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Fabrication of engineered biochar from paper mill sludge and its application into removal of arsenic and cadmium in acidic water

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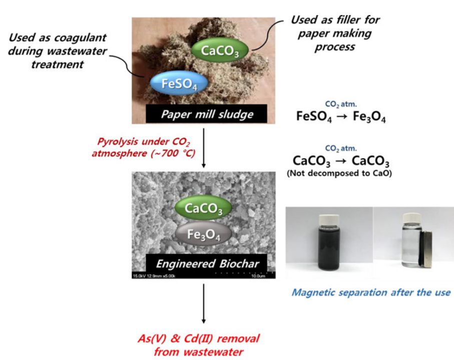
HIGHLIGHTS

- Fabrication of engineered biochar with paper mill sludge in a single step.
- High fraction of Fe- and Ca solid minerals in the biochar.
- pH neutralization of acidic wastewater with addition of biochar.
- Simultaneous adsorption capability of the biochar for As(V) and Cd(II).

GRAPHICAL ABSTRACT



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ABSTRACT

An engineered biochar was fabricated via paper mill sludge pyrolysis under CO_2 atmosphere, and its adsorption capability for As(V) and Cd(II) in aqueous solution was evaluated in a batch mode. The characterization results revealed that the biochar had the structure of complex aggregates containing solid minerals (FeO, Fe_3O_4 and $CaCO_3$) and graphitic carbon. Adsorption studies were carried out covering various parameters including pH effect, contact time, initial concentrations, competitive ions, and desorption. The adsorption of As(V) and Cd(II) reached apparent equilibrium at 180 min, and followed the pseudo-second-order kinetics. The highest equilibrium uptakes of As(V) and Cd(II) were 22.8 and 41.6 mg g^{-1}, respectively. The adsorption isotherms were better described by Redlich-Peterson model. The decrease in As(V) adsorption was apparent with the increase in PO_4^{3-} concentration, and a similar inhibition effect was observed for Cd(II) adsorption with Ni(II) ion. The feasibility of regeneration was demonstrated through desorption by NaOH or HCl.

1. Introduction

Environmental pollution by heavy metals has markedly accelerated with rapid industrialization in recent decades. Heavy metals can pose detrimental threats to human health since they are highly toxic and carcinogenic even at very low concentration levels (Beyki et al., 2016). Contamination of surface water and groundwater

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bodies by heavy metals originates from various industrial activities including mining, metal plants, textile, batteries, pulp/paper, and cloth industries (Chang et al., 2016). Among these contamination sources, acid mine drainage (AMD) arising from mining activities is of a significant concern, and treatment of AMD is one of the greatest environmental challenges in the world (Hedrich and Johnson, 2014). The AMD has a very low pH value (<3), and contains diverse inorganic contaminants such as anionic metalloids and cationic metals (Gurung et al., 2017).

Arsenic (As) and cadmium (Cd) are anionic and cationic heavy metals commonly found in AMD, respectively. Arsenic occurs as two species of arsenate (As(V)) and arsenite (As(III)), and is mainly found in mining regions rich in arseno-metal sulfide minerals (Le Pape et al., 2017). Due to the high toxicity and adverse effects of arsenic, the recommended standard in drinking water level is set up at 10 ppb in the WHO guideline (Mahimairaja et al., 2005). Cadmium has been also reported to be very toxic, and the exposure to Cd can lead to fatal damages to human organs including kidney, nervous system, and blood vessel (Bolan et al., 2013a,b). Various technologies such as chemical precipitation (Guo et al., 2016), membrane separation (Arevalo et al., 2013), and adsorption (Streat et al., 2008) have been employed to treat waters contaminated with As and Cd. Among these technologies, adsorption has gained much recognition as a viable method because of its simplicity, low operation cost, technical flexibility (Jiang et al., 2016).

In the treatment of acidic metal-contaminated water by adsorption, it is highly desirable to restore the quality of water by increasing the solution pH to neutral values. In this regard, the use of alkaline adsorbent that can neutralize the acidity is preferable. For example, limestone ($CaCO_3$) or steel slag containing Fe, Mn, Ca, and Si have been used as treatment medium for acidic wastewater due to their great potential in increasing the solution pH as well as adsorbing/precipitating the metals (Lee et al., 2016). However, liming is not suitable for the treatment of As-contaminated wastewater because limestone has little ability to adsorb anionic metalloids, whereas steel slag has demerits such as leaching problem of heavy metals in acidic conditions.

Most biochars are alkaline due to the release of alkaline minerals (i.e., Ca, Mg) from thermal degradation of biomass feedstocks during pyrolysis. Biochar has received considerable interests as a treatment medium for environmental remediation because of its advantageous physical properties associated with high surface area and porous structures (Ahmad et al., 2014). Biochar prepared from poultry litter has been applied to treat acidic wastewater, and synergistic effect for metals removal was demonstrated (Oh and Yoon, 2013). However, the issues associated with separation of used biochar and low adsorption ability toward anionic metalloids of biochar were not fully resolved in the study.

Paper mill sludge (PMS) is generated during wastewater treatment in pulp and paper industry, and contains high concentrations of inorganics (*i.e.*, Ca and Fe species) due to addition of those chemicals in the treatment process (Kunhikrishnan et al., 2012). Our previous work has used PMS as a feedstock of pyrolysis to obtain renewable energy (*i.e.*, syngas) in the presence of CO_2 (Cho et al., 2017a). It also produced magnetic biochar rich in Fe/Ca minerals with high alkalinity. These characteristics of PMS-derived biochar could be advantageous to the treatment of acidic wastewater containing cationic metals and anionic metalloids.

In this work, engineered biochar was fabricated with PMS via pyrolysis under CO_2 atmosphere, and applied for the adsorption of As(V) and Cd(II) in strongly acidic solution. The physicochemical properties of the biochar were characterized using various microscopic/spectroscopic instruments. The adsorption ability of the biochar was evaluated under various parameters such as solution pH, contact time, initial concentrations, and effect of competitive ions. Desorption kinetics experiment was conducted to investigate the regeneration possibility of used biochar.

2. Materials and methods

2.1. Chemical reagents

Paper mill Sludge (PMS) was obtained from a wastewater treatment plant of Moorim Paper Co., South Korea. Sodium arsenate dibasic heptahydrate ($Na_2HAsO_4{\cdot}7H_2O$), cadmium nitrate tetrahydrate ($Cd(NO_3)_2{\cdot}4H_2O$), sodium phosphate dibasic (HNa_2O_4P), sodium bicarbonate ($NaHCO_3$), sodium chromate (Na_2CrO_4), nickel nitrate ($Ni(NO_3)_2$), calcium nitrate ($Ca(NO_3)_2$) and ammonium nitrate (NH_4NO_3) were purchased form Sigma Aldrich, USA. Inductively coupled plasma (ICP) standard solution (multi-element standard solution XVI, 100 mg L^{-1} of As, Cd, Ca, Cr, Fe, Pb etc.) in diluted nitric acid (2%) was purchased from Merck Millipore Co., USA.

2.2. Preparation of engineered biochar

A batch type tubular reactor (TR) was used to fabricate engineered biochar. A 25.4 mm of stainless Ultra Torr Vacuum Fitting (Swagelok SS-4-UT-6-400) was used to connect the both ends of the TR that was housed in a quartz tubing (25.4-mm outer diameter and 610 mm in length, Chemglass CGQ-0900T-13, USA). The atmospheric gas of CO_2 used in the experiments was obtained from Daesung Gas Co., South Korea and was ultra-high purity (UHP) grade. The gas flow rate was controlled with mass flow controller (5850E, Brooks, USA). The flow rate was increased from 500 mL min^{-1} set up in the previous study (Cho et al., 2017a) to 600 mL min^{-1} to provide enough amount of CO_2 in the production of a large amount of biochar. A split-hinged programmable furnace (FT-830, DAIHAN Scientific) was used to manipulate the pyrolysis temperature. The loaded amount of PMS was 40 g inside the TR and the heating rate of 10 °C min^{-1} ranged from 270 to 720 °C (45 min). This temperature condition has been fully justified by our previous work to generate highly porous biochar from diverse biomass feedstocks (Cho et al., 2017 b). The resulting biochar is denoted as paper mill sludge-derived biochar (PMSB).

2.3. Characterization of the biochar

The morphology and elemental information of the biochar were examined using a field emission-scanning electron microscope (FE-SEM, Hitachi S-4700, Japan) and energy-dispersive X-ray spectroscopy (EDS). Brunauer–Emmett–Teller (BET) analysis was conducted with a surface analyzer (Belsorp-mini II, USA). X-ray diffraction (XRD, D8 Advance, Bruker-AXS) analysis was performed to indentify the mineral phases on the biochar. Thermogravimetric analysis (TGA, Q600, TA Instrument) was carried out to identify the chemical composition. High-performance X-ray photoelectron spectrometer (XPS, K-ALPHA$^+$, Thermo Scientific) was used to investigate the composition and chemical state of elements on the surface of the biochar. Raman spectra were obtained using a Dimension P1 Raman spectroscopy (Lambda Solution Co., USA).

2.4. Adsorption experiments

All the adsorption experiments were performed using 25 mL high-density polyethylene (HDPE, Fisher Scientific, USA) vials in duplicate at room temperature (25 ± 2 °C), and the HDPE caps were used to seal the vials. The pH values of solution were adjusted with 5 M HNO_3 and 5 M NaOH. The solution was shaken at 200 rpm using an orbital shaker (Stuart, UK). The samples were filtered with