Nature Environment and Pollution Technology An International Quarterly Scientific Journal	p-ISSN: 0972-6268 e-ISSN: 2395-3454	Vol. 17	No. 3	pp. 933-937	2018

Original Research Paper Open Access

Optimization of Copper Ion Removal in Aqueous Solution by the Biochar Derived from the Modified Corncob

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Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 28-10-2017
Accepted: 19-12-2017

Key Words:
Copper ion removal
Biochar
Corncob

ABSTRACT

Copper ion in aqueous solution is an essential nutrient for humans, animals and microorganisms. However, the excess of copper ion in aqueous solution produces many toxic and harmful effects on living organisms. Therefore, it is necessary to remove the copper ions in aqueous solution prior to discharge into water bodies. The main aim of this study is to test biochars obtained from the modified corncob as adsorbent for copper ion from aqueous solution. The operating parameters, such as adsorbent dosage, initial solution pH, contact time and pyrolysis temperature of the biochars, were investigated in detail. The operation parameters have an important effect on the removal of copper ion from aqueous solution by biochars derived from the modified corncob. The biochars derived from the modified corncob exhibited an excellent adsorption performance of copper from aqueous solution and can be applied in the removal of copper ions in aqueous solution.

INTRODUCTION

With the rapid development of industrial activities, a large amount of industrial effluents containing heavy metals is released into surface and underground water, which has resulted in a number of environmental problems (Astals et al. 2015, Jin et al. 2016). Heavy metals, such as copper, lead, cadmium and so on, are toxic and non-biodegradable. They can accumulate in living organisms, and may thus pose a threat to human health (Barakat 2011, Cantu et al. 2014). Copper ion in aqueous solution is an essential nutrient for humans, animals and microorganisms. However, the excess of copper ion in aqueous solution produces many toxic and harmful effects in living organisms (Regmi et al. 2012, Wang et al. 2015a). So, many countries have stringent standards for copper ion discharge in the effluents (Budinova et al. 2006, Cao et al. 2009). In China, the permissible limit for copper ion for electroplating effluents that are to be discharged to surface water is 0.5 mg/L (Shen et al. 2015). Therefore, it is necessary to remove the copper ions in effluents prior to discharge into water bodies. It is also very important to develop effective technologies to treat copper ion polluted wastewater (Meng et al. 2014).

A number of purification methods have been applied. Conventional methods for the removal of copper ions from wastewater are based on ion exchange processes, chemical precipitation, separation techniques through membranes, electrochemical techniques and adsorption (Kaušpėdienė et al. 2010, Fernando et al. 2011, Duan et al. 2014). However, most of these methods are expensive, because they require specialized reagents and apparatus, and they may also produce a large amount of waste. Adsorption is considered a cost effective choice for copper ion removal from aqueous solution, especially at medium or low ion concentrations because it is economical, easy to handle and highly efficient. The use of adsorbents involving activated carbon, natural clay minerals, green plant waste, synthetic inorganic materials, synthetic nano-particles and bio-adsorbents have all been optimized for the removal of copper ion from aqueous solution (Martin et al. 2011, Vanessa et al. 2014). In recent years, the investigation of low cost materials such as biochars has been studied (Wu et al. 2011). They are generated from agricultural residues and may be used as adsorbents for the removal of heavy metals from aqueous solutions. Natural materials such as plant waste are widely available in large quantities and they also have great potential as low cost and, most importantly, environmentally friendly adsorbents. The production of biomass derived materials also has several positive effects on environmental conditions and climate protection (Tong & Xu 2013, Jiang et al. 2016).

The main aim of this study is to test biochars obtained from the modified corncob as adsorbent for copper ion removal from aqueous solution. The possibility of enhancing the adsorption process was investigated by optimizing the adsorbent dosage, initial solution pH, the contact time and pyrolysis temperature of the biochars.

MATERIALS AND METHODS

Materials

The corncobs were obtained from croplands in a suburb of Shaoxing, China. They were washed with the distilled water, dried at room temperature, ground into powder and sieved into 40 meshes for the experiments.

A stock solution of copper ion concentration was prepared by dissolving $CuSO_4·5H_2O$ in deionised water, which was diluted to achieve the desired ranges of copper ion treatment.

Experimental Methods

Preparation of biochars: The ground corncob samples were placed in ceramic crucibles, which were covered with a tightly fitting lid and pyrolyzed for 8 h under oxygen limited conditions in a muffle furnace. The pyrolysis temperature was raised to 773 K. Then, the biochars were allowed to cool to room temperature and ground to pass through 80 meshes. The biochars were obtained, and stored for adsorption experiments.

Adsorption of copper ion in aqueous solution by biochar: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.1 g biochar and 200 mL of Cu^{2+} ion solutions with various initial concentrations between 10 mg/L and 50 mg/L. The initial pH was adjusted to 3.0 with 1 mol/L HCl. The flasks were placed in a shaker at a constant temperature of 298 K and 200 rpm. The samples were filtered and analysed.

Analytical methods: The concentration of Cu^{2+} ion was analysed by atomic absorption spectrophotometry.

The amount of adsorbed Cu^{2+} ion q_t (mg/g) at different time, was calculated as follows:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad ...(1)$$

Where, C_0 and C_t (mg/L) are the initial and equilibrium liquid-phase concentrations of Cu^{2+} ion respectively. V (L) is the solution volume and m (g) is the mass of adsorbent used.

Statistical analyses of data: All experiments were repeated in duplicate and the data of results were the mean and the standard deviation (SD). The value of the SD was calculated by Excel Software. All error estimates given in the text and error bars in figures are standard deviation of means (mean±SD). All statistical significance was noted at α=0.05 unless otherwise stated.

RESULTS AND DISCUSSION

Characterization of Biochar

The surface physical morphology of biochar was observed by a scanning electron microscope. The surface morphology of biochar is shown in Fig. 1. It can be seen that the biochar contains irregular and porous structures, indicating that the biochar presents adequate morphology for copper ion adsorption. They can be applied to the treatment of copper wastewater. In this study, the obtained biochars will be tested for their adsorption ability.

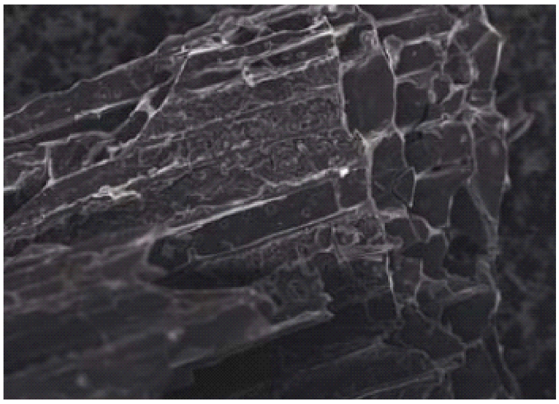

Fig. 1: SEM micrograph of biochar.

Effect of Contact Time

In the adsorption process, the contact time is an important operation parameter. To test the effect of contact time on the adsorption of copper ion in aqueous solution, the following adsorption experiment was carried out. Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.1 g biochar and 20 mL of Cu^{2+} ion solutions with initial concentration of 20 mg/L. The initial pH was adjusted to 3.0 with 1 mol/L HCl. The flasks were placed in a shaker at a constant temperature of 298 K and 200 rpm. The contact time was ranged from 0 min to 480 min. The samples were filtered and analysed. The effect of contact time on the adsorption of copper ion in aqueous solution by the biochars is shown in Fig. 2.

From Fig. 2, it can be seen that the contact time had an important effect on the adsorption capability of copper ion in aqueous solution by the biochars. The removal rate of copper ion was increasing with the increasing of reaction time. When the reaction time reached 200 min, the adsorption process reached to equilibrium. At the beginning of the adsorption, there are many vacant positions on the surface of the biochars. The removal rate of copper ion was increased quickly at this stage. When the adsorption process reached to equilibrium, there were no vacant positions on the surface of the biochars.

Effect of Initial pH in Solution

The initial pH conditions in the solution had a significant impact on the copper ion adsorption capacities of the biochar. It is a key factor determining the efficiency of copper ion removal in solution. The amount of copper ion precipitation at different pH values in solution is generally a

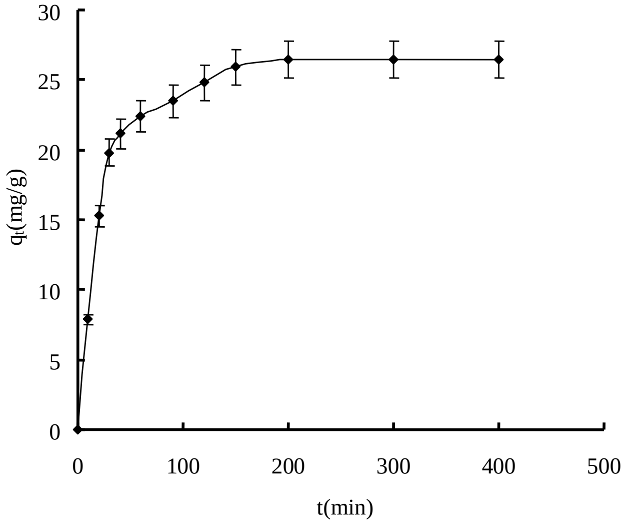

Fig. 2: The effect of contact time on the adsorption of copper ion in aqueous solution by the biochars.

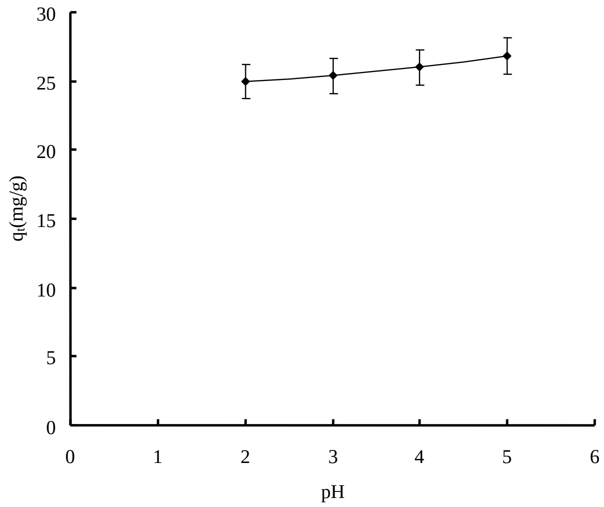

Fig. 3: The effect of initial pH in solution on the adsorption of copper ion in aqueous solution by the biochars.

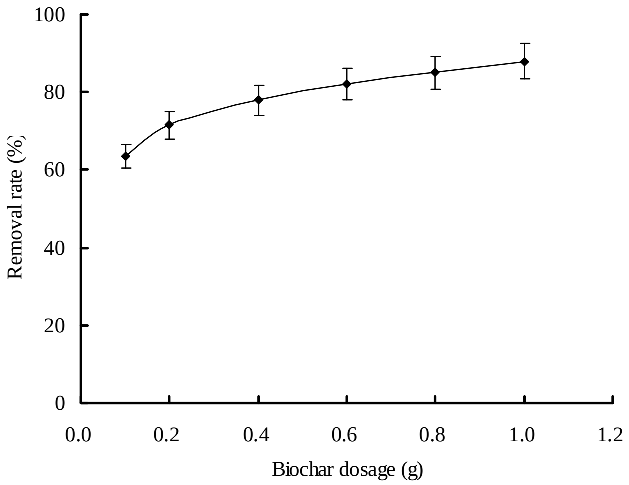

Fig. 4: The effect of biochar dosage on the adsorption of copper ion in aqueous solution by the biochars.

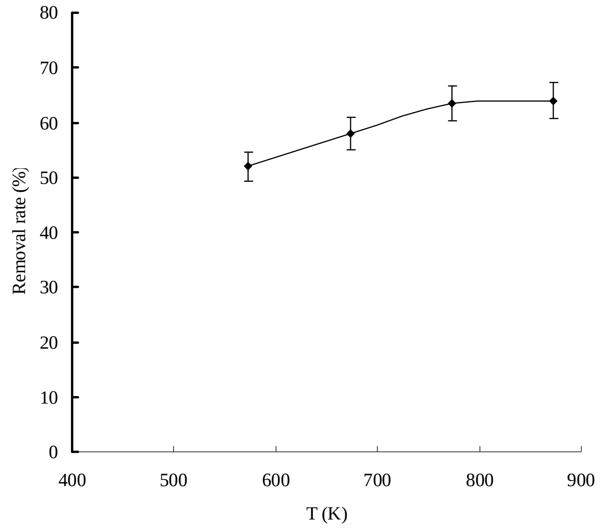

Fig. 5: The effect of the pyrolysis temperature on the adsorption of copper ion in aqueous solution by the biochars.

concern in distinguishing the copper removal phenomenal because of adsorption. Therefore, the effect of solution pH on copper ion precipitation in the absence of biochar was first confirmed. To test the effect of initial pH in solution on the adsorption of copper ion in aqueous solution by the biochars, the following experiments were carried out: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.1 g biochar and 200 mL of Cu^{2+} ion solutions with initial concentration of 20 mg/L. The initial pH was adjusted from 2.0 to 5.0 with 1 mol/L HCl. The contact time is 200 min. The flasks were placed in a shaker at a constant temperature of 298 K and 200 rpm. The samples were filtered and analysed. The effect of initial pH in solution is shown in Fig. 3.

From Fig. 3, it can be concluded that the initial pH in solution had an important influence on the adsorption capacity of copper ions in aqueous solution by the biochars. Along with the increase of the initial pH value in solution, the adsorption capacity of copper ion in aqueous solution was increased slowly. This result is similar to some other researches. At low initial pH value in solution, the copper ions on the biochar surfaces might be positively or neutrally charged, which hindered the adsorption of positively charged copper ions. As a result, increase in pH of the solution promoted the removal the copper ions (Ahmad et al. 2014, Wang et al. 2015).

Effect of Biochar Dosage

The effect of biochar dosage on the adsorption of copper ion in aqueous solution by the biochars was studied by varying the amount of biochars from 0.1 g/L to 1 g/L. The other reaction parameters were maintained constant. The initial pH was adjusted to 3.0 with 1 mol/L HCl. The flasks were placed in a shaker at a constant temperature of 298 K and 200 rpm. The contact time is 200 min. The initial concentrations of copper ion in solution is 20 mg/L. The effect of biochar dosage is shown in Fig. 4.

As seen from Fig. 4, adsorption of copper ion in aqueous solution was increased with the increase of the biochar dosage. This suggests that the biochar was acting as adsorbent and the increase in removal was related to the increased availability of exchangeable sites or sites for surface complexation.

Effect of Biochar Pyrolysis Temperature

To test the effect of the pyrolysis temperature on the adsorption capacity of biochar, the following experiments were carried out. The pyrolysis temperature was raised to 573 K, 673 K, 773 K and 873 K respectively, and then the three biochars were obtained. The adsorption experiments were carried out in order to test the adsorption capacity for copper ion. The removal rate of copper ion by three biochars is shown in Fig. 5.

From Fig. 5, it can be seen that the pyrolysis temperature was beneficial to enhance the adsorption capacity of copper ion in aqueous solution by the biochars. This indicated that the pyrolysis temperature might have different effects on the copper ion within the biochar structure.

CONCLUSIONS

The biochar was obtained from the modified corncob as adsorbent for copper ion removal from aqueous solution. The possibility of enhancing the adsorption process was investigated by optimizing the adsorbent dosage, initial solution pH, the contact time and pyrolysis temperature of the biochars. The experimental results suggested that these operation parameters had an important effect on the removal of copper ion from aqueous solution.

ACKNOWLEDGMENTS

This study was financially supported by the project of Science and Technology Plan in Shaoxing City (2014B70041).

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