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Facile synthesis of nano ZnO/ZnS modified biochar by directly pyrolyzing of zinc contaminated corn stover for Pb(II), Cu(II) and Cr(VI) removals

Changjing Li, Lei Zhang, Yuan Gao, Aimin Li *

School of Environmental Science and Technology, Dalian University of Technology, Linggong Road 2, Dalian 116024, PR China

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ABSTRACT

Nowadays, nano mineral modified biochars show a promising adsorption capacity for pollutants removals by combining the advantages of porous structure of biochar and unique property of nano minerals. In this work, nano ZnO/ZnS modified biochar was synthesized from slow pyrolysis of the zinc contaminated corn stover obtained from a biosorption process. The characterization results indicated that the zinc mineral modified biochar had a better porous structure (BET = 397.4 $m^2\ g^{-1}$ and TPV = 0.43 $cm^3\ g^{-1}$) than the common biochar (BET = 102.9 $m^2\ g^{-1}$ and TPV = 0.20 $cm^3\ g^{-1}$), and zinc minerals were evenly anchored on the biochar surface as nano ZnO/ZnS. Batch sorption experiments show that the obtained nano ZnO/ZnS modified biochar had strong sorption ability to Pb(II), Cu(II) and Cr(VI) with maximum sorption capacities of 135.8, 91.2 and 24.5 mg g^{-1}, respectively, which were significantly higher than the common biochar (63.29, 27.05 and 15.23 mg g^{-1}, respectively). The adsorption kinetics of heavy metal ions on nano ZnO/ZnS modified biochar were well described by the pseudo-second-order model, and the adsorption behavior coincided with heterogeneous adsorption materials as reflected by well fitting the Freundlich model. The thermodynamic results indicated that the adsorption process was an endothermic and spontaneous process. Based on the comprehensive characterizations and adsorption performance, the enhancement of the metals removal by the nano ZnO/ZnS modified biochar were mainly attributed to the hydroxyl groups on the surface of nano ZnO/ZnS particles and well-developed porous structure catalyzed by zinc salt during pyrolysis process. These findings suggested that generation of nano mineral modified biochar from heavy metals polluted biomass could be an attractive approach to treating and utilizing the waste biomass with a highly technical and economic feasibility.

1. Introduction

Heavy metal pollution in soil, water body and/or wastewater is a serious issue worldwide. Due to the non-degradable feature, phytoremediation and biosorption are two most often used methods to extract and enrich heavy metals by diverse plants from contaminated soil and water body (Singh et al., 2003). Especially, the biosorption by biomass is a low-cost and readily available method for heavy metals removal (Fomina and Gadd, 2014). Phytoremediation and biosorption based on the use of plants to the contaminated soil or groundwater has been applied in Hunan Province and Sichuan Province in China. The application of plant repair is widely reported in Chinese media. As a consequence, a large amount of heavy metal polluted biomass is generated in both phytoremediation and biosorption process, which needs to be further treated. Traditionally, the heavy metal polluted biomass was burned, and thus the most of heavy metals were retained in solid residue (ash), which needed to be solidified for landfill or submitted to metallurgy process for metal recovery. Although this approach could produce additional values by recovering energy and metal resources, the low energy value from burning the biomass and potentially environmental risk of heavy metals emission during the high-temperature combustion (higher than 850 °C) limited its application. Therefore, the searching of a more technically and economically viable method for this dangerous waste material is still a major task.

Recently, the utilization of waste biomass for biochar generation is becoming more popular. Biochar is a carbonaceous product derived from pyrolyzing biomass in an oxygen-limited atmosphere (Lonappan et al., 2016, Veni et al., 2017). Originally, biochar was exploited for soil amendment to enhance crop yield (Marris, 2006, Yao et al., 2013). From environmental aspect, biochar could serve as a carbon sequestration function to mitigate climate

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* Corresponding author.
E-mail address: leeam@dlut.edu.cn (A. Li).

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change (Lehmann et al., 2006, Liu et al., 2013). More recently, biochar was recognized as an important adsorbent to remove organic contaminants and heavy metals from wastewater due to its relatively low cost, wide availability, abundant porous structure and surface functional groups (Chen et al., 2008; Cao et al., 2009). By co-producing bio-oil and fuel gas, the biochar production process is becoming more economically attractive than combustion for biomass utilization.

As for the application of biochar as an adsorbent, the adsorption capacity for pollutants was still lower than typical adsorbents, e.g. activated carbon. In order to enhance the adsorption ability of biochar, a lot of efforts have been made to modify the biochar with special porous structures and surface properties (Liu et al., 2015; Kah et al., 2017). Among all modification methods, loading minerals on the surface of biochar to make a mineral modified biochar is the most promising one by combining the advantages of biochar and minerals (Ahmed et al., 2016; Tan et al., 2016; Sizmur et al., 2017). Within the composites, biochar could provide some porous structure for heavy metal adsorption and serve a carrier for minerals by carrying and stabilizing them. On the other hand, the minerals, especially nano-size minerals in the composites exhibited a high activity and selectivity upon heavy metal adsorption helping by a size-quantization effect and high surface area (Hua et al., 2012). Compared with common biochar, the biochars modified by nano minerals exhibited excellent adsorption abilities to a range of contaminants from aqueous solutions (Liou and Chen, 2009, Zhang et al., 2012, Zhang and Gao, 2013). For instance, Wang et al. reported a MnO_x-loaded biochar with a strong sorption ability to Pb(II), Cu(II), and Cd(II) with maximum sorption capacities of 153.1, 34.2, and 28.1 mg g^{-1}, respectively, which were significantly higher than that of pristine biochar (H. Wang et al., 2015; S. Wang et al., 2015).

The biochar could be inserted by mineral nanoparticles through surface modification by depositing minerals or nanocrystals on virginal biochar. For example, Yosuke et al. loaded zinc oxide on the commercially available granular activated carbon by the equilibrium adsorption of zinc ions from aqueous solution followed by calcination in air at 350 °C for 2 h, and the removal efficiency of the resulting ZnO-GAC on Pb(II) was 5.1 times higher than the commercial activated carbon (Kikuchi et al., 2006). Yan et al. synthesized magnetic biochar/ZnS composites by a two-step method, by which the biochar was produced from rice hull through slow pyrolysis at 400 °C for 5 h in a muffle furnace, and ZnS was deposited on biochar by continuously and simultaneously injecting the mixture of zinc chloride and thiourea in a polyol solution at 180 °C. The magnetic biochar/ZnS composites exhibited 10 times higher adsorption capacity for Pb(II) than the control magnetic biochar (Yan et al., 2015). Although these composites by depositing minerals, especially by loading zinc minerals, showed good adsorption capacities, the complex preparation procedure and relatively weak adhesion strength between minerals and biochar limited their practical application.

More recently, the catalytically pyrolysis of biomass by metal salts, where biomass feedstocks were soaked with metal salt solution, is an interesting way to decrease the activation energy and improve the bio-oil quality (Song et al., 2014; H. Wang et al., 2015; S. Wang et al., 2015). The directly pyrolysis of metal salt loaded biomass might have several advantages for the synthesis of mineral modified biochar: (1) the metal salts could have some catalytic effects on the pyrolysis of biomass, thus improving the porous structure of biochar; (2) the generation of biochar and the formation of minerals even with nano size proceeded simultaneously; and (3) the entire synthetic process involves only one pyrolysis step, which made it easy to scale up. Although a few studies showed some promising results by directly pyrolyzing biomass pretreated by potassium permanganate ($KMnO_4$) or zinc nitrate ($Zn(NO_3)_2$) (Gan et al., 2015; H. Wang et al., 2015; S. Wang et al., 2015), due to the selections of loading metal salts and pyrolysis conditions, the porous structure and minerals phase in the resulting modified biochars were far below expectation. The nano minerals modified biochar could also be prepared by pyrolysis heavy metal contaminated biomass. Compared with post-modification biochar or biochar made from impregnation method, biochar made from polluted biomass could provide a win-win approach by recycling polluted biomass into useful materials and avoiding the addition of chemical reagents (Mosa et al., 2018).

In this study, the zinc polluted corn stover, which was collected from biosorption process, was used as the feedstock instead of the biomass externally supplemented by metal salts. Zinc content was controlled at 5%, which was the average sorption capacity of biological adsorption and much lower than the amount of metal required for impregnation method. The zinc polluted biomass was pyrolyzed under a broad temperature range to obtain the modified biochar with well-developed porous structures and nano ZnO/ZnS mineral phases. The specific objectives of this study are (1) to analyze the zinc nanostructures in the biochar scaffold; (2) to investigate the physical and chemical properties of the modified biochar; (3) to evaluate the adsorption ability of the zinc mineral modified biochar to lead, copper, and chromium; and (4) to tentatively elucidate the adsorption mechanisms of heavy metal sorption on the biochar derived composites.

2. Experimental methods

2.1. Materials

In this study, corn stover used as a typical biomass was obtained from a local village in Dalian, China. The corn stover mainly consisted of 35.88% of cellulose, 8.20% of lignin, and 29.72% of hemicellulose by weight with undetermined protein, fat, starch, sugar and inorganic salts. As for elemental composition, the raw corn stover contained 39.21% of carbon, 5.00% of hydrogen, 1.23% of nitrogen, 5.71% of ash and 48.85% of oxygen. For preparing the metal polluted biomass, the corn stover was crushed, sieved to 0.18 mm (80 mesh) and then dried in an oven at 105 °C overnight, the resulting corn stover powder was used as a bio-adsorbent for zinc ions removal. For biosorption process, 5.0 g of corn stover was mixed with a 200-mL $ZnSO_4$ solution at Zn^{2+} concentration of 1250 mg/L, and was shaken in a water bath at 150 rpm for 300 min at room temperature. After the adsorption was accomplished, the mixture was dried at 105 °C. The weight ratio of Zn^{2+} in the resulting zinc loaded corn stover was 5%, which was the highest Zn^{2+} percentage in biomass gathered from biosorption process.

2.2. Biochar preparation

The slow pyrolysis experiments were performed in a lab-scale fixed-bed pyrolysis reactor. Ten grams of raw biomass or zinc loaded biomass was placed in a horizontal tubular reactor (60 mm I.D. and 300 mm length). Then, the reactor was purged with a nitrogen gas with a flow rate of 200 mL min^{-1} for 20 min to remove oxygen from the pyrolysis system. Thereafter, the temperature was raised at a 5 °C min^{-1} of heating rate to designated pyrolysis temperatures of 500, 600, 700, or 800 °C, and maintained for additional 60 min to ensure the completed conversion of the raw material. The biochar prepared from raw corn stover pyrolysis was named as C500, C600, C700, and C800, respectively, where the suffix number represents the pyrolysis temperature. The biochar prepared from zinc loaded corn stover pyrolysis at different