



## Sonolytic degradation of butyric acid in aqueous solutions



Meral Dükkancı, Gönül Gündüz\*

Ege University, Chemical Engineering Department, 35100 Bornova, İzmir, Turkey

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### ABSTRACT

The sonolytic degradation of butyric acid was investigated in an ultrasonic reactor emitting waves at 850 kHz. The effects of the ultrasonic power, the initial concentration of butyric acid, and the addition of H<sub>2</sub>O<sub>2</sub> were studied on the degradation of butyric acid. In the sonication of butyric acid, degradation degrees as high as 31.5% could be achieved at a power of 31 W, at an initial concentration of 2.8 mM butyric acid with the addition of 0.34 M H<sub>2</sub>O<sub>2</sub> for a sonication time of 5 h. The degradation of butyric acid increased with irradiation time, indicating first order kinetics.

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### 1. Introduction

The application of ultrasound irradiation for the degradation of organic pollutants in water has received considerable attention from environmental scientists and engineers, due to their undesirable effects in the water environment. Water irradiation using ultrasound causes decomposition of water molecules into extremely reactive radicals, such as H<sup>\*</sup> and HO<sup>\*</sup>. These generated radicals either react with each other to form new molecules and radicals, or diffuse into a bulk liquid to serve as an oxidant (Xu et al., 2013). In the oxidation of wastewaters containing aromatic compounds such as phenol results in the formation of several intermediates including unsaturated carboxylic acids such as muconic, maleic, fumaric, and acrylic acids. The unsaturated acids undergo further oxidation to more refractory, short chain mono and dicarboxylic acids such as acetic (AA), oxalic (OA), propionic (PropA), and butyric (BA) acids (Gomes et al., 2002).

Among these acids, butyric and propionic acids have a low odour threshold with unpleasant sour odours. They have become recognized world-wide as a problem in the treatment of industrial waste water. BA is particularly a good model system because it is formed in most of the degradation pathways of more complex organic compounds and it is a precursor of AA, which is a typical end product of oxidation reactions (Gomes et al., 2004).

High temperatures and pressures are required to oxidize carboxylic acids when traditional oxidation techniques are used (Gomes et al., 2004; Sanchez-Oneto et al., 2006; Kim and Ihm, 2011; Tran et al., 2011; Dobrynkin et al., 2012). However, oxidation of carboxylic acids by Advanced Oxidation Processes (AOPs), such as photocatalytic oxidation (Lucena et al., 2012; Wetchakun et al., 2013; Turki et al., 2013; Mattsson et al., 2013), photoFenton oxidation (Sannino et al., 2013), photocatalytic ozonation (Mehrijouei et al., 2011), catalytic ozonation (Orge et al., 2012), electrochemical oxidation (Huang et al., 2011; Shih et al., 2013), photoelectrochemical oxidation (Chen et al., 2013), and photoelectrocatalytic oxidation (Shinde et al., 2012), has the advantage of carrying out the reaction under ambient conditions. Among various AOPs, sonication has attracted considerable interest in recent years by virtue of its particular comparative advantages, such as avoidance of chemical dosing and catalysts, safety, a lower demand for solution clarity, etc. (Xu et al., 2013).

Sonolytic degradation of some carboxylic acids has been reported in literature. It was found that high frequency of irradiation was more beneficial in degrading carboxylic acids (Yoo et al., 1997; Gogate et al., 2003; Dükkancı and Gündüz, 2006; Fındık and Gündüz, 2007; Okitsu et al., 2009). The impact of a collapsing bubble on the contents of the surrounding liquid depends on the vibrational frequency: If the frequency is low (20–100 kHz) mechanical effects overcome, whereas, in a high frequency medium (100–1200 kHz) the chemical effects dominate (Kidak and Ince, 2006; Larpparisudthi et al., 2009; Mason et al., 2011; Dükkancı et al., 2012). The efficiency of acoustic cavitation can be increased by using high frequencies instead of low frequencies. Even though

\* Corresponding author. Tel.: +90 232 3112292.

E-mail address: [gonul.gunduz@ege.edu.tr](mailto:gonul.gunduz@ege.edu.tr) (G. Gündüz).

cavitation is less violent, more cavitation events occur at higher frequencies, providing more opportunities for free radicals to be produced. In literature, many studies have been reported by using high frequency in sonolytic degradation of organic pollutants (Ince and Tezcanlı, 2001; Jiang et al., 2002; Tezcanlı-Guyer and Ince, 2004; Bremmer et al., 2009; Sáez et al., 2010).

However, no study on sonolytic degradation of butyric acid at a high frequency, such as 850 kHz, was previously reported. In the study done by Sáez et al. (2010) in the sonochemical degradation of perchloroethylene aqueous solutions, the frequency of 850 kHz gave the best results among the other studied frequencies of 380, 580 and 1142 kHz in terms of degradation efficiency. In another study done by Dükkançı et al., (2012), sonochemical treatment of Orange II textile dye was studied using ultrasound at frequencies of 20, 40, 380, 850, 1000, and 1176 kHz with different power inputs. They concluded that 850 kHz ultrasonic bath was not only highly effective on Orange II decolorization but also had the highest electrical efficiency and was the best cost effective equipment. So, the present study aims to contribute to the literature by presenting the sonolysis of butyric acid in an aqueous solution in an ultrasonic reactor with a frequency of 850 kHz. The effects of ultrasonic power, initial concentration of butyric acid, and the addition of H<sub>2</sub>O<sub>2</sub> were investigated on the sonolytic degradation of butyric acid.

## 2. Experimental

The system includes an ultrasonic signal generator (Meinhardt, K8) operating at different powers and a piezoelectric transducer with a titanium diaphragm (Meinhardt, E/805/T) emitting ultrasound waves at 850 kHz. The solution to be sonicated was placed in a 0.75 dm<sup>3</sup> glass reactor (Meinhardt, 5/1575) surrounded by a water cooling jacket to control temperature inside the reactor ([http://www.meinhardt-ultraschall.de/page06\\_e.html](http://www.meinhardt-ultraschall.de/page06_e.html), 2013).

In a typical run, a butyric acid solution (99% + purity, Aldrich, 0.35 dm<sup>3</sup>) at a known concentration was placed in the reactor. The temperature of the reaction mixture was kept constant at 293 K by adjusting the flow rate of the cooling water. At the desired ultrasonic power the solution was sonicated for 5 h. The input powers of 25, 50 and 75 W from the generator were applied to the sonication system. The powers given in the study are the actual powers (4, 8 and 31 W) determined by the calorimetric method (Mason, 1999). Samples were taken periodically from the reaction mixture and analyzed by HPLC (Agilent 1200) equipped with a UV detector at 210 nm. Separation of the components was achieved by a ZORBAX Eclipse XDB-C18 column (4.6 mm, 5 μm, Agilent). Elution was performed at 1 mL/min flow rate of the mobile phase H<sub>2</sub>O:MeOH:H<sub>3</sub>PO<sub>4</sub> = 9:6:0.005 volume ratio and at a pH ~2.73. The percentage degradation of butyric acid was followed as a function of time.

The reduction in the chemical oxygen demand (COD) of the butyric acid solution was determined by measuring initial and final COD values (after sonication for 5 h) of the aqueous BA solution with a Lovibond Checkit Direct COD Vario device.

## 3. Results and discussion

### 3.1. Effect of ultrasonic power

The experiments for the effect of ultrasonic power on the sonication of butyric acid were performed with a butyric acid concentration of 2.8 mM, at a frequency of 850 kHz and at actual powers of, 4, 8, and 31 W. Each run was repeated at least four times, but, mostly seven times. Fig. 1 displays the time variation of the degradation degree ( $x$ ) of butyric acid under various ultrasonic powers. The inset presents the kinetic study. A linear dependence

of  $-\ln(1-x)$  versus time ( $t$ ) is observed at different powers indicating that the degradation of butyric acid follows first order kinetics with respect to the butyric acid concentration. A higher degradation degree (14.1%) could be achieved with 31 W than those with 4 and 8 W (3.0% and 4.6%, respectively) after a sonication time of 5 h.

The initial degradation rates were calculated using Equation (1):

$$(-r_{A0}) = C_{A0}(dx/dt)_{0-60 \text{ min}} \quad (1)$$

where  $(-r_{A0})$  is the initial degradation rate of butyric acid in mM min<sup>-1</sup>,  $C_{A0}$  is the initial concentration of butyric acid in mM, and the  $dx/dt$  is the slope of the straight line in min<sup>-1</sup> obtained from the degradation degree ( $x$ ) versus the time graph in Fig. 1 for the first 60 min.

The initial degradation rate of the BA solution increased from  $8.4 \times 10^{-4}$  mM min<sup>-1</sup> to  $1.4 \times 10^{-3}$  mM min<sup>-1</sup>, and to  $3.1 \times 10^{-3}$  mM min<sup>-1</sup> with the increase in power from 4 W to 8 W and to 31 W, respectively.

When the power was increased from 4 W to 8 W and then to 31 W, the rate constant of BA increased from  $1.2 \times 10^{-4}$  min<sup>-1</sup> to  $1.5 \times 10^{-4}$  min<sup>-1</sup>, and to  $6.6 \times 10^{-4}$  min<sup>-1</sup>, respectively, because of the increase in the transmittance of the ultrasonic energy into the reactor. Due to this energy, in the reactor, the pulsation and collapse of bubbles occur more rapidly, the number of cavitation bubbles increases, and a higher concentration of OH radicals is achieved in the aqueous solution of the organic pollutant. These hydroxyl radicals react with the pollutant in the solution (Jiang et al., 2002).

A very slight decrease in the solution pH was observed during the sonication time of 5 h with the 2.8 mM BA solution at 4 W and 8 W. It remained almost constant at the initial butyric acid pH value of 4.1. However, the solution pH changed from 4.1 to 3.8 after a reaction time of 5 h when it was sonicated at 31 W. Taking into account the pKa value of butyric acid (4.63 at 298 K), it is clear that the major chemical structure is C<sub>3</sub>H<sub>7</sub>COOH rather than C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup> under the conditions used. It means that the hydrophobic property of butyric acid is higher in the pH studied. Hydrophobic compounds are more easily decomposed by the hot cavitation bubble interface and/or hydroxyl radicals formed from the water sonolysis. Therefore, decomposition of the neutral butyric acid (C<sub>3</sub>H<sub>7</sub>COOH) molecule proceeds faster than that of the ionized one (C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>) and decomposition of butyric acid proceeds at the interface region of the cavitation bubble where the concentration of local hydroxyl radicals is reported to be very high (Okitsu et al., 2009).

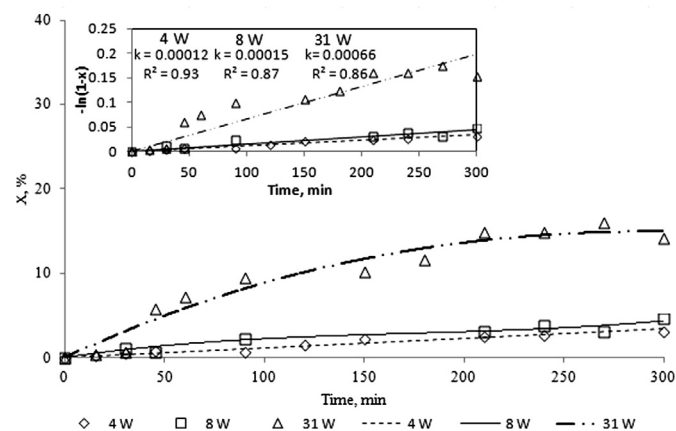


Fig. 1. Effect of ultrasonic power on the degradation of butyric acid. Inset presents the first order kinetic. (Frequency = 850 kHz, Initial concentration = 2.8 mM, and Volume = 0.35 dm<sup>3</sup>).

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