Decolorization of azo dyes Orange G using hydrodynamic cavitation coupled with heterogeneous Fenton process

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ABSTRACT

The present work demonstrates the application of the combination of hydrodynamic cavitation (HC) and the heterogeneous Fenton process (HF, Fe^0/H_2O_2) for the decolorization of azo dye Orange G (OG). The effects of main affecting operation conditions such as the inlet fluid pressure, initial concentration of OG, H_2O_2 and zero valent iron (ZVI), the fixed position of ZVI, and medium pH on decolorization efficiency were discussed with guidelines for selection of optimum parameters. The results revealed that the acidic conditions are preferred for OG decolorizaiton. The decolorization rate increased with increasing H_2O_2 and ZVI concentration and decreased with increasing OG initial concentration. Besides, the decolorization rate was strongly dependent on the fixed position of ZVI. The analysis results of degradation products using liquid chromatography–ESI–TOF mass spectrometry revealed that the degradation mechanism of OG proceeds mainly via reductive cleavage of the azo linkage due to the attack of hydroxyl radical. The present work has conclusively established that the combination of HC and HF can be more energy efficient and gives higher decolorization rate of OG as compared with HC and HF alone.

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1. Introduction

Azo dyes, generally characterized by the presence of one or more azo bonds (–N=N–) in association with aromatic systems and auxochromes (–OH, –SO₃, etc.), are important synthetic colorants that represent the largest class of dyes in common use especially applied in textile processing. Textile effluents have been shown to be toxic, mutagenic, carcinogenic and non-biodegradable, making it a public health concern. Several conventional techniques including physical, chemical, and biological processes have been developed to remove the azo dyes in the aquatic environment, such as adsorption [1–3], coagulation [4], photo-catalysis [5,6], ozonation [7], and biosorption [8–10]. Nevertheless, these adopted methods have proven to be costly, time-consuming and impractical.

As these dyes are typically recalcitrant to conventional wastewater treatment, many studies are now focused on advanced oxidation processes (AOPs). Cavitation-based AOPs have been widely developed as a promising and efficient method for the removal of azo dyes, which are classified as acoustic cavitation (AC), hydrodynamic cavitation (HC), optic cavitation and steam bubble cavitation [11–13]. The AC is widely studied by sonochemical research group including Hoffmann, Weavers, Pandit, Grieser and Asakura. The temperature (on the order of 5000 K) and pressure (on the order of 5000 K) in collapsing microbubbles can reach extreme levels [14,15], leading to the thermal dissociation of water vapor into reactive hydroxyl free radicals and hydrogen atoms [15–17]. These highly reactive species are vital to the subsequent oxidation and reduction reactions. Despite such promising information, use of acoustic cavitation reactors in commercial scale does not appear to being progressing robustly, and only one study in pilot-scale conducted by Hoffmann in 2001 was reported [18]. The major hindrance of using this technique rests with efficient operation of ultrasound transducers at a commercial scale operation due to substantially lower energy efficiencies and higher investment costs [12,19].

Hydrodynamic cavitation, which is induced by subjecting the liquid to velocity variations by introducing constrictions in the flow, can be a serious contender as an alternative to AC. Several reports appear in literature confirming that HC is better energy

efficient, lower investment costs, and higher scale-up possibilities than AC [19–21]. However, time-consuming has proven to be a major hindrance of alone HC process. Consequently, individual HC process is not yet considered commercially feasible due to this limitation. Moreover, the previous results suggested that the combination of various AOPs was deemed as essential step in their further development. Therefore, numerous research programs aimed at the combination of HC with AOPs in order to intensify degradation rate or achieve complete mineralization, such as catalytic oxidation, Fenton process and Fenton like processes [22,23]. Especially, the effect of applicability of combination of HC and Fenton chemistry has been also widely studied. The overall aim of these combined processes is to mineralize the initial organic pollutants completely or at least lower chain compounds, obtain higher degradation rate, and convert the initial compounds into less harmful final products than the individual techniques [23,24]. Conventionally, Fenton chemistry is based on the use of Fe^{2+} ions conjunction with hydrogen peroxide (H_2O_2) to generate highly reactive hydroxyl radicals ($\cdot OH$) which then oxidize the organic pollutants to CO_2, H_2O and relatively smaller molecules [25–27]. In heterogeneous Fenton process (HFP), it is hypothesized that initially iron metal is corroded to Fe^{2+} in the presence of H_2O_2 under acidic conditions, which then further reacts with H_2O_2 in a Fenton-like process to generate $\cdot OH$ and Fe^{3+}. The Fe^0 then reduces the Fe^{3+} back to Fe^{2+} and the cycle continues [28].

The combination of HC and HFP is considered to obtain an improved degradation efficiency attributed to the higher quantum free radicals production [29]. Researches confirmed that the combination of HC and HFP is very energy efficient and cost effective as compared to individual technique to treat the wastewater, such as the efficacy of combination of HC and Fenton chemistry for the removal of p-nitrophenol studied by Pradhan et al. [30], and HC coupled with the HFP for the treatment of real industrial wastewater reported by Bremner et al. [31]. As was pointed out by Bagal et al. in recent literature [22], the role of sequential addition of Fenton's reagent on degradation efficiency of pollutant in combined process of HC and AFP must be optimized and the heterogeneous Fenton like processes must be developed on the pilot scale for reduction or elimination of the sludge formation [32].

The Orange G (OG), which is a typical symbol of azo dye and extensively used in dyeing the textile fabrics, has been the subject of investigations. The chemical structure of OG is shown in Fig. 1. Mostly, the degradation of OG using traditional techniques including adsorption [33,34], sonolysis [35], biotransformation [36], UV/TiO$_2$ [37,38], and Fenton processes [39] has been reported. Currently, it should be noted that in spite of extensive research, very limited information exists regarding the evaluation on OG decolorization through the combination of HC with HFP. Cavitation is a dynamic phenomenon and its effects strongly depend on the operational parameters. In this study, experiments on OG decolorization were conducted by coupling of HC and HFP (Fe^0/H_2O_2). The objective of this study was to investigate the effects of main affecting operation conditions such as the inlet fluid pressure, initial concentration of OG, H_2O_2 and ZVI, the fixed

position of ZVI, and medium pH on decolorization efficiency. To our knowledge, this is the first comprehensive investigation of operation parameters on the decolorization of OG and degradation mechanism in HC–HFP system, thus paving the way for pilot-scale application.

2. Experimental

2.1. Chemicals and solvents

Hydrogen peroxide (30%, w/v) and ZVI powder were purchased from Kelong chem. (ShangHai, China). HPLC grade acetonitrile and acetic acid were obtained from Merck Co. (Darmstadt, Germany). Orange G and other reagents with analytic reagent grade were purchased from Huipu chemical&apparatus Co. (Hangzhou, China). Solutions were prepared using Millipore water supplied by a Milli-Q water purification system (Molsheim, France).

2.2. Apparatus setup

Schematic representation of experimental setup of hydrodynamic cavitation system and the dimensions of the applied orifice plate are shown in Fig. 2. The system consists of a feed vessel tank with 1.25 L capacity, a vortex pump (25WB-65, Shanghai Hongya Machine Pump Making Co., LTD, 3 kW, 2900 rmp, 0.3 m³/h), and valves. The discharge pipe of pump is connected to the suction side on the bottom of the tank and bifurcated into main and bypass lines. The main line and the bypass line discharge the material back into the tank. The main line has the facility to incorporate an orifice plate located over the pressure gauge to generate cavitation of different intensities. The bypass line has a throttling valve for adjusting pressure and flow rate into the main line. The water passes through the orifice plate, causing the central pressure at the cavity falls below the vapor pressure of the water and generating a number of cavities. The pressure gauges are provided and recorded both in inlet line and downstream of the orifice plate. During the experiment, control valve (in bypass line) was left open until the pump reaches its maximum speed, and thus the desired pressure and flow rate were obtained in the mainline.

2.3. Experimental methodology

A dimensionless parameter called cavitation number, is generally used in hydrodynamic cavitation and is defined as

$$\sigma = \frac{p_d - p_v}{p_u - p_d} \approx \frac{p_d}{p_u} \tag{1}$$

where p_d, p_u, and p_v are the downstream, upstream, and vapor pressures, respectively, and the approximation holds when $p_u \geqslant p_d \geqslant p_v$, as they do under this experimental conditions.

All experiments were performed with reaction time of 120 min, and samples were withdrawn from the reaction vessel every 20 min. The concentration of OG was analyzed by measuring the absorbance of dye solution at 478 nm using a UV-spectrophotometer (TU-1901). The concentration of dissolved Fe^{2+} concentration was determined using the standard phenanthroline colorimetric method [40]. The extent of mineralization was measured on a total organic carbon analyzer (TOC-V CPN5000 A, Shimadzu). All experiments were carried out in triplicate to check the reproducibility and the average value for each run was calculated as the presented data.

The temperature of the reaction mixture was maintained at 25 °C by circulating cooling water through the surrounding water jacket. The optimal pH value at 3 was selected and adjusted by sulphuric acid and sodium hydroxide considering the cavitation
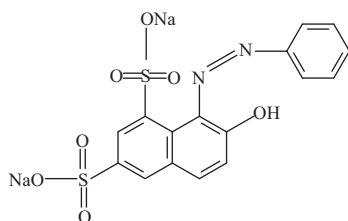

Fig. 1. Molecular structure of OG.