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Serial parameter: CN 11-2629/X\*1989\*m\*211\*en\*P\*25\*2013-4



## Removal of Cu(II) from acidic electroplating effluent by biochars generated from crop straws

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Received 11 July 2012; revised 06 September 2012; accepted 01 November 2012

### Abstract

The removal efficiency of copper (Cu(II)) from an actual acidic electroplating effluent by biochars generated from canola, rice, soybean and peanut straws was investigated. The biochars simultaneously removed Cu(II) from the effluent, mainly through the mechanisms of adsorption and precipitation, and neutralized its acidity. The removal efficiency of Cu(II) by the biochars followed the order: peanut straw char > soybean straw char > canola straw char > rice straw char  $\gg$  a commercial activated carbonaceous material, which is consistent with the alkalinity of the biochars. The pH of the effluent was a key factor determining the removal efficiency of Cu(II) by biochars. Raising the initial pH of the effluent enhanced the removal of Cu(II) from it. The optimum pyrolysis temperature was 400°C for producing biochar from crop straws for acidic wastewater treatment, and the optimum reaction time was 8 hr.

**Key words:** adsorption; biochar; Cu(II) removal; electroplating effluent; precipitation

**DOI:** 10.1016/S1001-0742(12)60118-1

### Introduction

Large quantities of annual crop residues such as crop straws accumulate due to agricultural practices in China. Although some residues are used as feed, fuel or straw returned to the fields, about  $2 \times 10^8$  tons are still burned in the fields, which not only constitutes a waste of resources but is also a source of air pollution. Concurrently, heavy metals such as copper (Cu), nickel, chromium and zinc (Zn) are routinely detected in electroplating effluents (Algarra et al., 2005; Li et al., 2008; Pereira et al., 2010; Rao and Ikram, 2011). Like some of the other heavy metals, Cu(II) is an essential nutrient for humans, animals and micro-organisms, but excess Cu(II) produces many toxic and harmful effects in living organisms (Rao and Ikram, 2011). According to Emission Standard of Pollutants for Electroplating of China (GB21900-2008), the permissible limit of Cu for electroplating effluents that are to be discharged to surface water is 0.5 mg/L. Other countries also have stringent standards for Cu(II) discharge in effluent (Zhu et al., 2008). Therefore, it is necessary to remove Cu(II) and other heavy metals from electroplating effluents prior to discharge into water bodies (Sousa et al., 2009).

Several methods, namely chemical precipitation, ion exchange, solvent extraction, electrochemical treatment, reverse osmosis and the application of biological materials, have been proposed for treating effluents from the electroplating industry (Hunsom et al., 2005; Venkateswaran et al., 2007; Machado et al., 2010; Abdel-Aziz, 2011; Akbal and Camci, 2011; Peng et al., 2011). However, applications of these methods have been limited because of high capital costs, high operational costs and ineffective means of disposal of the resulting sludge (Venkateswaran et al., 2007; Zhang et al., 2010). The use of sorbents to remove and recover heavy metals from contaminated industrial effluents has emerged as a potential alternative to conventional methods (Ajmal et al., 2001; Lin et al., 2011). Techniques involving activated carbon, natural clay minerals, green plant waste, synthetic inorganic materials, synthetic nanoparticles and biosorbents have all been optimized for the removal of Cu(II) from aqueous solutions (Monser and Adhoum, 2002; Šćiban et al., 2007; Lu and Gibb, 2008; Zhu et al., 2008; González et al., 2011; Rao and Ikram, 2011). However, in recent years interest has been directed towards the investigation of low cost materials such as biochars, which are generated from agricultural residues and may be used as sorbents for the removal of heavy metals from aqueous solutions (Mohan et al., 2007; Qiu et

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al., 2008; Cao et al., 2009; Liu and Zhang, 2009; Beesley and Marmiroli, 2011; Chen et al., 2011; Kong et al., 2011; Inyang et al., 2012; Kołodyńska et al., 2012). Activated carbon is usually used as an adsorbent to remove heavy metals from aqueous solutions; however, dairy-manure derived biochar was found to be six times more effective for lead (Pb) adsorption than a commercial activated-carbon (Cao et al., 2009). A similar trend was observed for adsorption of Pb(II) and cadmium (Cd(II)) by oak bark char (Mohan et al., 2007). The biochar produced from corn straw at 600°C showed great adsorption capacity of 12.52 mg/g for Cu(II) and 11.0 mg/g for Zn(II) (Chen et al., 2011). Kołodyńska et al. (2012) found that Cu(II), Zn(II), Cd(II) and Pb(II) were strongly adsorbed by biochars produced from pig and cow manure at 400°C and 600°C. The effectiveness of removal of these metals increased with the increasing initial concentration of biochar and metal ion, pH and as well as contact time (Kołodyńska et al., 2012). Although the adsorption of several heavy metals by biochars has been previously investigated, few studies involved the adsorptive removal of heavy metals from real wastewaters.

Wastewaters discharged from the electroplating industry not only contain heavy metals, but are also strongly acidic. Biochars are characterized by alkaline pH (Yuan et al., 2011) and thus can neutralize acidic fluids and simultaneously remove heavy metals and, thus, may be ideal for treating electroplating effluents.

The objective of this study was to examine the efficiencies of biochars derived from crop straws for Cu(II) removal from real effluent obtained from the electroplating industry. The possibility of enhancing the sorption process was also investigated by optimizing the adsorbent dosage, initial solution pH, contact time and pyrolysis temperature of the biochars.

## 1 Materials and methods

### 1.1 Preparation of biochars

Straws from peanut, soybean, canola and rice were collected from croplands in a suburb of Nanjing, China. The straw samples were air-dried at room temperature and ground to pass through a 0.83-mm sieve. These straw samples were used as feedstock for producing biochars. The ground straw samples were placed in ceramic crucibles, covered with a tightly fitting lid and pyrolyzed under oxygen-limited conditions in a muffle furnace. The pyrolysis temperature was raised to 300°C, 400°C or 500°C at approximately 20°C/min and held for 225 min (Chun et al., 2004; Yuan et al., 2011). Then, the biochars were allowed to cool to room temperature and ground to pass through a 0.25-mm sieve before further experiments.

The alkalinity of the biochars was determined by titration (Yuan et al., 2011). Samples of 0.25 g of the biochars were weighed into 100-mL plastic bottles and 50 mL of

46.08 mmol/L HCl solution was added to each bottle. The suspensions were then shaken in a constant temperature water bath at  $(25 \pm 1)^\circ\text{C}$  for 8 hr. After standing for 24 hr at 25°C in a constant temperature box, each suspension was filtered and the solution titrated against 91.62 mmol/L NaOH using an automatic titrator (Mettler Toledo T50, Switzerland). A pH of 7.0 was set as the titration end point and the titration rate was 0.5 mL/min, with 0.25 g of each biochar added to 50.0 mL of deionized water as a control. The recorded volume of NaOH was used to calculate the alkalinity of the biochars. All results were the average of three parallel experiments.

A commercial activated carbon sample obtained from the Shanghai Tongshi Chemical Engineering Company, China, was used for comparison.

### 1.2 Acidic electroplating effluent

Upon completion of the acid washing process with  $\text{H}_2\text{SO}_4$ , the acidic electroplating wastewater was collected from an electroplating factory in a suburb of Nanjing, China in June 2011. The concentration of Cu(II) in the electroplating effluent was 773.61 mg/L and its pH was 1.87.  $\text{SO}_4^{2-}$  is the main anion in the effluent.

### 1.3 Effect of contact time

The biochars derived from peanut and canola straw pyrolyzed at 400°C were used to investigate the effect of contact time on the efficiency of Cu(II) removal from the effluent. Duplicate samples of 0.400 g of biochar were weighed into 100-mL plastic bottles, and 25 mL of acidic electroplating effluent was added to each bottle. The suspensions were then shaken in a constant temperature water bath at  $(25 \pm 1)^\circ\text{C}$  for 0.5, 1, 2, 4, 8 and 24 hr, respectively. Afterwards, the suspensions were filtered to separate the solution from the solid phase (Tong et al., 2011). Cu(II) in the solutions was determined by atomic absorption spectrometry. The amount of Cu(II) removed by the biochar was calculated from the difference between the total amount present initially and the amount remaining in the solution at equilibrium. The pH of the solution was measured using a pH meter (Orion 720, USA) with a combination electrode.

### 1.4 Effect of biochar pyrolysis temperature

Samples of biochars derived from peanut straw that was pyrolyzed at 300°C, 400°C or 500°C were weighed into 100-mL plastic bottles in duplicate, and 25 mL of acidic electroplating effluent was added to each bottle. The suspensions were then shaken in a constant temperature water bath at  $(25 \pm 1)^\circ\text{C}$  for 2 hr. After standing at 25°C for 22 hr, the suspensions were filtered and the Cu(II) concentration and pH of the solutions were determined.

### 1.5 Effect of biochar dosage

Of each biochar generated at 400°C, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 g was weighed into 100-mL plastic bottles,

and 25 mL of acidic electroplating effluent added to each bottle. The suspensions were then shaken in a constant temperature water bath at  $(25 \pm 1)^\circ\text{C}$  for 2 hr. After standing at  $25^\circ\text{C}$  for 22 hr, the suspensions were filtered and the Cu(II) concentration and pH of the solutions were determined.

### 1.6 Effect of initial pH of wastewater

The pH of the electroplating effluent was adjusted to 4.0 by the addition of NaOH. Of biochar, 0.500 g samples were weighed into 100-mL plastic bottles and 25 mL of electroplating effluent with the pH adjusted was added to each bottle. The suspensions were then shaken in a constant temperature water bath at  $(25 \pm 1)^\circ\text{C}$  for 2 hr. After standing at  $25^\circ\text{C}$  for 22 hr, the suspensions were filtered and the Cu(II) concentration and pH of the solutions were determined.

## 2 Results and discussion

### 2.1 Effect of pyrolysis temperature of the biochars on removal of Cu(II)

The pyrolysis temperature affected the chemical properties of biochar (Yuan et al., 2011) and thus the adsorption of heavy metals by the biochar (Liu and Zhang, 2009). The removal rates of Cu(II) by the biochars generated at  $400^\circ\text{C}$  and  $500^\circ\text{C}$  were similar but greater than that produced by the biochar generated at  $300^\circ\text{C}$  (Fig. 1). The biochars (20 g/L) generated at 400 and  $500^\circ\text{C}$  increased the effluent pH to 5.88 and 6.88 (Fig. 2), respectively, and the removal rate of Cu(II) reached 99.3%. In comparison, the same amount of biochar generated at  $300^\circ\text{C}$  increased the effluent pH to 4.82 and removed 76.1% of Cu(II) from the effluent. Therefore, the biochar produced at the higher temperature showed a greater removal efficiency for Cu(II) from wastewater than that produced at lower temperature, which was similar with previous report for removal of Pb(II) by biochars prepared from pinewood and rice husk (Liu and Zhang, 2009).

The alkalinity of the biochars generated at  $400^\circ\text{C}$  and  $500^\circ\text{C}$  was greater than that of the biochar generated at  $300^\circ\text{C}$  (Table 1) because the biochars generated at higher temperature contained more carbonate (Yuan et al., 2011). Thus, the addition of biochars generated at  $400^\circ\text{C}$  and  $500^\circ\text{C}$  had a greater neutralizing effect and resulted in a greater increase in effluent pH than the addition of biochar generated at  $300^\circ\text{C}$  when the quantities of biochars added were the same. The superior removal rate of Cu(II) by the biochars generated at higher temperatures could be attributed to the greater increase in effluent pH, which enhanced both the adsorption of Cu(II) by the biochars and the precipitation of Cu(II) in the systems. In a previous study, we found that at pH 5.0 only 2.4% of Cu(II) formed precipitates after 24 hr in Cu(II) solution with initial concentration of 1.0 mmol/L; however, when the

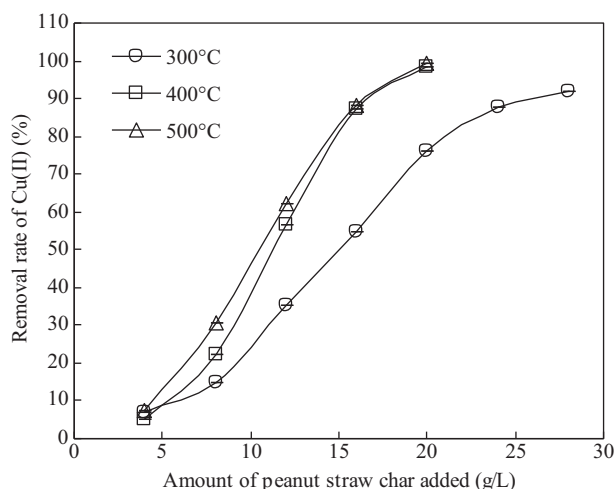


Fig. 1 Removal rate of Cu(II) from electroplating effluent by peanut straw char generated at different temperatures.

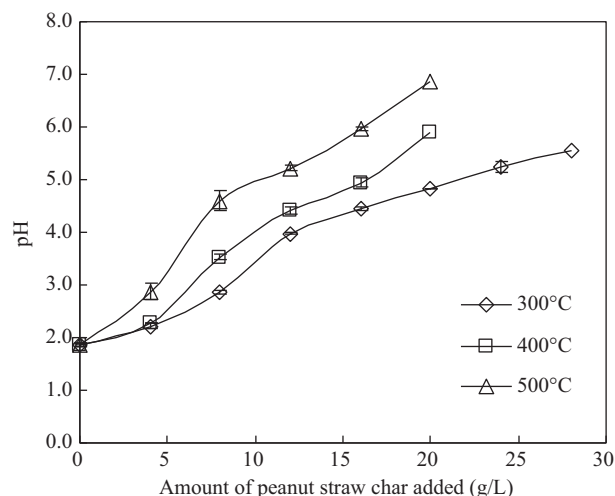


Fig. 2 Solution pH after reaction of electroplating effluent with peanut straw char generated at different temperatures.

solution pH was increased to 6.0, 78.2% of Cu(II) formed precipitates (Tong et al., 2011). Therefore, at pH < 5.0 Cu(II) was removed from electroplating effluent mainly through adsorption; at pH 5.0–6.0, both adsorption and precipitation had important contributions to the removal of Cu(II); while at pH > 6.0, Cu(II) was removed mainly through precipitation. At an addition level of 20 g/L, the biochar generated at  $300^\circ\text{C}$  removed Cu(II) mainly through adsorption on the biochar, while both adsorption and precipitation had important contributions to Cu(II) removal by biochar generated at  $400^\circ\text{C}$ ; however, precipitation was the main mechanism for Cu(II) removal by biochar produced at  $500^\circ\text{C}$ .

Compared with biochar generated at  $400^\circ\text{C}$ , addition of biochar generated at  $500^\circ\text{C}$  led to a greater increase in effluent pH, whereas both biochars had similar removal rates of Cu(II) due to the greater contribution of functional groups on biochar generated at  $400^\circ\text{C}$  to Cu(II) adsorption. The concentrations of carboxylic and phenolic groups on

**Table 1** Alkalinities of biochars generated from peanut, soybean, canola and rice straws compared to that of activated carbon

Temperature (°C)	Peanut straw char			Canola straw char	Soybean straw char	Rice straw char	Activated carbon
	300	400	500	400	400	400	–
Alkalinities (mol/kg)	9.49	14.08	18.94	9.60	11.49	6.65	3.96

“–”: not determined.

biochars have previously been reported to decrease with rising pyrolysis temperature (Yuan et al., 2011). There were similar trends in the present study. The contents of the two types of groups on biochar generated at 400°C were greater than on that generated at 500°C (**Table 2**). These functional groups can complex with Cu(II), consequently the higher concentration of functional groups on biochar generated at 400°C led to the formation of more Cu(II) complexes on the biochar and, thus, there was a greater specific adsorption of Cu(II) on this biochar compared with that generated at 500°C.

The characteristics of the biochars combined with their abilities to remove Cu(II) from electroplating effluent suggest that the optimum pyrolysis temperature for producing biochar from crop straws for acidic wastewater treatment was 400°C. At this temperature, both organic anions and enhanced alkalinity can contribute significantly to the removal of Cu(II) and the neutralization of the effluent. In addition, at this temperature a moderate biochar production rate can be achieved because the production rate decreases with rising pyrolysis temperature.

## 2.2 Effects of biochar type and their dosages on removal of Cu(II)

The biochar dosage had a direct influence on the Cu(II) removal efficiency. Biochars generated from peanut, soybean, canola and rice straws at 400°C were used to examine the efficiency of Cu(II) removal from acidic electroplating effluent, and were compared to a commercial activated-carbon. The effluent pH and percentage removal of Cu(II) increased when larger amounts of biochars were added, as they contained alkaline substances and could neutralize the effluent. The quantities of alkaline substances and adsorption sites for Cu(II) increased in proportion to the amount of biochar added, and thus the amount of acid neutralized and Cu(II) removed from the electroplating effluent increased in consequence. However, there were significant differences in neutralization and Cu(II) removal produced by the different biochars. At 20 g/L, the addition of biochars made from peanut, soybean, canola and rice straws increased the effluent pH from

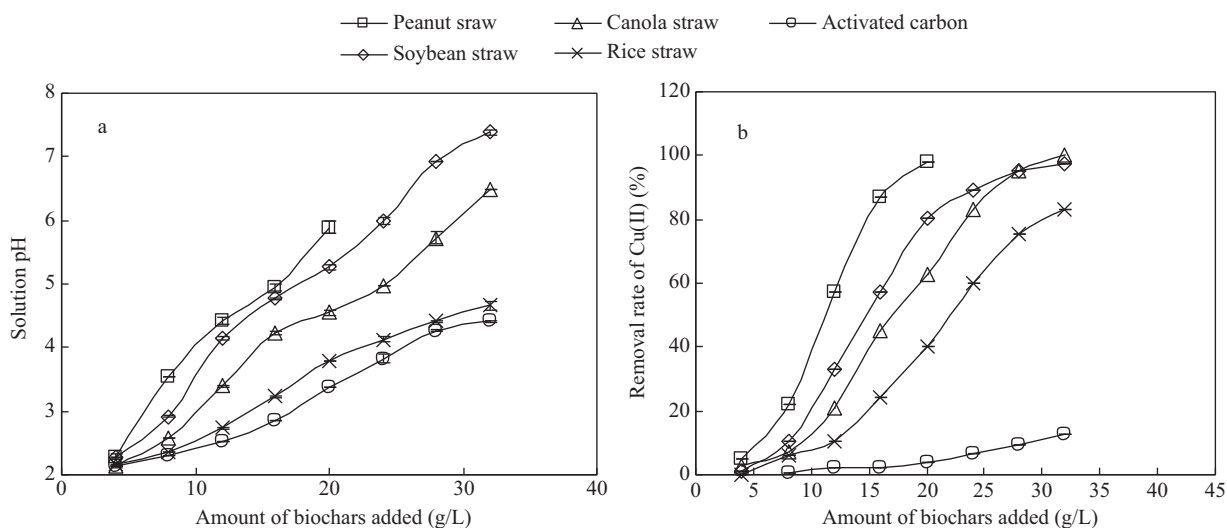
**Table 2** Oxygen-containing functional groups in the biochars produced from peanut straw at different pyrolysis temperatures (unit: cmol/kg)

Temperature	Carboxylic	Lactonic	Phenolic	Total groups
300°C	18.3	35.0	191.0	244.3
400°C	6.4	37	160	203.4
500°C	4.2	39.0	87.0	130.2

1.87 to 5.88, 5.27, 4.55 and 3.79, respectively (**Fig. 3a**), correspondingly, 98%, 80%, 62% and 40% of Cu(II) was removed. The removal percentages of Cu(II) by these biochars were much higher than that by the commercial activated-carbon (3.4%; **Fig. 3b**). The efficiency of Cu(II) removal and increase in pH as a result of the addition of the biochars followed the order: peanut straw char > soybean straw char > canola straws char > rice straw char ≫ activated carbon (**Fig. 3**). This order is consistent with the alkalinity of these biochars (**Table 1**) and the adsorption capacities of these biochars for Cu(II) as reported in our previous study (Tong et al., 2011).

The relative contribution of adsorption and precipitation to Cu(II) removal depended on suspension pH, therefore the mechanisms for Cu(II) removal varied with the type of biochars and the amounts of the biochars added. At low addition level, Cu(II) was removed mainly through Cu(II) adsorption on the surface of the biochars, due to relatively low pH. With increased amounts of biochar added, the suspension pH rose and consequently the contribution of precipitation to Cu(II) removal by biochars increased. Using soybean straw char as an example – when the amount of the biochar added was ≤ 16 g/L, the adsorption of Cu(II) was the main mechanism for Cu(II) removal because suspension pH was < 5.0. When 20 g/L of the biochar was added, both adsorption and precipitation had important contributions to Cu(II) removal. However, when the amount of the biochar added was > 24 g/L, precipitation of Cu(II) on the surface of the biochar was the main mechanism for Cu(II) removal because suspension pH was > 6.0. When the four biochars were compared, at the addition level of 20 g/L both adsorption and precipitation made important contributions to Cu(II) removal by peanut straw and soybean straw chars; while adsorption was the main mechanism for Cu(II) removal for canola straw and rice straw chars because the suspension pH was < 5.0 for the systems with the biochars added.

Due to the different abilities of the biochars to remove Cu(II) and to neutralize acidic solutions, different amounts of the biochars were needed to treat electroplating effluent. Addition of 20 g/L of peanut straw char raised the effluent pH from 1.87 to 5.88, and the removal rate of Cu(II) reached 98%, whereas 28 g/L of soybean and canola straw chars increased the effluent pH from 1.87 to 6.92 and 5.72, respectively, with 95.2% of Cu(II) removed by the two biochars. Although the final effluent pH for the canola straw char system was much lower than that for soybean straw char, the removal rate of Cu(II) by the two biochars was the same. This suggests that the contribution



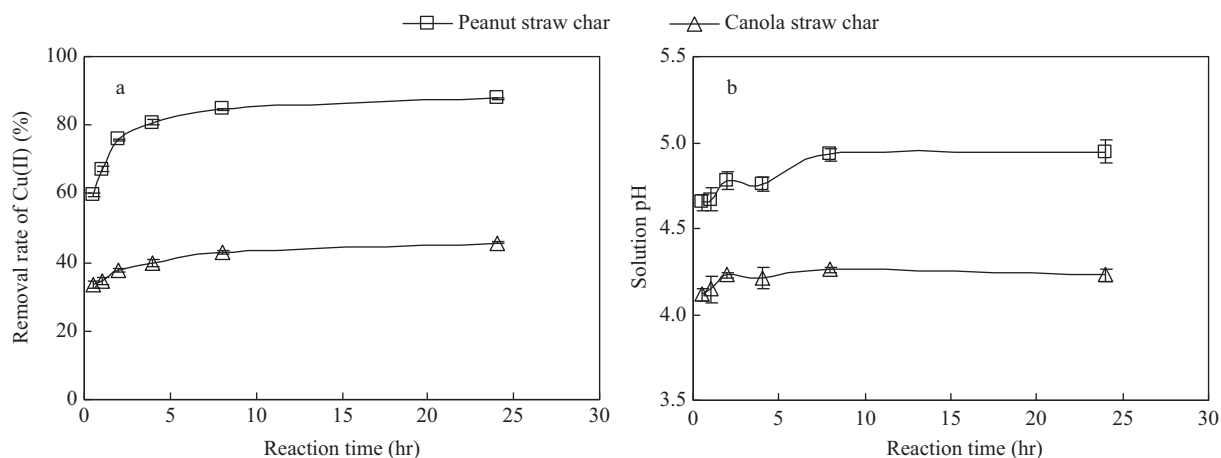
**Fig. 3** Effect of dosages on the solution pH (a) and the removal efficiency of Cu(II) (b) with biochars and activated carbon from electroplating effluent.

of Cu(II) adsorption on canola straw char to Cu(II) removal was greater than that for soybean straw char. Similarly, there was a greater contribution towards Cu(II) removal of adsorption on peanut straw char compared to soybean straw char because the removal rate reached 98% for the peanut straw char system at pH 5.88. The efficiency of Cu(II) removed by rice straw char was lower than that for the other three biochars. Addition of 32 g/L of rice straw char increased the effluent pH from 1.87 to 4.66, and the corresponding removal rate of Cu(II) was 82.9%, much lower than that for soybean straw and canola straw chars (**Fig. 3b**). Therefore, the biochars generated from peanut, soybean and canola straws could be used to neutralize the acidity of actual electroplating effluent and effectively remove Cu(II) from effluent.

### 2.3 Effect of contact time on Cu(II) removal and solution pH

The efficiency of Cu(II) removal from the acidic electroplating effluent increased rapidly as contact time increased, until equilibrium was reached at 8 hr (**Fig. 4a**). The overall

removal process may be controlled by one or more steps (e.g., film or external diffusion, intra-particle diffusion and adsorption on the surface of the adsorbent) (Lin et al., 2011). The solution pH increased with reaction time in a similar manner (**Fig. 4b**). Biochar contains alkaline substances and, when it is added to an acidic solution, these alkaline substances are released and neutralize the solution, leading to a rapid increase in solution pH. This process enhances the efficiency of Cu(II) removal through several mechanisms. The pH rise accelerates the hydrolysis of Cu(II) to form  $\text{Cu}(\text{OH})^+$ , which is adsorbed much more easily by biochar than  $\text{Cu}^{2+}$  (Tong et al., 2011). The pH rise also leads to the formation of  $\text{Cu}(\text{OH})_2$  precipitates on the biochar, especially at  $\text{pH} > 6.0$  (Tong et al., 2011). When the suspension  $\text{pH} < 5.0$ , enhanced adsorption was the mechanism of Cu(II) removal as mentioned above. The surface charge on the biochars becomes more negative with rising pH due to the dissociation of the oxygen-containing functional groups, which augments the electrostatic adsorption of Cu(II) onto the biochars. The dissociation of the oxygen-containing functional groups also increases



**Fig. 4** Effect of reaction time on the removal efficiency of Cu(II) (a) from electroplating effluent by biochars and the effluent pH (b).



the quantity of organic anions on the biochars, which form complexes with  $\text{Cu}^{2+}$  and thus increase the specific adsorption of Cu(II) by the biochars.

## 2.4 Effect of initial pH of the electroplating effluent on Cu(II) removal

The initial pH of the electroplating effluent is a key factor determining the efficiency of Cu(II) removal. The pH of the effluent was adjusted from 1.87 to 4.0 with NaOH, and then 20 g/L of canola straw, soybean straw and rice straw chars were added to compare removal efficiencies of Cu(II) by the biochars. The removal rate of Cu(II) increased significantly after the initial pH was adjusted (Table 3). The removal rate of Cu(II) increased from 63.5%, 80.0% and 40.0% in the systems without pH adjustment to 97.1%, 94.1% and 88.4% for canola straw, soybean straw and rice straw chars, respectively. The main reason for the enhanced efficiency of Cu(II) removal was the change in final pH of the effluent, which rose to 7.17, 7.51 and 5.0 for the canola straw, soybean straw and rice straw chars, respectively (Table 3). The greatest increase in removal rate of Cu(II) was for rice straw char, and the enhanced Cu(II) adsorption by the biochar was the mechanism for this increase—because at pH 5.0 the formation of precipitates made only a small contribution to the removal of Cu(II) (Tong et al., 2011).

**Table 3** Effect of initial effluent pH on the removal rate of Cu(II) by different biochars

Biochar	Initial effluent pH	Final effluent pH	Cu(II) removal (%)
Canola straw char	1.87	4.65	63.5
	4.0	7.17	97.1
Soybean straw char	1.87	5.04	79.9
	4.0	7.51	94.1
Rice straw char	1.87	3.71	40.0
	4.0	5.0	88.4

Initial concentration of Cu(II) was 773.61 mg/L.

## 3 Conclusions

Biochars from crop straws contain alkaline substances and have significant adsorption capacities, and can be used to simultaneously neutralize the acidity of and remove Cu(II) from electroplating effluent. Increased pH in effluent enhanced the adsorption and precipitation of Cu(II) on the biochars and thus improved the Cu(II) removal efficiency. The biochars generated from peanut, soybean and canola straws were better choices for the treatment of acidic electroplating effluent than rice straw char and commercial activated carbon. The optimum pyrolysis temperature was 400°C for producing biochar from crop straw for acidic wastewater treatment, and the optimum reaction time was 8 hr. Biochars can be obtained by simple methods and their feedstock is cheap and available locally in large

quantities. Biochars are also biofuel. The biochars with heavy metals adsorbed can be treated through burning, and thus secondary pollution can be avoided. Therefore, although relatively high addition levels of biochars (20–32 g/L) are needed, the crop straw biochars can be used in the treatment of real wastewater containing heavy metals.

## Acknowledgments

This work was supported by the Knowledge Innovation Program Foundation of the Chinese Academy of Sciences (No. KZCX2-EW-405) and the National Key Technology R&D Program of China (No. 2012BAJ24B06).

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## Journal of Environmental Sciences (Established in 1989)

Vol. 25 No. 4 2013

<b>Supervised by</b>	Chinese Academy of Sciences	<b>Published by</b>	Science Press, Beijing, China
<b>Sponsored by</b>	Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences	<b>Distributed by</b>	Elsevier Limited, The Netherlands
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		<b>Domestic price per issue</b>	<b>RMB ¥ 110.00</b>

ISSN 1001-0742

