Preparation of Biochars from Bio-Waste for Removing Pollutants from River Water

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Abstract
As a low-cost adsorbent, biochar can be used as a great tool for water treatment. Instead of using expensive woody biomass for biochar production, this study aimed to investigate the feasibility of using biowaste such as sugarcane skins, orange peels, and peanut shells to produce biochars through pyrolysis at 700°C. The optimal time length, dosage, and temperature for water purification were explored afterwards in batch tests. The ammonia nitrogen (NH₄⁺-N) removal efficiencies of sugarcane skin, orange peel, and peanut shells were 74.4%, 96.3% and 90.8%, respectively, and the simultaneous permanganate index removal efficiencies were 26.6%, 31.0% and 26.6%, respectively. There was no significant difference in NH₄⁺-N and permanganate index removal efficiencies when the dosage of three kinds of biochars was higher than 1.0 g/100 ml water. Greater adsorption capacity of biochars was observed for pollutants when temperature was increased from 10 to 30°C. These results confirmed our assumption that biowaste could make for good raw materials in producing biochars.

Keywords: biochars, shells, COD removal, ammonia nitrogen

1. Introduction
The tremendously fast growth of the urban populations and the expansion of urban construction in China, along with the discharge of sewage and waste into river waters, have deteriorated Chinese river water quality, which has posed increasing risks to aquatic ecosystems. Finding a method to economically remove the pollutants from river water is a great challenge (Ternes, 2007; Rozic et al., 2000).

Among many approaches, adsorption of contaminants by using activated carbon is a well-developed and effective technique for water purification. Compared with expensive activated carbon, biochar prepared by biomass also has a greater surface area due to its high porosity, which make it a low-cost and high-efficiency adsorbent for water treatment (Kumar et al., 2010; Pajooheshfar et al., 2009). Commercially available biochar is commonly made from woody biomass and its high cost limits its wide application. Therefore, low-cost materials for biochar production need to be explored. Converting biowaste into biochar has the potential to not only eliminate the amount of pollutants in water bodies, but also to solve the problem of the household waste disposal. (Issabayeva et al., 2010; Rosenfeld and Henry, 2001). Some biowaste consists largely of stable carboniferous substance which can serve as promising raw materials for biochar production. This study aimed to investigate the potential production of biochars through pyrogenic decomposition by using sugarcane skin, orange peels, and peanut shells as biomass materials. We also investigated the removal of water- pollutants using the biowaste derived biochars produced.

2. Materials and Methods

2.1 Preparation of Biochars from Sugarcane Rind, Orange Peel and Peanut Shells
Pyrogenic decomposition was conducted to produce biochars from the biowastes. Sugarcane rind, orange peel, and peanut shells were selected, cut into small pieces of approximately 0.3 cm× 0.5 cm, and dried in an oven at 50°C for 20 hours. About 15 g each of dried sugarcane rind, orange peel and peanut shells were placed in a vacuum tube furnace. The temperature increased at a rate of 5°C/min to 700°C and remained stable for 0.5 hours for carbonization under the protection of nitrogen gas. The experimental apparatus is shown in Figure 1. Generated biochar samples were weighed after carbonization.
Figure 1. Apparatus for preparing biochars

2.2 Removing Pollutants Using Biochars

Batch tests were performed to explore the performance of generated biochars. An aliquot of 300 mL of water sampled from a local river in East Hangzhou (Zhejiang Province, China) was put into three 250-ml Erlenmeyer flasks, and various dosages (0.5, 1, 1.5 and 2.0g/100 mL) of biochars made from sugarcane rind, orange peel or peanut shells were added to flasks with the river water. The Erlenmeyer flasks were placed in a temperature controlled shaker for 9 hours at 200 rpm. Water samples (5 ml) were collected every hour during the 9 hours, and then filtered through filter membranes with pore size of 0.22 μm and then tested immediately. NH$_4^+$-N and permanganate indexes were tested to track changes in the concentration of NH$_4^+$-N and organic matters in the water during the adsorption process.

2.3 Analysis and Calculations

Surface morphologies of sugarcane rind, orange peel and peanut shells were characterized by using a scanning electron microscope (Philips XL30ESEM, the Netherlands) before and after carbonization at the Analysis and Testing Center of Zhejiang University. The permanganate index was determined by using the acidity method, and the NH$_4^+$-N concentration were determined by using Nessler’s reagent spectrophotometric method.

3. Results and Discussion

3.1 Morphology Changes of Sugarcane Rind, Orange Peel and Peanut Shells before and after Pyrogenic Decomposition

To understand changes in surface morphology of sugarcane rind, orange peel and peanut shells before and after pyrogenic decomposition, we employed a scanning electron microscopy (SEM) for characterization (Figure 2). According to the images, the morphology of the raw materials changed and rendered high porosities. During pyrolysis and carbonization, the biomass in biochars decomposed and reacted with active agents such as water vapor, carbon dioxide, forming a large number of micro pores. The biochars that developed the most micropores have large specific surface area, high porosity and superior adsorption capacity (El-Hendawy et al., 2008). Previous studies have shown that remarkable improvements regarding specific surface area, total specific pore volume, microporous volume, average pore size and cation exchange capacity occur when the burning temperature is above critical temperature (700°C) (Nguyen et al., 2004; James et al., 2005; Lehmann and Joseph, 2009).
3.2 Pollutant Removal Using Biochars

3.2.1 Effect of Treatment Time

To determine the optimal water treatment duration using biochars made from sugarcane rind, orange peel and peanut shells, samples were collected on an hourly basis during the 9-h test. Changes in the concentrations of NH$_4^+$-N and permanganate index of the water are shown in Figure 3.
Figure 3. NH$_4^+$-N and organic matters removal efficiencies by the biochar made from sugarcane rind, orange peel and peanut shells over time

(Dosage: 1g; reaction temperature: 30°C)

As shown in the Figure 3, the removal efficiencies of NH$_4^+$-N by the three types of biochars increased as the reaction proceeded. The adsorption rates of the three types of biochars in the first 2 hours were higher than that in the rest of the time. The NH$_4^+$-N removal efficiencies after 9h by the biochars made from sugarcane rind, orange peel and peanut shells were 74.4%, 96.3% and 90.8%, respectively. Unlike the NH$_4^+$-N removal efficiencies, the decrease of permanganate indexes by biochars was comparatively lower, and the removal efficiencies of organic matter by the biochars made from sugarcane rind, orange peel and peanut shells were 26.6%, 31.0% and 29.4% after 9h of reaction, respectively. The adsorption equilibrium was reached after approximately 4h of reaction for the three types of biochars. As seen in figure 3, the organic matter and NH$_4^+$-N removal efficiencies by the biochars made of orange peel were greater than that by the biochars made of sugarcane rind and peanut shells. The results of study by Shaaban and Dimin (2004); Chia et al., (2014); Ahmad et al., (2014) show that there are many oxygen-containing functional groups on the biochar surface, such as hydroxyl group, carboxyl group and sulfonic acid group, which contribute to ammonia removal. In addition, biochars have a large amount of negative charges and high charge density which also benefit the superior removal of ammonia. It was reported that the organic matter removal by biochars is caused by the combination of adsorption and partitioning (Chen et al., 2008; Han et al., 2016). Most biochar contains positive and negative ion on its surface, and has a high capacity of ion exchange. Given that the NH$_4^+$-N removal by biochars was obviously better than that of organic matter, ion exchange might play a leading role.

3.2.2 Effect of Dosage on Pollutant Removal

To determine the optimal dosage for treating polluted river water with the biochars made of sugarcane rind, orange peel and peanut shells, 0.5, 1.0, 1.5 or 2.0 g of biochars was added into every 100 ml of water, respectively, and the reaction time was set as 6h. The results regarding ammonia and organic removal under different biochar doses are shown in Figure 4.
As seen in Figure 4, with the increasing doses of biochars from 0.5 g to 1.0 g, the NH$_4^+$-N and organic matter removal efficiencies also significantly increased, but further increased biochar dose had no significant effect on the removal of NH$_4^+$-N or permanganate index. Therefore, under the experimental conditions, the optimal dosage of 1.0 g biochar/100 ml water was selected for the treatment of river water. It was also observed that adsorption processes with all three types of biochars displayed similar patterns. The removal rates increased with the increasing biomass dosage, which is consistent with other previous studies (El-Sikaily et al., 2011; Hussain et al., 2006). The improved performance with high dosage is mainly attributed to the increased adsorbent surface area.

3.2.3 Effect of Temperature on Pollutant Removal

To determine the optimal temperature for treating the polluted water with the biochars made from sugarcane rind, orange peel and peanut shells, the adsorption processes under the temperature of 10, 20, or 30°C were investigated. After 6 h, samples were collected to measure the changes in the NH$_4^+$-N and permanganate index of the water.

As seen in Figure 5, the removal efficiencies of pollutants by three types of biochars increased with increasing temperature. The higher the temperature, the greater the adsorption rates of NH$_4^+$-N and organic matter. Therefore, high temperatures in the summer could provide more favorable conditions for treating river water using biochars.
When the temperature was 40°C, the NH$_4^+$-N removal efficiencies by the biochars made of sugarcane rind, orange peel and peanut shells were 73.7%, 90.0% and 74.0%, respectively, and the removal efficiencies of the permanganate index were comparatively lower: 29.7%, 35.0% and 32.0%, respectively. The organic matter and NH$_4^+$-N removal efficiencies by the biochars made of orange peel were higher than that by the biochars made of sugarcane rind and peanut shells.

4. Conclusion

Results suggest that biochars made from sugarcane rind, orange peel and peanut shells are promising adsorbents for water purification on a large scale. Under the same conditions, the permanganate index and NH$_4^+$-N removal efficiencies by the biochars made of orange peel are higher than those by the biochars made of sugarcane rind and peanut shells. Under experimental conditions, the optimal dosage of biochars was 1.0 g for 100 mL of river water, and 30°C was the best temperature for removal. Using the biochars made of biowaste as adsorbents to purify water could not only reduce domestic solid waste, but could also provide a low-cost approach to treating polluted river water.

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References


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