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Preparation of green alga-based activated carbon with lower impregnation ratio and less activation time by potassium tartrate for adsorption of chloramphenicol

Xiuzhen Zhu, Yuan Gao, Qinyan Yue*, Yujiao Kan, Wenjia Kong, Baoyu Gao*

Shandong Provincial Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Jinan 250100, China

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ABSTRACT

Potassium tartrate ($C_4H_6K_2O_7$) was utilized as a novel activating agent to prepare activated carbon with relatively high specific surface area by using less activating agent and activation time from marine waste–green alga (*Enteromorpha prolifera*) for the first time. The influences of activation temperature, impregnation ratio and activation time on the pore structure were investigated to obtain the optimum conditions (activation temperature: 700 °C, impregnation ratio: 1:1, and activation time: 30 min). Meanwhile, the activation temperature was evaluated to be the essential factor that dominated the form of pore structure in activated carbon. The green alga-based activated carbon that was prepared under optimum conditions has shown the high surface area of 1692 m^2/g and total pore volume of 1.22 cm^3/g, which could be used as an effective adsorbent to remove chloramphenicol. The thermodynamic data of chloramphenicol were well fitted by Langmuir isotherm model and the green alga-based activated carbon has showed high adsorption capacity of 709.2 mg/g towards chloramphenicol.

1. Introduction

Antibiotics have been widely used for high-efficiency killing bacteria in a century (Nie et al., 2015). Nevertheless, their detriments for the aqueous eco-system and human health have been considered to be an intractable issue in recent years. Chloramphenicol (CAP) is one of the broad-spectrum antibiotics (Giri and Golder, 2014). In many countries, CAP has been banned in feed production (Chatzitakis et al., 2008), due to the possibility of aplastic anemia, myelosuppression and cancer etc. Unfortunately, the drug of CAP is still used in some low-income regions for livestock due to its low-cost, efficient bacteriostasis and stability (Nie et al., 2015). The CAP was difficult to be metabolized, therefore, the non-degradable CAP is ejected by the faeces of fowl and aquatic animals and discharged into water or soils (Dai et al., 2016). There were many reports about the findings of the CAP in the sewage (Mohd Din et al., 2015; Qin et al., 2016). In addition, traditional pathways of sewage disposal are unavailable to dislodge the CAP. Therefore, there is an insistent demand for developing a technology to remove the CAP with high efficiency and low-cost to decrease the potential harm to human health and ecosystem.

For removing antibiotics from hospital or pharmaceutical wastewater, adsorption has been regarded as an attractive technique owing to its high adsorption capacity, low-cost and high operability (Liao et al., 2013; Pezoti et al., 2016). Activated carbon (AC) is an excellent material for the treatment of sewage as a result of its larger porosity, chemical stabilization and low selectivity compared to other adsorbents (Pezoti et al., 2016; Yahya et al., 2015). A large number of carbon-rich resources have been used as the raw precursors to product the AC, e.g. coal, lignite and pitch (Arami-Niya et al., 2016; Cho et al., 2016; Xing et al., 2015). It was reported that more and more biomass materials have been used as carbon precursor to fit the demands of environment sustainability and reduce costs, such as Arundo donax linn (Sun et al., 2013), guava seeds (Pezoti et al., 2016) and cow-hairs (Kong et al., 2015). In recent years, some AC materials have been developed from the common green alga, *Enteromorpha prolifra* (EP), because of its rich in carbon and special channel-like microstructure (Gao et al., 2013; Li et al., 2011). Considering the environmental degradation and eutrophication of oceans caused by the green alga, the employment of green alga as the raw material for AC production not only supported the resource utilization, but also provided a favorable choice for controlling the deterioration of marine eco-systems caused by green alga.

In addition, activating agent is also a key factor for the pore

* Corresponding authors.
E-mail addresses: qyyue58@aliyun.com (Q. Yue), bygao@sdu.edu.cn (B. Gao).

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structure and physicochemical properties of AC. Activation methods of manufacturing AC can be divided into physical and chemical activation (Li et al., 2011). There are many advantages for chemical activation including low temperature, well-developed pore structure and high yield. Unfortunately, some drawbacks still exist in chemical activation. Especially for strong acid/alkali activating agents, such as KOH (Li et al., 2017), NaOH (Cho et al., 2016), and H_3PO_4 (Kundu et al., 2015), which are extremely corrosive to the apparatus, and thus alleviating the corrosion of reaction during the AC preparation was required. Potassium tartrate is a kind of organic potassium salt with low-corrosive, and widely employed in food, medicine and chemical industry. There were few previous studies that were reported to apply potassium tartrate as an activating agent to manufacture AC.

The objectives of this study were to (i) employ potassium tartrate as the activating agent to obtain AC with relatively high specific surface area; (ii) evaluate the impacts of key factors (activation temperature, impregnation ratio and activation time) on specific surface areas of different ACs; (iii) estimate the adsorption behavior of activated carbon prepared using Potassium Tartrate (AC-PT) under the optimal preparing conditions.

2. Materials and methods

2.1. Materials

Enteromorpha prolifera was collected from the seaside (Qingdao, Shandong province), air-dried, ground and sieved (powder with a size less than 0.425 mm) before usage. All the chemical reagents were analytical grade. Potassium tartrate ($C_4H_6K_2O_7$) and Chloramphenicol (CAP) were provided by Aladdin (Shanghai, China). The structural formula of CAP is displayed in Fig. S1.

2.2. Preparation of activated carbon

Before chemical activation processes, the raw material was carbonized at the pyrolysis temperature of 700 °C with a heating rate of 10 °C/min, and keeping for 90 min by using a resistance furnace (KSY-4D-16) to gain the EP-based char (Gao et al., 2016). To get the optimum conditions for the AC preparation, the EP-based char was activated at different conditions. Different mass of $C_4H_6K_2O_7$ was mixed with 10 g of EP-based char at various mass ratios of 1:1, 2:1, 3:1, 4:1 and 5:1. Thereafter, the mixtures were placed in the middle of tube type resistance furnace (SKQ-3–10) under N_2 atmosphere. They were heated with a rate of 10 °C/min from room temperature to the activation temperature (500, 600, 700, 800 or 900 °C) and kept for 15, 30, 60, 90 or 120 min at the target temperature. After the reaction, the system was naturally cooled to room temperature. The products were washed by hydrochloric acid to remove the redundant activating agents, and then the products were washed by hot deionized water to remove the impurities. Finally the samples were dried, grounded, sieved to average diameter of 0.150 mm and stored in seal bags for further use.

2.3. Characterization methods

The thermogravimetric curve of EP-based char dipped in $C_4H_6K_2O_7$ was acquired by using a TGA instrument (SHI-MADZU, TGA-50) at ambient temperature to 900 °C with a rate of 10 °C/min at N_2 atmosphere. The differential thermal analysis (DTG) was based on the differential TGA curve. The textural structure of AC was obtained from a JW-BK122W (Beijing JWGB Sci. & Tech. Co., Ltd China) apparatus under −196 °C by N_2 adsorption-desorption isotherm. Scanning electron microscope (SEM, FEI, Quanta FEG 250) was used to investigate microstructure of activated carbon. The samples were characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB 250) to obtain relative amounts and valence states of carbon, nitrogen, oxygen and chlorine with Al Kα X-ray (1486.6 eV) as an excitation source.

2.4. Adsorption of chloramphenicol

Thermodynamics studies were investigated to identify the adsorption of chloramphenicol in terms of adsorption temperature. Typically, 0.025 g AC-PT was blended with 50 mL of CAP solution with different concentration of chloramphenicol (400–1000 mg/L) in a 250 mL Erlenmeyer flask. The suspension was shocked with a speed of 130 rpm for 4 h in a water bath to reach adsorption equilibrium at different temperatures (20, 40 and 60 °C).

Samples were filtrated by 0.45 μm membranes, and the residual concentration of CAP solution was determined by UV–VIS spectrophotometer (UV-754, Shanghai) at 277 nm. The amount of CAP adsorbed onto AC-PT was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentration of CAP, respectively (mg/L); q_e is the amount of adsorption CAP on activated carbon (mg/g), V is the volume of CAP solution (L) and w is the amount of AC-PT (g).

3. Results and discussion

3.1. Thermal analysis

The pyrolysis behavior of the mixture of EP-based char with $C_4H_6K_2O_7$ (EP-based char impregnated with $C_4H_6K_2O_7$ at a ratio of 1:1) was shown in Fig. S2. The pyrolysis process can be divided into two stages. The first section (27–312 °C) showed a mass loss of 25% with a peak at 267 °C in DTG curve, which indicated that vast moisture and volatile were pyrolyzed with the increasing temperature (Sun et al., 2016). The second stage representing the temperature from 312 to 894 °C indicated the a mass loss of 51% with a significant peak appeared at 852 °C in DTG curve, which could be associated with the decomposition of organic matters, such as fatty acid, ether extract and proteins. This phenomenon could be attributed to the breakdown of the long chain to reform the new structure under the effect of activators (Li et al., 2010). As with other activators , potassium tartrate was used as dehydrating agent which can release tars that occupied the pores of char and restrain consumption of carbon during the pyrolysis process (Laksaci et al., 2017).

3.2. Activation parameters

3.2.1. Activation temperature

Activation temperature is a dominating factor for preparing ACs, which affects the pore structure, the specific surface area, and chemical properties of ACs. The influence of activation temperature was estimated at the impregnation ratio of 3:1 (Potassium tartrate: EP-char) and activation time of 60 min. The textural characteristic of ACs is showed in Fig. 1.

As the activation temperature increased from 500 to 900 °C, the BET surface area of ACs increased from 1018 m^2/g (500 °C) to 1893 m^2/g (700 °C), then it was decreased to 1364 m^2/g at 900 °C (Fig. 1a). The decrease in the BET surface area at higher temperature (900 °C) could partially attributed to transformation of micropores to mesopores and the break or collapse of cross-linked structure under strong gasification (Yahya et al., 2015). Meanwhile, the micropore surface area in the ACs showed the similar trend as compared with that of BET surface area in terms of activation temperature. The increasing of external surface area with activation temperature which was attributed that mesopores increased. As a result, the highest surface area of AC can be obtained at the activated temperature of 700 °C and it was chosen as optimal condition in the activating process and employed in the following experiments.

The average pore size of AC samples slightly decreased from 2.60 to