat to aquatic environments around the world (Codd, 2000). Massive growth of algae in natural water increased the difficulty and cost of water purification (Xu et al., 2014), influenced the safety of drinking water (Dittmann and Wiegand, 2006). Till now, different technologies including biological (Ma et al., 2012), physical (Ahn et al., 2003) and chemical (Takaara et al., 2007) or a combination of these approaches (Liang et al., 2009) have been employed to control algae growth and to mitigate eutrophication. Current biological methods have focused on algae inhibition through biological filter-feeding (Ma et al., 2012) and microbial community stability adjustment (Ji et al., 2009); whereas physical approaches emphasized on algae growth condition adjustment through controlling light intensity (Chen et al., 2009), coagulation-flotation (Gao et al., 2010), ultrasonic radiation (Ahn et al., 2003), artificial mixing (Liu et al., 2012), and water-lifting aeration (Sun et al., 2014). Chemical approaches mainly managed phosphorus bioavailability or input (Yuan et al., 2016), developed algae inhibitors from chemical reagents (Costas and Lopez-Rodas, 2006) or phytogenic anti-algae extracts (Ferrier et al., 2005). Although these measures had achieved acceptable feasibility in water treatment plant, the challenge with all the above-mentioned technologies remain. For those lakes or reservoirs with large surface area, the methods like ultrasonic irradiation and water-lifting aeration are difficult to carry out in practice due to high cost and complicated process (Chen et al., 2009). The direct use of chemical or phytogenic algae inhibitors in the water body could cause negative effects on ecosystems, such as toxin release and bioaccumulation, although these methods can be quickly performed especially as an emergency strategy application (Garlich et al., 2016). Therefore, it is important to develop a new algal inhibitor that is effective for inhibition of algae communities as well as economically and environmentally benign. In addition, the inhibitor should be capable of *in-situ* algal control, which removes algae cell in water source area rather than in water treatment plant (Asaeda et al., 1996).

It is well known that copper and Cu(II) salt are blue-green algae (cyanobacteria) killers in aqueous environment (Costas and Lopez-Rodas, 2006; Garlich et al., 2016). The Cu(II)-loaded biomass harvested from the bioremediation or biosorption process is expected to have similar inhibition function in cyanobacteria growth. However, the direct use of the Cu(II)-loaded biomass in anti-algae practice could probably pose serious water pollution due to the unstable form of biomass in nature (Huang et al., 2018a,b). If the Cu-containing biochar originated from carbonization of Cu(II)-loaded biomass can be employed as a blue-green algae inhibitor, it will be a win-win strategy for disposal of Cu(II)-contaminated biomass and mitigation of water eutrophication. However, this potential has not been well explored. Moreover, although Liu et al. (2012, 2014) had thermally treated the Cu(II)-loaded fir sawdust at 450–600 °C as catalyst (Cu nanoparticles (NPs) embedded biochar) for improving bio-oil production and reducing 4-nitrophenol in wastewater, the chemical form and environmental behavior of Cu(II) as well as the ecotoxicity of resulted biochar were not thoroughly investigated. Because the properties of biochars are closely related to pyrolysis temperatures and feedstock which determines the ecological risks of produced biochar (Jin et al., 2016), research is still needed to investigate the effect of pyrolysis temperature on the

behavior of similar materials with the aim to minimize the risk of hazardous component release into the environment.

To this aim, we (1) synthesized Cu NPs-embedded biochar composites by pyrolyzing Cu(II)-containing cotton leaf at temperature range of 350–750 °C, (2) characterized the basic physico-chemical property, environmental behavior, and the ecotoxicity of the as-prepared Cu(II) biochar composites, and (3) demonstrated the potential of algae inhibition performance experimentally on harmful cyanobacterium species *Microcystis aeruginosa*.

2. Materials and methods

2.1. Raw materials collection and Cu(II)-containing biomass pyrolysis

Chemicals including citric acid, ammonium ferric citrate, CuCl₂, NaNO₃, MgSO₄, KH₂PO₄, CaCl₂, Na₂CO₃, Na₂EDTA, CuSO₄, ZnSO₄, Na₂MoO₄, Co(NO₃)₂, MnCl₂, H₃BO₃, HCl, HNO₃, HClO₄, and diethylenetriamine pentaacetic acid (DTPA) of analytical grade were used as received after purchasing from Fisher Scientific (USA). All the chemical solutions were prepared using deionized water (DI water, 18.2 MU) throughout the experiment. Reference material GBW07604 GSV-3 (plant) was purchased from the National Center for Standard Materials of China. Feedstock biomass, cotton leaf (CL), was collected from Central Research Station, Louisiana State University Agricultural Center at Baton Rouge, LA. The CL was sequentially rinsed by tap and DI water to remove the dust and then oven-drying at 55 °C overnight and milling crushed to <2 mm pieces before use. Then, 50 g CL dry powder was mixed with Cu(II) solution (2000 mL, 300 mg L⁻¹) in a polypropylene bottle and shaken in an oscillator (150 rpm) at room temperature. After overnight shaking, the Cu(II)-loaded CL residue (named Cu-CL) was filtered and dried at 105 °C in an oven for 4 h before being carbonized. The carbonation was carried out by placing 30 g of Cu-CL dry powder in porcelain crucibles and pyrolyzed in a Thermo-lyne FA1730 muffle furnace under N₂ flow at 400 mL min⁻¹ for 30 min. After that, the Cu-CL sample was heated with temperature increase at a rate of 10 °C min⁻¹ and then maintained at desired temperatures (350, 550, and 750 °C) for 2 h with continuous N₂ flow at 200 mL min⁻¹ (Li et al., 2017). The produced biochar products were ground to size 0.12–0.2 mm, rinsed with DI water, and oven-dried at 105 °C for 6 h followed by storing in desiccators before use. Similarly, particles of CL without Cu(II) loading were pyrolyzed for comparison. For convenience of discussion, CB-x was used to represent the biochar without Cu(II) loading, Cu NPs-loaded biochar composite was recorded as CBC-x. The x in the CBC-x indicates the designated pyrolysis temperature.

2.2. Sample characterization

Total C, H and N contents of samples were determined using an elemental analyzer (Elementar Analysensysteme GmbH, Germany). Total Cu content was determined using a Hitachi atomic absorption spectrometer (Z-2000, Hitachi, Japan) after sample digestion with HCl-HNO₃-HClO₄ based on USEPA method 3050B. Meanwhile, the reference material GBW07604 GSV-3 was employed for the analysis quality control with Cu recovery rate (94.6%–104.3%) within the range of the certified limitation. The fractionation of Cu in sample is demonstrated by modified BCR sequential extraction test as procedure described by Huang et al. (2018a) with a solid/liquid ratio of 1:40 (g mL⁻¹); and four fractions including F₁ (water soluble, exchangeable and carbonate bound fractions), F₂ (fraction bound to Fe and Mn oxides, that is reducible), F₃ (fraction associated with organic matter, that is oxidizable), and F₄ (residual fraction) forms of Cu were categorized in the sequential extraction test. The surface

area (S_{BET}), total pore volume (TPV) and average pore diameter (AVP) of samples were measured by N_2 adsorption at 77 K using a V-Sorb 2800P analyzer (App-one, China). X-ray diffraction (XRD) analysis was also carried out to identify any crystallographic structure in the carbon samples by using a computer-controlled X-ray diffractometer (Philips Electronic Instruments, Mahwah, NJ, USA) with a scan rate (2 theta) of 0.02° per second. Morphological properties of the biochar were characterized using a field emission gun scanning electron microscope (FEG-SEM, JEOL 6335F, Japan) and a transmission electron microscopy (JEOL 200CX TEM, Japan). Finally, the change in composition and valence state of Cu(II) in the pyrolyzed samples was determined using X-ray photoelectron spectroscopy (Kratos, UK) with monochromatized Al $K\alpha$ radiation (1486.92 eV).

2.3. Composite stability and potential ecotoxicity evaluation

In order to study the stability of CBC sample, DI water (pH 6.89), DTPA (pH 7.31) and organic acid mixture (OAM, 10 mmol L^{-1} , pH 5.60) consisting of acetic, citric acid, formic, lactic, and malic with the molar ratio of 4:1:1:2:2 were used as extraction agents (Feng et al., 2005). Approximately 0.5 g CBC sample was weighed into a 50 mL centrifuge tube that contained 10 mL extraction solution followed by 24 h shaking (at 150 rpm, 25 °C) for reaction. The mixture was then centrifuged (at 8000 rpm, 15 min) and the supernatant was collected through a 0.45 μm nylon-membrane filter. Then, the filtrate was digested with $\text{HCl-HNO}_3\text{-HClO}_4$ before measuring total Cu(II) content.

The risk assessment code (RAC) (equation (1)) was applied to appraise the potential risk of biochar samples in environment (Liu et al., 2016b).

$$\text{RAC} = 100\% \times C_i/C_n. \quad (1)$$

where C_i is the mobile fraction (F_i) of Cu in sequential extraction test, C_n is the total content of the Cu in sample. The toxic response coefficient of Cu is 5. Generally, RAC with value <1, 1–10, 11–30, 31–50, and >50 indicates no risk, low risk, medium risk, high risk and very high risk, respectively (Huang et al., 2018a).

Moreover, plant germination test was employed to evaluate the potential ecotoxicity of the prepared CBC. In brief, CBC samples of 2 g were weighed into a series of 50 mL centrifuge tubes which contained 20 mL DI water each and shaken at 150 rpm for 4 h. The supernatants were filtered with 0.45 μm nylon-membrane filters. Approximately 5 mL filtrate from each treatment was added to the pre-sterilized Petri dish to wet the filter paper, followed by distributing 10 seeds of Chinese cabbage on the filter paper. The Petri dishes were covered and then placed in an incubator under dark at 25 °C. After 72 h incubation, the measurement was taken for the number of seeds germinated and the primary root length. DI water was used as a control. The experiments were conducted in triplicates. The germination rate (%) was calculated by equation (2) (Huang et al., 2018a).

$$\text{Germination rate} = 100\% \times \frac{\text{Germination number in treatment}}{\text{Germination number in control}}. \quad (2)$$

2.4. Algal cultivation and inhibition test

In this experiment, all the facilities including pipette tips, medium, carbon samples, filters, and glassware were sterilized before use. *Microcystis aeruginosa* (FACHB-905), a cyanobacterium species that cause harmful algal blooms, was obtained from the Freshwater

Algae Culture Collection at the Institute of Hydrobiology (Wuhan City, China). *Microcystis aeruginosa* culture was conducted at the laboratory of the Northwest A&F University with a sterilized BG11 medium using the method described by Ni et al. (2012). All cultures were grown in 250 mL flasks with 150 mL of sterilized culture medium at 25 °C with a 14:10-h light-dark cycle. The light intensity was 50 $\mu\text{mol photons m}^{-2} \cdot \text{s}^{-1}$. To ensure that the experiments were conducted with the algae in the exponential growth phase, the algae were cultivated in batch cultures (transferred and inoculated once every 5 d).

The effectiveness of algal inhibition of the prepared carbon samples were tested using the algal bioassays method ISO 8692-2004. In brief, *Microcystis aeruginosa* was inoculated into a culture medium in a 500 mL flask using $(1.65\text{--}1.96) \times 10^8 \text{ cells} \cdot \text{L}^{-1}$ as the initial algal density. About 0.5 g of each prepared carbon sample sealed in a polythene mesh bag was added to a 500 mL flask with an initial algal density of $(1.65\text{--}1.96) \times 10^8 \text{ cells} \cdot \text{L}^{-1}$. The algae culture with no carbon sample added was labelled as control, and carbon samples pyrolyzed at 550 °C and 750 °C without Cu were used for comparison with CBC samples. There were three replicates for each treatment. All flasks were cultured at 25 °C under 14 h light + 10 h dark conditions, and algal growth was monitored every 3 d during the culturing. Cell numbers were calculated by using an optical microscope (Olympus CX31, Olympus Corporation) at 400 magnifications with a hemocytometer before the cells were homogenized using an ultrasonic cell pulverizer (VCX130, US Sonics) for 10 min. The content of chlorophyll-a in *Microcystis aeruginosa* were assayed according to the classical ethanol extracting method (Ni et al., 2012). Algal cells were harvested by suction filtration 10 mL algae mixture with a 0.45 μm cellulose membrane. All the cell pellets entrapped by the membrane were resuspended in a centrifuge tube with 10 mL ethanol (95%), transferred into a 75 °C water bath for 10 min, moved into a 4 °C refrigerator without light for 24 h extraction. After that the tubes were centrifuged at 8000 rpm for 10 min, the extraction supernatant was collected to measure the absorbance (A) at wavelengths of 665 nm and 750 nm with a Shimadzu UV-2600 spectrophotometer, ethanol (95%) was used as a blank. The contents of chlorophyll-a ($C_{\text{chlorophyll-a}}$, $\text{mg} \cdot \text{L}^{-1}$) were calculated with formula (3) (Ni et al., 2012). The specific growth rates were calculated with the equation (4) (Wang et al., 2011).

$$C_{\text{chlorophyll-a}} = 11.93(A_{665} - A_{750}) \quad (3)$$

$$\text{Specific growth rate} = \ln(D_t/D_0)/\Delta t \quad (4)$$

where D_t and D_0 are the contents of chlorophyll-a at time t and at initial, respectively, and Δt is the duration of the incubation in days.

3. Results and discussion

3.1. Effect of pyrolysis on biochar properties

The basic properties of the biochar samples produced at different temperatures are presented in Table 1. As suggested in previous studies (Huang et al., 2018a; Li et al., 2018b), the increase of pyrolysis would enhance the decomposition of organic substance, resulting in more alkaline carbon materials with less carbon contents. In the present study, with the increase of pyrolysis temperature from 350 °C to 750 °C, the pH values of biochar samples increased from 8.3 to 10.2 with the decomposition of biomass. In addition, there were the steadily declined biochar yield, carbon (C) and nitrogen (N) content due to the decomposition of organic matter in thermal treatment process with increasing temperature. These results suggested the decomposition of organic matter with

Table 1
Basic properties of the raw material and prepared biochar samples (“—” indicates no determination).

Parameters	CL	CB-350	CB-550	CB-750	CBC-350	CBC-550	CBC-750
pH (1:10)	6.59 ± 0.03	8.33 ± 0.06	9.93 ± 0.02	10.23 ± 0.05	8.38 ± 0.07	9.96 ± 0.02	10.19 ± 0.04
Yield (%)	—	44.03 ± 0.05	36.66 ± 0.06	28.85 ± 0.09	43.53 ± 0.02	36.61 ± 0.02	28.75 ± 0.03
C (%)	44.07 ± 0.15	49.51 ± 0.12	48.43 ± 0.12	46.35 ± 0.06	49.41 ± 0.22	48.34 ± 0.11	46.17 ± 0.16
H (%)	5.47 ± 0.19	2.98 ± 0.07	2.19 ± 0.07	0.92 ± 0.12	2.89 ± 0.13	2.19 ± 0.05	0.91 ± 0.14
N (%)	2.27 ± 0.04	1.10 ± 0.04	0.76 ± 0.02	0.53 ± 0.03	1.07 ± 0.02	0.75 ± 0.03	0.54 ± 0.06
S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	—	107.0	269.4	284.4	5.78	57.15	208.42
TPV ($\text{cm}^3 \cdot \text{g}^{-1}$)	—	0.09	0.19	0.22	0.03	0.07	0.18
AVP (nm)	—	3.28	3.08	2.84	12.3	4.67	3.39

the enhanced aromatization in biochar samples during pyrolysis (Jin et al., 2016).

It had been reported that during the thermal treatment process of organic matter, some porous carbon materials would be generated (Ahmed and Hameed, 2018; Liu and Huang, 2018). The biochar surface morphology presented in SEM images also reflected this point (Fig. 1a–d). As displayed in Fig. 1a, the surface of Cu-CL sample was flat, while the CBC sample surface morphology showed porous structure with some small particles dispersed (Fig. 1b–d). As the pyrolysis temperature increased, due to the decomposition of the primary constituents of raw feedstock, the surface of CBC became rougher with some pores collapsed and smaller particles adhered on internal pores and the outer surface of CBC. Such observations were also reported by other researchers during thermal treatment of the Cu contaminated sewage sludge (Jin et al., 2016). These results indicate that increasing the pyrolysis

temperature benefits the generation of biochar porosity.

Aiming to explore the pyrolysis temperature on biochar porosity variation, the related biochar samples were further determined with N_2 adsorption–desorption (Fig. 1e). In this study, the N_2 adsorption–desorption curves of all the biochar samples showed an archetypal Type IV curve, implicating the biochar belongs to mesoporous material as classified by the IUPAC. The calculated S_{BET} and TPV of all biochar samples increased with the temperature increasing from 350 °C to 750 °C (Table 1), while the AVP of the samples was lowered gradually. The reduction in AVP might be due to the higher pyrolysis temperature that makes more formation of smaller pores, it was also probably because more particles were adhered to the outer biochar surface and/or internal pores of biochars that caused the blockage (Jin et al., 2016).

Thermal treatment of organic biomass waste was considered to be an effective in waste volume reduction and harm mitigation (Das et al., 2016). Herein, the potential ecotoxicity of all the prepared biochar samples were further evaluated with plant germination test and the results are showed in Fig. 1f. In general, germination rates greater than 50% indicated little or no ecotoxicity for plant growth (Huang et al., 2018a). Among all the prepared biochar samples, only the germination rate of CBC-350 sample was relatively lower (33.67%) with shorter plant seedling root length around 7.34 mm. The CB-350 showed an acceptable germination rate (99.31%) but a reduced low root length (10.10 mm) compared with the control (Blank, 18 mm). This acute toxicity of CBC-350 sample was probably due to the existence of high toxic concentration of PAHs generally produced at 300–400 °C pyrolysis temperature (Lyu et al., 2016) as well as relatively higher leachable Cu(II) content (Fig. 2). On the other hand, for CB-350, it could be due to the relatively low pyrolysis temperature (350 °C) that could not transform all the nutrients in the feedstock biomass into stable form, and the plant seedlings could easily reach the nutrients supply during their growth so the toxicity effect on the root growth was only mild. With increasing pyrolysis temperature, more Cu(II) and nutrients are expected to turn into stable form in biochar with less toxicity. This was evident with CB-550 and CBC-550 treatments, which had germination rate of 93.67% and decent root growth (17 mm). As the pyrolysis temperature was further increased to 750 °C, the germination rates of CB-750 and CBC-750 samples showed slight reduction when compared with those of biochars from 550 °C. These phenomena were likely due to the high pH value of biochars pyrolyzed at 750 °C since strong alkaline biochars were not good for plant growth (Huang et al., 2018a). These results demonstrated that higher pyrolysis temperatures especially at 550 °C probably favored the Cu(II) laden biochar detoxification.

3.2. Effect of pyrolysis on copper chemical form and behavior

In order to further understand the effect of thermal treatment on the Cu(II) laden biochar detoxification, the effect of pyrolysis on

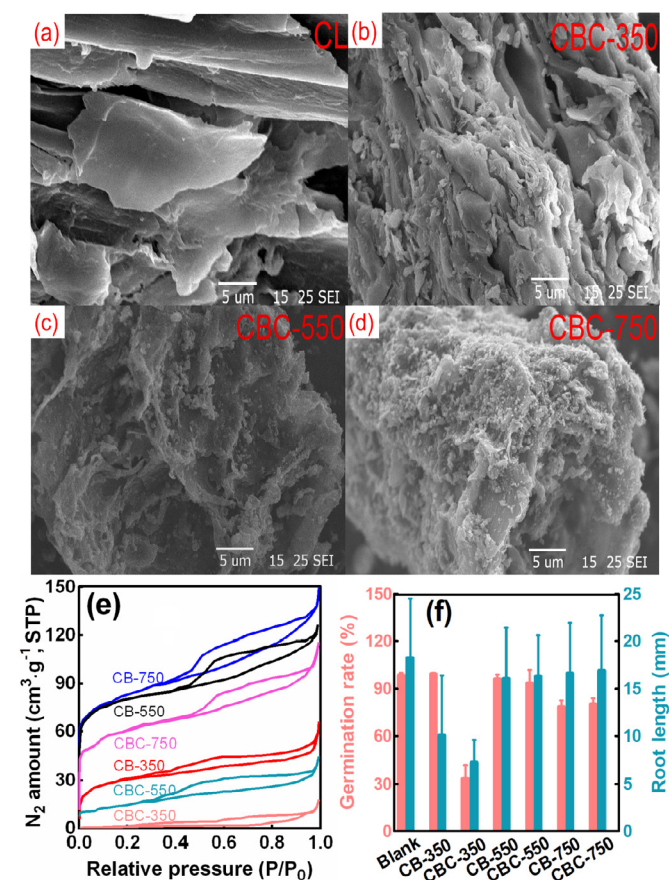


Fig. 1. SEM images of CL (a), CBC-350 (b), CBC-550 (c), and CBC-750 (d); N_2 adsorption–desorption curves (e) and ecotoxicity test results (f) of all the prepared biochar samples.

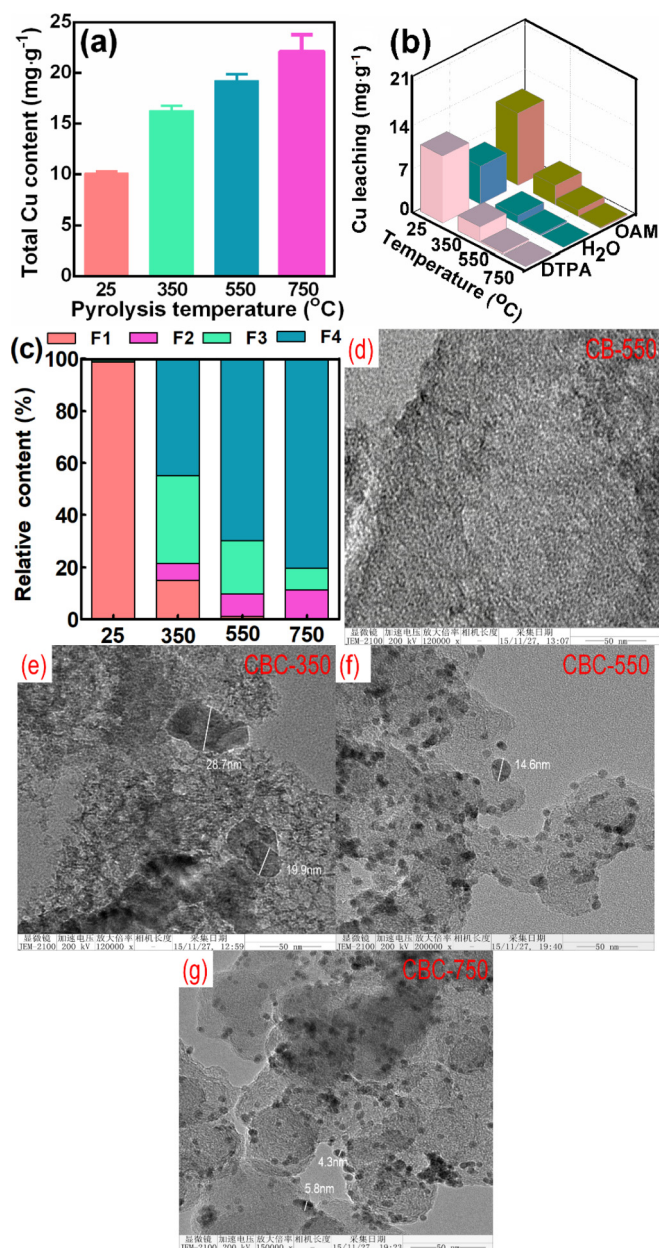


Fig. 2. Total Cu concentration (a), leachable Cu concentration (b) and fractionation of Cu (c) in feedstock and biochars influenced by various pyrolysis temperatures; TEM images of CB-550 (d), CBC-350 (e), CBC-550 (f), and CBC-750 (g).

copper behavior during the biomass thermal treatment process was investigated. Total Cu was increased significantly with the pyrolysis temperature changed from 350 °C to 750 °C (Fig. 2a). After pyrolysis, the Cu levels in biochar obtained at temperature of 350, 550 and 750 °C were 16.29, 19.24 and 22.11 mg g⁻¹, which were about 1.6, 1.9 and 2.2 times of that in raw Cu-CL (10.16 mg g⁻¹), respectively. Elevating of pyrolysis temperature facilitated more Cu remained within the biochar (Liu et al., 2012, 2014). The increase of Cu contents in biochar samples were in line with the nature of biomass thermal conversion approach since the mineral elements (e.g. Cu) were more stable than the C, N, and H etc. (Liu et al., 2012).

To analyze the stability of the as-prepared sample, the Cu leachability in CBC sample was evaluated by selecting DI water (pH 6.98), DTPA solution (pH 7.3) and OAM (pH 5.6) as extraction reagents. As seen in Fig. 2b, for the DI water extraction, the leaching

content of Cu from the Cu-CL, CBC-350, CBC-550, and CBC-750 samples were 6.06 mg g⁻¹, 1.03 mg g⁻¹, 0.12 mg g⁻¹, and 0.02 mg g⁻¹, respectively. For OAM solution extraction, the leaching content of Cu from the Cu-CL, CBC-350, CBC-550, and CBC-750 samples were 10.03 mg g⁻¹, 2.46 mg g⁻¹, 0.22 mg g⁻¹, and 0.16 mg g⁻¹, respectively. And for DTPA solution extraction, the leaching content of Cu from the Cu-CL, CBC-350, CBC-550, and CBC-750 samples were 10.06 mg g⁻¹, 3.06 mg g⁻¹, 0.19 mg g⁻¹, and 0.11 mg g⁻¹, respectively. The results indicated that the greater pyrolysis temperature generally immobilized more Cu in the biochar matrix and reduced Cu leachability. The efficiency of Cu immobilization of CBC was higher at 550 °C and 750 °C than 350 °C. The results were in line with the observations of Cu partitioning in feedstock and biochars (Fig. 2c) and the findings reported by Yousaf et al. (2018) during the biomass thermal disposal. It is clear that the fractionations of Cu in feedstock and biochar samples are strongly dependent on the pyrolysis temperature. For example, there was more than 98% of Cu in F₁ fraction, while it was decreased to <1% and <0.01% at pyrolysis temperature of 550 °C and 750 °C, respectively. In addition, the content of the mobile and bioavailable fraction (F₁) of Cu in biochar was lowest followed by the potentially bioavailable fractions (F₂ and F₃) and the highest content was noticed to be in non-bioavailable form (stable fraction of F₄), which were remarkably different from those in feedstock. Moreover, the values of RAC of feedstock and CBC were found to be 98.7, 15.07, 1.03, and <0.01 with the pyrolysis temperature of 25, 350, 550, and 750 °C, respectively, indicating the very high potential risk of feedstock, medium risk of CBC-350, low risk of CBC-550, and no risk of CBC-750, respectively. These results were also in accordance with the observations in the of potential ecotoxicity test as illustrated in Fig. 1f. Overall, these results suggested that the pyrolysis temperature at above 550 °C was more potentially favorable for the disposal of Cu-containing waste biomass.

The thermal stabilization mechanism for metals in organic waste is the increasing temperature that could lead to the trap and enclosure of metals in the carbon matrix and even turning into insoluble matters during biomass carbonization process (Liu et al., 2016b; Yuan et al., 2015). This would result in the inhibition of metal leaching ability. To evaluate this possibility, TEM analyses of different biochar composites were performed. Compared with the TEM image of CB-550 (Fig. 2d), there were many solid particles embedded detected in the carbon matrix of CBC-350 (Fig. 2e), CBC-550 (Fig. 2f) and CBC-750 (Fig. 2g). Additionally, the size of the embedded spherical particle on CBC sheets was found decreased from around 28.7 nm–5.8 nm with the pyrolysis temperature increasing from 350 °C to 750 °C. This result indicated that Cu-containing particles loaded on biochar sheets were in nanoscale in this study, suggesting the formation of Cu NPs embedded in the biochar during pyrolysis process.

The XRD analysis was used to investigate the nature of Cu in the biochar samples. As illustrated in Fig. 3a, the broad XRD reflection peaks existed between 15° and 30° of the biochars, indicating amorphous property of the biochar materials. In the XRD pattern of CB-550, the diffraction peaks located at 2 theta of 20.1° and 26.2° were corresponding to the formation of SiO₂ particle during the pyrolysis process (Fu et al., 2017). In the XRD pattern of CBC-350, the diffraction peaks centered at 2 theta of 35.4°, 38.7°, 48.7°, 58.3°, and 68.1° were indexed as the crystal planes of (11-1), (111), (20-2), (202), and (31-1) of CuO (JCPDS 48-1548), confirming the existence of CuO in the CBC-350 sample. With the temperature increased to 550 °C, besides the peaks of CuO, the new peaks appeared at 2 theta of 36.4° and 61.4° were assigned to (111) and (220) planes of Cu₂O (JCPDS 05-0667), and the peaks located at 2 theta of 43.3° and 50.4° agreed well to the values of the metallic copper Cu⁰ (Fu et al., 2017; Xu et al., 2016). These results implicated

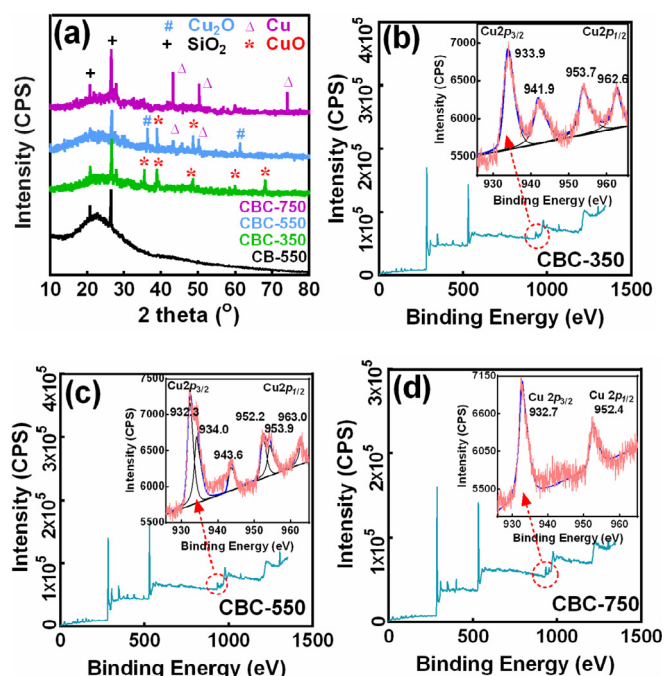


Fig. 3. XRD patterns of the prepared biochars (a); XPS spectra of the CBC-350 (b), CBC-550 (c) and CBC-750 (d) after pyrolysis.

the formation of CuO , Cu_2O and Cu^0 mixture during the N_2 protected biomass carbothermal conversion process. After the temperature increase to 750°C , there were only reflection peaks of 43.3° , 50.4° and 74.1° in CBC-750 biochar sample, which were corresponding to the (111), (200) and (220) planes in Cu^0 phase (JCPDS 01-089-2838), demonstrating the thorough reduction of Cu(II) into Cu^0 . These processes were possible due to strong reducibility of volatile species (e.g., H_2 , CO , and $\text{C}_x\text{H}_y\text{O}_z$, etc.) produced at high pyrolysis temperature (400 – 800°C) as well as biochar (mainly Carbon). The strong reducibility of the volatile species and biochar carbon can facilitate the absorbed Cu(II) into low valence state Cu(I) or Cu(0) . Similar observations were also reported on the formation of Ag NPs and Cu NPs during the pyrolysis of the Ag(I) sorbed fir sawdust (500°C) (Liu et al., 2016a) and Cu(II) polluted fir sawdust (Cu 3% in wt., 450 – 600°C) (Liu et al., 2012, 2014).

The XPS analysis was further used to elucidate the valence state, chemical bonding, and surface composition characteristics of the Cu biochar composites. The high sensitivity XPS survey spectrum of the CBC sample obtained after the thermal process was displayed in Fig. 3b–d. As displayed in Fig. 3b, the high resolution XPS spectrum of CBC-350 showed the doublet high intensity peaks of $\text{Cu } 2p_{3/2}$ (933.9 eV) and $\text{Cu } 2p_{1/2}$ (953.7 eV) excitation, and two satellite peaks at binding energy of about 941.9 and 962.6 eV , respectively, which are the typical features of Cu(II) oxidation state in CuO (Barreca et al., 2007). The presence of CuO in CBC-350 sample was due to the decomposition of CuCl_2 , which could not be avoided during the biomass pyrolysis process. With the temperature increasing to 550°C , the CBC-550 sample showed not only peaks centered at 934.0 , 943.6 , 953.9 , and 963.0 eV but also peaks located at 932.3 and 952.2 eV , respectively (Fig. 3c). Since higher binding energy corresponds to a more oxidized state, the clear peaks at binding energy of 934.0 , 943.6 , 953.9 , and 963.0 eV for CBC-550 sample may be attributed to the Cu(II) in CuO ; whereas the presence of peaks at 932.3 and 952.2 eV were related with the Cu(I) in Cu_2O (Barreca et al., 2007). Further increasing pyrolysis

temperature to 750°C led to the existence of $\text{Cu } 2p_{3/2}$ and $\text{Cu } 2p_{1/2}$ peaks with binding energies of 932.7 and 952.4 eV , respectively (Fig. 3d), and these values closely matched to the literature values for metallic copper (Barreca et al., 2007; Panzner et al., 1985). The later could be caused by more reducing species (e.g., H_2 , CO , $\text{C}_x\text{H}_y\text{O}_z$ etc.) and the biochar (mainly Carbon) generated at the anaerobic pyrolysis process (Liu et al., 2014). The XPS results further confirmed the formation of low valence state copper (Cu(I) and Cu(0)) in the biomass pyrolysis process, which were consistent with XRD observations. Overall, these results demonstrated the production of Cu NPs embedded biochar composites during the biomass pyrolysis.

3.3. Inhibition effects of biochars on *Microcystis aeruginosa* growth

Due to the relatively higher Cu leaching content in the CBC-350 sample (Fig. 2b), it might pose a Cu(II) contamination risk to the water environment, herein only the stable CBC-550 and CBC-750 samples were used in the anti-algal test with CB-550 and CB-750 samples as comparison. The effects of CBC for anti-algal performances on *Microcystis aeruginosa* ($p < 0.05$) are illustrated in Fig. 4. The results clearly showed that the CBC-550 and CBC-750 samples inhibited the growth of *Microcystis aeruginosa* while CB-550 and CB-750 did not in terms of the measured chlorophyll-a content (Fig. 4a), algae biomass density (Fig. 4b), and algae growth rate (Fig. 4c) during the 21-day incubation. There was no significant difference between the CB-550 and CB-750 biochar samples and the control. At the end of experiment, the chlorophyll-a contents were around 6.8 mg L^{-1} , algae biomass density were around $(6.58\text{--}6.78) \times 10^8\text{ cell mL}^{-1}$, and algae growth rates were around 0.76 , respectively for CB-550 and CB-750 treatments, while they were remarkably inhibited throughout the experiments by the CBC-550 and CBC-750 treatments (Fig. 4a–c). The results indicated that direct addition of CBC-550 and CBC-750 into algae incubation medium could inhibit *Microcystis aeruginosa* growth. In addition, during the incubation experiment, the electrical conductivities of

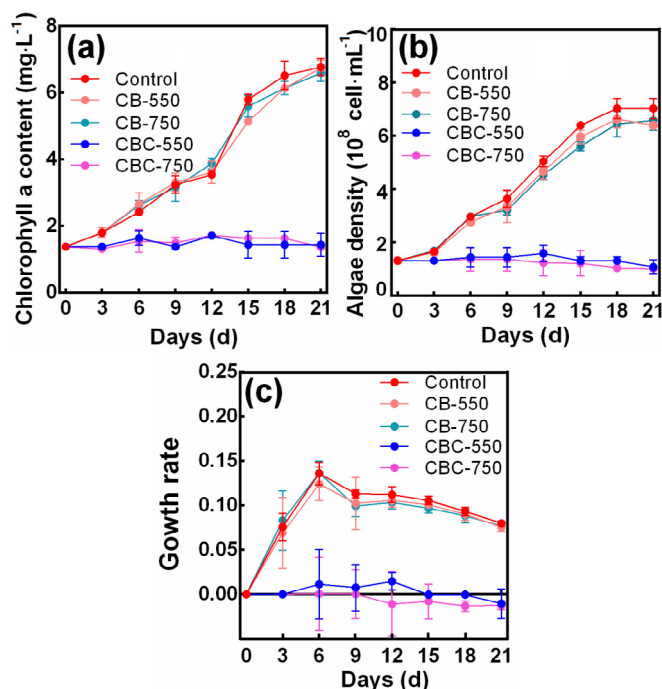


Fig. 4. Changes in chlorophyll-a content (a), blue-green algae biomass density (b) and growth rate (c) during the incubation experiment.

algae incubation mediums were found to range from 2.7 to 3.4 dS cm⁻¹ with the medium pH kept in slightly alkaline condition (pH 9.1–9.5) (Figures not shown). At this condition, the existed Cu₂O particles in the CBC-550 could not be decomposed into Cu(II). Therefore, inhibition effect of CBC-550 was unlikely from the presence of Cu(II). Besides this, since the CBC-750 was mainly the Cu⁰ NPs embedded biochar and the leachable Cu(II) in the sample was unnoticeable (Figs. 2 and 3), the inhibition effect of the CBC-750 sample was possibly attributable to the embedded Cu⁰ contained NPs, which was known to affect algae growth (Adam et al., 2015; Melegari et al., 2013). Since it is well known that Cu salts such as CuSO₄ and others have been widely used for improving water quality as well as aquaculture production (Boyd and Massaut, 1999; Garlich et al., 2016), this demonstrated that CBC-550 and CBC-750 could be used to mitigate toxic algae in eutrophic surface water bodies such as lakes and ponds or employed as a preventive strategy with much reduced environmental risks due to minimum release of leachable Cu(II) ions.

3.4. Economic and environmental implications and relevant future study

Currently, more than 19% of agricultural soil in China is suffering from serious contamination with Cu being one of the dominating toxic pollutants, which can pose a severe threat to environmental and human health (Zhao et al., 2015). Owing to their long-term efficiency, environmental friendliness and cost-effectiveness for removal of Cu from effluent and/or soil system, bioremediation technologies including biosorbent enrichment, phytoextraction and phytostabilization, etc. had been advocated as an alternative for the contaminated water and/or soil *in-situ* remediation (Qu et al., 2016; Suzakia et al., 2017). However, the main features of these technologies are their high volume of bio-waste production, high Cu content in biomass tissue and the challenge in safe management of bio-waste (Sas-Nowosielska et al., 2004). At present study, the results showed that the controllable carbonation of biomass waste at temperature above 550 °C was an effective approach for stabilizing the toxic Cu compared to the raw feedstock material. Besides a remarkable decline in the mobile fraction of Cu in biochar, thermal treatment also converts Cu-accumulating bio-waste into value-added carbon composite product with negligible potential ecological risk. Although this study focused only on Cu-rich biomass waste from biosorption, it is expected that the conversion of biochar from biomass of plants growing in Cu-contaminated soils to exhibit similar characteristics of Cu stability. The carbonation of plant biomass from phytoremediation of other heavy metals also showed significant reduction in Cd, Pb, and Zn release (Huang et al., 2018a). Additionally, pyrolysis of spent biomass waste into safe carbon composite by industrial process will be an acceptable choice of disposal with economic benefits. For instance, considering the expenditure involved in the bio-waste collection, transportation, drying, grinding, and pyrolysis, etc. (Huang et al., 2018b), the total cost for bio-waste thermal disposal was only about \$ 6.2 t⁻¹ in U.S. dollar (¥ 42 t⁻¹ in Chinese Yuan), which is much lower than the cost of landfill disposal (~\$13 t⁻¹) (Zhou et al., 2015). Moreover, considering the value of value-added carbon composite produced, the practical expenditure of the biomass waste thermal disposal will be even lower than the estimated (Väisänen et al., 2016). Meanwhile, the present study proved that CBC-550 and CBC-750 could be used to mitigate toxic algae in eutrophic surface water bodies such as lakes and ponds or employed as a preventive strategy. Further study is needed to evaluate the potential use of Cu carbon composite for algae growth inhibition in specific eutrophic surface water under specific field conditions.

4. Conclusion

This study demonstrated that pyrolysis is an effective disposal method of Cu(II)-laden bio-waste. The increase of pyrolysis temperature from 350 °C to 750 °C decreased the biochar yield, enhanced the mesoporous structure development, facilitated the Cu(II) stabilization within biochar matrix, and promoted the Cu-containing NPs embedded carbon composite formation. Pyrolysis temperature higher than 550 °C relieved the ecotoxicity of Cu-laden biomass waste. In addition, Cu-containing NPs in the biochar composite were CuO, CuO/Cu₂O/Cu⁰ mixture, and Cu⁰ crystal forms at 350, 550 and 750 °C, respectively. Compared with the biochar without Cu, the Cu NPs embedded composites obtained at 550 and 750 °C remarkably inhibited the *Microcystis aeruginosa* algae growth. This research indicated pyrolysis of the Cu(II) laden biomass at temperature higher above 550 °C was not only a suitable strategy for thermal treatment of spent bio-waste for disposal with low environment risk but also a promising method for producing Cu NPs *in-situ* embedded biochar nanocomposite, which could be used as cyanobacteria inhibitor with low ecotoxicity for treating eutrophic ponds.

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