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Heavy metal removal from aqueous solutions using engineered magnetic biochars derived from waste marine macro-algal biomass

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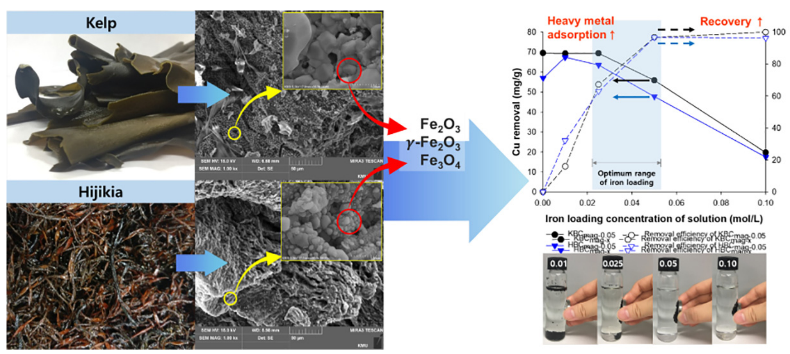
HIGHLIGHTS

- Magnetic biochar derived from marine macro-algae was made for heavy metal adsorption.
- Physicochemical properties and isotherms were characterized using various techniques.
- Iron-loaded condition was optimized for Cd, Cu, and Zn removal and magnetic separation simultaneously.
- Magnetic macro-algae biochar had high selectivity for Cu with plentiful O-containing groups.
- Adsorption and recovery ability showed an opposite tendency as iron doping increased.

GRAPHICAL ABSTRACT



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ABSTRACT

Despite the excellent sorption ability of biochar for heavy metals, it is difficult to separate and reuse after adsorption when applied to wastewater treatment process. To overcome these drawbacks, we developed an engineered magnetic biochar by pyrolyzing waste marine macro-algae as a feedstock, and we doped iron oxide particles (e.g., magnetite, maghemite) to impart magnetism. The physicochemical characteristics and adsorption properties of the biochar were evaluated. When compared to conventional pinewood sawdust biochar, the waste marine algae-based magnetic biochar exhibited a greater potential to remove heavy metals despite having a lower surface area (0.97 m^2/g for kelp magnetic biochar and 63.33 m^2/g for hijikia magnetic biochar). Although magnetic biochar could be effectively separated from the solution, however, the magnetization of the biochar partially reduced its heavy metal adsorption efficiency due to the biochar's surface pores becoming plugged with iron oxide particles. Therefore, it is vital to determine the optimum amount of iron doping that maximizes the biochar's separation without sacrificing its heavy metal adsorption efficiency. The optimum concentration of the iron loading solution for the magnetic biochar was determined to be 0.025–0.05 mol/L. The magnetic biochar's heavy metal adsorption capability is considerably higher than that of other types of biochar reported previously. Further, it demonstrated a high selectivity for copper, showing two-fold greater removal (69.37 mg/g for kelp magnetic biochar and 63.52 mg/g for hijikia magnetic biochar) than zinc and cadmium. This high heavy metal removal performance can likely be attributed to the abundant presence of various oxygen-containing functional groups (—COOH and —OH) on the magnetic biochar, which serve as potential adsorption sites for heavy metals. The unique features of its high heavy metal removal performance and easy separation suggest that the magnetic algae biochar can potentially be applied in diverse areas that require biosorbents for pollutant removal.

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1. Introduction

Biochar is a porous carbonaceous material derived from pyrolyzing organic biomass under oxygen-limited conditions. Biochar has attracted considerable attention in recent years due to its notable properties, for example, its low cost, eco-friendliness, and the wide range of available feedstock materials, as well as mechanical and thermal stability, which facilitate the application of biochar in many environmental areas (Mohan et al., 2015; Tan et al., 2015). Recently, the removal of heavy metals has become a key area of research interest in relation to the potential of biochar for wastewater remediation. Due to the rapid development of industries, heavy metals are gradually discharged into the environment. Moreover, heavy metals are non-biodegradable and bio-accumulating substances, which are known to be toxic to living organisms even at very low concentrations (Fu and Wang, 2011; Ju et al., 2009). Hence, heavy metal removal is necessary.

In many previous studies, biochar exhibited a great potential for heavy metals adsorption in wastewater due to the presence of a highly porous structure and diverse functional groups (Li et al., 2017; Lu et al., 2012). For example, various biochars derived from sawdust (Kaczala et al., 2009), peanut shells (Zhang et al., 2015), and energy cane (Mohan et al., 2015) have previously been studied as sorbents to remove heavy metals. The most commonly used feedstock materials for biochar are agricultural wastes such as wood, rice straws, and fruit peel. As the research into biochar has been particularly active in recent years, various kinds of raw materials have been applied to remove heavy metals. Daily manure (Cantrell et al., 2012; Kołodyńska et al., 2012), wastewater sludge (W. Zhang et al., 2013), micro algae (Bird et al., 2011), and marine macro-algae (Jung et al., 2016; Kim et al., 2016) represent some examples of these raw materials. Among them, according to our preliminary work, marine macro-algae has a relatively high pH and various oxygen-containing functional groups on the biochar surface, which suggests it is beneficial for the removal of cationic heavy metals.

Despite the good sorption ability of biochar, powdered biochars are difficult to separate from the aqueous solution when applied in the wastewater treatment process due to the small particle sizes and lower density (Chen et al., 2011). Not only biochars but also many adsorbents such as activated carbon (Ai et al., 2010) and zeolite (Mthombeni et al., 2015) have difficulties in use due to the same reasons. To overcome this disadvantage, several trials have been performed to modify adsorbents with magnetic materials so as to achieve better separation after use (Ifthikar et al., 2017; Mohan et al., 2014; Trakal et al., 2016). However, many investigations of magnetic biochars have been biased toward the study of anionic heavy metals and organic materials in order to emphasize the adsorption ability of biochars, whereas studies concerning cationic heavy metals adsorption are lacking. Therefore, it is necessary to evaluate the effect of magnetic loading on biochar in terms of the cationic heavy metals adsorption capacity as well as to determine the optimum production conditions for magnetic biochar with regard to cationic heavy metal removal and biochar recovery after use.

In this study, a new type of magnetic biochar was developed using wasted marine macro-algae. The base carbonaceous materials used in the study were wasted kelp and hijikia, which is a common seaweed found in South Korea that causes waste problems, and iron oxide particles (Fe_2O_3, γ-Fe_2O_3, and Fe_3O_4) were doped onto the pristine biochar surface in order to impart magnetism. The iron oxides were doped onto the biochars in order to improve the recovery and reuse potential after adsorption without sacrificing the heavy metal adsorption efficiency. Cationic heavy metals such as copper, cadmium, and zinc were selected as the target substances for removal in this study. This study aims to (1) produce magnetic biochars with iron oxides using wasted kelp and hijikia, (2) evaluate the properties and adsorption capabilities of the magnetic biochars, and (3) optimize the manufacturing condition for the magnetic biochars in terms of the cationic heavy metals adsorption ability and used magnetic biochar recovery.

2. Materials and methods

2.1. Manufacture of magnetic algae biochars

In order to evaluate the properties of the magnetic biochars, both pristine biochars and magnetic biochars were manufactured and investigated. The raw biomasses used for the biochar production in this study were wasted kelp and hijikia collected from Busan, Korea. The kelp and hijikia were thoroughly washed, air-dried for 24 h, and then exsiccated for more than 12 h in a drying oven. The prepared materials were ground using a home grinder into 0.18–1.7 mm diameter particles.

The magnetic biochars were prepared by modifying the approach of Zhang et al. (M. Zhang et al., 2013). A diagram of the manufacturing procedure for the magnetic biochars is shown in Fig. 1. $FeCl_3 \cdot 6H_2O$ was used for the biochar magnetization. Each 30 g sample of the prepared kelp and hijikia was immersed in 500 mL of $FeCl_3$ solution at different molar concentrations (0.01–0.1 mol/L) for 30 min with vigorous magnetic stirring. Additionally, the mixture was aged in a drying oven at 70 °C for 30 min and then separated from the $FeCl_3$ solution. Subsequently, the collected materials were pyrolyzed in a muffle furnace (Nabertherm, Germany) at 500 °C with N_2 gas flow. The N_2 gas injection was performed to prevent the ignition of the organic materials until the internal temperature of the furnace was below 100 °C. The heating rate for pyrolysis was 7 °C/min, while the residence time was 2 h. The pyrolyzed magnetic biochars were washed with deionized (DI) water and oven dried before use. The magnetic biochars derived from kelp and hijikia are hereinafter named as KBC_{mag-x} and HBC_{mag-x}, with x indicating the molar concentration of the Fe loading solution, which ranged from 0.01 to 0.1 mol/L.

Additionally, as a control, non-magnetic biochars were prepared using marine algae according to the same pyrolyzing conditions. The attained kelp biochar and hijikia biochar are referred to as KBC and HBC, respectively.

2.2. Characterization of the surface properties

The specific surface area was quantified using an N_2 multilayer surface area and porosity analyzer (Micromeritics ASAP 2020N, USA). The biochar samples were degassed under a vacuum at 623 K for 4 h, before being filled with N_2 gas at different vapor pressures. The measured data were fitted according to the Brunauer-Emmett-Teller (BET) method. The element C, H, N, O, and S composition in the biochar samples was determined using an elemental analyzer (Elementar vario MICRO cube, Germany) with a detection limit of 0.1%. The presence of the functional groups on the surface of the biochars and magnetic biochars was observed using a Fourier transform infrared spectrometer (FTIR; Bruker Vertex 80 V, USA). The FTIR spectra of the materials were recorded from a range of 4000 to 400 cm^{-1} with a resolution of 0.96 cm^{-1}. A scanning electron microscope (SEM; Tescan MIRA-3, Czech Republic) was employed to determine the surface physical morphology. The magnetic properties of the kelp magnetic biochar and hijikia magnetic biochar were assessed using a vibrating sample magnetometer (VSM; Lake Shore 7404, USA) with an extended field (−15,000 to 15,000 G) at room temperature. The crystallographic structures of the biochars were observed using X-ray diffraction (XRD; RIGAKU SmartLab, Japan), and the samples were scanned from 5 to 90° with a scan speed of 2°/min. The zeta potentials of the biochars were measured by a zeta potential analyzer (ELSZ-2000, Otsuka Electronics, Japan).

2.3. Heavy metals adsorption experiments

In order to measure the heavy metal removal of the prepared biochars, batch adsorption experiments were conducted by mixing 0.5 g of the biochar with 30 mL of cadmium, copper, and zinc solutions in 50 mL vials at room temperature. The metal solutions (500 to