Chemosphere 150 (2016) 40–48

Contents lists available at ScienceDirect

Chemosphere

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

Efficient degradation of Acid Orange 7 in aqueous solution by iron ore tailing Fenton-like process

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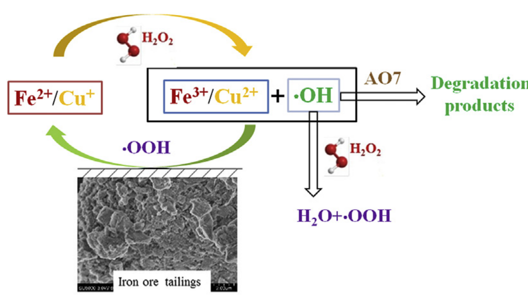
HIGHLIGHTS

- The iron ore tailing was first applied as heterogeneous Fenton catalyst.
- Acid Orange 7 was oxidized completely within 60 min by using the tailing and H_2O_2.
- The mechanism of the tailing as an efficient heterogeneous Fenton catalyst has been explored.
- $\cdot OH$ is the main active radicals for the Fenton-like reaction.
- The tailing can be reused more than nine times without apparent decrease of the catalytic capacity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 June 2015
Received in revised form
8 January 2016
Accepted 1 February 2016
Available online xxx

Handling Editor: Jun Huang

Keywords:
Iron ore tailing
Heterogeneous Fenton-like process
Acid Orange 7
Degradation
Mechanism and pathway
Catalyst stability

ABSTRACT

An effective method based on iron ore tailing Fenton-like process was studied for removing an azo dye, Acid Orange 7 (AO7) in aqueous solution. Five tailings were characterized by X-ray fluorescence spectroscope (XFS), Brunner–Emmet–Teller (BET) measurement, and Scanning Electron Microscope (SEM). The result of XFS showed that Fe, Si and Ca were the most abundant elements and some toxic heavy metals were also present in the studied tailings. The result of BET analysis indicated that the studied tailings had very low surface areas (0.64–5.68 $m^2\ g^{-1}$). The degradation efficiencies of AO7 were positively correlated with the content of iron oxide and cupric oxide, and not related with the BET surface area of the tailings. The co-existing metal elements, particularly Cu, might accelerate the heterogeneous Fenton-like reaction. The effects of other parameters on heterogeneous Fenton-like degradation of AO7 by a converter slag iron tailing (tailing E) which contains highest iron oxide were also investigated. The tailing could be reused 10 times without significant decrease of the catalytic capacity. Very low amount of iron species and almost undetectable toxic elements were leached in the catalytic degradation of AO7 by the tailing E. The reaction products were identified by gas chromatography-mass spectrometry and a possible pathway of AO7 degradation was proposed. This study not only provides an effective method for removing azo dyes in polluted water by employing waste tailings as Fenton-like catalysts, but also uses waste tailings as the secondary resource.

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http://dx.doi.org/10.1016/j.chemosphere.2016.02.001
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1. Introduction

Textile industries' production of dyestuffs creates huge volumes of wastewater. It is estimated that over 15% of the total world production of dyes is lost in the textile effluents (Liu et al., 2007). Azo dyes constitute the largest and the most important class of synthetic dyes for industrial applications (Yang et al., 2010). The discharge of azo dyes into water streams is undesirable not only because of their color but also their toxicity, non-biodegradability, and potential carcinogenic characteristics (Clarke and Johnson, 2010). Therefore, the urgent removal of azo compounds from wastewater has attracted worldwide attention.

Among various treatment methods, advance oxidation processes (AOPs) are becoming important technologies for removing azo compounds (Yang et al., 2010; Stylidi et al., 2004; Guo et al., 2010; Yuan et al., 2011). AOPs based on the in situ generation of hydroxyl radical (·OH), which is a highly powerful oxidizer and can attack organic compounds in a non-selective way, leading them to be mineral end-products. AOPs, including ozonation (Muthukumar and Selvakumar, 2004), Fenton reaction (Guo et al., 2010; Gutowska et al., 2007), and photocatalysis (Bandara et al., 1999), have been applied to the degradation of azo dyes. Among them, Fenton process has its own unique advantages, including high degradation efficiency, simple operation, environmentally benign property, and low cost (Zhao and Hu, 2008). The classical Fenton reagent consists of a homogeneous solution of iron ions and hydrogen peroxide. However, its practical application in dealing with industry wastewater has some disadvantages. It is efficient only at low pH ($pH < 4$) (Hu et al., 2011), and it is costly to remove the iron ions from the system after the treatment (Pariente et al., 2008; Luo et al., 2009). In order to overcome the above shortages, developing heterogeneous Fenton-like catalysts such as iron-containing solid compounds, iron-coated particles, and supported iron compounds, is necessary. For heterogeneous processes, main oxidative reactions occur at the solid–liquid interface where the iron remains substantially in the solid phase, either as a mineral or as an adsorbed ion (Hu et al., 2011). The heterogeneous Fenton-like reaction can effectively destroy organic pollutants in a wider pH range with much less iron loss than the homogeneous Fenton process. However, most of the procedures for preparing heterogeneous Fenton-like catalysts are tedious, time-consuming and costly.

A continuous increase of hazardous industrial wastes like iron ore tailings generated by iron and steel industry, is becoming a serious problem. A total of 59.7 billion tons of tailings has been discarded as waste, and the production of iron ore tailings is estimated to be one third of all stockpiled tailings. The stockpiles of waste tailings not only occupy a large area of land and pollute the environment, but can also easily flow and topple, leading to vegetation deterioration and injuries, resulting even in natural disaster, like when a tailing dam collapses (Wu et al., 2013; Liakopoulos et al., 2010). At the same time, waste tailings as secondary resources are very important to all countries in the world. There is growing interest in possible alternative uses of solid wastes as adsorbents and catalysts or as the starting materials before their discharge into the environment (Zeng et al., 2004; Li et al., 2010; Santos et al., 2015; Lin et al., 2013). Waste tailings have already been used as absorbents or oxidants to remove dye compounds (Clarke et al., 2010, 2013; Wu et al., 2013). Clarke and Johnson (2010) found that Mn oxide (Mn_xO_y) containing mine tailings from South Africa could decolorize a number of acid azo dyes including Acid Orange 7 (AO7), decolorizing 42% of AO7 after 2 h reaction. The waste tailings have rarely been applied as heterogeneous Fenton-like catalysts for the treatment of compounds. Ali et al. (2013) reported steel industry waste was effectively employed as a Fenton-like catalyst for the efficient decolorization of methyl orange dye, but the iron-containing waste used in their study contained about 90% iron, which could not be considered as real waste. Therefore, it is important to investigate real waste tailings for application as Fenton-like catalysts to treat organic pollutants.

In the present study, iron ore tailings were applied as the Fenton-like catalyst for the treatment of simulated dye wastewater. Acid Orange 7 was chosen as a model dye since it displays the "core-structure" of a number of commercial dyes and thus has similar physiochemical properties as more complex dye compounds (Coen et al., 2001). Reaction parameters on heterogeneous Fenton-like degradation of AO7 by iron ore tailings were investigated in detail. In addition, the intermediates were identified and the degradation pathway was proposed for AO7 in the Fenton-like process.

2. Experimental

2.1. Materials

Iron ore tailings composite samples were collected from five different tailings' dumps. The tailings were dried after collection. Acid Orange 7 was obtained from Sigma–Aldrich (China Division, Shanghai of China). H_2O_2 (30%, v/v) was purchased from Fisher Company (Utah, USA). HPLC-grade ethanol and dichloromethane (CH_2Cl_2) were obtained from Merck (Darmstadt, Germany). The spin-trapping agent 5,5-dimethyl-pyrroline-N-oxide (DMPO) was purchased from J&K Scientific Ltd (Beijing, China). Ultrapure deionized water produced by a Milli-Q water purification system (Millipore, Beldford, MA) was employed throughout this study. Stock solution was prepared by dissolving desired amount of AO7 into methanol and then stored at 4 °C in a refrigerator. Working solutions were obtained by diluting stock solution with water to desired concentrations.

2.2. Degradation of AO7 by heterogeneous Fenton-like experiments

The iron ore tailings were mixed thoroughly to guarantee uniformity in their composition and then 0.5 g of iron ore tailings were added to 100 mL of working solution containing 30 mg L^{-1} of AO7 and 19.8 mM H_2O_2. The pH of the working solution was adjusted to 5.0. The above conditions were continued for the heterogeneous Fenton-like process, unless variables were examined during the investigation of reaction parameters. The mixture was then mechanically stirred at 100 rpm and 20 °C. Aliquots (5 mL) of the sample were taken at different time intervals and filtered through syringe membrane filters (0.2 μm) for the determination of UV–Visible absorption. All experiments were carried three times. The recovery of AO7 in the filtered samples determined before heterogeneous Fenton-like experiments was 97.8% (RSD = 3.2%, n = 6), which shows adsorption of AO7 by the tailings is very low and can be negligible.

2.3. Analytical methods

The components of the tailings were analyzed by X-ray fluorescence spectrometer (XFS) (S2 Ranger, Bruker AXS GmbH). The specific surface areas of the tailings were determined by multipoint N_2-BET analysis using an accelerated surface area and porosimetry analyzer ASAP 2020 (Micrometrics, USA) with analysis bath temperature of 77 K. Surface properties of the tailings were investigated by S-4800N II scanning electron microscope (SEM) (Hitachi, Japan). EPR experiments were performed on a Bruker A300-10/12 spectrometer (Bruker, Bremen, Germany) with DMPO as a spin-trapping agent for radical measurement.