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# Facile low-temperature one-step synthesis of pomelo peel biochar under air atmosphere and its adsorption behaviors for Ag(I) and Pb(II)

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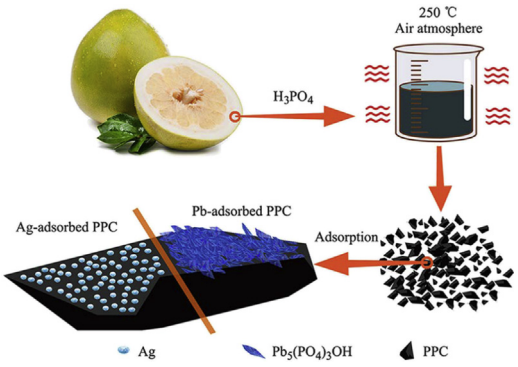
## HIGHLIGHTS

- Extremely low carbonization temperature and regular air atmosphere were used for biochar production from biomass waste.
- Amounts of oxygenic and phosphorous functional groups were introduced on the biochar surface.
- The prepared biochar could be used as an effective sorbent for Ag(I) and Pb(II) adsorption.
- Distinct mechanisms of the carbon material for Ag(I) and Pb(II) adsorption were proposed.

## GRAPHICAL ABSTRACT

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## ABSTRACT

This study prepared a novel low-cost surface functionalized carbon adsorbent (PPC) from biomass waste (pomelo peel) through a facile low-temperature (250 °C) one-step method under regular air atmosphere. The adsorption performance and mechanism of the carbon material for Ag(I) and Pb(II) were investigated by a range of sorption experiments and characterizations including SEM, EDX, XRD and FTIR. Sorption experimental results suggested that PPC had high adsorption capacities of 137.4 and 88.7 mg/g for Ag(I) and Pb(II), respectively, with adsorbent dosage of 2 g/L at unadjusted solution pH and room temperature (23 ± 1 °C). The characterization results indicated high-efficiency removal of the heavy metals by PPC was attributed to the strong chemical adsorption involving that Ag(I) ions were reduced as metallic Ag particles by oxygenic functional groups and Pb(II) ions were precipitated as $Pb_5(PO_4)_3OH$ crystals by phosphorous functional groups on the carbon surfaces. This study provides the possibility of synthesis high-efficient adsorbent using economic and environmental-friendly approach with low energy consumption.



## 1. Introduction

The treatment of industrial wastewater containing heavy metals is a major environmental and social issue, since toxic heavy metals are non-biodegradable and bioaccumulative, and some precious metals might be wasted along with wastewater discharge (Freitas et al., 2017; Ghassabzadeh et al., 2010). Silver and lead are classified as typical

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hazardous substances by the World Health Organization and the US Environmental Protection Agency, and sliver is a precious metal as well (Yao et al., 2015). As a relatively scarce raw material, silver has been widely used in varieties of industries such as coinage, electroplating, antimicrobial agents, medication and photography due to its outstanding thermal/electrical conductivity, photosensitivity and ductility (Sarı and Tüzen, 2013; Zafar et al., 2012; Zhang et al., 2017). Nevertheless, Ag(I) shows higher toxicity than other heavy metals such as mercury or copper even at very low concentration (Jeon, 2015; Jeon, 2016). Similarly, Pb(II) is water soluble with high toxicity, and harmful to human and other organisms (Zhang et al., 2016b). The main source of lead pollution is the discharge from many industries including battery manufacturing, oil refining, metal plating, leather tanning and paint producing (Liu et al., 2016; Wang et al., 2012). Thus, it's a substantial subject to exploit effective methods to remove and/or recover silver and lead from industrial effluents.

Currently, heavy metals wastewater treatment approaches, including chemical precipitation, membrane filtration, ion exchange and electrochemical treatment, have the drawbacks of secondary pollution, complicated operation and high operating cost (Fu and Wang, 2011; Zhang et al., 2017). Compared with these technologies, adsorption with the advantages of high efficiency, low cost and simple operation process is generally considered to be one of the best attractive options (Wan et al., 2016; Zare-Dorabei et al., 2016; Zhao et al., 2016). Commercial activated carbon (AC) is widely used adsorbent in the removal of heavy metals, showing excellent adsorption capacity due to its large specific surface area and abundant active adsorption sites on the surface (Ihsanullah et al., 2016; Kołodyńska et al., 2017; Rao and Kashifuddin, 2016; Zhou et al., 2015). But the precursors of AC are commonly fossil-based resources, which is high-priced, non-renewable and limited. So searching for substitutive adsorbent from inexpensive and renewable feedstock is of concern to researchers (Dawood et al., 2017). To solve this problem, biochar derived from various biomass has been proposed as an economical alternative adsorbent to remove heavy metals from wastewater, since its feedstock is abundant, low-cost as well as renewable (Alhashimi and Aktas, 2017; Oliveira et al., 2017; Tan et al., 2015b). On the other hand, using biomass from agricultural and industrial wastes as precursor of biochar could reduce their discarded quantity and thereby decrease environmental contamination.

The conventional method of converting biomass wastes to carbon adsorbents with good adsorption ability is high-temperature pyrolysis (400–800 °C) in an inert atmosphere accompanied by chemical activation (Boudrahem et al., 2011; Kyzas et al., 2016; Ramos et al., 2015; Santos et al., 2015; Yao et al., 2015). However, the high temperature process is one of the main drawbacks of biochar synthesis since it means large electricity consumption and huge environmental burden, and the yields of adsorbents are much lower than that of relatively low temperature method as more constituents of biomass are thermally decomposed under higher temperature (Inyang et al., 2015; Simsir et al., 2017). To date, there are very few literatures studied about relatively low temperature (≤350 °C) synthesis method especially in an air atmosphere. For example, B.V. Babu and S. Gupta prepared neem leaves activated carbon for Cr(VI) adsorption via HCl (36.5 wt%) activation at 150 °C in the air (Babu and Gupta, 2007). Low-temperature and regular air atmosphere make the adsorbent preparation process even more attractive and bring higher output. Nonetheless, the preparation method, characteristics of the obtained material and the mechanism of the heavy-metal adsorption process need further examination.

Pomelo peels, take up about 40% of total pomelo weight, are abundant waste agricultural biomass which have not been recycled and might further pollute the environment (Bhatnagar et al., 2015). There are few researches have synthesized adsorbents from pomelo peels, but their prolonged and high temperature pyrolysis procedure boost the cost dramatically. For example, Zhu et al. prepared a modified pomelo peel carbon through a complex multi-step pyrolysis process with KOH activation and subsequent functionalization by $KMnO_4$ (Zhu et al., 2017). In our study, a novel low-cost and high-efficiency carbon adsorbent was synthesized from pomelo peels through a facile one-step method at extremely low carbonization temperature of only 250 °C under regular air atmosphere with phosphoric acid ($H_3PO_4$) and its adsorption capacity of Ag(I) and Pb(II) was evaluated. Meanwhile, the physicochemical properties of the pristine and post-sorption carbon were characterized to investigate the intrinsic adsorption mechanisms of Ag(I) and Pb(II).

## 2. Materials and methods

All chemical reagents used in this study including $Pb(NO_3)_2$, $AgNO_3$, $Mg(NO_3)_2 \cdot 6H_2O$, $NaNO_3$, $Cd(NO_3)_2$, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $H_3PO_4$ (85%, wt%) were obtained from Beijing Chemical Works Co. Ltd. (Beijing, China) and were analytical grade. All solutions were prepared with deionized (DI) water (Direct-Q3UV, Millipore, USA).

### 2.1. Biochar production

The white sponge-like part of pomelo peel was separated and dried at 80 °C and grinded into powder. 10 g of the dry pomelo peel powder was impregnated with 100 mL of 85% (wt%) $H_3PO_4$, stirred evenly, and then it was carbonized in an oven under air atmosphere for 2 h at 250 °C. The mixture was washed with DI water and vacuum filtered for several times until the pH is neutral as well as no white precipitate generation when adding lead nitrate solution into the filtrate. The obtained pomelo peel biochar (PPC henceforth) material was dried in an oven at 80 °C for 24 h and grinded into powder for further use.

### 2.2. Characterizations

Contents of organic elements (C, H, N and S) in the PPC were determined with a CHNOS Elemental Analyzer (vario macro cube, Elementar), and major inorganic elements were examined by an inductively-coupled plasma atomic emission spectroscopy (ICP-OES) via a PerkinElmer Optima 8300 instrument after acid digestion. Surface morphology of PPC before and after silver and lead adsorption were analyzed using a scanning electron microscope (SEM) via a Hitachi S-4800 instrument equipped with an energy dispersive X-ray fluorescence spectroscopy (EDS, Oxford instruments) for assessing surface elemental composition. Before scanning, the samples were spread on a carbon adhesive tape and sputtered with Pt. Crystal structures on the PPC before and after silver and lead adsorption were identified by a computer-controlled X-ray diffractometer (XRD) via a Rigaku Ultima IV instrument with scanning range from 10 to 90° in the 2θ range and rate of 8°/min. Functional groups on the materials were investigated by Fourier transform infrared spectrometer (FTIR, PerkinElmer) through pressing mixture of spectroscopic grade KBr and samples at a ratio of 100:1 into a flake and recording the transmittance in the spectrum range from 450 to 4000 $cm^{-1}$.

### 2.3. Adsorption experiments

To investigate the adsorption properties of PPC toward Ag(I) and Pb(II), a range of adsorption experiments were conducted including adsorption kinetics, adsorption isotherm and effects of initial pH. Typically, 0.1 g of PPC was added to 50 mL plastic centrifuge tube containing 50 mL of Ag(I) or Pb(II) solutions at unadjusted pH (about 6.0) with initial concentration of 50 mg/L, at room temperature (23 ± 1 °C), and the tubes were subsequently shaken in a mechanical shaker at 200 rpm. After shaking for 24 h, the mixtures were filtered with membrane filters (0.22 μm pore size mixed cellulose membrane), and the concentrations of initial heavy metals solutions and filtrates were measured by ICP-OES. For adsorption kinetics, the concentration of initial solutions is 50 mg/L, and the tubes were immediately withdrawn from shaker and filtered after different time intervals between 0 and 48 h. In the adsorption isotherm tests, the concentration of Ag(I) initial solutions were in