Ecological Engineering xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Ecological Engineering

journal homepage: www.elsevier.com/locate/ecoleng

Short communication

Engineered biochar derived from eggshell-treated biomass for removal of aqueous lead

Hongyu Wang[a,b], Bin Gao[b,*], June Fang[b], Yong Sik Ok[c], Yingwen Xue[a], Kai Yang[a], Xinde Cao[d]

[a] School of Civil Engineering, Wuhan University, Wuhan 430072, China
[b] Department of Agricultural and Biological Engineering, University of Florida, Gainesville, FL 32611, USA
[c] Korea Biochar Research Center, Kangwon National University, Chuncheon 200-701, Gangwon Province, Korea
[d] School of Environmental Science and Engineering, Shanghai Jiaotong University, Shanghai 200240, China

ARTICLE INFO

Article history:
Received 23 January 2017
Received in revised form 18 May 2017
Accepted 14 June 2017
Available online xxx

Keywords:
Designer biochar
Biosorption
Heavy metal
Remediation
Conservation

ABSTRACT

Engineered biochars were prepared by slow pyrolysis of three types of biomass pretreated with eggshell waste. The resulting biochars were composite materials with eggshell particles on carbon surface within the pore networks, which were confirmed by various characterization tools. The engineered biochars showed relatively fast adsorption kinetics to Pb^{2+} aqueous solutions. In addition, adsorption isotherms showed that the Langmuir maximum Pb^{2+} adsorption capacities of the engineered biochars (103–261 mg/g) were higher than those of the pristine biochars (32.9–56.0 mg/g). The adsorption of Pb^{2+} onto the biochars were affected by adsorbent dosage, initial solution pH, and ionic strength. Findings from this work indicated that the engineered biochar from eggshell-treated biochar can be used as an effective agent for soil and water remediation and conservation.

1. Introduction

Biochar is a fast-growing research topic because of its promising potentials in various environmental applications, particularly in soil improvement and carbon sequestration (Zhang and Ok 2014). A number of studies have also suggested that biochar and its derivatives (e.g., engineered biochar) can be used as low-cost adsorbents for the removal of various contaminants from aqueous solutions (Inyang et al., 2012; Mohan et al., 2014; Xie et al., 2015). In comparison to pristine biochar, engineered biochar, prepared through either modifying the pristine biochar or direct pyrolysis of pretreated biomass feedstock, often shows enhanced sorption ability for both heavy metals and organics (Ok et al., 2015; Zhang and Gao 2013; Zhou et al., 2013)

Various engineering methods have been developed to make engineered biochars such as biochar-based composites for environmental applications (Inyang et al., 2014; Zhang et al., 2012a; Zhou et al., 2014). Most of these methods, however, require the usage of chemical reagents, which may add additional cost. Recent studies have demonstrated that low-cost materials such as clay and natural minerals can be used to pretreat the biomass for the preparation of novel engineered biochars (Wang et al., 2015; Yao et al., 2014). For example, engineered biochar with clay particles implanted within biochar pores (biochar-clay composites) is a promising low-cost adsorbent for environmental applications because of its unique properties and functions inherited from both clay and biochar (Yao et al., 2014). It is thus feasible and more desirable to use low-cost or waste materials with excellent sorption abilities as the engineering reagents to prepare biochar composites (Reddy et al., 2014).

Eggshell, a biodegradable waste material, is a common household byproduct that is abundant and available at a very low cost. Because of its unique natural porous structures and high content (~95%) of calcite, eggshell has been utilized in many applications including as a biosorbent for environmental remediation (Ahmad et al., 2012b; Guru and Dash 2014). Eggshell-based materials have shown strong affiliations to heavy metal ions (e.g., Pb^{2+}, Cu^{2+}, and Cd^{2+}) and thus can be used as a low-cost adsorbent for soil remediation and wastewater treatment (Ahmad et al., 2012a; Almaroai et al., 2014; Zheng et al., 2007).

To take advantage of the good adsorption ability of the eggshell and the development of engineered biochar technology, this work developed a novel eggshell-biochar adsorbent for the removal of heavy metals from aqueous solutions. The eggshell-biochar was prepared through direct pyrolysis of three types of biomass (bam-

* Corresponding author.
E-mail address: bg55@ufl.edu (B. Gao).

http://dx.doi.org/10.1016/j.ecoleng.2017.06.029
0925-8574/

boo, hickory, and peanut hulls) pretreated with eggshell powder. The three biomass materials are not only abundant, but also among the most commonly used feedstock for biochar production (Inyang et al., 2016; Mohan et al., 2014; Sun et al., 2014). The resulting engineered biochars were characterized with various analytical tools. A range of batch adsorption experiments was conducted to evaluate the adsorption ability of the engineered biochars to Pb^{2+} in aqueous solutions. The specific objectives were as follows: 1) prepare and characterize eggshell-biochar composites; 2) determine the adsorption kinetics and isotherms of Pb^{2+} on the biochars; and 3) determine the effects of initial solution pH, sorbent dosage, and ionic strength on Pb^{2+} removal.

2. Materials and methods

2.1. Materials

All chemicals and reagents used in this work were of analytical grades and solutions were prepared using deionized (DI) water (18.2 MΩ) (Nanopure water, Barnstead). Lead nitrate ($Pb(NO_3)_2$) was purchased from Fisher Scientific. Bamboo chips, hickory chips, and peanut hulls were collected locally in Gainesville, FL, and were milled to obtain powders between 0.5 mm and 1 mm and dried prior to use.

2.2. Sorbent preparation and characterization

For each feedstock, 40 g of the dried biomass was pyrolyzed in a tube furnace under N_2 flow at a temperature of 450 °C for 3 h. The obtained pristine biochar samples was rinsed with DI water several times, oven dried at 80° C, and placed in an air-tight container prior to use. The basic physicochemical properties of the pristine biochars derived from the three types of feedstocks have been reported in several previous studies (Sun et al., 2014; Yao et al., 2012). They were label as BB, HB, and PB using the first initials of the feedstock type and biochar.

Waste eggshells were used as the reagent to prepare the engineered biochars (eggshell-biochar composites). The eggshells were first clean with DI water and dried in an oven at 80 °C for 24 h. The dried eggshells were ground with a grinder to produce fine powder and sieved to a size between 20 and 95 μm. After that, 0.3 g of the eggshell particles were irradiated through bath sonication with Misonix S3000 ultrasonicator (QSonica, Newtown, CT) in the presence of 200 mL dimethylformamide (DMF) in a glass beaker for 5 h. Previous studies have demonstrated that this process can make colloidal and nanosized eggshell particles (Hassan et al., 2014). In the next step, 40 g of each biomass were immersed in the eggshell particle suspension and the mixture was stirred for 24 h using a magnetic stirrer. The mixture was then oven dried at 80° C for 24 h. The pre-treated biomass was pyrolyzed in the tube furnace under N_2 flow at a temperature of 450 °C for 3 h. The obtained engineered biochar samples were treated with the same procedures as the pristine biochars and were labeled as EBB, EHB, and EPB.

Surface morphology and element composition of the engineered biochars were examined using a scanning electron microscopy (SEM) (JEOL JSM-6400, Japan) equipped with an energy dispersive X-ray fluorescence spectroscopy (EDS, Oxford Instruments Link ISIS). A computer-controlled X-ray diffractometer (XRD) (Philips APD 3720) equipped with a stepping motor and graphite crystal monochromator was used to investigate the crystalline of one of the engineered biochars (EBB).

2.3. Adsorption experiments

Adsorption kinetics were investigated by adding 0.05 g of each biochar into digestion vessels (Environmental Express) containing 25 mL of Pb^{2+} solution (105 mg/L) at room temperature. The vessels were then shaken at 50 rpm in a mechanical shaker. At different time intervals (0, 0.5, 1, 2, 4, 8, 12, 24 and 48 h), vessels were withdrawn and the mixtures were subsequently filtered through 0.22 μm pore size nylon membrane filters (GE cellulose nylon membrane). The Pb^{2+} concentrations in the filtrates were determined by an inductively coupled plasma-atomic emission spectrometry (ICP-OES, Optima 2300, Perkine-Elmer SCIEX, USA). The amounts of Pb^{2+} sorbed onto the biochar samples were calculated based as the differences between initial and final aqueous concentrations.

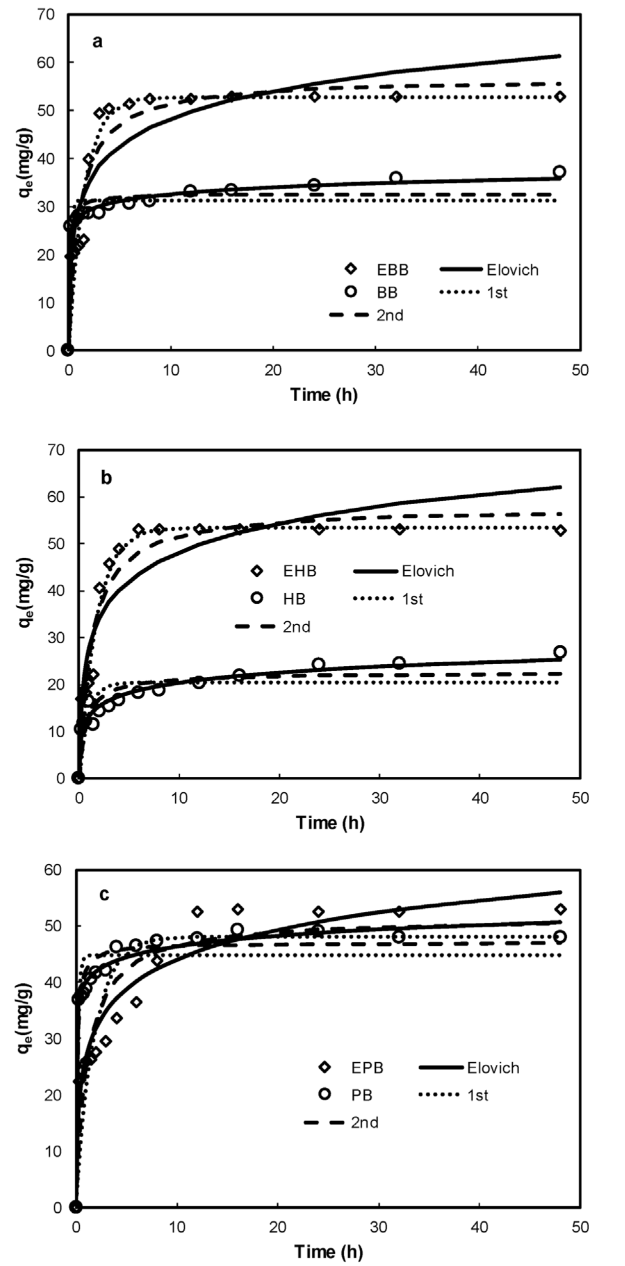

Fig. 1. Kinetics data and fitted models of Pb^{2+} adsorption onto biochars: a) BB and EBB; b) HB and EHB; and c) PB and EPB.

Adsorption isotherms were determined by adding 0.05 g of adsorbent to digestion vessels (Environmental Express) containing 25 mL of Pb^{2+} solutions (2–500 mg/L) at room temperature. The vessels were shaken in the mechanical shaker for 24 h at room temperature, and the samples were then withdrawn and subsequently filtered to determine Pb^{2+} concentrations in the filtrate by the same