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Research article

Activated carbon doped with biogenic manganese oxides for the removal of indigo carmine

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ABSTRACT

Indigo carmine (IC) is one of the oldest, most important, and highly toxic dyes which is released from the effluents of many industries and results in serious pollution in water. In this study, the biogenic Mn oxides were activated by NaOH and then heated for 3 h at 350 °C to produce activated carbon doped with Mn oxide (Bio-MnO_x-C), which were produced by culturing Mn (II)-oxidizing bacterial strain MnI7-9 in liquid A medium at 28 °C with 10 mmol/L $MnCl_2$. Bio-MnO_x-C was characterized by SEM, TEM, IR, XPS, XRD, *etc*. It contained C, O, and Mn which comprised Mn (IV) and Mn (III) valence states at a ratio of 3.81:1. It had poorly crystalline ε-MnO_2 with a specific surface area of 130.94 m^2/g. A total of 0.1 g Bio-MnO_x-C could remove 45.95 g IC from 500 mg/L IC solution after 0.5 h contact time. IC removal by Bio-MnO_x-C included a rapid oxidation reaction and the removal reaction followed second-order kinetic equation. These results confirmed that Bio-MnO_x-C could be a potential material for wastewater remediation.

1. Introduction

Indigo carmine (3,3-dioxo-2,2-bisindolyden-5,5-disulfonic acid disodium salt, IC) was one of the oldest, most important, and highly toxic dyes. It was released by many industries, such as textile, papers and plastics processors, and caused serious pollution in water bodies (Attia et al., 2006). During the "Eleventh Five Year Plan" period (2006–2010), China had been the largest indigo producer with a production of more than 60% of the global total (Si et al., 2013). Due to its symmetrical structure and stable properties, it is difficult to be oxidized and cracked. Recently, some IC wastewater treatment methods, such as physical adsorption (Valix et al., 2004), chemical oxidation (Zaied et al., 2011), and the use of biological enzyme (Podgornik et al., 2001), have shown certain efficacy. However, the physical method can only remove IC by surface absorption of the adsorbent using weak van der Waals attractive forces and result in reversible adsorption. The chemical oxidation method is expensive, and the biological enzyme method is restricted because the enzyme is complex, diverse, and some mechanisms and processes therein remain unclear.

Activated carbon is widely used in environmental protection to remove organic toxins and heavy metals in water (Park et al., 2007) because of its large surface area, well developed porosity, and high adsorption capacity (Newcombe et al., 1993). Activated carbon was also widely used as a catalyst carrier to enhance the catalytic activity to best utilize its other advantages, such as ease of preparation and low-cost (Arana et al., 2003). The carbon-coated TiO_2 showed higher activity in the decomposition of methylene blue in water under UV irradiation and was able to be used repeatedly to a greater extent than TiO_2 (Tsumura et al., 2002).

Manganese (II) can be oxidized to manganese (Mn) oxides by biotic and abiotic processes, which is mainly composed of Mn (IV). Mn (II)-oxidizing microorganisms can accelerate the rate of Mn (II) oxidization compared to the abiotic process (Hastings and Emerson, 1986). Studies have demonstrated that biogenic Mn oxides were highly reactive minerals that had much higher sorption and oxidation capacities for a lot of organic compounds and metal ions than abiotic Mn oxides (Murray and Tebo, 2007). For example, Diclofenac™ oxidation with biogenic Mn oxides produced by *Pseudomonas putida* MnB6 was 10-times faster than that with chemically produced MnO_2 at neutral pH (Forrez et al., 2010).

The successful use of biogenic Mn oxides for IC removal, Ag (I)

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removal and As (III) oxidation has been reported in the authors' prior study (Chen et al., 2014a; Pei et al., 2013; Liao et al., 2013). The biogenic Mn oxides produced by manganese-oxidizing bacteria adhere tightly to the bacterial capsular (Liao et al., 2013), which is composed of organic compounds. In this study, biogenic Mn oxides were activated by NaOH and then heated to produce activated carbon doped with Mn oxides (Bio-MnO_x-C). This study was designed to prepare new, efficient, cheap eco-materials, and to examine their effect and mechanism of removing toxic organic pollutants using IC as a model contaminant. The results of this study explained the possible removal mechanism of Bio-MnO_x-C for toxic organics and were valuable for the application of biogenic Mn oxides.

2. Material and methods

2.1. Materials

A Mn (II)-oxidising bacterial strain *Marinobacter* sp. MnI7-9 which has a strong oxidizing capability was provided by Dr Zongze Shao from The Third Institute of Oceanography, Xiamen in China. The strain was isolated from the sediment of the outer part of a hydrothermal vent chimney in the deep water of the middle Indian Ocean (25.32 °S, 70.04 °E; 2474 m deep) in 2009. IC was purchased from Aladdin (Shanghai) Co., Ltd. Analytically pure chemical Mn oxide (γ-MnO_2) was purchased from Sinopharm Chemical Reagent Co., Ltd, China. Activated carbon (AC, CAS registry number: 7440-44-0) was purchased from Sinopharm Chemical Reagent Co., Ltd, China.

2.2. Preparation of activated carbon doped with biogenic Mn oxides

The Mn(II)-oxidizing bacterial strain *Marinobacter* sp. MnI7-9 was cultured in liquid A medium at 28 °C with 10 mmol/L $MnCl_2$, as described in Liao et al. (Liao et al., 2013). The biogenic Mn oxides were produced after 7 d, collected and dried in a vacuum freeze-dryer at −60 °C for 24 h. The biologic Mn oxides and NaOH were added to a clean crucible at a mass ratio of 1:4, then deionized water was added into the crucible to immerse the mixture for 24 h. After the water in the crucible had evaporated at 80 °C, the residue was not covered with a ceramic fiber paper and some sands on the top of the paper to generate reducing conditions, then baked in a muffle furnace at 350 °C for 3 h. The product was first washed with 10% HCl, then washed with deionized water to neutrality and finally dried with a freeze-dryer to generate Bio-MnO_x-C.

2.3. Characterization of the activated carbon doped with Mn oxides

2.3.1. Morphological characterization and Mn-content analysis

Scanning electron microscopy (SEM) observations were made by a JSM-6390/LV equipment using copper stubs with Bio-MnO_x-C powders. Transmission electron microscopy (TEM) observations were performed using Tecnai G2 20s-TWIN equipment with Bio-MnO_x-C powders supported on Cu grids.

Bio-MnO_x-C was dissolved with 20 mL of 2.5 mol/L sulphuric acid and Mn oxides were redoxed with 0.2 g of sodium oxalate in a water bath at 70 °C (Katz et al., 1956), then centrifuged and filtered through a 0.22 μm filter. The filtrate was diluted to 50 mL with 1% of concentrated HNO_3 and stored at 4 °C prior to analysis. The Mn^{2+} concentration in the filtrate was measured by an atomic absorption spectrometer (AAS, 986A, Beijing Puxi General Instrument Co., Beijing, China) (Liao et al., 2013). The Mn content of Bio-MnO_x-C was 44.22%.

2.3.2. EDS, IR, XPS, and XRD analysis

Energy-dispersive spectroscopy (EDS) was recorded by a JSM-6390/LV equipment. The samples were ground with 100 mg KBr to form a fine powder. This powder was then compressed into a thin pellet. The sample was then analyzed using a Nicolet Avatar 330FT-IR (Thermo Electron Corporation, USA) spectrometer and the spectrum recorded over the spectral range of 400–4000 cm^{-1}.

X-ray photoelectron spectroscopy (XPS) analysis was acquired using a VG Multilab2000 X-ray photoelectron spectrometer with an Al Kα X-ray source (1486 eV). Samples were prepared by adherence of a thin layer of the powdered sample to a platen using double-sided adhesive graphite tape and a vacuum pressure of 10^{-7} Pa. The survey spectrum was collected using a fixed pass energy of 100 eV and an energy step size of 1.0 eV, while the regional spectrum had a pass energy of 25 eV and an energy step size of 0.05 eV. The spectra were analyzed and the XPS peaks were identified using Avantage software from the Thermo Electron Corporation. All spectra were charge-corrected using the C (1s) spectral line at 284.80 eV as recommended.

The X-ray diffraction (XRD) patterns were performed on a Y-2000 diffractometer operated at 30 kV and 20 mA with Cu Kα radiation ($\lambda = 0.1543$ nm) and a diffracted beam monochromator over the range $5 \leq 2\theta \leq 90°$.

2.3.3. Surface characterization

The determination of specific surface area of the samples was based on the N_2 adsorption method (Brunauer–Emmet–Teller, BET) with an AUTOSORB-1MP-CR surface analyzer (Jiang et al., 2011). The pore size was calculated by the Barrett–Joyner–Halenda (BJH) equation. The test temperature was 77 K. The range of relative pressures (P/P_0) in this test was 10^{-6} to 1. The point of zero charge (PZC) was determined by salt titration method (Chen et al., 2014a). The acidic and basic site concentrations were determined using the Boehm titration method (Boehm, 1994).

2.4. IC removal by activated carbon doped with biogenic Mn oxides

Each 100 mL IC solution with different pH values was added to flasks containing 0.1 g Bio-MnO_x-C using the activated carbon as a control. The flasks were stoppered and shaken at 160 rpm for 5 h at different temperatures (25 °C, 35 °C, 45 °C). Then, 5 mL of the reacted solution was withdrawn at specific time intervals, and filtered through a 0.22 μm filter. Mn^{2+} concentration in the filtrate was measured using the AAS as described above. The IC concentration in the filtrate was determined by ultraviolet spectrophotometer (UV-3000, Shanghai Mapada Instrument Co., Shanghai, China) at $\lambda = 610$ nm (Gemeay et al., 2003). The amount and percentage adsorptions of IC were computed using Eqns (1) and (2), respectively, as follows:

$$\text{Removal amount} = \frac{\left(C_i - C_f\right) \times V}{m(\text{Bio} - \text{MnO}_x - \text{C})} \quad (1)$$

$$\text{Removal percentage} = \frac{C_i - C_f}{C_i} \times 100\% \quad (2)$$

where m(Bio-MnO_x-C) is the mass of Bio-MnO_x-C, V is the volume of the IC solution, C_i and C_f represent the initial and final IC concentrations (mg/mL), respectively.

IC and its degradation products were analyzed by high performance liquid chromatography (HPLC, Aglient1200) at 30 °C with a reversed-phase C18 column (150 mm × 4.6 mm) and an ultraviolet detector which was adjusted to 235 nm. The mobile phase was a