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Unraveling sorption of lead in aqueous solutions by chemically modified biochar derived from coconut fiber: A microscopic and spectroscopic investigation

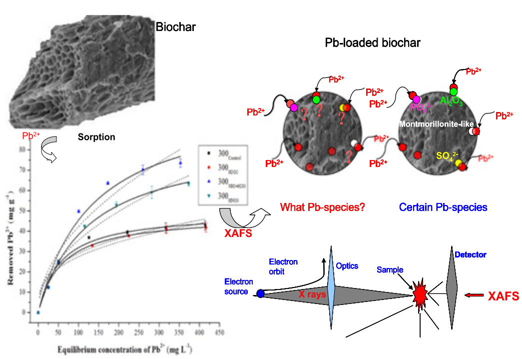
Weidong Wu [a,b], Jianhong Li [b], Tian Lan [b], Karin Müller [c], Nabeel Khan Niazi [d,e,f], Xin Chen [a], Song Xu [a], Lirong Zheng [g], Yingchao Chu [b], Jianwu Li [h], Guodong Yuan [i], Hailong Wang [a,h,i,*]

[a] School of Environmental and Chemical Engineering, Foshan University, Foshan, Guangdong 528000, China
[b] Ministry of Education Key Laboratory of Protection and Development Utilization of Tropical Crop Germplasm Resources, Hainan University, Haikou, Hainan 570228, China
[c] The New Zealand Institute for Plant and Food Research Limited, Ruakura Research Centre, Private Bag 3123, Hamilton, New Zealand
[d] Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad 38040, Pakistan
[e] MARUM, University of Bremen, Bremen D-28359, Germany
[f] Department of Geosciences, University of Bremen, Bremen D-28359, Germany
[g] Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, China
[h] Key Laboratory of Soil Contamination Bioremediation of Zhejiang Province, School of Environmental and Resource Sciences, Zhejiang A & F University, Lin'an, Hangzhou, Zhejiang 311300, China
[i] Guangdong Dazhong Agriculture Science Co. Ltd., Hongmei Town, Dongguan, Guangdong 523169, China

HIGHLIGHTS

- Chemical modification increased Pb adsorption of the biochars pyrolyzed at 300 °C.
- Modification enhanced free carboxyl and hydroxyl groups on biochars' surfaces.
- Pb-montmorillonite and $Pb(C_2H_3O_2)_2$ were the dominant species of the Pb-loaded biochars.
- The chemical modification decreased the exchangeable Pb on the Pb-loaded biochars.
- Chemical modification reduced Pb adsorption on the biochars pyrolyzed at 700 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we examined the efficacy of nine different types of coconut-fiber derived biochars (CFBs), prepared at different temperatures and chemically modified with ammonia, hydrogen peroxide and nitric acid, to remove lead (Pb^{2+}) from aqueous solutions. Langmuir-q_m values of the biochars pyrolyzed at 300 °C and modified with ammonia and nitric acid increased from 49.5 to 105.5 and 85.2 mg g^{-1}, respectively, compared to control (unmodified), whereas hydrogen peroxide treatment had no effect. The maximum amount of Pb adsorbed on biochars was in the order of CFB-700 > MCFB-300-$NH_3 \cdot H_2O$ > CFB-500 > MCFB-300-HNO_3 > CFB-300. X-ray absorption fine structure (XAFS) spectroscopy results revealed that Pb-montmorillonite, $Pb(C_2H_3O_2)_2$, $PbSO_4$, Pb-Al_2O_3 and $Pb_3(PO_4)_2$ were the five most important Pb species observed in Pb-loaded biochars, and as such,

Abbreviations: CFBs, coconut fiber-derived biochars; MCFBs, chemical modified coconut fiber-derived biochars; CEC, cation exchange capacity; SEM-EDX, scanning electron microscope-energy dispersive X-ray spectra; XAFS, X-ray absorption fine structure; FTIR, Fourier Transformation Infra-Red Spectrophotometry; EXAFS, extended x-ray absorption fine structure; LCF, linear combination fitting.

* Corresponding author at: School of Environmental and Chemical Engineering, Foshan University, Foshan, Guangdong 528000, China
E-mail addresses: nzhailongwang@163.com, hailong@zafu.edu.cn (H. Wang).

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favoring Pb immobilization in aqueous solutions. Overall, the sorption capacity of CFBs pyrolyzed at 300 °C substantially increased for Pb^{2+} with ammonia and nitric acid modification. However, these chemical modifications did not improve the sorption of Pb on CFBs pyrolyzed at temperatures ≥500 °C, thereby highlighting a temperature dependent response of chemically modified biochars to Pb sorption in this study.

1. Introduction

Several heavy metal pollutants have been released into the soil and water environments due to a rapid population growth, development of social economy, industry, smelting and mining operations, waste disposal, and the extensive application of pesticides and chemical fertilizers in agriculture. This has led to serious heavy metal pollution throughout the world including China (Zhang et al., 2013, 2015). The pollution of surface water and groundwater bodies by heavy metals is endangering ecosystems, food safety and human health (Jiang et al., 2012).

There are various methods for removing heavy metals from water including adsorption, chemical precipitation, ion exchange and membrane filtration (Duan and Su, 2014; He et al., 2015; Shen et al., 2016). Among multifarious remediation treatment technologies for heavy metals, adsorption has seen significant attention in recent years given to its fast metal removal rate, eco-friendly nature low cost, profitability, ease of operation, and high efficiency (Xu et al., 2013; Genç-Fuhrman et al., 2016; Lu et al., 2016). Nano-materials, industrial byproducts (e.g., steel-making slag, starfish), charcoal, and other materials are commonly used as adsorbents for heavy metals in soils and aqueous solutions (Duan and Su, 2014; Yu et al., 2015; Abdolali et al., 2016; Lim et al., 2016). More recently, biochars derived from various biowastes have been tested extensively for environmental remediation of soil and water systems (Zhang et al., 2013; He et al., 2016; Yang et al., 2016a). Coconut fiber is available in large quantities as a waste product of coconut orchards in tropical regions of Asia. For example, >250 million coconuts are produced and consumed annually in Hainan Island, China (Wang et al., 2015). Coconut fiber has been tested as a sorbent to remove contaminants from wastewater (Loffredo et al., 2014; Henryk et al., 2016). Coconut fiber-derived biochar (CFB) is regarded as the low-cost and environmental-friendly remediation material because of its large specific surface area, presence of a variety of active functional groups, micro porous structure and high cation exchange capacity (Bhatnagar et al., 2010; Shen et al., 2012; Wu et al., 2016). Although yet to be carried out Pb^{2+} adsorption on coconut fiber derived biochar, the efficacy of coconut-derived char or activated carbons to remove heavy metals from aqueous solution has been evaluated (Inyang et al., 2011; Shen et al., 2012; Wu et al., 2016).

The techniques like scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDX) and X-ray absorption fine structure (XAFS) spectroscopy have been used to examine the sorption mechanisms for heavy metals bound to a variety of environmental media and biochars (Lu et al., 2012; Xu et al., 2013; Nevidomskaya et al., 2016; Yang et al., 2016b). The XAFS spectroscopy is a powerful tool to delineate the composition, crystallinity and bonding environments of the metallic elements and those sorbents (Xiong et al., 2013).

Lead (Pb) is a widespread heavy metal pollutant in the environment and considered to be toxic to plants, animals and humans. Major anthropogenic sources of Pb contamination include mining, industrial and recycling activities. Lead exposure is estimated to account for 674,000 deaths each year and 9.8% of the global burden of idiopathic intellectual disability. Young children are particularly vulnerable to Pb toxicity which can adversely affect their brain and nervous system (World Health Organization, 2016). The often observed discrepancies between Pb bioavailability and toxicity in Pb polluted soil might be related to uncertainties in the estimation of model parameters for Pb binding to soil humic substances (Xiong et al., 2013).

Although yet to be resolved, an understanding of the Pb sorption mechanisms to biochars and knowledge about the binding stability are critically-important for assessing their potential for immobilization of Pb in aqueous environments, such as modified coconut-fiber derived biochar (MCFB) yielded at different pyrolysis temperatures for Pb removal. It has been reported that hydrogen peroxide (H_2O_2) modification significantly enhanced Pb^{2+} sorption on peanut hull-derived hydrochar due to increased O-containing functional groups, particularly carboxyl groups, on hydrochar surfaces (Xue et al., 2012; Rajapaksha et al., 2016). Amino-modified wood biochar substantially enhanced Cu^{2+} sorption, because the amino moiety efficiently complexes with heavy metals in view of high stability constants of metal complexes (Yang and Jiang, 2014). In the current study, we applied XAFS spectroscopy coupled with isotherm modeling and microscopy to examine sorption mechanisms at biochar-Pb interface under environmentally-relevant aqueous conditions. The objectives of this study were to: (1) examine the sorption capacity of a variety of chemically modified biochars obtained at different pyrolysis temperature for Pb in aqueous solutions, (2) explore the solid-phase speciation of Pb in Pb-loaded CFBs and MCFBs, and (3) investigate the stability of Pb^{2+} sorption to CFBs and MCFBs.

2. Materials and methods

2.1. Production of biochars

Coconut (*Cocos nucifera* L.) was collected from a coconut grove in the eastern suburbs of Wenchang (110.9°E, 19.6°N), Hainan Province, China, for biochar production. The coconut-fiber was separated from coconut fruit and chopped into cubes of about 1 cm length, width and height and air-dried at room temperature to obtain a moisture content of approximately 7–8%. It was then placed in the lid-covered ceramic crucibles and pyrolyzed at 300, 500 and 700 °C under oxygen-limited conditions in a SX210–12 Muffle furnace (Longkou Xian Ke Electricity Furnace Inc., Shandong, China) with a heating rate of approximately 20 °C min^{-1} (Chun et al., 2004). The biochars produced at different pyrolysis temperatures were ground and passed through a 2 mm sieve and stored in air-tight plastic bags prior to use for sorption experiments and spectroscopic analysis. The controls in sorption experiments are referred to as CFB-300, CFB-500 and CFB-700, respectively. Collectively, we refer to them as coconut fiber-derived biochars (CFBs).

For chemical modification of the biochars, we adapted the procedure as described by other researchers (Chen, 2012; Xue et al., 2012; Liu et al., 2013). The control CFBs were mixed at a 1:10 (w/v) ratio with (a) 5% ammonia (NH_3) solution and shaken in a constant temperature water bath at 50 °C for 9 h; (b) 5% hydrogen peroxide (H_2O_2) solution and shaken in a reciprocating shaker at 25 °C for 8 h; and (c) 2 M nitric acid (HNO_3) shaken in a reciprocating shaker at 30 °C for 8 h.

Then the biochars were rinsed 3–4 times with de-ionized water to remove the chemical reagents, oven dried at 60 °C for 48 h, and stored in air-tight plastic bags prior to use for sorption experiments and spectroscopic/microscopic analyses. The chemically modified biochar samples are hereafter collectively referred to as modified coconut fiber-derived biochars (MCFBs). The biochars produced at 300, 500 and 700 °C temperatures and treated with ammonia, hydrogen peroxide and nitric acid aqueous solution are referred to as MCFB-300-$NH_3 \cdot H_2O$, MCFB-500-$NH_3 \cdot H_2O$, MCFB-700-$NH_3 \cdot H_2O$, MCFB-300-H_2O_2,