



Catalytic ozonation of organic pollutants from bio-treated dyeing and finishing wastewater using recycled waste iron shavings as a catalyst: Removal and pathways



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ABSTRACT

Catalytic ozonation of organic pollutants from actual bio-treated dyeing and finishing wastewater (BDFW) with iron shavings was investigated. Catalytic ozonation effectively removed organic pollutants at initial pH values of 7.18–7.52, and the chemical oxygen demand (COD) level decreased from 142 to 70 mg·L⁻¹ with a discharge limitation of 80 mg·L⁻¹. A total of 100% and 42% of the proteins and polysaccharides, respectively, were removed with a decrease in their contribution to the soluble COD from 76% to 41%. Among the 218 organic species detected by liquid chromatography-mass spectrometry, 58, 77, 79 and 4 species were completely removed, partially removed, increased and newly generated, respectively. Species including textile auxiliaries and dye intermediates were detected by gas chromatography-mass spectrometry. The inhibitory effect decreased from 51% to 33%, suggesting a reduction in the acute toxicity. The enhanced effect was due to hydroxyl radical (•OH) oxidation, co-precipitation and oxidation by other oxidants. The proteins were removed by •OH oxidation (6%), by direct ozonation, co-precipitation and oxidation by other oxidants (94%). The corresponding values for polysaccharides were 21% and 21%, respectively. In addition, the iron shavings behaved well in successive runs. These results indicated that the process was favorable for engineering applications for removal of organic pollutants from BDFW.

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1. Introduction

The textile industry is a water-consuming and heavily polluting industry. Water is primarily consumed during the dyeing and finishing processes, and the wastewater accounts for approximately 80% of the total discharge from the textile industry (Lin, 2008; Lin and Chen, 1997). Dyeing and finishing wastewater (DFW) is characterized by a high content of organic pollutants. Dyestuffs and textile auxiliaries, which are the main components of DFW, are potentially toxic and exhibit poor biodegradability, which results in a threat to aquatic organisms (Arslan-Alaton and Alaton, 2007; Pereira and Freire, 2006; Sharma et al., 2007). Although DFW is typically treated by primary sedimentation, biological treatment and secondary sedimentation, the effluent chemical oxygen demand (COD) and soluble COD (SCOD) still barely meet the latest strict discharge limitation of 80 mg·L⁻¹ in GB 4287-2012 for dyeing and finishing in the textile industry.

Effluent organic matters (EfOM), which are mainly composed of refractory compounds and soluble microbial products (SMPs), contribute to the high COD level in bio-treated DFW (BDFW). SMPs, which primarily consist of proteins, polysaccharides and organic colloids, are derived from biological treatment and constitute a majority of the soluble EfOM (Barker and Stuckey, 1999; Jarusutthirak and Amy, 2007). To further reduce the COD value, further treatment is necessary to remove residual organic pollutants.

In recent years, catalytic ozonation, which is an advanced oxidation process (AOP), has attracted increasing attention in wastewater treatment, especially for the removal of refractory organics, due to its capacity for degradation and mineralization of these pollutants (Ghatak, 2014). Catalysts may promote the decomposition of ozone and the generation of highly reactive radical species, especially the hydroxyl radical (•OH).

Iron is the fourth most abundant element in the Earth's crust, and iron-based materials have been widely employed in wastewater treatment. Currently, catalytic ozonation with iron ions (Fe²⁺, Fe³⁺), iron oxides (Fe₂O₃, Mn-Fe-O, Fe-Cu-O) and iron-bearing minerals (Fe₃O₄, α-FeOOH) has been applied for the removal of various

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compounds, such as dyes (Chen et al., 2010), phenol (Shahamat et al., 2014), *p*-chlorobenzoic acid (Lan et al., 2013), nitrobenzene (Zhang and Ma, 2008) and tertiary treatment of industrial wastewater, such as heavy oil refining wastewater (Chen et al., 2014), and Lurgi coal gasification wastewater (Zhuang et al., 2014).

In general, zero-valent iron (ZVI) has been used as a reductant and catalyst for Fenton-like systems. Some pollutants, such as heavy metals (Li and Zhang, 2007), organochlorine pesticides (Sayles et al., 1997) and dyes (He et al., 2012), can be effectively removed by chemical reduction using ZVI. Bergendahl and Thies (2004) reported the Fenton oxidation of methyl *tert*-butyl ether using ZVI as a source of Fe²⁺. According to Joo et al. (2004), the reaction between oxygen and ZVI (O₂/ZVI) may lead to the formation of reactive oxygen species (ROS) that are capable of oxidizing organic pollutants, and this process is pH dependent. At a pH < 5, the oxidation reaction is due to •OH. However, at higher pH values, this reaction may be due to the oxidation product of Fe²⁺ with oxygen, such as the ferryl ion (Keenan and Sedlak, 2008a). Nevertheless, some studies have indicated that the oxidant yield during the O₂/ZVI process in the absence of chelating agents or electron-transfer mediator is too low for practical application (Keenan and Sedlak, 2008b; Liu et al., 2014). Only a few studies on the catalytic ozonation of wastewater using ZVI have been reported. According to Ziylan and Ince (2015), ZVI nanoparticles can increase the mineralization of ibuprofen during ozonation. According to Martins et al. (2014), iron shavings can effectively enhance ozone for the treatment of olive mill wastewater. Zhang et al. (2014) reported that supported ZVI particles exhibited a catalytic effect during the ozonation of methylene blue. However, the preparation of the catalyst was complicated, and the pH was restricted to 3. Pan et al. (2012) reported that ZVI chippings performed well in the catalytic ozonation of bio-treated dye wastewater but only conventional parameters were considered. Few studies on the catalytic ozonation of BDFW have been reported.

In this study, the catalytic ozonation with iron shavings (O₃/ZVI) was applied for the removal of EfOM from actual BDFW under the initial pH to reduce the COD level and meet the discharge limitation (i.e., 80·mg L⁻¹). The iron shavings were prepared in a simple procedure and characterized. The biodegradability and toxicity of the treated BDFW were evaluated. The variations in the EfOM characteristics including SMPs concentration, molecule weight (MW) distribution and three-dimensional excitation-emission matrix fluorescence (3DEEM) were investigated. In addition, the variations in organic pollutant species were analyzed. By comparing the removal efficiencies from the O₃/ZVI, O₃ and O₂/ZVI processes along with the quenching tests and electron paramagnetic resonance (EPR) experiments, different removal pathways in the O₃/ZVI process were determined, and the corresponding proportions were determined. The stability of the iron shavings was also investigated.

2. Materials and methods

2.1. Materials and reagents

The wastewater was obtained from the effluent of a full scale wastewater treatment plant located in a typical dyeing and

finishing industry cluster in southeast China. With a designed capacity of 200,000 m³·d⁻¹, the plant is responsible for the centralized treatment of wastewater from more than one hundred mills in this industry cluster. The plant employed a typical secondary treatment process including primary sedimentation, hydrolytic acidification, oxidation ditch and secondary sedimentation in sequence.

All of the chemicals used were analytical grade or above. 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO) was purchased from Aladdin Chemistry Co., Ltd, China. The luminescent bacteria *Photobacterium phosphoreum* were purchased from Hamamatsu Photon Techniques Inc., China. Sodium sulfite, *tert*-butanol (TBA) and the other chemicals were purchased from Sinopharm Chemical Reagents Co., Ltd, China. All the solutions were prepared with ultrapure water.

2.2. Preparation of catalysts

Iron shavings consisting of 38CrMoAl steel were purchased from a metal machinery plant and used as a catalyst for ozonation. The main composition of the iron shavings is listed in Table 1. The iron shavings were characterized by XRD. As shown in Fig. S1, the catalyst exhibited strong diffraction peaks at 2θ of 44.7°, 65.0° and 82.3°, which are characteristic of ZVI (JCPDS 06-0696). The preparation process was based on the method reported by Fu et al. (2010). First, the catalyst was immersed in 1 mol·L⁻¹ NaOH for 24 h to remove oil stain and impurities. After an alkaline wash, the catalyst was rinsed and immersed in 0.1 mol·L⁻¹ HCl for 1 h for activation. After acid pickling, the catalyst was rinsed to neutralize it. Finally the catalyst was dried using a vacuum freeze dryer and stored for subsequent use.

2.3. Experimental procedure

The O₃/ZVI, O₃ and O₂/ZVI experiments were conducted in the three same reactors at room temperature (298 ± 1 K) as a set of parallel controlled tests. The O₃/ZVI and O₃ experiments in the presence of 148 mg·L⁻¹ TBA, which is a strong •OH scavenger, were conducted as quenching tests. The O₂ and N₂/ZVI experiments were conducted as blank tests. Each reactor was ozonized for 5 min and rinsed to remove impurities. First, BDFW (2.1 L) was added and circulated in the reactor once the reaction started. BDFW was bubbled with N₂ for 20 min prior to removal of the dissolved oxygen (DO) in the N₂/ZVI process. For each process, O₃, O₂ or N₂ gas was continuously delivered into the reactor through a porous plate at the bottom immediately after the addition of 42 g (20 g·L⁻¹) of iron shavings for the O₃/ZVI, O₂/ZVI and N₂/ZVI processes, which corresponds to the beginning of the reaction. The flow of the O₃, O₂ or N₂ gas was maintained at 500 mL·min⁻¹, and the gaseous concentration of ozone was 10.8 mg·L⁻¹ in the O₃/ZVI and O₃ processes. Ozone was generated using a corona discharge ozone generator (CONT KT-OZ-10G, China) with air as the feed gas. The off-gas was absorbed by a KI solution. The oxygen was generated using an air pump. The pH value of the BDFW was not adjusted. The entire reaction lasted for 120 min. Samples were removed from the sampling port and quenched with the addition of a suitable amount of sodium sulfite. The unsettled samples were used for total iron

Table 1
Main composition of the iron shavings.

| Element | Fe | C | Si | Cr | Mn | Mo |
|-------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Content (%) | >95 | 0.35–0.42 | 0.20–0.45 | 1.35–1.65 | 0.30–0.60 | 0.15–0.25 |
| Element | Al | P | S | Ni | Cu | |
| Content (%) | 0.70–1.10 | ≤0.035 | ≤0.035 | ≤0.030 | ≤0.030 | |

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