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Capture of perchlorate by a surface-modified bio-sorbent and its bio-regeneration properties: Adsorption, computations and biofouling

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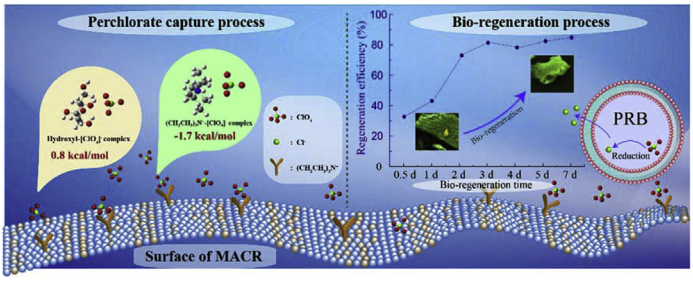
HIGHLIGHTS

- We created a bifunctional bio-sorbent for ClO_4^- capture.
- Laden perchlorate was directly reduced by the perchlorate reducing bacteria.
- A small biofouling was formed on bio-regenerated bio-sorbent due to the EPS.
- DFT analysis corresponded well to the competitive adsorption results.

GRAPHICAL ABSTRACT



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ABSTRACT

A magnetic amine-crosslinked reed (MACR) was synthesized by an insitu precipitation method and used for perchlorate uptake. The morphological properties of clean MACR, perchlorate-saturated MACR and bio-regenerated MACR samples were determined using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and zeta potential measurements. The adsorption capacities of perchlorate by clean and bio-regenerated MACRs were determined. The density functional theory (DFT) method was employed to evaluate the binding free energies between various anions and ammonium/hydroxy groups. The maximum adsorption (Q_{max}) of perchlorate by MACR was calculated to be 195.5–232.8 mg/g at 30–50 °C. The theoretical computation of adsorption-free energies indicated that ammonium groups were dominant in the process of perchlorate adsorption; other anions, such as $[H_2PO_4]^-$, $[NO_3]^-$ and $[SO_4]^{2-}$, showed relatively higher binding free energies than $[ClO_4]^-$, which corresponded to the results of competitive adsorption. The spent MACR was then bio-regenerated in a sealed 250-ml conical flask with perchlorate-reducing bacteria (30 °C, 160 rpm) and reached 81.4% of recovery within 3 days. Some hydrophobic macromolecules of

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extracellular polymeric substances (EPS) might have attached to the surface of MACR, which was validated by the zeta potential, SEM and excitation emission matrix (EEM) fluorescence spectroscopy results.

1. Introduction

Perchlorate is known as an emerging trace inorganic contaminant (Duncan et al., 2005; Hao et al., 2012; Lee et al., 2012; Park et al., 2012) and has been detected in soil, groundwater, surface water and even vegetables/fruits/milk in the United States and China (Duncan et al., 2005; Srinivasan and Sorial, 2009; Bardiya and Bae, 2011; McLaughlin et al., 2011; Hao et al., 2012; Gu et al., 2015; Song et al., 2015a,b,c; Faccini et al., 2016; Yang et al., 2016). Various perchlorate salts employed in rocket fuel (ammonium perchlorate), firework and explosive (perchlorate contaminant) production have contributed to perchlorate pollution worldwide (Lee et al., 2012; Park et al., 2012; Gu et al., 2015; Song et al., 2015a,b,c). Perchlorate is suspected of disrupting the thyroids uptake of iodide, an essential nutrient for the synthesis of thyroid hormones, and subsequently causing the malfunction of nervous system (Wu et al., 2010; Bardiya and Bae, 2011; Gu et al., 2015; Faccini et al., 2016) derived from the interference of iodine uptake by perchlorate. As a result, the U.S. Environmental Protection Agency (EPA) has set a drinking water equivalent level of 15 μg/L for perchlorate; a relevant equivalent level for perchlorate is still not set in China (Ucar et al., 2017).

However, considering its high solubility, trace level, low volatility and chemical inertness in water, decontamination of perchlorate from surface water/groundwater or industrial wastewaters appears somewhat difficult (Son et al., 2006). As a result, a number of studies have focused on multiple perchlorate-decontaminating techniques (Xu et al., 2013; Yang et al., 2016; Zhu et al., 2016; Yao et al., 2017), e.g., membrane separation, adsorption, ion-exchange, bio-remediation/biological treatment, chemical reduction, and electrochemical reduction. These commonly used methods can be divided into two categories: separation techniques (adsorption, ion-exchange, membrane separation) (Giblin et al., 2002; Son et al., 2006; Sanyal et al., 2015) and decomposition techniques (Son et al., 2006; Wang et al., 2014; Song et al., 2015a,b,c; Yang et al., 2016; Yao et al., 2017) (bio-treatment and chemical/electrochemical reduction). Among all these techniques, pore adsorption through activated carbon was proved to be inefficient for perchlorate uptake, and although the membrane filtration technology was effective, the expense of this technology was very high (Srinivasan and Sorial, 2009). In contrast, adsorption through electrostatic attraction or chelate action is an effective and accepted physicochemical technique for perchlorate removal through a convenient operational process. These adsorbents allow for the decontamination of a large bed volume of perchlorate-contaminated water before breakthrough occurs (Srinivasan and Sorial, 2009; Tan et al., 2012; Xu et al., 2014; Song et al., 2015a,b,c), although the innocuous disposal of spent resins and the eluent after the brine techniques requires additional expense. Decomposition efforts for perchlorate have focused primarily on biological treatment methods because the perchlorate in water can be directly decomposed into Cl^- through microbial reduction. However, the application of microbial reduction in perchlorate decontamination remains limited, partially due to (i) large amounts of organic matter discharged into the effluent after the biological process; (ii) trace perchlorate levels in surface water/groundwater (Song et al., 2015a,b,c); and (iii) sensitivity of perchlorate-reducing bacteria (PRB) to pH, temperature and salinity (Song et al., 2015a,b,c).

In this study, microbial reduction was integrated with adsorption for perchlorate decontamination. The perchlorate was first adsorbed by a new magnetic bio-sorbent from water, and the resulting perchlorate-laden bio-sorbent was separated and placed in contact with a perchlorate-reducing bacterial culture for bio-regeneration. Perchlorate-degradation bacteria were cultivated from the seeds of active aerobic sludge. To collect all spent/bio-regenerated bio-sorbents from adsorption and bio-regeneration systems, magnetic bio-sorbent using Giant reed as the starting material was presented. The Giant reed was first magnetized by a magnetization reaction with $FeCl_3$ and $FeSO_4$; then, the magnetic sample was modified by an amine cross-linked reaction, forming a magnetic amine cross-linked reed (MACR) (Song et al., 2015a,b,c; 2016a,b). The composition properties of the magnetic bio-sorbent were determined by X-ray photoelectron spectroscopy (XPS). The bio-regeneration efficiency of spent bio-sorbent was evaluated by comparing the adsorption capacity of MACR with that of bio-regenerated MACR; the biofouling of bio-regenerated adsorbent was also evaluated. Three-dimensional fluorescence spectra were used to detect bacteria transformation during the cultivating process, and a cladogram was also performed. Perchlorate-adsorption tests were conducted under different conditions (pH, temperature, co-existing anions and time). The density functional theory (DFT) method was employed to calculate the adsorption energies between $CH_2CH_3)_3N^+$ and different anions (NO_3^-, ClO_4^-, and $H_2PO_4^-$).

2. Materials and methods

2.1. Chemical reagents and materials

The Giant reed bio-material was collected from Nansi Lake in Shandong Province, China. The raw material was dried at 100 °C for 24 h and crushed into small pieces ranging from 1 to 4 mm. The pieces of Giant reed were then sieved to a proper size (300–600 μm) for further usage. All reagents used in this study were of analytical reagent grade, which were provided by Tianjin Kermel Chemical Reagent Co. (China). All solutions were prepared by ultrapure water (0.055 μS/cm). The pH was adjusted with NaOH solution (1 mol/L) and HCl solution (1 mol/L).

2.2. Preparation of MACR

In this work, we prepared the magnetic bio-sorbent for two purposes: (i) preparing a new magnetic adsorbent with functional groups for preferential adsorption of perchlorate; (ii) improving the separation of spent or bio-regenerated MACR from adsorption/bio-regeneration systems.

MACR was first introduced with nano-Fe_3O_4 and then functionalized with amine groups. Four grams of sieved Giant reed were mixed with 240 ml of a solution containing 0.125 mol/L $FeSO_4$ and 0.25 mol/L $FeCl_3$ in a 500-ml three-neck round-bottom flask. The flask was purged with N_2 for 5 min to keep the reaction system in an oxygen-free condition. The temperature was controlled at 70 °C after adding 25 ml of $NH_3 \cdot H_2O$ (25%), and this temperature was