



Fabrication of magnetic biochar as a treatment medium for As(V) via pyrolysis of FeCl₃-pretreated spent coffee ground[☆]



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ABSTRACT

This study investigated the preparation of magnetic biochar from N₂- and CO₂-assisted pyrolysis of spent coffee ground (SCG) for use as an adsorption medium for As(V), and the effects of FeCl₃ pretreatment of SCG on the material properties and adsorption capability of the produced biochar. Pyrolysis of FeCl₃-pretreated SCG in CO₂ atmosphere produced highly porous biochar with its surface area ~70 times greater than that produced in N₂ condition. However, despite the small surface area, biochar produced in N₂ showed greater As(V) adsorption capability. X-ray diffraction and X-ray photoelectron spectrometer analyses identified Fe₃C and Fe₃O₄ as dominant mineral phases in N₂ and CO₂ conditions, with the former being much more adsorptive toward As(V). The overall results suggest functional biochar can be readily fabricated by necessary pretreatment to expand the applicability of biochar for specific purposes.

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1. Introduction

A concept of utilizing waste biomass for energy recovery has been gaining increasing attention as a sustainable approach to cope with massive amounts of organic wastes generated by human activities (Kwon et al., 2015). Pyrolysis is considered as a promising fuel processing technique since virtually all biomass wastes can be converted into hydrocarbons such as synthetic gas and oil, which can be further purified and/or upgraded with/without catalytic applications to meet the standard fuel properties. Biochar is another byproduct mainly composed of carbon with highly porous structure and biological/chemical stability (Ghaffar et al., 2015). Due to these favorable properties, biochar has been utilized in agricultural practices including land restoration (Lehmann, 2007), crop yield improvement (Zhang et al., 2014), and soil amendment (Li et al., 2016).

The use of biochar as a treatment medium for environmental remediation has attracted much research interests because of its

effectiveness and economic feasibility. Despite the material properties varies in largely depending on the type of feedstock biomass and pyrolytic parameters, biochar commonly contains a large number of functional groups capable of binding various type of contaminants (Cho et al., 2016b). Biochar has been tested as adsorbent in the removal of various heavy metals and organic contaminants from water (Clemente et al., 2017; Sun et al., 2016). For example, Clemente et al. (2017) assessed the adsorption performance of diverse biochar fabricated in different conditions (feedstock, temperature, reaction time etc.) toward Cd(II), Ni(II), Pb(II), Cu(II) and Zn(II). Sun et al. (2016) examined the adsorption of sulfamethoxazole by biochar in the presence of low molecular weight organic acids.

However, most biochar for environmental application exhibit high pH due to the escape of hydrogen molecules as well as the accumulation of highly alkaline mineral ash during pyrolysis (Jung et al., 2016; Luo et al., 2015; Tian et al., 2016), and this limits their application to treat anionic contaminants, especially As(V) that is highly mobile in high pH conditions (Zheng et al., 2012). In addition, carboxyl group, one of the most common functional groups in biochar, has low affinity to As(V). Thus, it is desirable to find suitable ways to modify or functionalize biochar for better treatment of As(V)-contaminated soils or waters.

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In an effort to produce functionalized biochar, several researchers have manipulated different pyrolysis parameters including ash content (Li et al., 2017), pressure (Azuara et al., 2016), feedstock type (Higashikawa et al., 2016), and pyrolysis temperature (Lyu et al., 2016) to impart desired functionalities to biochar, but little study has investigated in depth such modifications specifically for As(V) treatment. In addition, recent studies revealed that magnetic biochar adsorbents had good adsorption ability for arsenic adsorption and they can be facilely separated after use by external magnet (Tian et al., 2011; Wang et al., 2015b; Zhang et al., 2016).

For the synthesis of magnetic biochar, several researchers have pretreated biomass with iron salts prior to pyrolysis or have modified as-prepared biochar via co-precipitation of ferrous/ferric ions on the biochar surface (Zhang et al., 2013, 2016). Such different synthesis methods resulted in different degrees of arsenic removal (Baig et al., 2014). For example, Fe-biochar prepared by co-precipitation showed greater As(V) adsorption capability than that prepared by pretreatment (Wang et al., 2015a).

To our knowledge, the influence of atmospheric gas in pyrolysis on the performance of magnetic biochar in As(V) adsorption has yet been reported. In our recent study, the effectiveness of using CO₂ as a pyrolytic medium in the production of syngas, and enhancement of pore structure of produced biochar has been demonstrated (Cho

et al., 2015; Kim et al., 2016; Kwon et al., 2012). In this study, spent-coffee ground (SCG) was used as initial feedstock for fabricating biochar because a considerable amount of SCG is generated daily from commercial coffee beverage consumption, and SCG contains various organic carbon components (i.e. fatty acids, lignin, cellulose, hemicellulose, and other polysaccharides) that could offer advantageous properties as an environmental medium upon heat treatment. Magnetic biochar adsorbents were produced from FeCl₃-pretreated SCG in two different atmospheres (N₂ and CO₂), and their As(V) adsorption capability was evaluated. The magnetic biochar samples were characterized using various spectroscopic instruments, a magnetometer and a surface analyzer. As(V) adsorption tests with the biochar samples were conducted under varying experimental parameters including equilibrium pH, contact time, and initial As(V) concentration.

2. Experimental section

2.1. Materials

Quartz tubing with a dimension of 25.4 mm outer diameter and 610 mm length (Chemglass CGQ-0900T-13) was used as the tubular reactor (TR) for pyrolysis. Alumina crucible (1 cm × 1.5 cm × 7 cm, Ohyunstar Co., South Korea) was used as a sample container that

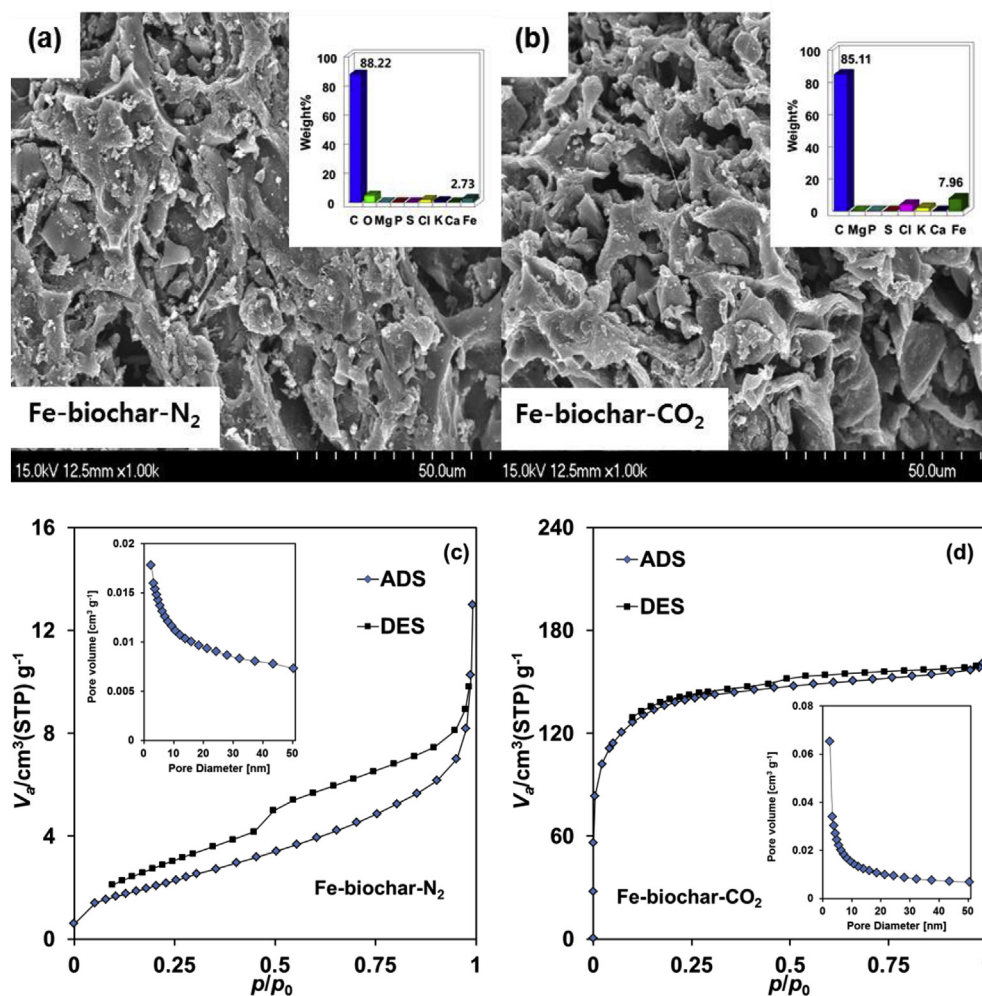


Fig. 1. (a,b) FE-SEM/EDX data and (c,d) N₂ adsorption/desorption isotherm of Fe-biochar generated in N₂ and CO₂ (ADS: N₂ adsorption, DES: N₂ desorption) and inset figure of pore volume with pore diameter.

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