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Adsorption behavior and mechanism of Cr(VI) by modified biochar derived from *Enteromorpha prolifera*

Youyuan Chen, Baoying Wang, Jia Xin*, Ping Sun, Dan Wu

Key Laboratory of Marine Environment and Ecology, Ministry of Education; Shandong Provincial Key Laboratory of Marine Environment and Geological Engineering (MEGE); College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China

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ABSTRACT

Biochar that was derived from *Enteromorpha prolifera* and magnetically modified (BCF600) was evaluated for its physicochemical properties and Cr(VI) adsorption behavior and mechanism. The results showed that the modified biochar was less porous on surface and loaded with γ-Fe_2O_3 particles. BCF600 exhibited a maximum adsorption capacity for Cr(VI), which acquired from the Langmuir model of 88.17 mg g^{-1} and a removal efficiency of 97.71%, for 100 mg L^{-1} of Cr(VI). The adsorption of Cr(VI) by BCF600 decreased with increasing pH and background ion intensity. Based on the FTIR results, the change in the -OH groups on the surface after adsorption confirmed that electrostatic interaction was likely the preponderant mechanism. In addition, the BCF600 could be easily separated using a magnet and displayed high recyclability. Therefore, this magnetic biochar derived from *Enteromorpha prolifera* has the potential to serve as a highly efficient adsorbent for water pollution control.

1. Introduction

Biochar is a carbon-rich product of biomass pyrolysis under hypoxic or anaerobic conditions (Dawood et al., 2017). It has a strong ability to adsorb various pollutants in water because of its stable porous structure, high specific surface area, and enriched oxygen-containing functional groups; thus, it has attracted much attention (N. Zhou et al., 2017). Presently, many raw materials exist for biochar preparation, such as sawdust (Y.Y. Zhou et al., 2017), rice straw (Qian et al., 2017), bamboo (Fan et al., 2010), rice husk (Ma et al., 2014), safflower seed (Angın, 2013), pinewood (Wang et al., 2015b), olive busk (Demirbas, 2004), *Alternanthera philoxeroides* (Yang et al., 2014), and other ligneous and cellulosic plant carbon, as well as fecal carbon and sludge carbon (Agrafioti et al., 2014a). However, finding cheap biomaterials with superior performance and easy steps for biochar preparation remains a major challenge in conventional wastewater treatment (Inyang et al., 2016). *Enteromorpha prolifera* is a marine macroalgal species that has high reproductive capacity owing to eutrophication and easily forms green tides, which negatively affect marine transportation, tourism, and water quality (Zhou et al., 2010). For instance, in the summer of 2008, an unprecedented outbreak of *Enteromorpha prolifera* occurred in China's Yellow Sea in the port city of Qingdao, with a total salvage of 100 million metric tons (Zhang et al., 2012). In the past ten years since that event, *Enteromorpha prolifera* has maintained its prosperity, thus threatening the economic development of many cities along the coast of the Yellow Sea. Determining how to use and dispose of *Enteromorpha prolifera* in an efficient and environmentally friendly manner is critical for marine environmental protection and efficient resource utilization. Therefore, the feasibility of using *Enteromorpha prolifera* to prepare biochar that can be applied in wastewater treatment has piqued interest.

Until now, the literature on algal biochar and its application remains very limited (Shukla et al., 2017). Studies to date have indicated that biochars produced from algal biomass are fundamentally different from biochars produced from lignocellulosic feedstock (Maddi et al., 2011). Generally, biochars produced from various algal species tend to have low cation exchange capacity, carbon content, and specific surface area, but are high in pH, nitrogen, and extractable inorganic nutrients including P, K, Ca, and Mg (Yu et al., 2017). Given these characteristics of algal biochar, in most studies, it has been used as a soil improver in soil remediation (Li et al., 2011), but little attention has been paid to its adsorption potential. Later, some studies found that the cell wall of algae was composed of sugars, proteins, cellulose, lipids, etc. These constituents comprise hydroxyl, ketonic, phenolic, aldehydic, carboxylic, and other polar functional groups, which could serve as potential adsorption binding sites (Nautiyal et al., 2016), thus inspiring some researchers to hypothesize that algal biochar could be used as an adsorbent. In particular, for macroalgae, Roberts et al. (2015) observed

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* Corresponding author.
E-mail address: xinj15@ouc.edu.com (J. Xin).

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that the specific surface area of biochar produced from macroalgae was relatively higher than that produced from other algal species. Subsequently, studies were conducted on the absorption capacity of algal biochar [*Scenedesmus dimorphus* (Bordoloi et al., 2017), *Enteromorpha prolifera* (Qiao et al., 2017), *Spirulina platensis* (Nautiyal et al., 2016), and *Porphyra tenera* (Park et al., 2016)] for Co(II), polycyclic aromatic hydrocarbons (PAHs), Congo red dye, and copper(II), respectively. However, the findings in these studies concerning algal biochar as an adsorbent for water pollutants were not as ideal as expected. Although these algal biomass sources are readily available and abundant, their adsorption capacities generally lie between 0.05 and 23.00 $\mathrm{mg\,g^{-1}}$ (Bordoloi et al., 2017; Nautiyal et al., 2016; Park et al., 2016; Qiao et al., 2017), which is significantly lower than that of biochar prepared from lignocellulosic feedstock. Therefore, the need to find technical methods to improve the adsorption capacity of algal biochars is urgent.

Recently, many different biochar modification methods have been discussed: (1) chemical modification by increasing surface functional groups, aromaticity, and pore structures (Fan et al., 2010; Ma et al., 2014); (2) simple physical modification by improving biochar carbon structure, surface area, and pore volume (Lima et al., 2010); and (3) load modification by loading metals, oxides, or ions (Han et al., 2015; M. Zhang et al., 2013; Zhou et al., 2014). Among them, magnetic modification, an oxide load-modification method that can both increase adsorption capability and generate recyclability, is an efficient and promising alternative modification method. Wang et al. (2015b) synthesized a magnetic biochar using pinewood that had a As(V) adsorption capacity about 1.6 times higher than that of its corresponding original biochar. The adsorption capacity for As(V) of a magnetic biochar derived from chestnut shell (Z. Zhou et al., 2017) was 45.8 $\mathrm{mg\,g^{-1}}$, which was much greater than that of the pristine biochar (17.5 $\mathrm{mg\,g^{-1}}$). Han et al. (2015) used peanut hull to prepare magnetic biochar, yielding a product that had a Cr(VI) adsorption capacity about 1–2 orders of magnitude greater than that of its corresponding pristine biochar. However, according to our current knowledge, no attempt has ever been made to modify *Enteromorpha prolifera* with this method. Hence, whether the magnetic modification of *Enteromorpha prolifera* derived biochar could significantly increase its adsorption capability and magnetic properties is unknown and needs to be investigated. If the response is positive, deeper insights into the governing sorption mechanism of this modified biochar should be sought.

In this study, a magnetic biochar was synthesized from macroalgae *Enteromorpha prolifera* biomass for the first time and its adsorption behavior and mechanism regarding the target heavy metal Cr(VI) were studied. The main purposes of this study were to: (1) synthesis and characterize the magnetic *Enteromorpha prolifera* derived biochar; (2) explore the adsorption properties and adsorption mechanism of Cr(VI) by magnetic *Enteromorpha prolifera* derived biochar; (3) evaluate the recyclability of the magnetic *Enteromorpha prolifera* derived biochar, and provide scientific guidance for the utilization of *Enteromorpha prolifera*.

2. Materials and methods

2.1. Chemicals and materials

Enteromorpha prolifera powder was purchased from Qingdao Seawin Biotech Group Co, Ltd. The *Enteromorpha prolifera* powder was thoroughly washed using deionized (DI) water and dried in an oven at 80 °C. Then, the biomass was stored in a container before pyrolysis. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), potassium dichromate ($K_2Cr_2O_7$), and other chemicals used were of analytical grade. A 1000 $\mathrm{mg\,L^{-1}}$ Cr(VI) stock solution was produced via dissolving 0.2829 g of K_2CrO_7 in 100 mL of DI water. The diverse concentrations of Cr(VI) solution used in this study were acquired via diluting the stock solution.

2.2. Preparation of magnetic Enteromorpha prolifera derived biochar

The preparation of magnetic *Enteromorpha prolifera* derived biochar was based on the method reported by M. Zhang et al. (2013). Briefly, 50 g of *Enteromorpha prolifera* biomass was added to 500 mL $FeCl_3$ solution at a concentration of 2 $\mathrm{mol\,L^{-1}}$ and stirred for 2 h with a magnetic stirrer at 80 °C. Then, the *Enteromorpha prolifera* biomass was separated from the solution and dried at 70 °C. The *Enteromorpha prolifera* biomass was then placed into a porcelain crucible and capped. The porcelain crucibles were subjected to heating in a muffle furnace for pyrolysis at desired temperature (400 or 600 °C) at the rate of 10 $\mathrm{°C\,min^{-1}}$ and then keep constant for 2 h. After naturally cooling to room temperature (25 °C), the biochar was sieved through a 0.6 mm sieve to produce particles less than 0.6 mm and washed with DI water a few times, then dried at 70 °C for 6 h, and finally put in a closed container before use. The pristine *Enteromorpha prolifera* derived biochar was prepared in the same way, except it was not pretreated with $FeCl_3$. The original biochar samples were designated “BC” and the magnetic biochar samples were designated “BCF” with a suffix indicating the peak temperature of pyrolysis (i.e., BC400, BC600, BCF400, and BCF600).

2.3. Biochar characterization

The surface morphology of the samples was characterized using scanning electron microscopy (SEM) (Hitachi S-4800, Japan). The surface functional groups of the samples were determined via Fourier transform infrared spectroscopy (FTIR) (Bruker TENSOR 27, Germany). The crystallographic structure of the samples was examined through X-ray diffraction (XRD) analysis (Ultima IV, Japan). The specific surface area was quantified using the Brunauer, Emmett, Teller (BET) method (Autosorb-iQ$_3$, USA). The elemental composition of biochars were determined via an elemental analyzer (Vario EL III, Elementar, Germany).

2.4. Sorption experiments

2.4.1. Optimization of preparation parameters

Based on our previous study (Chen et al., 2017), two pyrolysis temperatures (400 and 600 °C) were chosen for biochar preparation. The pristine biochars (BC400 and BC600) and magnetic biochars (BCF400 and BCF600) were prepared at these two temperatures. BCF600, which had a greatest adsorption capacity, was selected based on preliminary experiments; hence, the physicochemical properties and the adsorption behavior and mechanism of BCF600 were further explored.

2.4.2. Adsorption and desorption characteristics

To 50 mL conical vessels, 0.06 g of biochar and 30 mL of Cr(VI) solution were added. The initial pH of the Cr(VI) solutions with no biochar was tested as 5.03 ± 0.02 using a pH meter (HQ30D, Hach, USA). Then, the conical vessels were sealed and shaken in a 25 °C thermostat oscillator with 140 $\mathrm{r\,min^{-1}}$ shock oscillation for 120 h. After the adsorption equilibrated, the suspension was centrifuged at 3000 $\mathrm{r\,min^{-1}}$ for 5 min and the resultant supernatant was filtered at 0.45 μm. The concentration of Cr(VI) was tested with a UV–vis spectrophotometer (Pgeneral T6, China) using diphenylcarbazide spectrophotometry (C.Q. Chen et al., 2011). As a blank, different concentrations of Cr(VI) solution without biochar were separately measured via colorimetric analysis in experiments. No change in absorbance intensity of the solution illustrated that the Cr(VI) solution was stable.

To determine the best dosage of each biochar, different dosages (1, 1.5, 2, 3, 4, 6, 8, 10, 12, 14, and 16 $\mathrm{g\,L^{-1}}$) of the four biochars (BC400, BC600, BCF400, and BCF600) were added to 30 mL of a 100 $\mathrm{mg\,L^{-1}}$ Cr (VI) solution and the adsorption capacities were compared. The kinetic experiments of Cr(VI) adsorption by BCF600 were carried out in 30 mL of 100, 300, and 500 $\mathrm{mg\,L^{-1}}$ Cr(VI) solution, and the concentration of

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