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Role of extracellular polymeric substances in efficient chromium(VI) removal by algae-based Fe/C nano-composite

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HIGHLIGHTS

- Optimal carbonization temperature and Fe(III) addition were determined.
- EPS results in high reductive Fe content and specific surface area.
- EPS affects Cr(VI) removal efficiency of the Fe/C composite owing to the stabilizing property.
- Algae-based Fe/C nano-composite has a 236.9 mg/g removal capacity for Cr(VI).

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ABSTRACT

Subsequent application of the obtained algae by chemical coagulation (e.g. Fe(III) addition) presents a challenge because of various iron compounds in algae. In this study, algae obtained by chemical coagulation were carbonized to yield an algae-based Fe/C nano-composite with a high capacity for hexavalent chromium (Cr(VI)) removal (236.9 mg/g), which is attributed to the high reductive Fe content (e.g., FeS, Fe(0), and FeO) and specific surface area. The optimal conditions—that is, 100 mg/L Fe(III) addition and 800 °C—were determined. Moreover, the role of extracellular polymeric substances (EPS) in carbonization was examined as it affected the product composition and efficiency of Cr(VI) removal, owing to the stabilizing property effect of EPS in algae. Algal EPS induced the homogeneous distribution of Fe compounds on the surface of the algae, and the generated α-FeOOH nanoparticles were wrapped in organic carbon matrix, resulting in a sufficient reaction between Fe compounds and organic carbon during carbonization. X-ray photoelectron spectroscopy showed that reduction and adsorption contributed 83.44% and 16.56% to Cr(VI) removal, respectively. This study provides a new insight into the role of EPS in the efficient Cr(VI) removal by algae-based Fe/C nano-composite and presents a promising application of this Fe/C nano-composite in environmental remediation.

1. Introduction

Algae have uncontrolled growth (algal bloom) in aquatic systems and negatively affect water quality, aquatic ecosystems, and public health; as such, algae have drawn global interest in recent decades (Anderson et al., 2002; Heisler et al., 2008; Hochmuth et al., 2014; Villacorte et al., 2015). Hydrolyzing metal salts, such as iron, aluminum, and their polymers (e.g., polyaluminum chloride and polyferric chloride), are typically used as coagulants to separate or remove algae from water (chemical coagulation) (Hao et al., 2016). Upon adding Fe(III), the positively charged Fe(III) prompts the aggregation of suspended algal cells into larger particles as a result of the electrostatic interaction of the coagulant with the algal cells (Papazi et al., 2010).

Traditionally, the obtained algae are used as potential feedstock for biodiesel production or anaerobic digestion for methane production (Milledge and Heaven, 2013; Ward et al., 2014). However, this application of these obtained algae presents a challenge because of various iron compounds in algae. Therefore, an effective method to deal with these obtained algae has to be developed.

Previous studies have reported on the strong adsorption

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capacity of algae-based biochars for aqueous heavy metal removal (Inyang et al., 2016; Yu et al., 2017). This capacity can be attributed to the considerably high proportion of oxygen-rich functional groups in algae (Bird et al., 2011). Peng et al. (2014) prepared iron-laded biochar derived from microalgae to remove tetracycline. Dried microalgae powder and different amounts of iron salt ($(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$) were mixed for hydrothermal carbonization. This iron-loaded algae-based biochar exhibited excellent removal of tetracycline. However, microalgae and iron salt were simply mixed before carbonization. Johansson et al. (2016) produced Fe–biochar from two algal sources, *Gracilaria* and *Oedogonium*, to remove selenium, arsenic, and molybdenum in an ash disposal effluent from a power station. *Gracilaria* and *Oedogonium* biomass was soaked into the $FeCl_3$ solution before carbonization. This method differs from that employed in the study by Peng et al. (2014). This process yielded iron-impregnated algae, similar to the algae obtained by chemical coagulation. Thus, carbonization of algae can effectively obtain an algae-based Fe/C nano-composite, which may be used for contaminant removal. The Fe/C nano-composite is supposed to exhibit excellent adsorption, attributed to porous carbon structure, as well as reductive property from Fe(II).

Extracellular polymeric substances (EPS), which are excreted by bacteria or algae and consist of various organic substances have different applications in various fields (Wang et al., 2009). In general, among the most important functions of EPS are as fundamental structural elements to determine the mechanical stability of biofilms and to protect the biological system against noxious influences from the environment (Wingender et al., 1999). Moreover, EPS were typically used as stabilizers to avoid the aggregation of nanoparticles. The adsorption of EPS on silver nanoparticles (SNPs) can significantly impart a negative charge to the SNP surface and increase their surface potential, thereby improving the stability of SNPs (Khan et al., 2011). The negatively charged algal EPS play a key role in algal removal by chemical coagulation (Salehizadeh and Shojaosadati, 2003). EPS have been demonstrated as a crucial factor in various fields, however the effect of EPS on the final product composition of algae-based Fe/C nano-composite has not been reported.

Therefore, this study aims to determine the optimal Fe(III) dosage and carbonization temperature and to evaluate the effect of algal EPS on the final product composition of an algae-based Fe/C nano-composite at the optimal Fe(III) dosage and carbonization temperature. Moreover, Cr(VI), as one of the most common representative pollutant, was chosen to verify the removal efficiency of this algae-based Fe/C nano-composite under different EPS conditions. The mechanism of EPS affecting the product composition of the Fe/C nano-composite and Cr(VI) removal was examined. This study can provide a new insight into the role of EPS in efficient Cr(VI) removal by an algae-based Fe/C nano-composite and present an outstanding application of this Fe/C nano-composite for environmental remediation.

2. Materials and methods

2.1. Chemicals

$Fe_2(SO_4)_3$, NaOH, HCl, NaCl, $K_2Cr_2O_7$, and *o*-phenanthroline were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All solutions were prepared with deionized (DI) water.

2.2. Chemical analysis

Cr (VI) concentration was determined spectrophotometrically using 1,5-diphenylcarbazide (Radmila MilaW et al., 1992). Ferrous ions were detected spectrophotometrically using *o*-phenanthroline (Leupin et al., 2005; Wu et al., 2017). Specifically, Fe(II) was sampled and mixed with 1 mL of acetate buffer and 0.4 mL of *o*-phenanthroline; it was then quantified by a UV–vis spectrophotometer (AOE UV-1900, AOE Instruments, China) at 510 nm after 10 min. Total iron was detected using 10% hydroxylamine hydrochloride as reductive reagent to reduce Fe(III) to Fe(II); the concentration of Fe(II) was then measured with the described method (Herrera et al., 1989). The total C, N, H, and S contents were measured by dry combustion (950 °C) with an Elementar Vario EL elemental analyzer (Elementar Analysensysteme GmbH, Germany). Fe content was determined based on spectrophotometry that was described below. The O content was calculated by the difference.

2.3. Algae cultivation and EPS extraction

Chlorella vulgaris, one of the most remarkable green eukaryotic microalgae (Safi et al., 2014), was used in this study. The specific medium and condition of cultivation are presented in the Supplementary Material. A heat extraction method described in previous studies was used to extract algal EPS (Li and Yang, 2007; Wang et al., 2014) and detailed procedure can be found in Supplementary Material. The specific compositions of algal EPS from *Chlorella* (e.g., proteins, polysaccharides, and humus) have been reported in a previous study (Wang et al., 2014).

2.4. Fe(III) addition and Fe/C nano-composite preparation

After cultivation, the algae solution was diluted to $OD_{680} = 1.0$ (0.275 g/L biomass) using DI water to maintain the consistent experimental conditions for all groups. The concentrated $Fe_2(SO_4)_3$ (10 g/L–Fe(III)) solution was then added to the algae solution to achieve four final concentrations of Fe(III) (0, 50, 100, and 200 mg/L). After being deposited for an appropriate time, the supernatant was poured out, and the algal sediment containing Fe compounds was dried in a vacuum freeze drier (Boyi Kang FD-1C, Beijing Boyi Kang Laboratory Equipment Co. Ltd., China). The dry algal sediment was carbonized to 800 °C at a heating rate of 10 °C/min and then maintained at 800 °C for 2 h in a tube furnace under N_2 atmosphere. Other nano-composites were similarly produced at different temperatures (400 °C, 600 °C) and with various concentrations of Fe(III). The obtained samples were referred to as *C.V.*(+)–Fe a or *C.V.*(−)–Fe a (*C.V.* is the abbreviation of *Chlorella vulgaris*), where "-" and "+" indicate that the algal EPS were extracted and not extracted, respectively, and "a" denotes the concentration of Fe(III) addition. The reductive Fe content in the obtained Fe/C nano-composite was measured by adding 0.1 g of the product into 50 mL of 1 M HCl solution, followed by detecting the concentration of Fe(II). Similar experiments in an EPS solution and a non-EPS algae solution were performed consistent with the aforementioned description.

2.5. Cr(VI) removal experiments

Batch equilibrium studies were performed by mixing 0.002 g of Fe/C nano-composite with 19 mL of purged DI water. The reaction was then initiated by adding 1 mL of Cr(VI) stock solution (400 mg/L) to the aforementioned three experimental sets to attain a Cr(VI) concentration of 20 mg/L. Glass vials were then placed in a shaker (at 170 rpm) at room temperature (25 °C). The solution was sacrificially sampled at a predetermined time to measure the concentration of Cr(VI). Unless otherwise stated, all the aforementioned batch experiments were performed in duplicate in 50 mL glass vials sealed with an aluminum cap and under anoxic conditions. The initial pH was adjusted to 5.0 ± 0.2 with 1 M HCl or NaOH solution.