Chemical Engineering Journal 315 (2017) 274–282

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Combination of photocatalysis with hydrodynamic cavitation for degradation of tetracycline

Xiaoning Wang, Jinping Jia *, Yalin Wang

School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China

HIGHLIGHTS

- Coupling photocatalysis with hydrodynamic cavitation shows synergistic effect.
- HCO_3^- improves degradation rate of tetracycline in combined process.
- Degradation pathway of tetracycline involved hydroxylation and loss of some groups.

ARTICLE INFO

Article history:
Received 29 July 2016
Received in revised form 4 January 2017
Accepted 5 January 2017
Available online 5 January 2017

Keywords:
Tetracycline
Hydrodynamic cavitation
Photocatalysis
Synergistic effect
Degradation mechanism

ABSTRACT

Hydrodynamic cavitation is a promising technology for wastewater treatment. In this study, TiO_2 (P25) photocatalytic degradation of tetracycline, an antibiotic compound extensively used and environmentally hazardous, was conducted with hydrodynamic cavitation employed simultaneously. Many factors, such as initial tetracycline concentration, solution pH and presence of inorganic anions, were explored. Kinetics were investigated at varied contaminant concentrations, and the pseudo-first-order rate constant for tetracycline photocatalysis coupled with hydrodynamic cavitation was 1.5–3.7 times of the sum of those for the individual processes. These results indicated that a synergistic effect occurred in the combined method. Tetracycline degradation was pH-dependent and favored at alkaline pH. The presence of HCO_3^- in the medium induces promotive effect on the photocatalytic degradation of tetracycline in the presence of hydrodynamic cavitation, while sulfate and chloride exhibit only minor effect. UV/Vis spectra, Fourier transform infrared (FTIR) adsorption spectra and liquid chromatography–mass spectra (LC–MS) were used to evaluate the degradation mechanism. Scanning electron microscopic (SEM) images of TiO_2 confirmed that hydrodynamic cavitation can prevent photocatalytic particles from agglomeration.

1. Introduction

Antibiotics, one of the largest groups of pharmaceutical compounds used as therapeutic medicine and feed supplements in livestock, have been detected in various water bodies at levels of ng L^{-1} to μg L^{-1} [1]. Although the antibiotic concentration in aquatic environment is low, they are considered to pose a potential threat to ecosystem and human health due to ecotoxicity and the development of antibiotic resistance genes [2,3]. Tetracyclines are the second most common antibiotic group in both production and usage throughout the world. According to a report of the Animal Health Institute, in European Union, about 4990 tons of tetracyclines were used in animal feeding in 2007 [4]. In the U.S., tetracyclines sold and used were more than 5900 tons in 2012 [5]. The usage of tetracyclines in China in 2013 was estimated to be 6950 tons [6]. As tetracyclines are poorly metabolized or absorbed in the body, most of the drugs are discharged in unchanged and active forms in the excreta [1]. Moreover, tetracyclines are designed to be stable and biorefractory, and their removal by conventional water treatment methods is ineffective [7]. So, it is of great interest for global researchers to develop effective techniques for rapid degradation of tetracyclines.

Photocatalysis with TiO_2 is a promising method for the degradation of organic pollutants [8–10]. During this process, highly reactive radical species, predominantly hydroxyl radicals, are generated and responsible for the degradation as well as mineralization of organics in wastewaters. Several studies on the photocatalysis of tetracycline have been published, and the intermediates, toxicity and possible pathway of tetracycline photocatalytic degradation were addressed [8,11,12]. However, photocatalytic oxidation technique is affected by mass transfer

* Corresponding author.
E-mail address: jpjia@sjtu.edu.cn (J. Jia).

http://dx.doi.org/10.1016/j.cej.2017.01.011
1385-8947/

limitations and by gradual deactivations from accumulation of contaminant and its byproducts on the catalyst surface [13], which might be a significant obstacle for its large-scale application in real wastewater treatment.

To solve this problem, many researchers have been attempting to introduce cavitation into photocatalytic reaction systems to improve the light utilization efficiency of suspended TiO_2 [13–15]. Cavitation is the phenomena of formation, growth, and violent implosion of vapor bubbles in a liquid medium [16]. Ultrasonically and hydrodynamically induced cavitations are the two simple means. The former technology has been studied extensively to degrade organic pollutants in waters [14,17,18], but ultrasound irradiation is not economically applicable for industrial plants due to its ineffective distribution of the cavitational activity on a large scale and inefficient transfer of electric power into the liquid [19].

An alternative technique is the hydrodynamic cavitation, which can overcome the problems of ultrasonic cavitation. As liquid passes through constrictions such as orifice and venturi, the pressure at the throat or vena contracta falls below the vapor pressure of the liquid, and the liquid flashes, generating a number of bubbles which will subsequently collapse when the pressure recovers downstream of the constriction [20]. Bubble collapse during cavitation generates localized transient hot spots with high temperatures and pressures, which induce the cleavage of water and volatile pollutant molecules to yield free radicals [16,21]. The collapsing cavities can also generate high-speed micro-jets and intensive shockwaves, which may be responsible for the surface cleaning and/or erosion, fragmentation of friable solids and enhancement in local mass transport rates [22]. Hydrodynamic cavitation is a green technology for the degradation or even mineralization of water contaminants performed at moderate conditions and without assistance of any external chemicals or catalysts [23]. Its combination with other advanced oxidation processes, such as H_2O_2 [20,24], Fenton [20,25] and ozonation [26], has also been studied. However, reports on the combination of hydrodynamic cavitation and photocatalysis are seldom [15,27], and there is no study, to the best of our knowledge, has been reported using this hybrid method to treat tetracycline solutions.

In this study, the combined system of photocatalysis and hydrodynamic cavitation using a venturi tube was explored to degrade tetracycline in an aqueous solution with relatively large volume of 4.0 L. The effect of several experimental conditions, including initial concentration of tetracycline, solution pH and addition of inorganic anions was investigated. To estimate the role of hydrodynamic cavitation in photocatalytic process, a straight pipe instead of venturi tube with the same length and inlet diameter was fixed at the termination of main line, and the fluid was also circuiting in the loop during the photocatalytic degradation of tetracycline. Several analytic methods, UV/Vis, FTIR and LC–MS spectroscopy as well as SEM technique, were utilized to analysis and confirm the experimental results.

2. Material and methods

2.1. Materials

Tetracycline hydrochloride (molecular weight: 480.90 g mol^{-1}; molecular formula: $C_{22}H_{24}N_2O_8{\cdot}HCl$) was of USP grade and purchased from Aladdin Chemistry Co., Ltd. The commercial TiO_2 (Degussa P25, 80% anatase and 20% rutile, surface area 50 $m^2\,g^{-1}$) was purchased from Degussa and used as a photocatalyst. Acetonitrile and formic acid (HPLC grade) were purchased from Aladdin Industrial Corporation (Shanghai, China). All other reagents used were of analytical grade. HCl and NaOH were used to adjust solution pH. NaCl, $NaHCO_3$ and Na_2SO_4 were chosen to explore the influence of inorganic anions on tetracycline degradation. Ultrapure water used in chromatographic analysis was obtained from a Hitech-Kflow water purification system (Hitech Instruments Co. Ltd., Shanghai, China). Solutions for other uses in this study were prepared with deionized water.

2.2. Experimental setup

Degradation runs were performed in an experimental setup as shown in Fig. 1, which allows us to investigate the individual and combined processes of photocatalysis and hydrodynamic cavitation. It consists of a jacketed cylindrical glass reactor (capacity 5.0 L) and a jet flow loop. The solution temperature in the reactor was kept at 30 ± 3 °C through a cooling water circulator. UV254 irradiation was provided by a 9 W mercury lamp, which was hosed in a 30 mm diameter quartz tube and vertically placed inside the reactor. The light intensity at a distance of 1 cm from the housing lamp was 27.8 mW cm^{-2}, as measured with a UV radiometer (Light and Electric Instruments Factory of Beijing Normal University).

Aqueous solution in the reactor was circulated through the jet flow loop, which was driven by a high-pressure, self-priming stainless steel pump (Shanghai Qiquan Pump Co., Ltd., China) with an electric power of 0.75 kW. The intake side of the pump was connected to the bottom of the reactor, while the discharge side of the pump branched into main and bypass lines. Throttle valves and pressure gauge at the lines were provided for adjusting and measuring the pressure in the main line. A venturi tube as shown in Fig. 1b was made of Pyrex glass and provided to act as the producer of cavitation. The inner diameter of throat of the venruti tube is 2 mm. Its expansion and contraction angles are both 20°. The venturi tube was equipped at the termination of the main line and submerged in the solution. The distance between the UV254 lamp and venturi tube is 6 cm.

To achieve high cavitation activity, inlet pressure and flow rate through the cavitation tube should be improved [28,29]. In this study, the throttle valve in the main line was left open and the valve in the bypass line was totally closed. Thus, the highest pressure of 0.34 MPa and highest flow rate of 105.7 mL s^{-1} were obtained in the mainline. The cavitation number was calculated to be 0.59 according to literature [30]. During the sole process of photocatalysis, circulation of the fluid without venturi tube in the loop system was employed to enhance the mass transfer in solution.

2.3. Experimental procedure

All experiments were performed for 90 min with 4.0 L aqueous solution of tetracycline. The venturi tube and straight pipe with the same length and inlet diameter were altered, and the UV254 lamp was switched on as needed to conduct the individual or combined experiment. Unless specifically mentioned, the initial concentration of tetracycline was 30 mg L^{-1}, TiO_2 dose was 100 mg L^{-1}, initial pH was natural 4.2, and no matrix component was added. Before each test, the reaction mixture was mechanically stirred in the dark for 1 h to ensure the catalyst-substrate equilibration. For all the conditions investigated, the total amount of tetracycline adsorbed on TiO_2 was less than 1 wt%. The experiments were repeated for two times.

2.4. Analytical methods

Samples were withdrawn at designated times and filtered through Millipore 0.45 μm filters prior to analysis. The absorbance spectra of the untreated and treated samples were scanned using a UV/Vis spectrophotometer (UV-2102, Unico, USA). The amount of