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Highly efficient simultaneous adsorption and biodegradation of a highly-concentrated anionic dye by a high-surface-area carbon-based biocomposite

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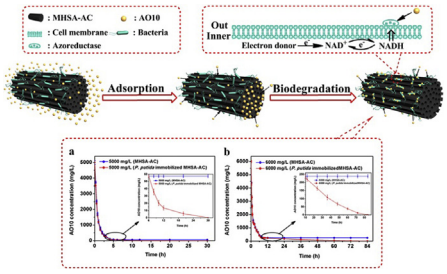
HIGHLIGHTS

- Agricultural waste as an eco-friendly strategy for dye removal from wastewater.
- Simultaneous chemical-physical activation technique promoted surface area.
- MHSA-AC could adsorb AO10 effectively to protect bacteria from harm.
- High-concentrated AO10 could be removed completely by SAB process.

GRAPHICAL ABSTRACT



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ABSTRACT

Mesoporous high-surface-area activated carbon (MHSA-AC), which has a honeycomb structure, was produced from coconut shells by simultaneous chemical and physical activation and used for the rapid adsorption of an anionic dye, namely acid orange 10 (AO10), from water. Owing to its porosity and high Brunauer–Emmett–Teller surface area (2283.91 m^2g^{-1}), MHSA-AC is a highly efficient adsorbent. It also has good biocompatibility and is a good immobilization carrier; the grooves on the MHSA-AC surface facilitate immobilization. Here, a new, highly efficient, and environmentally friendly simultaneous adsorption and biodegradation (SAB) process was developed. Highly concentrated AO10 (6000 mg L^{-1}, 20 mL) was removed with an efficiency of 100% (pH = 7, 35 °C) by SAB using cells immobilized on MHSA-AC (500 mg). The immobilized cells were used directly, without pretreatment; the SAB process is therefore simple and has good potential for application in the treatment of dyes in industrial wastewater.

1. Introduction

Rapid industrial development in recent years has caused the discharge of dyes to become a global environmental concern and a threat to human health (Wang et al., 2005, 2011; Salima et al., 2013). Synthetic dyes are widely used in the textile, paper, leather, pharmaceutical, and printing industries (Hao et al., 2010;

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Liu et al., 2012; San et al., 2014), and the removal of azo dyes, a large group of synthetic dyes, has become a major issue (Anbia et al., 2010). The highly substituted aromatic rings of azo dyes make these molecules recalcitrant and difficult to deal with (Khehra et al., 2005; Liu et al., 2007). Various techniques have therefore been developed to remove dyes from wastewaters, for example, coagulation and flocculation (Moghaddam et al., 2010; Lau et al., 2015), membrane separation (Allegre et al., 2004; Lee et al., 2006; Liu et al., 2012; Shao et al., 2013; Wei et al., 2013; Thamaraiselvan and Noel, 2015), oxidation (Chacón-Patiño et al., 2013; Yadav et al., 2013; Labiadh et al., 2015), photocatalysis (Chen et al., 2006; Gupta et al., 2012; Xu et al., 2013), adsorption (Pereira et al., 2003; Lei et al., 2006; Liu et al., 2015; Zhao et al., 2015), and biological treatments (Jain et al., 2012; Rodrigues et al., 2014). Biological treatments, which are cost-effective and environmentally friendly techniques, have been used for many years, but there are only a limited number of microorganisms that can degrade contaminants at high concentrations. Combined treatment processes are therefore needed to remove azo dyes from wastewater.

Simultaneous adsorption and biodegradation (SAB) methods, which involve adsorption followed by biological treatment, have been developed for removing dyes at high concentrations. Pollutants can be removed efficiently and completely using this new strategy. The biodegradation step in the SAB process can convert pollutants to harmless compounds. Although some pollutants are degraded by inorganic materials through advanced oxidation processes (AOPs) based on hydroxyl radical reactions, many harmful intermediate products can be produced during such processes. In addition, ultraviolet (UV) or high-energy light is needed for AOPs, and these are expensive and harmful (Filice et al., 2015; Wang et al., 2015). SAB, which is an economically viable, highly efficient, and environmentally friendly process, therefore has advantages over other methods in practical applications.

Carbon-based materials (Asfaram et al., 2016a, b), such as activated carbon (AC) (Hadi et al., 2016), carbon nanotubes (Graf et al., 2016), and graphene (Tiwari et al., 2013), are currently attracting much attention. AC in particular has various advantages, such as low cost, adjustable porosity, high surface area, easy processing, wide applicability, and high adsorption capacity (Din et al., 2009). Because of these advantages, various pollutants, for example, dyes (Ghaedi et al., 2012; Roosta et al., 2014, 2015), heavy metals, and gases, can be removed using AC. In addition, the maximum adsorption of AC at equilibrium is similar to that of other adsorbents. However, commercially available AC derived from coal is still relatively expensive. Much research has therefore been devoted to developing AC from inexpensive, abundant, and renewable materials, such as orange peel (Foo and Hameed, 2012), oil palm shells (Tan et al., 2007), sawdust (Prakash Kumar et al., 2005), bamboo (Hameed et al., 2007), and bagasse (Mohan and Singh, 2002). Coconut shells, which make up a large amount of agricultural solid waste, are suitable for conversion to AC because of their stiffness and abrasion resistance.

In this study, SAB was used to treat highly concentrated acid orange 10 (AO10), an anionic azo dye, using surface-immobilized bacteria and mesoporous high-surface-area AC (MHSA-AC). $ZnCl_2$ chemical activation and CO_2 physical activation have been widely used for the development of pore networks in AC (Hu et al., 2000). In this study, we prepared MHSA-AC with uniform pores and a honeycomb structure from coconut shells by simultaneous chemical and physical activation (Fig. 1). MHSA-AC efficiently removed AO10 from water because of its high Brunauer–Emmett–Teller (BET) surface area (2283.91 m^2g^{-1}) and because its pores provide channels that allow molecules to easily enter the internal pores. As well as acting as an adsorbent, MHSA-AC also acts as a superior carrier for the immobilization of bacterial cells owing to its biocompatibility and because the grooves on its surface make cell immobilization easy. A strain of *Pseudomonas putida*, which has been widely used to degrade AO10, was used in the biodegradation process. *P. putida* immobilized on MHSA-AC was used directly in the SAB process without any pretreatment, making the process simple and practical. A high concentration of AO10 (6000 mg L^{-1}) was removed continuously and completely by cells immobilized on MHSA-AC using the SAB process. The results show that this SAB process is more efficient and has greater potential than traditional treatment methods.

2. Materials and methods

2.1. Materials

Coconut shells were obtained from the local market in Suzhou, China. Tryptone and yeast extract were purchased from the Suzhou Biogene Biotechnology Co., Ltd. AO10, $ZnCl_2$, HCl, and inorganic salts were obtained from the Sinopharm Chemical Reagent Suzhou Co., Ltd.

2.2. Cultivation of bacteria

A pure strain of *P. putida* (CICC 21,906) was purchased from the China Center of Industrial Culture Collection. The strain was grown in Luria–Bertani (LB) liquid medium (tryptone, 10 g L^{-1}; yeast extract, 5 g L^{-1}; NaCl, 10 g L^{-1}). The pH of the medium was adjusted to 7.0. The LB liquid medium, phosphate-buffered saline (PBS) solution, and all equipment were autoclaved at 30 °C for 20 min, and the AO10 solution was separately sterilized using a 0.22-μm membrane filter before the biological experiments.

2.3. AO10 biodegradation assays

The *P. putida* strain was cultured in LB liquid medium (100 mL) in a constant temperature oscillator (30 °C, 120 rpm). The free cells were harvested by centrifuging for 10 min and then washed twice with PBS solution. The cell pellets were used in subsequent experiments.

We systematically investigated various factors that affect the efficiency of AO10 biodegradation by *P. putida*. First, we examined the effects of various culture mediums (water, glucose, and LB) and conditions (aerobic and anaerobic) on the AO10 biodegradation efficiency at the same cell concentrations after 24 h, using an initial AO10 concentration of 50 mg L^{-1}. The effects of temperature (20–50 °C) and pH (3–10) on the AO10 biodegradation efficiency, using the same initial AO10 concentration (50 mg L^{-1}), were also studied.

Batch experiments were then performed under the optimum conditions to study the effects of various AO10 concentrations on biodegradation by *P. putida* cells.

2.4. Preparation of MHSA-AC

Coconut shells were washed with distilled water and dried overnight. The dried shells (1.0 g) were impregnated with concentrated solutions of $ZnCl_2$ (30 mL) at various $ZnCl_2$/shell weight ratios (0.5, 1.0, 1.5, 2.0, 2.5, and 3.0) for 24 h. The mixtures were dried at 110 °C overnight. The dried solid mixtures were carbonized in a tube furnace under a constant flow of argon (150 cm^3min^{-1}) at a heating rate of 10 °C min^{-1} until the desired temperature (800 °C), was reached. The carbon samples were activated at the carbonization temperature for 2 h in a CO_2 atmosphere (100 cm^3min^{-1}). The activated products were cooled to