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Repeated oxidative degradation of methyl orange through bio-electro-Fenton in bioelectrochemical system (BES)

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HIGHLIGHTS

- Composite Fe_2O_3/ACF electrode was prepared with ACF treated with nitric acid oxidation.
- H_2O_2 production reached steadily at 88.63 μmol/L with the optimized BES parameters.
- Methyl orange degradation was repeated eight batches through bio-electro-Fenton in BES.

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ABSTRACT

Composite Fe_2O_3/ACF electrode facilitated methyl orange (MO) oxidative degradation using bio-electro-Fenton in bioelectrochemical system (BES) was investigated. Characterized by both XPS and FT-IR techniques, it was found that the composite Fe_2O_3/ACF electrode with highest Fe loading capacity of 11.02% could be prepared after the carbon felt was oxidized with nitric acid. Moreover, hydrogen peroxide production reached steadily at 88.63 μmol/L with the external resistance as 100 Ω, cathodic aeration rate at 750 mL/min, and the pH of the bio-electro-Fenton system adjusted to 2. Significantly, not only the electrochemical profiles of the BES reactor as electrochemical impedance spectroscopy (EIS) was bettered, but the MO oxidative degradation could be accomplished for eight repeated batches, with the MO removal efficiency varied slightly from 73.9% to 86.7%. It indicated that the bio-electro-Fenton might be a promising eco-friendly AOP method for Azo-dye wastewater treatment.

1. Introduction

With the development of the textile industry, dyes account for a very large proportion of wastewater in the organic pollution. Featured for substituted aromatic rings joined by one or more azo groups (—N=N—), azo dye is now one of the largest number of species adopted in dyeing industry (Cardenas-Robles et al., 2013). Due to their high colority, non-degradability, potential mutagenicity and poor biochemical purification ability, azo dyes would not only directly endanger people's health, but pose a major risk on the soil and the aquatic ecosystems, and finally bring about unimaginable consequences (Mu et al., 2009). Traditionally, various treatment methods as adsorption, coagulation, oxidation, electro-chemistry method have been adopted for the processing of the dye wastewater (Li et al., 2012; Punzi et al., 2015; Türgay et al., 2011). Regardless of their convenient operation and excellent decolorization efficiency, these methods cost too much and always lead to the secondary environmental pollution.

Based on the classical chemical oxidation water treatment, advanced oxidation process (AOP) is now regarded as a new technology for dye wastewater processing (Pignatello et al., 2006). Harboring powerful oxidation capacity, hydroxyl radicals (·OH) generated by AOP could react with various organic compounds, further induce chain oxidative reactions assisted with the intermediate products of reaction, and finally generate H_2O, CO_2 and other unharmful substances (Asghar et al., 2015). As one of the powerful AOP methods, Fenton's reagents have, been used to treat the phenol and benzene early in 1964 for the first time, creating a wastewater treatment precedent (Xu, 2004). Till now, Fenton's reagents have been employed to treat various kinds of organic compounds like penicillin wastewater, anionic surfactants, etc., and achieved prefect effects. Apart from its convenience and degradability, this

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method was strictly limited by controlling pH, massive sludge production and high price of hydrogen peroxide.

To date, the electro-Fenton has been widely studied for the destruction of organic compounds with hydroxyl radicals formed using electro-generating hydrogen peroxide (Yu et al., 2015). As a competitive option for the removal of pollutants against conventional methods, bioelectrochemical system (BES) has been widely investigated and considered (Sun et al., 2013). Recently, many researchers tried to integrate BES with Fenton's reagents, namely the bio-electro Fenton, of which electrons and protons could be produced by oxidizing organic matter in the anode to maintain the process of electro-Fenton within the cathode chamber. It was reported that dye decolorization could be accomplished with electro-Fenton at BES cathode powered by anodic Fungus–bacterium (Fernandez de Dios et al., 2013). So far, azo dyes as Orange II, Rhodamine B and so on have been reported to be degraded with the bio-electro Fenton system (Feng et al., 2010). In addition to the electricity production via microbial metabolism at anode, more iron or iron oxide was expected to be loaded onto the cathode surface to provide sustained release of ferric ions (Ozcan et al., 2013). Reportedly, Fe@Fe_2O_3 could be loaded onto the active carbon felt (ACF) using sonication after $FeCl_3$ was reduced using $NaBH_4$ to prepare composite electrode Fe@Fe_2O_3/ACF (Li et al., 2009; Zhuang et al., 2010). However, the loosely-bound physical attachment of Fe@Fe_2O_3 might not extend the duration of bio-electro-Fenton period as expected. It would be more meaningful to modify the surface of ACF in order to improve the fixedness of Fe_2O_3 loading. However, few publications could be tracked in this field.

In order to construct the robust bio-electro-Fenton system for dye wastewater treatment, the preparation of composite Fe_2O_3/ACF electrode with high iron loading, the adjustment of reactor parameters for H_2O_2 production, electrochemical performance of the optimized BES reactor, and the repeated oxidative degradation of methyl orange (MO), were all investigated in this study.

2. Methods

2.1. Preparation of the composite Fe_2O_3/ACF electrode

Firstly, 2 g of ACF (YB-20, YiBang, China) was washed at reflux with a volume ratio of acetone and ethanol at 1:1 for about 8 h in the Soxhlet extractor, and was dried at 80 °C to constant weight. Next, the washed ACF was modified with specific oxidant as nitric acid, acid potassium dichromate, sodium hypochlorite, concentrated sulfuric acid, and hydrogen peroxide for 2 h at 100 °C, respectively. After that, oxidized ACF (oACF) of each group was washed with deionized water several times, and was dried to constant weight as before. As for the loading of Fe_2O_3, oACF was soaked in 300 mL of $FeCl_3{\cdot}6H_2O$ (3 g/L), and was then sonicated for 1 h at 30 °C by 40 kHz. Meanwhile, 15 g/L of $NaBH_4$ solution was dropped into the ferric solution slowly at 60 rpm (BT100-2 J, Longer Pump, China) to reduce ferric irons onto ACF surface (Li et al., 2009). Afterward, the soaked oACF was washed and dried as before, and was finally assembled into titanium wire to fabricate the composite Fe_2O_3/ACF electrode. The Fe Loading capacity was calculate as:

$$\text{Fe Loading}\ (\%) = 100 * (\text{Weight of } Fe_2O_3\text{/ACF-Weight of oACF})/\text{Weight of oACF}$$

2.2. Characterization of the Fe_2O_3/ACF electrode

For Fourier-transform infrared (FT-IR) detection, the samples were cut into about 1.5 cm × 1.5 cm, and then dried in a vacuum dryer at 80 °C for 2 h. FT-IR spectra of the Fe_2O_3/ACF electrode was recorded by an FT-IR spectrometer (Nicolet iS50, USA), with the scanning range varying from 4000 to 400 cm^{-1} at the scanning speed of 0.158–6.28 cm/s.

The element analysis of the Fe_2O_3/ACF electrode was characterized by X-ray photoelectron spectrometer (XPS) (Thermo ESCALAB 250, USA). The surface analysis was performed in the ultrahigh vacuum system (1×10^{-8} Pa) equipped with a 180° hemispherical energy analyzer. With an incident monochromatic X-ray beam focused on the sample surface, the electron energy analyzer was operated with a fixed pass energy of 30 eV enabling high spectra resolution.

2.3. Reactor setup

The dual-chamber BES reactor was made of polycarbonate (16 cm in external diameter, 14 cm in height) and separated by cationic exchange membrane (CMI-7000s, Yuejin, China). The anode electrode was made of graphite fiber brushes (6 cm in diameter, 12 cm in length, TOHO, Japan), cathode electrode consisted of the composite Fe_2O_3/ACF electrode as assembled previously. Each chamber of the BES reactor had a working volume of 0.55 L. For all tested groups, the both electrodes were connected via a copper wire with a 100 Ω high-precision resistor in between except otherwise mentioned.

2.4. Reactor operation

Prior to starting the BES reactor, the anode chamber was inoculated with anaerobic sludge obtained from Genencor bio-products (Wuxi, China), with the cathode was filled using deionized water until the anode potential across electrodes poised at −0.55 V (Keithley 2700, USA) every 10 min. Containing 5 mg/L of MO and 0.05 mol/L of Na_2SO_4, 550 mL of electrolyte (pH adjusted to 3) was injected into the cathode chamber, and was then magnetically stirred at 1000 rpm/min for about 30 min to establish adsorption equilibrium between the solution and electrodes. During the degradation process, fresh air was fed into the cathode providing oxygen at the rate of 750 mL/min (YZ2515X, Longer Pump, China) except otherwise mentioned. For sampling, 5 mL of electrolyte was collected every 15 min for the detection of residual hydrogen peroxide and MO.

2.5. Analytic method

Testing of the polarization curves were conducted as described previously (Liu et al., 2014). Also, volumetric current density and power density were normalized with the 0.55 L of net cathode compartment (NCC).

Electrochemical impedance spectroscopy (EIS): EIS analysis was performed using the electrochemical workstation (CHI660D, Chenhua, China) with a two electrode mode as described previously (Liu et al., 2014).

The concentration of MO was determined spectrometrically at 464 nm as described previously (Zhang et al., 2015), and the MO removal was calculated as ratio of the residue concentration (C) after every batch to the initial concentration (C_0) of MO.

The concentration of total iron ions (Fe^{2+} and Fe^{3+}) was determined spectrometrically with the phenanthroline method according to the standard protocol of State Environmental Protection Administration (SEPA) of China (SEPA, 2000).

The detection of hydrogen peroxide was conducted using the 2,9-dimethyl-1,10-phenanthroline (DMP, Sigma, USA) method (Kosaka et al., 1998). After being centrifuged for 5 min at 800 rpm/min, the same volume (0.5 mL in each) of supernatant DMP (10 g/L), $CuSO_4{\cdot}5H_2O$ (0.01 mol/L), and phosphate buffer solution was added into 3 mL of deionized water in a 5 mL colorimeter