Chemosphere 208 (2018) 408–416

Contents lists available at ScienceDirect

Chemosphere

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

Enhanced sorption of hexavalent chromium [Cr(VI)] from aqueous solutions by diluted sulfuric acid-assisted MgO-coated biochar composite

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HIGHLIGHTS

- MgO coated biochar composite can effectively remove Cr(VI) from solutions.
- Acid pretreatment enhanced Cr(VI) removal by MgO coated biochar.
- Reduced secondary pollution risks [Cr(III)] in MgO-coated biochar treatments.
- 74.3% of sorbed Cr(VI) on MgASHR$_{550}$ existed in the hexavalent oxidation state.
- MgSHR$_{550}$ and MgASH$_{R550}$ demonstrated high reusability.

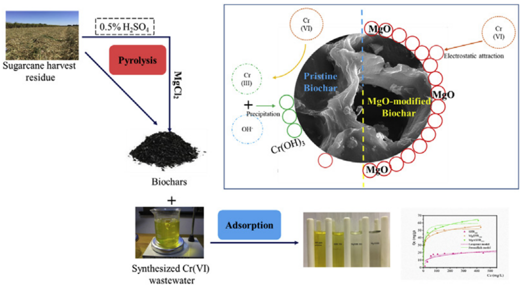
ARTICLE INFO

Article history:
Received 4 January 2018
Received in revised form
8 May 2018
Accepted 28 May 2018
Available online 31 May 2018

Handling Editor: Patryk Oleszczuk

Keywords:
Cr(VI) ions
Sulfuric acid hydrolysis
Sugarcane harvest residue
MgO coated biochar composite
Sorption

GRAPHICAL ABSTRACT



ABSTRACT

Metal oxide-Carbon composites have aroused great interesting towards specific anionic contaminants removal from the polluted environment. In this study, aiming at removing toxic chromate ion [Cr(VI)] from aqueous solutions, a novel approach was developed to produce surface-enhanced MgO-coated biochar adsorbent from sugarcane harvest residue (SHR). It was found that sulfuric acid hydrolysis and MgO-coating both facilitated the removal of Cr(VI) by biochars, and the maximum sorption capacities for the pristine biochar (SHR$_{550}$), MgO-coated biochar (MgSHR$_{550}$), and acid-assisted MgO-coated biochar (MgASHR$_{550}$) that derived from the Langmuir isotherm model were 20.79, 54.64, and 62.89 mg g^{-1}, respectively. Additionally, the Cr(VI) removal was a pseudo-second-order kinetic model controlled process with equilibrium reached within 24 h. The mechanism investigation revealed that Cr(VI) ions was directly sorbed by the MgO-coated biochars via the chemical interaction between MgO and Cr(VI), whereas the sorption-coupled reduction of Cr(VI) to Cr(III) governed the sorption of Cr(VI) on the SHR$_{550}$. Although the increases of solution pH (>2.0) and KNO_3 concentration (>0.05 mol L^{-1}) reduced the Cr(VI) removal by biochars, while there were lower secondary pollution risks in MgO-coated biochar treatments due to the suppressed release of Cr(III) in solutions. This work could provide guidance for the production of efficient biochar for the removal of Cr(VI) from wastewater.

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https://doi.org/10.1016/j.chemosphere.2018.05.175
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1. Introduction

Chromium (Cr) is a common contaminant in the wastewater from several industries such as leather tanning, pigment manuscript, metal finishing, and wood preservation (Miretzky and Cirelli, 2010; Lyu et al., 2017). In the aquatic environment, Cr generally exists in either trivalent [Cr(III)] or hexavalent [Cr(VI)] oxidation states (Lyu et al., 2017). Chromium (III) is less toxic and at low dosages is essential for the sugar and lipid metabolism of organisms (Pechova and Pavlata, 2007), whereas Cr(VI) is highly toxic and carcinogenic/mutagenic for both animals and plants (Miretzky and Cirelli, 2010). Moreover, Cr(VI) exhibits higher solubility and mobility than Cr(III) in aqueous solutions (Dong et al., 2017; Yu et al., 2018). Therefore, the detoxification of Cr(VI)-containing effluent before discharge is imperative for environmental and ecological safety.

So far, biochar has proved a universal adsorbent for pollutants due to its favorable physicochemical properties and relatively low cost (Ahmad et al., 2014; Tan et al., 2015; Niazi et al., 2018a; b). However, the use of biochar in wastewater treatment has been restricted by its limited sorption capacities for anionic pollutants such as phosphate (PO_4^{3-}), nitrate (NO_3^-) and arsenate (AsO_4^{2-}) due to the electrostatic repulsion between the predominantly negatively charged biochar surface and the anions (Yao et al., 2012; Niazi et al., 2018a; b). Therefore, the elimination of the electrostatic repulsion and the enhancement of the removal efficiencies of biochars has become a problem of significant interest.

The coating of biochar with metal oxides/hydroxides is an effective method for the alteration of the biochar surface electrochemical properties (i.e., from the negatively-charged surface to the positively-charged surface) (Rajapaksha et al., 2016; Li et al., 2018). Three methods that are commonly utilized for engineered biochar production are: 1) pyrolysis of element enriched biomass, 2) impregnation of the biomass with metal salts followed by pyrolysis, and 3) insertion of metal oxide into pristine biochars (Tan et al., 2016). Using these methods, numerous biochars have been produced with significantly improved removal efficiencies for anionic pollutants such as PO_4^{3-} (Yao et al., 2011; Zhang et al., 2012; Li et al., 2016, 2017), NO_3^- (Zhang et al., 2012; Usman et al., 2016), and AsO_4^{2-} (Zhang et al., 2013; He et al., 2017). Among these engineered adsorbents, MgO-coated biochars have shown excellent performance for the removal of anionic pollutants that was better than that of other produced biochars (Yao et al., 2011; Zhang et al., 2012; Li et al., 2017). Unfortunately, few studies have focused on the removal of Cr(VI) from aqueous solutions with the MgO-coated biochar composite. Moreover, a prevalent challenge associated with Cr(VI) sorption on pristine/engineered biochars was the release of Cr(III) cations during the sorption process (Dong et al., 2011; Huang et al., 2016), which could result in secondary pollution once the Cr(III) was oxidized to Cr(IV) (Shi et al., 2018). Therefore, this defect should be addressed when designing biochar-based Cr(VI) adsorbents.

Furthermore, a higher removal efficiency is always favorable for the commercial utilization of biochar as an adsorbent. The improvement of the adsorbent physical structure is an optimal method for enhancing its performance in pollutant removal. For example, a significantly improved PO_4^{3-} removal efficiency ($620\ mg\ g^{-1}$) was obtained by a porosity-enhanced MgO/biochar (Jung and Ahn, 2016). Additionally, Wang et al. (2015) considered that the increased biochar surface and the existence of surface MnOx particles were the main reasons for the improved adsorption capacities of Pb^{2+}, Cu^{2+}, and Cd^{2+}. Therefore, we hypothesized that enhanced physical properties of the feedstock coupled with the introduction of metal oxides/hydroxides into biochars would lead to significantly increased anionic pollutant removal efficiencies.

Biomass surficial physical properties can be enhanced via electrochemical modification, microwave, steam exploration, and acid/base hydrolysis, among which hydrolysis with diluted acid is the most widely applied approach due to the simplicity, safety, and low cost (Baral and Shah, 2017). The original structure of the biomass is destroyed with the formation of the pores because the majority of the hemicellulose is removed and converted into fermentable sugars through acid hydrolysis (Rezende et al., 2011; Asadieraghi and Daud, 2014). Nevertheless, few studies have focused on the preparation of biochars from feedstocks that were pretreated with acid hydrolysis.

Therefore, in this study, surface-enhanced MgO-coated biochars composite were produced from sugarcane harvest residue (SHR) pretreated with diluted sulfuric acid (H_2SO_4) and used for the removal of Cr(VI) from aqueous solutions. The effects of the initial solution pH, ionic strength, Cr(VI) concentration, and contact time on the Cr(VI) removal by the engineered/unmodified biochars were investigated. Furthermore, multiple characterization techniques were employed to explore the possible mechanisms involved in the Cr(VI) removal on the biochars.

2. Materials and methods

2.1. Biochar production

Biomass used in this study was sugarcane harvest residue (SHR), which includes the tops and leaves that deposited on the soil surface after sugarcane harvest using a chopper harvester. The SHR samples were collected from Louisiana State University Agcenter Sugar Research Station at St. Gabriel (LA, USA). After the collection, the samples were washed thoroughly with deionized water (DW, 18.2 MΩ) to remove the surface dust. The biomass was then oven-dried, milled, and sieved to particles with diameter <0.5 mm.

For acid hydrolysis pretreatment, 100 g of SHR were soaked in a flask containing 1000 mL 0.5% H_2SO_4. Sulfuric acid was selected due to its high availability, low cost, and specific effects on cellulose/hemicellulose hydrolysis (Rezende et al., 2011; Baral and Shah, 2017). Additionally, the H_2SO_4 concentration was chosen based on our preliminary experiments (data not shown). The flask was vigorously shaken at 240 rpm for 2 h. Then, the solid-phase material was separated and washed with DW until neutralization. The acid-hydrolyzed SHR (hereafter referred as ASHR) was oven-dried at 80 °C for 24 h. For magnesium (Mg) impregnation pretreatment, 50 g of SHR or ASHR were mixed, respectively, with 1000 mL of $7.5\ g\ L^{-1}$ $MgCl_2 \cdot 6H_2O$ in the flasks and shaken for 12 h. The samples were then oven dried at 80 °C for 48 h prior to the pyrolysis process.

Biochars were then produced by pyrolyzing various precursors [i.e., SHR, ASHR, magnesium modified SHR/ASHR (MgSHR and MgASHR, respectively)] in a muffle furnace at 550 °C for 1 h under the N_2 flow condition. The produced biochars were milled and passed through a 0.25 mm nylon sieve for further usage in sorption experiments and characterization. For the convenience of discussion, biochar samples were referred to as SHR_{550}, $MgSHR_{550}$, and $MgASHR_{550}$, where the SHR, MgSHR, or MgASHR refers to the precursor material and the suffix (550) indicates the production temperature (i.e., 550 °C).

2.2. Biochar characterizations

Biochar pH values were determined at 1:20 (w/v) according to the international biochar initiative (IBI) recommended procedure (IBI, 2012). Total metal contents in biochars were measured using an inductively coupled plasma-atomic emission spectroscopy (ICP-AES, SPECTRO Plasma 3200, Germany) after microwave digested