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Effect of phosphoric acid on the surface properties and Pb(II) adsorption mechanisms of hydrochars prepared from fresh banana peels

Nan Zhou [a, 1], Honggang Chen [a, 1], Qiuju Feng [b], Denghui Yao [a], Huanli Chen [a], Haiyan Wang [c], Zhi Zhou [a, *], Huiyong Li [a, **], Yun Tian [d], Xiangyang Lu [d]

[a] College of Science, Hunan Agricultural University, Changsha 410128, China
[b] College of Chemistry and Chemical Engineering, Jishou University, Jishou 416000, China
[c] College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China
[d] College of Bioscience and Biotechnology, Hunan Agricultural University, Changsha 410128, China

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ABSTRACT

The acidic environment has been confirmed to have significant influence on the biochar products through hydrothermal carbonization. To investigate the effect of H_3PO_4 on the surface properties and adsorption mechanisms of the biochar, fresh banana peels were used as feedstock and transformed into hydrochars under the catalysis of H_3PO_4 with concentration ranges from 0% to 50%wt. The addition of H_3PO_4 greatly impacted the physicochemical properties of the as-obtained hydrochars, such as carbonization degrees, pH values, amount of surface acidic functional groups and then further affected the adsorption mechanisms of lead ions on those hydrochars. Hydrochars catalyzed by H_3PO_4 with higher concentration showed higher degree of carbonization, lower value of pH and fewer amount of acidic functional groups, while lower content of H_3PO_4 could not completely catalyze the degradation reactions and resulted in larger quantity of intermolecular locked oxygen containing groups that could not be participated into the adsorption process. Among all six samples, hydrochar generated in 30%wt H_3PO_4 exhibited the best adsorption property of 241 mg g^{-1}, possibly due to the largest concentration of the acidic functional groups on the surface rather than in the intermolecular structure of the carbon. It had been confirmed that the adsorption mechanisms were the combination of surface complexation, cationic exchange and part of precipitation. Hydrochars derived from fresh banana peel via hydrothermal carbonization catalyzed by phosphoric acid could be excellent adsorbents for lead removal in aqueous environments.

1. Introduction

Biochar, a carbon-rich material, is the solid post product of the carbonization of biomass resources under oxygen free or limited environment. Due to the attractive characteristics, low density, high stability, developed surface property and environmental benign nature, biochar can have widely application in pollutants amendment including heavy metals (Kołodyńska et al., 2017; Tong et al., 2011), organic compounds (Klasson et al., 2014; Li et al., 2014) and green house gases (Awasthi et al., 2017). Combined with abundant feedstock resources, a cost-effective conversion process and simple handing procedure, biochar has become a promising candidate to substitute the current costly adsorbents, such as activated carbon, silica and alumina in wastewater treatments. The adsorption behavior of biochar towards heavy metals is the result of the cooperation of physical attraction and chemical reaction (Tan et al., 2017). The former largely depends on the surface area and porosity, since high surface energy can strengthen the molecular and intermolecular force and high quantity of holes can apply more storing places for heavy metal ions; while the latter significantly relies on the surface functional groups and chemical fractions, due to which chemical reactions including ion exchange, complexation, precipitation, electrostatic attraction and π-interaction between

* Corresponding author.
** Corresponding author.
E-mail addresses: zhouzhi@hunau.edu.cn (Z. Zhou), lhy5321@hunau.net (H. Li).
[1] Nan Zhou and Honggang Chen contributed equally to this work.

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the biochar and heavy metal ions can take place. Therefore, it is very important to improve the surface property for adsorption performance development of biochars.

It is well known that the composition of biomass has a great influence on the surface property of biochar, however, the surface characteristics of biochar can be significantly changed by using different carbonization methods and adjusting the reaction conditions, especially when combined with the in situ or after activation processes (Li et al., 2014). The after activation is widely used presently to improve the surface property of the products after pyrolyzation of the biomass through physical or chemical or physicochemical ways. During which, specialized reagents are commonly used and complicate apparatus are usually required, coproducing a large quantity of waste and by-products, resulting in requirement of disposal and further treatments (Xue et al., 2012). Recently, wet pyrolysis, also named hydrothermal carbonization (HTC), has attracted tremendous attentions for biochar synthesis and modification. HTC is a thermochemical process performed in water within the temperature range of 120–260 °C for several hours under saturated pressure (autogenous or provided by a gas). Besides of the mild reaction environment and lower energy consumption, the overwhelm capability of HTC is the directly use of biomass with high content of moisture, which comes for most of biomass naturally obtained. The cutting of the pre-dehydration process that is required for dry pyrolysis can deeply reduce the costs in industrial applications, and the firsthand use of those high moisture-containing resources like banana peels can greatly enlarge the scope of biomass feedstock. However, most of the related literature were still utilizing dehydrated and pulverized raw materials rather than fresh biomass (Nizamuddin et al., 2016; Pellera et al., 2012), cutting the HTC out of the main market for biochars preparing. To develop the wide-scope application of HTC, increasing efforts and more investigation are urgently required.

During the HTC process, the biomass is undergoing thermal degradation in water and contrariwise affects the physicochemical properties of water (Brunner, 2009), which will reduce the dielectric constant of water and turn it to be a good solvent for non-polar substances, such as organic staff under supercritical conditions. With the increase amount of the ionic species in water, acid-base-catalyzed reactions can be facilitated (Elliott, 2011). Although detailed reaction mechanisms of biomass during HTC process are yet unknown due to the complexity of natural materials (Funke and Ziegler, 2010), adding chemicals especially an acid during the HTC procedure to transform pure carbohydrates and/or biomass into functional char coal materials has been proven to be highly feasible (Fernandez et al., 2015; Lynam et al., 2011; Titirici et al., 2007). Thus, the in situ activation taken place with the pyrolysis of biochar simultaneously becomes possible and much easier. It was confirmed that adding acetic acid and salts like lithium chloride into the reacting system could effectively reduce the vapor pressure and enhance the fuel value of biochars (Lynam et al., 2011, 2012). Later, HCl, NaOH and NaCl solutions were employed to produce biochars with strengthened atrazine adsorption capability (Flora et al., 2013). It was reported that acetic acid and KOH could apply acidic and basic environment and influence the characteristics of the biochars. However, the study and utilization of transferring biomass into functional biochars through HTC is still in the embryonic stage, especially with the in situ activation by adding a specialized reagent. To accelerate the development of biochar, further studies and more efforts need to be devoted to explore the knowledge on the reaction mechanisms, the functionalization of additives, as well as application for various purposes.

Phosphoric acid is found to be an efficient activating agent to improve the property of carbon based materials before and/or after the carbonization (Elmouwahidi et al., 2017; Sun et al., 2016). Compared to other chemical activators, such as zinc chloride, hydroxide and nitric acid, H_3PO_4 has lower corrosivity and the as-obtained products contain less harmful residues, thus environmental benign (Prahas et al., 2008). Most recently, our group discovered that fresh and dehydrated banana peels could be transferred into highly effective sorbent biochars through a facile one-step hydrothermal carbonization approach by using 20%wt phosphoric acid as the reaction medium (Zhou et al., 2017). The phosphoric acid added here in the HTC process played a key role in the dehydration of the polysaccharides and the formation of large quantity of acidic surface functional groups, which was the dominant influence parameter on the removal capacity of the as-prepared biochars toward lead. It has been proven that in situ activation with wet pyrolysis of fresh banana peels into effective sorbents could be realized by using H_3PO_4 through HTC process. To figure out the feasible reaction mechanisms, herein, phosphoric acid with various concentrations ranging of 0%–50%wt were utilized as the reaction media to transfer fresh banana peels into biochar sorbents through hydrothermal carbonization. The pH value, the surface area, the micromorphology, the cationic ions, as well as the species and amounts of acidic functional groups of the as-obtained hydrochars were carefully investigated to illustrate the influence of the phosphoric acid on the surface properties of the hydrochars. The lead storage properties in aqueous solutions of those as-prepared hydrochars and the adsorption mechanism of the specific optimized sorbent were also studied to further demonstrate the relationship among the reaction media, the surface property and the adsorption capability.

2. Experimental

2.1. Preparation of banana peel based hydrochars

Bananas were purchased from a local market, washed and peeled. The banana peels were washed with distilled water (DW) for several times to completely remove the dust and other soluble impurities. After that, the cleaned banana peels were chopped into small pieces (0.5–1 cm), and then used as the feedstock to produce hydrochars directly. Analytical pure phosphoric acid H_3PO_4 was purchased from Aladdin Reagent Co. Ltd. (Shanghai, China) and used as received. The phosphoric acid was diluted with double distilled water into appropriate concentrations before the synthesis process. Typically, 4 g fresh banana peel pieces (containing about 90% moisture) were added into 50 ml phosphoric acid solutions with gradient concentration from 0 to 50%wt. After soaking in the H_3PO_4 solution for 2 h, the mixture was transferred into a 100 ml polytetrafluoroethylene (PTFE) inner steel autoclave and heated at 230 °C for 2 h. Then, the autoclave was taken out of the furnace and cooled to room temperature. The obtained product was vacuum filtered and washed with DW for several times until the washing liquid got neutral. Finally, the as-prepared sample was dried in oven at 80 °C overnight. For convenience, the obtained hydrochars were abbreviated as H-*x* hereafter, while *x* stands for the concentration of H_3PO_4, for example, H-20 is the hydrochar produced within 20%wt H_3PO_4.

2.2. Characterization

Scanning Electron Microscopy (SEM) was carried out to image the particle size and morphology of the samples through a JSN-6380LV instrument. Elemental analyzer was performed to define the elements contents and the atomic ratios via a Vario Micro cub Elementar (Germany). The surface areas of the hydrochars were calculated based on the results of N_2 sorption 77 K experiments performed in a Gemini VII 2390 Surface Area Analyzer according to