Chemosphere 146 (2016) 413-418

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Degradation of methyl orange by ozone in the presence of ferrous and persulfate ions in a rotating packed bed



Chemosphere

霐

Deming Ge ^{a, b}, Zequan Zeng ^c, Moses Arowo ^{a, b}, Haikui Zou ^{a, b, **}, Jianfeng Chen ^{a, b}, Lei Shao ^{a, b, *}

^a State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

^b Research Center of the Ministry of Education for High Gravity Engineering and Technology, Beijing University of Chemical Technology, Beijing 100029,

China

^c State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

HIGHLIGHTS

• Methyl orange was treated by the ferrous-catalyzed sodium persulfate and ozone (O₃/Fe²⁺/PS) process.

• A rotating packed bed was used to intensify the $O_3/Fe^{2+}/PS$ process.

• The $O_3/Fe^{2+}/PS$ process showed better degradation effect than the O_3/Fe^{2+} process.

• The intermediates of methyl orange degradation were identified.

ARTICLE INFO

Article history: Received 5 August 2015 Received in revised form 9 December 2015 Accepted 17 December 2015 Available online 30 December 2015

Handling Editor: Xiangru Zhang

Keywords: Ozone Ferrous ion Persulfate Methyl orange Rotating packed bed Degradation

ABSTRACT

This work investigated the degradation of methyl orange by ozone in the presence of ferrous and persulfate ions $(O_3/Fe^{2+}/S_2O_8^{2-})$ in a rotating packed bed. The effects of various operating parameters such as initial pH, rotational speed, gas–liquid ratio, ozone inlet concentration and reaction temperature on the degradation rate of methyl orange were studied with an aim to optimize the operation conditions. Results reveal that the degradation rate increased with an increase in rotational speed, gas–liquid ratio and ozone inlet concentration, and reached a maximum at 25 °C and initial pH 4. Contrast experiments involving ozone and ferrous ions (O_3/Fe^{2+}) were also carried out, and the results show approximately 10% higher degradation rate and COD removal in the $O_3/Fe^{2+}/S_2O_8^{2-}$ process than in the O_3/Fe^{2+} process. Additionally, the intermediates of the degradation process were analyzed to ascertain the degradation products.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The huge demand for dyestuffs has led to a considerable increase in the use of synthetic complex organic dyes in textile industries. Consequently, these industries discharge large volumes of dye effluents which constitute a significant category of environmental pollutants (Torrades and García-Montaño, 2014). Azo dyes, which contain at least one azo group (-N=N-) attached to substituted benzene or naphthalene rings, are the commonly used commercial dyes in the textile industries (Gutowska et al., 2007). However, these dyes with complex aromatic structures are refractory in nature and resistant to the degradative environmental activities (Saroj et al., 2014), and their presence in the environment is a threat to human and aquatic organisms. In fact, they not only cause aesthetic problems in water but also are toxic and possibly carcinogenic (Wu et al., 2008). Thus, they must be eliminated from industrial effluents prior to discharge into the environment.



^{**} Corresponding author. Beijing University of Chemical Technology, No. 15 Beisanhuan East Road, Beijing, 100029, PR China.

^{*} Corresponding author. Beijing University of Chemical Technology, No. 15 Beisanhuan East Road, Beijing, 100029, PR China.

E-mail addresses: zouhk@mail.buct.edu.cn (H. Zou), shaol@mail.buct.edu.cn (L. Shao).

Ozonation, which is a form of advanced oxidation processes (AOPs), is an efficient means of treating wastewater containing refractory organics and is regarded as one of the promising alternatives for solving the problem of dye wastewater pollution (Wang et al., 2007). Ozone can degrade many kinds of organic compounds in aqueous solutions owing to its ability to decompose and generate large amounts of the powerful oxidant, hydroxyl radicals (HO_{\cdot}) with the oxidation potential $E_0 = 2.7$ V. Consequently, it has been extensively applied in the treatment of organic wastewater in recent years (Turhan et al., 2012), and extra efforts such as the application of homogenous catalysts to effectively enhance its performance have been made (Li et al., 2004). These catalysts can promote the oxidation ability of ozone and thereby increase the degradation rate of the organics. The widely used catalysts include transition metals and metal ions, with ferrous ion being the most preferred due to its nontoxic nature.

Persulfate anion $(S_2O_8^{2-})$ whose standard oxidation potential $(E_0 = 2.01 \text{ V})$ is comparable to that of ozone $(E_0 = 2.08 \text{ V})$ (Qian et al., 2015), is also a strong oxidant that has been used in the chemical oxidation of organics in wastewater (Yan et al., 2015; Deng and Ezyske, 2011). It can act either directly on the organics or indirectly through the generation of sulfate radicals ($SO_4^-\bullet$, $E_0 = 2.6$ V) and hydroxyl radicals (HO ·, $E_0 = 2.7$ V) (Wang et al., 2014; Zhong et al., 2015). However, fast reaction rates cannot be achieved when persulfate is used alone in treating refractory pollutants, as is evidenced by the low total organic carbon removal efficiency of 39% reported by Shabiimam and Dikshit (2012). Yang et al. (2011) also reported low efficiencies when persulfate is used alone. This could be attributed to the slow decomposition rate of persulfate anion into sulfate radicals. However, persulfate systems exhibit high efficiency in heated solutions. For instance, ibuprofen can be completely degraded in thermally activated persulfate solutions at neutral pH (Ghauch et al., 2012a), and complete decolorization of methylene blue can also be achieved in thermally activated sodium persulfate solutions in a short time (Ghauch et al., 2012b). Nonetheless, these processes are energy-intensive. Consequently, micrometric Fe⁰ particles were introduced into the persulfate systems to activate persulfate through the release of Fe²⁺ and nascent iron oxides during the corrosion process (Ghauch et al., 2013). The mechanism of the activation of persulfate by Fe^{2+} is as follows (Ayoub and Ghauch, 2014; Ji et al., 2014):

$$Fe^{2+} + S_2O_8^{2-} \to Fe^{3+} + SO_4^{-} \cdot + SO_4^{2-}$$
(1)

$$SO_4^- \cdot + H_2O \rightarrow HO \cdot + HSO_4^-$$
⁽²⁾

$$SO_4^- \cdot + OH^- \to HO \cdot + SO_4^{2-} \tag{3}$$

Moreover, it has been reported that combined use of persulfate and ozone yields higher removal efficiencies for COD, color, and NH₃–N compared with the sole application of either ozone or persulfate (Abu Amr et al., 2013). This study therefore employed both persulfate activated by Fe^{2+} and ozone in an attempt to enhance the degradation of methyl orange. Also, due to the rapid consumption of ozone in the ozonation processes, the rate of gas–liquid mass transfer is the limiting step (Beltrán et al., 1997). Therefore, a reactor with good gas–liquid mass transfer performance is highly necessary.

A rotating packed bed (RPB) is an efficient gas—liquid contactor that was first proposed by Ramshaw and Mallinson (1981). A simulated high gravity environment is created by centrifugal force generated by rotation of a rotor in the RPB. Liquid flowing through the porous packing in the rotor is split into micro- or nano-droplets, threads and thin films, and there is also a huge and violently renewed gas—liquid interface. Therefore, RPB can significantly intensify mass transfer and mixing processes, and has been widely used in many applications such as ozonation (Zeng et al., 2012), absorption (Chiang et al., 2012), stripping (Gudena et al., 2012), distillation (Chu et al., 2013), etc.

This work employed O_3/Fe^{2+} /sodium persulfate (PS) and O_3/Fe^{2+} processes separately in an RPB to investigate the degradation of methyl orange. The effects of different operating parameters on the degradation rate of methyl orange were investigated in an attempt to optimize the operating conditions and to establish the suitable oxidation approach.

2. Experimental

2.1. Experimental procedure

2.1.1. $O_3/Fe^{2+}/PS - RPB$

Methyl orange (A.P., Sinopharm Chemical Reagent Co. Ltd., China) was dissolved in deionized water to obtain methyl orange solution (200 mg L⁻¹). The pH of the solution was adjusted to a certain value using H₂SO₄ (98%, Beijing Chemical Works, China) or NaOH (A.P., Beijing Chemical Works, China). Both sodium persulfate (A.P.) and FeSO₄·7H₂O (A.P.) were purchased from Sinopharm Chemical Reagent Co. Ltd., China while KI (A.P.) was obtained from Beijing Chemical Works, China.

Fig. 1 shows a schematic diagram of the experimental setup. The RPB consists mainly of a stationary casing and a packed rotor. The rotor has an inner diameter of 40 mm, an outer diameter of 120 mm and an axial length of 15 mm. The diameter of the stationary casing is 170 mm. Stainless steel wire mesh (Beijing Hongyahong Mesh Sale Center, Beijing, China) was used as the packing material.

Ozone was produced from pure oxygen using an ozone generator (Tonglin High-Tech Technology Co. Ltd., Beijing, China), and the ozone-containing gas was introduced into the RPB via the gas inlet and flowed inwards in the rotor. The methyl orange solution was divided into two portions: one was with the addition of Fe^{2+} while the other was with PS. Both were pumped into the RPB via two liquid inlets respectively at the same liquid flow rate (total liquid flow rate of 15 L h^{-1}) and flowed concurrently outwards in the rotor, and the two liquid streams mixed and formed Fe²⁺/PS containing methyl orange solution. The gas and the liquid streams contacted countercurrently in the RPB (the contact time was less than 1 s), leading to absorption of O₃ into the liquid stream and subsequent degradation of methyl orange by $O_3/Fe^{2+}/PS$. The gas and liquid streams then exited the RPB via the gas outlet and liquid outlet respectively. The gas stream was further introduced into a solution of KI (10 g L^{-1}) to absorb the effluent O_3 while the liquid stream was sampled for analysis.

The experimental parameters, except the one under investigation, were set as follows: temperature = 25 °C, inlet ozone concentration = 40 mg L⁻¹, Fe²⁺ concentration = 1.0 mM, PS concentration = 2.0 mM, initial methyl orange concentration = 200 mg L⁻¹, liquid flow rate = 15 L h⁻¹, gas flow rate = 300 L h⁻¹, rotational speed = 1000 rpm.

2.1.2. O_3/Fe^{2+} - RPB

The O_3/Fe^{2+} - RPB experiments were performed in the same way as the $O_3/Fe^{2+}/PS$ - RPB experiments but without the addition of PS in the methyl orange solution.

2.2. Analyses

UV-Vis optical spectra of the samples were recorded from 190 to 1100 nm using a UV5200 PC UV-Vis spectrophotometer (Shimadzu, Japan) and the concentration of methyl orange was Download English Version:

https://daneshyari.com/en/article/4407986

Download Persian Version:

https://daneshyari.com/article/4407986

Daneshyari.com