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Biochar pyrolytically produced from municipal solid wastes for aqueous As(V) removal: Adsorption property and its improvement with KOH activation

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HIGHLIGHTS

- Excellent adsorption performance of aqueous As(V) by MSW biochars.
- 2 M KOH activated MSW biochars were more favorable for As(V) adsorption.
- Second-order model and Langmuir equation for better description of adsorption.
- Porosity and functional group changes promoted As(V) adsorption on MSW biochars.

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ABSTRACT

Biochar converted from waste products is being considered as an alternative adsorbent for removal of aqueous heavy metal(loid)s. In this work, experimental and modeling investigations were conducted to examine the effect of biochars pyrolytically produced from municipal solid wastes on removing aqueous As(V) before and after activated by 2 M KOH solution. Results showed that the highest adsorption capacity of pristine biochars was 24.49 mg/g. The pseudo-second-order model and Langmuir adsorption isotherm model can preferably describe the adsorption process. The activated biochar showed enhanced As(V) adsorption ability with an adsorption capacity of 30.98 mg/g, which was more than 1.3 times of pristine biochars, and 2–10 times of modified biochars reported by other literatures. Increase of surface area and changes of porous texture, especially the functional groups on the surface of activated biochars are the major contributors to its more efficient adsorption of As(V).

1. Introduction

Biochar, the carbonaceous product of the pyrolysis of biomass, has attracted much research attention recently because of its potential applications in many environmental areas (Ahmad et al., 2014). Recent studies have also shown that biochar has potential as an environmental adsorbent to remove organic and inorganic pollutants from water systems (Mohan et al., 2014). Because of the relatively low cost and the abundance of biomass materials including agricultural and forestry wastes, biochar is becoming a practical alternative remediation agent for heavy metal(loid)s contaminants in the environment (Cao et al., 2009; Chen et al., 2011).

Municipal solid waste (MSW), all solid or semi-solid materials disposed by residents and businesses (excluding hazardous wastes and wastewater) is an inevitable consequence of human activity, and its management directly impacts the health of the people and environment surrounding it (Vergara and Tchobanoglous, 2012). Pyrolysis of MSW is a direct waste-to-energy process, which is suitable for production of gas, liquid and solid hydrocarbons or other valuable products (Ateş et al., 2013). Biochar produced from MSW could be used for energy production like coal or for production of adsorbent (Bernardo et al., 2012). However, the biochar used for heavy metal(loid) adsorbents were mainly obtained from crop straws (Agrafioti et al., 2014), manures (Cao et al., 2009; Meng et al., 2013), broiler litter (Uchimiya et al., 2010b), sewage sludge

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(Uchimiya et al., 2010a), and most of the biochars are directly produced from biomass without any modifications. Few studies were conducted to analyze the effect of MSW-derived biochar on heavy metal(loid) adsorption, especially for waste materials collected mainly from households that consist of paper, plastics, metals, textile, organic wastes, etc.

The main conclusion of previous studies is that biochars obtained from MSW have to be submitted to appropriate treatments in order to improve their quality if a reuse is to be considered (Bernardo et al., 2012; Cheng and Hu, 2010). A modification of biochar with chemical reagents may change porous structure as well as the amount and types of functional groups on the surface of biochar, and consequently change its adsorption capability (Lima et al., 2014; Liu et al., 2012; Trakal et al., 2014). In addition, chemical activation offers other several advantages since it can combine carbonization and activation in a single step, perform at lower temperatures, and enhance in-built catalytic oxidation capability (Liu et al., 2012). Thus, using chemically activated biochar produced from MSW to adsorb heavy metal(loid)s might offer an efficient, simple and low-cost approach for heavy metal(loid) removal from wastewater (Liu et al., 2012). To our knowledge, there is no published study about the MSW-derived biochar for metalloid adsorption.

Arsenic (As), one of the 6 commonly recognized metalloids, is notoriously poisonous to most multicellular life. Mining activities, combustion of fossil fuels, use of As pesticides, herbicides, and crop desiccants and use of As additives to livestock feed create environmental As problems (Fendorf et al., 2010). As contamination of natural waters is mostly caused by inorganic form as oxyanions of trivalent arsenite (As(III)) or pentavalent arsenate (As(V)), which is a problem that affects millions of people across the world (Ahmad et al., 2014). In order to control the As contamination and/or reduce As concentration in waters, numerous processes, such as chemical oxidation, precipitation, adsorption, ion exchange, reverse osmosis and membrane separation have been established (Mohan and Pittman, 2007). Among them, adsorption is an effective technology for the advantages of low cost and straightforward design (Agrafioti et al., 2014; Zhang and Gao, 2013). There have been some studies showed that biochars had high efficiency to remove inorganic As(III) and As(V) (Agrafioti et al., 2014; Samsuri et al., 2013) from aqueous solution, especially for the activated biochars produced from agricultural wastes (Samsuri et al., 2013; Zhang and Gao, 2013; Zhou et al., 2014). It has been reported that the maximum adsorption capacity of As(V) was 17.41 mg/kg adsorbed by modified cotton stalk-derived biochars (Zhang and Gao, 2013). However, the study for inorganic As removal from aqueous solution by MSW-derived biochars has not been reported.

In the whole project, biochars produced from MSW were obtained via slow pyrolysis at 400, 500 and 600 °C and were used to adsorb As(V) and As(III) in aqueous solution. Then the biochar with maximum adsorption capacity was chemically activated using 2 M potassium hydroxide (KOH). This study only focused on the adsorption characteristics of As(V) on pristine and KOH-activated biochars produced from MSW. The specific objectives were to: (1) examine adsorption kinetics and equilibrium isotherms of MSW-derived biochars for As(V); (2) compare physical and chemical properties and As(V) adsorption capacity of KOH-activated and pristine biochars; and (3) identify the mechanisms governing the efficient adsorption of As(V) onto the alkali activated biochars produced from MSW.

2. Methods

2.1. Pyrolysis of MSW

In this work, feedstock MSW was used as biomass obtained from Recycling Center in the City of Austin. Waste materials were collected mainly from households, which were consisted of paper, textile, organic wastes, and a small amount of plastics and metals, etc. The feedstock MSW was dried by air-forced oven at 60 °C for 1 d, then shredded into <2-mm size. The samples were kept in a desiccator for future analysis and pyrolysis.

The ground MSW sample was placed in fixed-bed batch type Parr pressure reactor (28-cm inner height × 14-cm inner diameter; Series 4580 HP/HT, Parr Instrument Company, Moline, IL) with automatic control equipped with a condenser. Detailed information about the batch reactor and pyrolysis process can be found in the previous study of laboratory (Capunitan and Capareda, 2012). The pyrolysis temperature is expected to be the most important factor because the thermochemical changes (e.g., the release of volatiles and condensable compounds from the unorganized phase of the biomass) are all temperature dependent (Tsai et al., 2012). Thus the temperature parameter and pyrolysis speed were considered in the present study. Three different peak temperatures, i.e., 400, 500 and 600 °C, were selected to pyrolysis MSW. Approximately 150 g of MSW sample was put into the reactor. Prior to starting each run, the reactor was purged with N_2 gas at less than 10 psi pressure for 20 min to ensure that the process would proceed in the absence of oxygen. The reactor was allowed to be heated under 100 mL/min N_2 gas flow rate until the desired temperature was attained. After maintaining 30 min, the heater was shut down followed by cooling to room temperature inside the reactor, then the products were collected and weighed. The pyrolysis residues (i.e., biochar) were stored in air-tight container, and hereafter referred to as BC400, BC500, BC600.

2.2. Biochar activation

The biochar with maximum adsorption capacity (i.e., BC500 in this study) was chemically activated based on the method reported by Regmi et al. (2012). Basically, 2 g of biochar with 500 mL of 2 M KOH solution were mixed and stirred for 1 h. The suspension was then filtered and the biochar was recovered on VWR Qualitative Filter Paper (Model 28321-077). After that, the filtered biochar was washed with deionized water and the suspension was stirred several times until the pH of the filtrate maintained stable. Then the solution was again filtered and the activated biochar recovered followed by drying overnight in an oven at 105 °C. The activated biochar samples were stored in air-tight container, and hereafter referred to as BCA500.

2.3. Adsorption experiment

2.3.1. Chemical reagents

Distilled deionized water (DDW) was used to prepare all solutions throughout this study. Sodium arsenate monobasic (NaH_2AsO_4) was purchased from VWR International, LLC. Stock solution (1000 mg/L) of As(V) was prepared by DDW. All other chemical reagents used were of analytical reagent grade purchased from VWR.

2.3.2. Adsorption dynamics of As(V)

For kinetic experiment, briefly, 50 mL As(V) solution (50 mg/L) and 0.1 g biochar samples were placed in a 150 mL triangle bottle with cover. The initial pH of the solution was adjusted to 6.0 ± 0.1 by 0.1 M NaOH and HNO_3 solution. All the triangle bottles were sealed and agitated in a temperature-controlled shaker (25 ± 1 °C) at a rate of 110 rpm. At regular time steps (0.5, 1, 2, 3, 4, 5, 6, 10, 15, 20 and 30 h), the suspension was centrifuged and filtered through a 0.45-μm membrane using a syringe. The concentration of As(V) in the filtrate was determined by an inductively-coupled plasma optical emission spectrometry (ICP-OES, Spectro CirOS, Germany). Meanwhile, the equilibrium pH was measured