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Electro-peroxone treatment of Orange II dye wastewater

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ABSTRACT

Degradation of a synthetic azo dye, Orange II, by electro-peroxone (E-peroxone) treatment was investigated. During the E-peroxone process, ozone generator effluent (O_2 and O_3 gas mixture) was continuously sparged into an electrolysis reactor, which was equipped with a carbon-polytetrafluorethylene (carbon-PTFE) cathode to electrochemically convert the sparged O_2 to H_2O_2. The in-situ generated H_2O_2 then reacted with the sparged O_3 to produce •OH, which can oxidize ozone-refractory organic pollutants effectively. Thus, by simply combining conventional ozonation and electrolysis processes, and using a cathode that can effectively convert O_2 to H_2O_2, the E-peroxone process degraded Orange II much more effectively than the two processes individually. Complete decolorization and 95.7% total organic carbon (TOC) mineralization were obtained after 4 and 45 min of the E-peroxone treatment, respectively. In comparison, only 55.6 and 15.3% TOC were mineralized after 90 min of the individual ozonation and electrolysis treatments, respectively. In addition to its high efficiency, the E-peroxone process was effective over a wide range of pH (3–10) and did not produce any secondary pollutants. The E-peroxone process can thus provide an effective and environmentally-friendly alternative for wastewater treatment.

1. Introduction

Synthetic dyes are used extensively in many industries, such as textile, printing, leather tanning, and paper production industries (Martinez-Huitle and Brillas, 2009; Nidheesh and Gandhimathi, 2012). Some of the dyes, however, are discharged in industrial wastewaters and can cause serious aesthetic and environmental damage to receiving water bodies. Most synthetic dyes are refractory to degradation in natural water (e.g., by sunlight or microbial attack) and can impart undesirable colors to water bodies even at very low concentrations (Martinez-Huitle and Brillas, 2009). In addition to aesthetic pollution, colors can decrease sunlight penetration through the water, and thus disturb the natural growth activity of aquatic organisms (Nidheesh and Gandhimathi, 2012). Moreover, some dyes and their degradation intermediates are toxic and carcinogenic, and can pose considerable hazards to aquatic life and human beings (Brown and Devito, 1993; Hammami et al., 2008; Silva et al., 2009). Wastewaters containing synthetic dyes should therefore be adequately treated before being discharged into the environment.

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Decolorization and pollutant degradation are two major tasks in dye wastewater treatment (Martinez-Huitle and Brillas, 2009). Because of the strong decolorization ability of ozone, it has been widely used in dye wastewater treatment. Ozone has a high selectivity in attacking conjugated double bonds (e.g., N═N, C═N, and C═C) that are often the chromophores of dye molecules, and can thus decolorize dye wastewater rapidly (Wu et al., 2008; Tehrani-Bagha et al., 2010). However, ozone usually has limited oxidation ability to mineralize refractory synthetic dyes effectively to CO_2 and H_2O. Consequently, ozonation effluents can still contain considerable amounts of degradation intermediates, some of which (e.g., aromatic amines from azo dye degradation) can actually have higher toxicity than the original dyes (Silva et al., 2009; Tehrani-Bagha et al., 2010; Hsing et al., 2007; Liakou et al., 1997a, 1997b). To minimize the threat associated with degradation intermediates, high degrees of pollutant mineralization are therefore desired in synthetic dye wastewater treatment (Martinez-Huitle and Brillas, 2009; Nidheesh and Gandhimathi, 2012).

To improve pollutant mineralization efficiency, ozone is often used in combination with other technologies such as H_2O_2, UV, and TiO_2 in dye wastewater treatment (Hsing et al., 2007; Shu, 2006; Lopez et al., 2004). Particularly, the use of O_3 and H_2O_2 together (i.e., the so-called peroxone process) has a significant synergistic effect on organic mineralization. This synergy is mainly because O_3 can react with H_2O_2 to form hydroxyl radicals (•OH) (Eq. (1)) (Staehelin and Hoigne, 1982), which are a very powerful oxidant and can oxidize most organic solutes at very high rates that can approach diffusion control limits (von Gunten, 2003). The addition of H_2O_2 in ozonation processes can therefore usually increase pollutant mineralization efficiencies considerably (Pocostales et al., 2010). In addition, H_2O_2 and O_3 do not produce secondary pollutants because they leave only H_2O and O_2 as by-products (Martinez-Huitle and Brillas, 2009; Xu et al., 2011). Peroxone processes have therefore been considered an effective and environmentally-friendly advanced oxidation (AO) technology for wastewater treatment (Pocostales et al., 2010; Rice, 1997).

$$H_2O_2 + O_3 \rightarrow \cdot OH + \cdot O_2^- + O_2 \quad (1)$$

However, conventional peroxone processes require addition of external H_2O_2, which is unsafe to transport, store, and handle due to its high reactivity. It is therefore desirable that H_2O_2 be generated in situ at controllable rates in peroxone systems. To this end, we have developed an electro-peroxone (E-peroxone) process that can drive the peroxone reaction using in situ electro-generated H_2O_2 (Yuan et al., 2013). In the E-peroxone process, O_3 is produced from O_2 using an ozone generator, which is the same as in conventional ozone and peroxone processes. The ozone generator effluent (O_3 and O_2 gas mixture) is then sparged into a reactor that has a carbon-polytetrafluorethylene (carbon-PTFE) cathode, which can electrochemically convert O_2 to H_2O_2 in acid solution (Eq. (2)) and HO_2^- (conjugated base of H_2O_2) in base (Eq. (3)) (Wang et al., 2012; Brillas et al., 1995). The in situ generated H_2O_2/HO_2^- then reacts with the sparged O_3 to produce •OH, which in turn oxidize organic pollutants. Thus, by using the O_2 that would otherwise be wasted in conventional ozonation or peroxone processes to electrochemically produce H_2O_2 in situ, the E-peroxone process can drive the peroxone reaction electrochemically for pollutant degradation without the addition of external H_2O_2.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \quad (3)$$

The E-peroxone process represents a simple combination of conventional ozonation and electrolysis processes, but can achieve much better pollutant mineralization than the two processes individually (Yuan et al., 2013). In a preliminary study, we compared the mineralization of methylene blue by ozonation, electrolysis, and E-peroxone treatment. Up to 93% of total organic carbon (TOC) in the wastewater was degraded in E-peroxone processes. In contrast, only 22% and 15% TOC were degraded in ozonation and electrolysis processes, respectively (Yuan et al., 2013). The results indicate that E-peroxone process is very effective at mineralizing ozone-refractory organics, and may thus provide an attractive way to treat synthetic dye wastewater.

The main objective of this work was therefore to further investigate E-peroxone treatment of synthetic dye wastewater. Orange II (C. I. Acid Orange 7), which is a widely used synthetic azo dye (see Supplementary Data for details), was used as the model compound in this study. The •OH production in the E-peroxone process was evaluated using a terephthalic acid (TA) trapping technique, which has been used to quantify •OH in various AO processes (Hua and Hoffmann, 1997; Milan-Segovia et al., 2007). Decolorization and mineralization of Orange II in the E-peroxone treatment were investigated and compared with conventional ozonation and electrolysis processes. The effects of the main operating parameters (e.g., current, ozone concentration, electrolyte, and solution pH) on E-peroxone performance were evaluated systematically.

2. Experimental

2.1. *Chemicals and reagents*

Analytical grade Orange II and potassium titanium (IV) oxalate were purchased from Sinopharm Chemical Reagent Co. Ltd, China. H_2O_2 (3 wt%) and hydroxyterephthalic acid (HTA, 97%) were from Sigma–Aldrich. Terephthalic acid (TA, > 99%) was from Alfa Aesar. Other chemicals (e.g., Na_2SO_4, NaOH, and H_2SO_4) were analytical grade and purchased from Beijing chemical Works Co., China. All solutions were prepared using deionized water.

2.2. *Ozonation, electrolysis, and E-peroxone treatment of Orange II solution*

Ozonation, electrolysis, and E-peroxone treatment of 400 mL Orange II (initial concentration of 200 mg/L) were conducted in an undivided acrylic column reactor. For ozonation treatment, an ozone generator (Tonglin Technology Co., China) was used

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