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Preparation of biochar from *Enteromorpha prolifera* and its use for the removal of polycyclic aromatic hydrocarbons (PAHs) from aqueous solution

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ABSTRACT

EP-biochar was produced from *Enteromorpha prolifera* (EP) at temperatures of 200–600 °C under limited-oxygen conditions and then activated using HCl and HF. To optimize the sorption of pyrene (PYR) and benzo[*a*]pyrene (BaP), the effect of the pyrolysis temperature was studied, and the results showed that EP-biochar produced at 500 °C gave the highest removal efficiency. The physiochemical properties of EP-biochar pyrolyzed at 500 °C were characterized. The examination indicated that the surface area of EP-biochar was 205.32 m^2/g. The effect of the EP-biochar dosage and initial solution pH on the adsorption were studied in batch adsorption experiments. Kinetic studies indicated that the adsorption processes of PYR and BaP agreed well with a pseudo second-order kinetic model. The sorption equilibrium data were well described by the Langmuir model. Desorption experiments were conducted to test the strength of binding interactions of EP-biochar. The results showed that PYR and BaP were difficult to dissolve in water after adsorption. Regeneration experiments demonstrated that the biochars regenerated at 200 °C retained approximately 48% and 40% of their initial PYR and BaP uptake.

1. Introduction

There has been increasing concern over the concentration of polycyclic aromatic hydrocarbons (PAHs) in the effluent of wastewater treatment plants (WWTPs) because WWTPs have been identified as the main contributors of PAHs in the aquatic environment (Tian et al., 2012; Qi et al., 2013; Qiao et al., 2014). PAHs constitute a class of chemical compounds with two or more benzene rings that are organic pollutants and ubiquitous in the environment (Li et al., 2014). PAHs are receiving attention because of their carcinogenicity, teratogenicity and mutagenicity. Some PAHs have already been identified as priority pollutants to be monitored and controlled by Environmental Protection Agencies in the United States and Environmental Monitoring of China (Zhai et al., 2011). Therefore, the concentrations of these pollutants need to be reduced in treated wastewater effluents. According to the physical and chemical properties, PAHs can be divided into low-molecular-weight PAHs (LMW-PAHs) and high-molecular-weight PAHs (HMW-PAHs). The two kinds of PAHs have two to three benzene rings and four to six benzene rings, respectively. The carcinogenicity increases with an increase in the number of benzene rings. Compared with LMW-PAHs, HMW-PAHs are difficult to be biodegraded in the natural environment because of their lower solubility and bioavailability, which means that HMW-PAHs are more harmful to humans.

In recent years, many methods such as chemical oxidation (Neyens and Baeyens, 2003), photocatalytic advanced oxidation (Vescovi et al., 2010) and biological degradation (Allègre et al., 2006) have been used to remove PAHs from wastewater. However, chemical remediation might cause secondary pollution because of the excessive use of chemicals, unreasonable proportions of the reagents and formation of oxygenated species that are potentially hazardous (Rivas et al., 2000). While biodegradation is identified as a promising method to remove PAHs, it is often limited as the survival rate of the PAHs degraders is low in WWTPs. Therefore, new methods must be used to remove PAHs. Biochar adsorption is a widely used method for removing PAHs because the material is easy to obtain, inexpensive and effective (Vijayaraghavan et al., 2006; Vilar et al., 2008). Biochar is widely used as an adsorbent because of the good adsorption performance resulting from the complicated surface structure (Ouyang et al., 2016). Li et al. (2010) reported that the surface properties of biochar could affect the adsorption capabilities of pollutants. El Qada et al. (2008) also showed that the adsorption process was influenced by the surface area and the distribution of pores. These physical and chemical characteristics of

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biochar mentioned above are strongly affected by the raw materials and modification methods. Sun et al. (2013) reported that biochars derived from plants (rice, wheat and maize straw) and biochars made from animal manure (chicken, swine and cow) had different sorption mechanisms. Many kinds of chemical agents have been used to activate biochar, including sulfuric acid, phosphoric acid, KOH and $ZnCl_2$ (Li et al., 2011). The nature of the resultant biochar is significantly influenced by pyrolysis parameters, especially pyrolysis temperature.

Many inexpensive raw materials such as bamboo (Yang et al., 2016), wheat straw (Cao et al., 2016) and sludge (Devi and Saroha, 2015) have been employed for the preparation of biochar, and this has provided prospective pathways for the use of *Enteromorpha prolifera* (EP) to remove the PAHs from water.

EP, a common green alga, is distributed widely in intertidal zones of coastal areas all over the world (Morales, 2005). However, in the past ten years, millions of tons of EP appeared along the coastal areas of the Yellow and East China Seas during May and July under the influence of climate change and sea tide, which caused a series of environmental issues (Ceylan and Goldfarb, 2015; Qiao et al., 2016; Yu et al., 2017). How to transform this waste biomass into high-value bioproducts became a worthy research topic. EP was usually used as traditional food and medicine, and previous studies suggested that biochar made from EP had good adsorption properties for dyes and zinc (Li et al., 2010, 2011). However, little work has been carried out to investigate the adsorption of PAHs on biochar obtained from *Enteromorpha prolifera* (EP).

To expand the application of EP in pollution treatment, EP-biochar was prepared at different pyrolytic temperatures in this study to remove pyrene (PYR) and benzo[*a*]pyrene (BaP), which are difficult for indigenous microorganisms to biodegrade. Physicochemical properties such as morphology, surface characteristics, elemental content, and type of surface functional groups were evaluated. We conducted batch experiments under various conditions such as reaction time, original concentration, biochar dosage and initial solution pH to evaluate the adsorption capacities and mechanisms of PAHs onto biochar.

2. Materials and methods

2.1. Materials and chemicals

EP was collected from the Laoshan coastal district in Qingdao, China; washed repeatedly with distilled water; and then dried in the air. All chemicals were of analytical grade or better. PYR and BaP standard solutions (100 mg/L in methanol) were purchased from AccuStandard, Inc. (New Haven, CT, USA).

2.2. Preparation of EP-biochar

Air-dried EP was ground and sieved through a 2-mm mesh. The pyrolysis process was conducted in a muffle furnace (HMX1400-30 China). The sieved EP was tightly packed into a crucible covered by aluminum foil in the middle of a quartz reactor under a N_2 environment inside the furnace. The pyrolysis temperature gradients were selected at 100 °C temperature intervals from 200 °C to 600 °C. The heating speed was 10 °C/min. The whole pyrolysis process lasted for two hours under a N_2 flow rate of 25 mL/min. After the pyrolysis process, the EP-biochar was sieved through a 0.154-mm mesh and then labeled BC200, BC300, BC400, BC500 and BC600. Then, 20-g EP-biochar samples were added to 200 mL of mixed acid containing 180 mL of hydrochloric acid (HCl) at a concentration of 1 mol/L and 20 mL of concentrated (40 wt%) hydrofluoric acid (HF) for 24 h. The residues were washed repeatedly with distilled water until the pH was neutral. Finally, the EP-biochar samples modified by acid solution were dried at 80 °C for approximately 12 h; labeled DBC200, DBC300, DBC400, DBC500, and DBC600; and then stored for future use.

2.3. Physicochemical characterization of EP-biochar

The surface area of EP-biochar was determined by using an ASAP-2020 surface area analyzer (Micromeritics Instrument Corporation, USA). A scanning electron microscope (SEM) (MIRA3, TESCAN) was applied to measure micrometrics and the surface morphology of the EP-biochar. The elemental analysis of the EP-biochar was recorded by a Vario Elemental Analyzer (Elementar Company, Germany). The functional groups were qualitatively analyzed by a Fourier transform infrared spectrometer (Tensor27, Bruker Company, Germany) in the range 400–4000 cm^{-1} at a resolution of 2 cm^{-1}.

2.4. Batch adsorption experiments

The application of EP-biochar as an adsorbent was explored to remove PYR and BaP from the synthetic solutions. Batch adsorption experiments were conducted in 150-mL glass conical flasks containing 100 mL of PYR or BaP solution. The background solutions contained $CaCl_2$ at a concentration of 0.01 mol/L to maintain constant ionic strength of the adsorption process and $HgCl_2$ at a concentration of 100 mg/L to eliminate the effect of biological activity. The standard solutions of PYR and BaP were diluted to predefined concentrations by adding certain volumes of background solutions as the synthetic wastewater in this study. The amount of methanol in 100 mL of synthetic wastewater should be no more than 1 mL to avoid co-solvent effects.

To determine the optimal pyrolysis temperature and the effect of the acid treatment for EP-biochar, the EP-biochars labeled BC200, BC300, BC400, BC500, BC600, DBC200, DBC300, DBC400, DBC500, and DBC600 were compared in aqueous PYR and BaP adsorption tests. Considering the concentrations of the wastewater and facilitating the study in the laboratory, the standard solutions were diluted with background solution to obtain PYR and BaP solutions with concentrations of 50 μg/L and 20 μg/L, respectively. The dosage of EP-biochar was 0.05 g. The mixtures were shaken in a temperature oscillator (XJ-III, Shaoguan Taihong Medical Instrument Co., Ltd., China) at a constant temperature of 25 °C and 150 rpm for 24 h to achieve adsorption equilibrium. Blank controls containing PYR or BaP solution without biochar were established. The supernatant liquids of the PYR and BaP were analyzed with a gas chromatograph-mass spectrometer (*GC-MS*).

To explore the kinetics of the adsorption process, we conducted batch experiments. The concentrations of PYR and BaP solutions were selected as 50 μg/L and 20 μg/L, respectively. EP-biochar (0.05 g) was added to 100-mL water samples and then the mixtures were shaken in a temperature oscillator at 25 °C and 150 rpm. The samples were taken at predetermined time intervals (10, 30, 60, 120, 300, 480 and 600 min) to measure the kinetics. The replicate tests of samples were carried out three times.

The sorption isotherm studies were described as follows. The concentrations of PYR samples were 10, 20, 50, 80, 100 and 150 μg/L. The concentrations of BaP samples were 10, 20, 30, 40, 50 and 60 μg/L. A total of 0.05 g of EP-biochar was added to 100-mL water samples, and then the mixtures were shaken in a temperature oscillator at 25 °C and 150 rpm to adsorption equilibrium.

Batch experiments were performed to investigate the effect of biochar dosage and pH. Conical flasks were separately filled with 100 mL PYR or BaP solutions and biochar and kept in an oscillator at 25 °C and 150 rpm for 24 h to equilibrium. The adsorption was tested under different biochar dosage from 0.1 to 1 g/L. The initial pH was adjusted to 2, 4, 7, 10 and 12 by NaOH (0.1 mol/L) and HCl (0.1 mol/L) solutions to investigate the effect of original solution pH. The amount of PYR and BaP adsorbed on EP-biochar and the removal rate was calculated by Eqs. (1) and (2).

$$q_e = (C_0 - C_t) \cdot V/m \tag{1}$$

$$\mathrm{R} = (C_0 - C_t)/C_0 \cdot 100\% \tag{2}$$