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Technical Note

$NaNO_2/FeCl_3$ catalyzed wet oxidation of the azo dye Acid Orange 7

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Abstract

A combination of ferric chloride and sodium nitrite significantly improved the wet oxidation of the azo dye Acid Orange 7 (AO7) in acid aqueous media (pH 2.6) under moderate conditions ($T = 150$ °C; oxygen pressure = 0.5 MPa). To evaluate the catalytic system, wet oxidation of AO7 was carried out at temperatures between 90 and 150 °C and oxygen pressures ranging from 0.1 to 0.5 MPa. The effect of initial solution pH from 2.6 to 11.4 and the amount of catalyst on the degradation of AO7 were also investigated. AO7 initial concentration was kept 200 mg L^{-1}. The degradation process was monitored by UV–visible spectroscopy, HPLC, IC (ion chromatography), GC–MS and TOC analysis. At 150 °C and 0.5 MPa oxygen pressure, 56% TOC was removed after 4 h of treatment, while no obvious TOC removal were achieved without catalyst at the same experimental condition. The main degradation products were some small organic acids: formic acid, acetic acid, pyruvic acid, oxalic acid, succinic acid (identified and quantified by IC) and phthalic acid (identified by GC–MS).

Keywords: Wet oxidation; Ferric chloride; Sodium nitrite; Azo dye; Acid Orange 7

1. Introduction

Textile industries produce a great deal of wastewater polluted with dyes. In fact, about 1 000 000 tons of different dyes are produced annually in the world (Stolz, 2001; Pandey et al., 2007), among which approximately 10–15% is lost in wastewater streams during manufacturing or processing operations (Zhao et al., 2005; Pekakis et al., 2006). Within the overall category of dyestuffs, azo dyes represent the largest class of dyes (Van der Zee et al., 2003; Özkan et al., 2004; Ramalho et al., 2004; Kusic et al., 2006; dos Santos et al., 2007) and therefore constitute a significant portion of dye pollutants. The release of these compounds into water streams is undesirable, not only because of their color, but also because many azo dyes and their breakdown products are toxic and/or mutagenic to the living organisms Prevot et al., 2001; Rajaguru et al., 2002; Van der Zee et al., 2003; Işik and Sponza, 2004; Umbuzeiro et al., 2005). Therefore they have to be removed before discharging into the environment. Many traditional chemical, physical and biological methods have been used to treat these dye-containing wastewaters, among them biological treatment is the most widely used method because of its minimal impact on the environment and cost effectiveness (Chen et al., 2003; Senan et al., 2003; Jadhav and Govindwar, 2006; Romero et al., 2006; Pandey et al., 2007). However, azo dyes are generally persistent under aerobic conditions (Shaul et al., 1991; Libra et al., 2004; Velegraki et al., 2006; Işik and Sponza, 2007). Although they are easily reduced under anaerobic conditions, they produce potentially more hazardous aromatic amines (Weisburger, 2002; Mantzavinos and Psillakis, 2004; Aksu and Tezer, 2005; dos Santos et al., 2005). Therefore, to protect the environment, new and more efficient technologies for azo dye-containing wastewater treatment are especially needed.

In the last decades, “advanced oxidation processes” (AOPs) aiming at treating persistent organic pollutants

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in industrial wastewaters have been actively explored (Gogate and Pandit, 2004; Mantzavinos and Psillakis, 2004; Perathoner and Centi, 2005). But these AOPs are only suitable for treating low-concentration wastewaters (Andreozzi et al., 1999; Gogate and Pandit, 2004; Stübera et al., 2005). For medium-high-concentration wastewaters, as often encountered in industrial streams, wet oxidation (WO) has proved to be an effective technique in the largest number of practical cases (Perathoner and Centi, 2005; Bhargava et al., 2006; Levec and Pintar, 2007). Because of utilizing molecular oxygen or air as an oxidant, the most economically attractive and environmentally friendly oxidizing agent, WO has been the subjects of considerable studies (Bhargava et al., 2006). However, the conventional WO is usually conducted at high temperature (200–320 °C) and high pressure (2–20 MPa) (Pintar et al., 2004; Minh et al., 2006; Levec and Pintar, 2007), which results in high capital and operating costs. To ease reaction conditions consequently reduce costs, appropriate catalysts can be used; thus, the process becomes catalytic WO (CWO). The addition of catalysts not only enables the process to be carried out at much milder conditions, but also improves conversion of organic pollutants that are refractory to non-catalytic oxidation and accelerates rates of oxidation (Cybulski, 2007; Levec and Pintar, 2007). CWO has been applied with some encouraging results to the treatment of various recalcitrant organic compounds, such as various azo dyes (Donlagić and Levec, 1998; Chen et al., 1999; Raffainer and von Rohr, 2001; Arslan-Alaton and Ferry, 2002; Chang et al., 2003; Garcia et al., 2005; Lei et al., 2007; Liu and Sun, 2007; Santos et al., 2007). And a wide range of homogeneous and heterogeneous catalysts have been developed (Bhargava et al., 2006; Levec and Pintar, 2007). Among these tested homogeneous catalysts, copper salts showed the highest catalytic reactivity (Mishra et al., 1995; Imamura, 1999; Kolaczkowski et al., 1999; Bhargava et al., 2006; Cybulski, 2007; Lopes et al., 2007), however, they must be removed from the treated effluent to prevent the contamination of the receiving water by toxic copper ion (Imamura, 1999; Kolaczkowski et al., 1999; Levec and Pintar, 2007; Lopes et al., 2007). Compared with homogeneous catalytic system, the major advantage of using heterogeneous catalysts is that the additional catalyst removal step is not required (Bhargava et al., 2006; Liu and Sun, 2007). However, heterogeneous catalysts, in many cases, undergo severe deactivation due to sintering, poisoning of active sites or fouling of the catalyst surface by deposition of reaction intermediates (Kolaczkowski et al., 1999; Bhargava et al., 2006; Levec and Pintar, 2007). Also, in hot acidic environment which is the typical reaction condition of WO, the active component may dissolve into the liquid phase, which is potentially toxic to the environment (Kolaczkowski et al., 1999; Bhargava et al., 2006; Cybulski, 2007). Thus, it is necessary to develop environmentally friendly, inexpensive and efficient catalysts for treating azo dyeing wastewater.

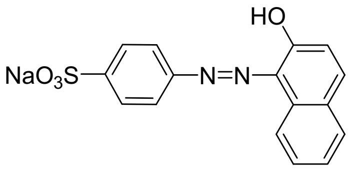

Fig. 1. The structure of AO7.

We have been interested in developing green methodologies for decomposing organic pollutants in water and have discovered a highly active catalyst (sodium nitrite), which exhibits the high catalytic capacity to activate molecular oxygen to destroy trichlorophenol, a kind of persistent environmental pollutant (Liang et al., 2005). Later, our investigation demonstrated that the incorporation of $FeCl_3$ into $NaNO_2$ could catalytically activate molecular oxygen for selective oxidation of alcohols (Wang et al., 2005). Recently, we disclosed that a combination of $FeCl_3$ and $NaNO_2$ could lead to efficient photocatalytic degradation for the steroid estrogens under natural light irradiation (Wang et al., 2007). Very recently, $FeCl_3/NaNO_2$ was found to be highly efficient for the WO degradation of dye pollutants especially anthraquinone dyes (Peng et al., in press). However, $FeCl_3/NaNO_2$ catalyzed WO of the azo dyes has not been investigated in detail. In the present work Acid Orange 7 (AO7, the molecular structure is shown in Fig. 1), a representative mono-azo dye, was used as a model pollutant to examine the WO destruction of azo dyes in the catalytic system. AO7 has been employed by some investigators to evaluate the effectiveness of some WO processes. For example, the homogeneous CWO experiments with AO7 catalyzed by $FeSO_4$ have been described in great detail in the paper of Raffainer and von Rohr (2001). They used an organic promoter to aid the catalytic destruction of AO7 because the catalytic activity of $FeSO_4$ was not enough high. The promoted CWO resulted in a TOC reduction of about 70% at 160 °C. However, the TOC removal was no more than 20% without the promoter at the same experiment condition. Based on above discussion, we postulated $NaNO_2$ might promote the $FeCl_3$-catalyzed WO degradation of AO7. The aim of our study is to show $NaNO_2$ can promote the $FeCl_3$-catalyzed oxidation of AO7 at moderate reaction conditions, since only using $FeCl_3$ as catalyst cannot efficiently oxidize the recalcitrant azo dye pollutant. Most notably, the catalytic system uses extremely abundant, cheap and environmentally friendly $FeCl_3$ as the catalyst, and cheap auxiliary agent ($NaNO_2$) as the co-catalyst.

2. Experimental

2.1. Materials

AO7 was purchased from Tianjin YuHua Economy and Trade Corporation (China) and used without further purification. NaCl, $NaNO_2$, Na_2SO_4, $FeCl_3 \cdot 6H_2O$, ammo-