Chemical Engineering Journal 242 (2014) 180–186

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Catalytic ozonation of basic yellow 87 with a reusable catalyst chip

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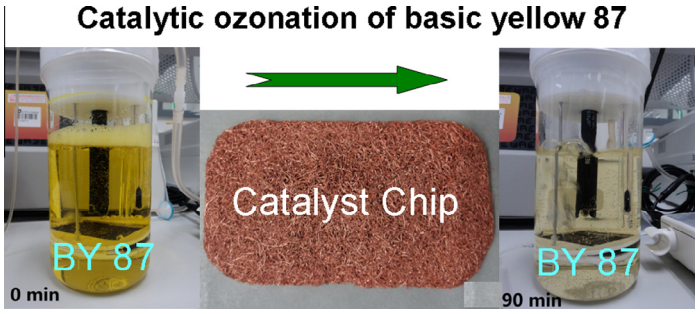
HIGHLIGHTS

- The catalyst chip significantly enhanced the mineralization of BY 87.
- The catalyst chip sustains a high catalytic activity under various conditions.
- Homogeneous and heterogeneous catalytic process occur simultaneously.
- The catalyst chip is reusable for successive ozonation process.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 August 2013
Received in revised form 22 November 2013
Accepted 18 December 2013
Available online 28 December 2013

Keywords:
Catalytic ozonation
Basic yellow 87
Catalyst chip
Kinetics
Mechanism

ABSTRACT

A porous copper fiber sintered sheet (PCFSS) with high porosity and large interfacial area, loaded with Cu/Zn/Al/Zr catalyst (i.e. CuO, ZnO, Al_2O_3 and ZrO_2), was evaluated for catalytic ozonation of Basic Yellow 87 (BY 87) in water. We investigated the influences of temperature, ozone dosage, BY 87 concentration and ozone/BY 87 molar ratios on the kinetics of BY 87 degradation, and the removal efficiency of BY 87. Compared to the ozonation process, the presence of the catalyst chip significantly improved the degradation of BY 87 (two times and five times more effective in the removal efficiency of COD and TOC, respectively). Batch experiments results demonstrated that the catalyst chip could sustain a high removal efficiency of BY 87 (around 99%), COD (about 60%) and TOC (around 30%) under a wide range of temperatures (0.5–61 °C), BY 87 concentrations (216–1078 ppm) and O_3/BY 87 mole ratios (0.98–21.3) within 4 h of reaction time. The decomposition rate of BY 87 was enhanced with increasing O_3 and BY 87 concentrations under the constant molar ratio. However, a shift from zero-order to pseudo-first-order kinetics (regarding BY 87) was observed when increasing O_3/BY 87 mole ratio from 0.98 to a value higher than 2.44. This work also demonstrated that homogeneous and heterogeneous catalytic processes could be integrated together in the presence of the catalyst chip, which shortens the half-life of BY 87 degradation. After reuse of the catalyst chip for ten times, the degradation efficiency of BY 87 and COD remained 99.2% and 58.9%, respectively, indicating a stable activity of the catalyst chip.

1. Introduction

Nowadays, color removal from industrial effluents is one of the most severe environmental issues faced by chemical industries. In most cases, conventional biological treatment systems are normally failed to apply for the destruction of the colorants, especially those containing azo chromophores (—N=N—), since they are hard to metabolize as carbon sources even by specific bacterial strains [1,2]. Ozone, can not only act as a 1,3-dipole to attack conjugated double bonds in colorants, but also can act as a nucleophilic agent and an electrophilic agent to react with activated aromatic system, finally resulting in the formation of biodegradable organic matter (e.g. carboxylic acids, carbonyl compounds)

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http://dx.doi.org/10.1016/j.cej.2013.12.041

[3]. Nevertheless, its efficiency is relatively low. Therefore, catalytic ozonation have been developed as one kind of advanced oxidation and have been widely explored for color removal of textile processing industrial wastewater, owing to its higher mineralization rates and effective ozone availability [4–8]. More recently, transition metal oxides were found to be a kind of promising catalyst for the heterogeneous catalytic ozonation, which aims to enhance the removal efficiency of refractory compounds through the transformation of ozone into more reactive species and/or through adsorption and reaction of the pollutants on the surface of the catalyst [9–12]. In heterogeneous catalytic ozonation process, reactions occur in both surface and liquid bulk, involving molecular ozone, $HO^{\cdot}$ radicals and surface oxygenated radical species. Moreover, metal ions, such as (Cu(II), Zn(II), et al.), will further facilitate the process of homogeneous catalytic ozonation [10]. Therefore, when transition metal oxides are used as the catalysts, both homogeneous and heterogeneous catalytic ozonation processes can be occurred at the same reaction system.

The efficiency of the catalytic ozonation process not only depends on the catalysts but also relies on the catalyst supports [4]. As a relatively new group of porous metals, porous copper fiber sintered sheet (PCFSS) have a three-dimensional reticulated structure featuring with high porosity and large specific surface area. PCFSS found many significant engineering applications particularly in filtration and separation, catalytic reaction, and thermal management [13]. These characteristics are useful not only for the catalyst to be firmly supported on the surface of the metal fiber but also for transferring heat, mass and promoting multiphase reaction. Nevertheless, to the best of our knowledge, transition metal oxides loaded PCFSS has not been reported as catalyst for ozonation process in solution.

In this paper, a novel catalyst chip (PCFSS loaded with transition metal oxides such as CuO, ZnO, Al_2O_3 and ZrO_2) with high porosity and large interfacial area was successfully fabricated. We explored the performance of the catalyst chip in catalytic ozonation of BY 87 which is one of the most commonly used hair dyes. Removal of BY 87 was compared in different systems including O_3 alone, O_3 + PCFSS, O_3 + catalyst chip, and O_2 + catalyst chip. For O_3 + catalyst chip, batch experiments were conducted at various reaction temperatures, ozone dosages, initial concentrations of BY 87, and O_3/BY 87 molar ratios. In addition, the reusability of the catalyst chip was evaluated in 10 successive ozonation process.

2. Experimental

2.1. Materials and reagents

A 2000 mg/L stock solution of BY 87 (Artenano Co. Ltd., Hong Kong) was prepared and stored in a reagent bottle at 4 °C. The structure of BY 87 was shown in Fig. S1(A) of SI. BY 87 solution of desirable concentration was obtained by successive dilutions of the stock solution with Milli-Q ultrapure water just before use.

In the PCFSS, copper fibers, with a coarse antler–like surface structure and 50–100 μm in diameter, were randomly aggregated, interlaced distributed and occluded with each other by point-to-point and line-to-line contacts, forming a three-dimensional reticulated metal backbone with an average pore size of >500 μm (Fig. S1(B) of SI). The porosity of PCFSS was about 75%. The catalyst chip was prepared by the reported method [14,15]. The dimension of the catalyst chip is 40 (W) × 70 (L) × 2 (H) mm. The catalysts were uniformly distributed on the surface of PCFSS using the impregnation method. The specific surface area of the catalyst chip is 3.65 m^2/g. The weight of the catalyst chip is 10.6875 g, among which the catalysts account for 9.66 wt.%. The catalysts are consisted of CuO (61.58 wt.%), ZnO (22.67 wt.%), Al_2O_3 (7.14 wt.%) and ZrO_2 (8.61 wt.%), respectively.

2.2. Experimental procedure

Catalytic ozonation of BY 87 were carried out in a cylindrical glass reactor (600 mL) equipped with ozone gas inlet and outlet, sampler, pH probe (Mettler-Toledo instrument MP220 pH meter), thermometer (0–100 °C) and Teflon catalyst holder (see Fig. S2 of SI). The catalyst chip was inserted into the holder near the bottom of the reactor. Ozone gas, generated from dried oxygen by an ozone generator (MEDOZONS-BM-O2, MEDOZONS Ltd., Russia), was continuously bubbled into the BY 87 simulated wastewater (400 mL) at a flow rate of 0.5 L/min through a pollen glass beetle (Φ20 mm) fixed under the catalyst holder. The reaction temperature was controlled with a water bath. Samples (5 mL) withdrawn at specific time intervals were immediately centrifuged at 6000 rpm for 15 min before analysis. The optical characteristics of the filtered samples, in the range of 190–1100 nm, were obtained from a Perkin Elmer Lambda 35 UV–vis spectrophotometer. The concentration of BY 87 was determined from its absorbance peak area at 411 nm. The chemical oxygen demand (COD) of samples was measured using a DRB200 digestion reactor and a DR890 Spectrophotometer (HACH). Total organic carbon (TOC) was analyzed by a TOC analyzer (TOC-5000A, Shimadzu). Two independent tests were conducted for each condition. The error is within ±5% for each test.

3. Results and discussion

3.1. Effect of the catalyst chip

In order to confirm the effect of the catalyst chip on BY 87 removal efficiency, the degradation of BY 87 in aqueous solution was performed in various systems such as O_3 alone, O_3 + PCFSS, and O_3 + catalyst chip, respectively. As shown in Fig. 1, the removal efficiency of COD was increased from about 28% to 41% with the presence of PCFSS in ozonation system. When catalysts were loaded on the PCFSS (i.e. the catalyst chip), the removal efficiency of COD was further increased to around 60% which is two times of the removal efficiency by the ozonation process. Meanwhile, TOC removal efficiency increased from about 7% to 13% and 36% in the presence of PCFSS and the catalyst chip, respectively. These results suggest that both the catalysts and the PCFSS have a synergistic effect with ozone for the degradation of BY 87. In Fig. 1, it should be noted that COD value was significantly reduced owing to the increase in saturation level (i.e. need less oxygen atom to

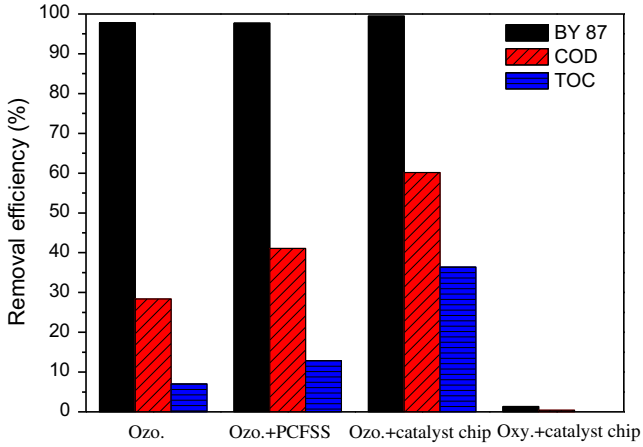

Fig. 1. Degradation efficiency of BY 87 and COD in different cases (conditions: temperature: 22 ± 0.5 °C; initial pH: 6.6; C_0(BY 87): 216 ppm; $C(O_3)$: 500 ppm; oxygen flow rate: 0.5 L/min; reaction time: 4 h).