



# The impact of selected parameters on the formation of hydrogen peroxide by sonochemical process



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## ABSTRACT

This study utilized 20 kHz ultrasonic irradiation as a mechanism of hydrogen peroxide production. The effects of various operating parameters were investigated, including ultrasonic amplitude, solution pH, source of water, initial dibutyl phthalate concentration and the presence of hydrogen peroxide. During the irradiation, the  $\text{H}_2\text{O}_2$  concentration arising was monitored. The results indicate that  $\text{H}_2\text{O}_2$  is produced by cavitation during ultrasonic irradiation. An increase in ultrasonic amplitude increases the amount of hydrogen peroxide produced. The initial pH of the solution does not affect the efficiency of processes substantially.  $\text{H}_2\text{O}_2$  is regarded as one of the most effective additives enhancing the sonochemical production of hydroxyl radicals, but too high a dose is known to exert a negative effect. Above a 0.1  $\mu\text{M}$  dose of  $\text{H}_2\text{O}_2$ , the amount of  $\text{H}_2\text{O}_2$  formed decreased as the concentration of  $\text{H}_2\text{O}_2$  increased. Thus, the concentration of hydrogen peroxide plays a crucial role in the extent to which effectiveness of the combined process is enhanced. The negative effect on reactions of the presence of additional components in the reaction solution was also confirmed. It was therefore concluded that experimental evaluation of optimum parameters of hybrid processes is a matter of importance.

## 1. Introduction

The range of ultrasound frequencies used commonly in sonochemistry is 20 kHz to 1 MHz [1,2]. Ultrasonic irradiation of liquids causes acoustic cavitations, i.e. the formation, growth and implosive collapse of bubbles. Such cavitation generates sites of locally high temperature and pressure for short periods of time, with these being responsible for unusual sonochemical effects [3,4]. The cavitation process is influenced by several factors such as frequency, gas properties (solubility, heat capacity ratio, thermal conductivity) and solvent properties (vapor pressure, density, viscosity, surface tension). The mechanism of the sonochemical degradation of organic pollutants is usually based on the formation of short-lived radicals generated in violent cavitation events [5]. The sonochemical destruction of pollutants in the aqueous phase generally involves several reaction pathways, such as pyrolysis inside the bubble and hydroxyl radical-mediated reactions at the bubble-liquid interface and/or in the liquid bulk (Fig. 1). The extreme temperature conditions generated by a collapsing bubble can also lead to the formation of radical chemical species. The radicals formed in this reaction are highly reactive and interact rapidly with other radical or chemical species in solution [6].

When ultrasound is applied, it will induce the sonolysis of water

molecules and thermal dissociation of oxygen molecules, if present, to produce different kinds of reactive species such as  $\text{OH}^\cdot$ ,  $\text{H}^\cdot$ ,  $\text{O}^\cdot$  and  $\text{OOH}^\cdot$ . Reactive-species production ensues by way of the following reactions, with ultrasound denoting the ultrasonic irradiation. Sonolysis of water also produces  $\text{H}_2\text{O}_2$  and  $\text{H}_2$  gas via  $\text{OH}^\cdot$  and  $\text{H}^\cdot$ . Though oxygen enhances sonochemical activity, its presence is not essential for water sonolysis, as sonochemical oxidation and reduction processes can proceed in the presence of any gas. However, the presence of oxygen also allows the  $\text{H}^\cdot$  forming  $\text{OOH}^\cdot$  to be scavenged, with this acting as oxidizing agent [4,7,8]. The hydroxyl radicals generated during cavitation can be used in the oxidative degradation of organic pollutants in an aqueous system [9–11].

During the past several years, ultrasound has been applied effectively as an emerging advanced oxidation process (AOP) for a wide variety of pollutants in wastewater treatment [12–14]. A growing number of studies have demonstrated that ultrasound irradiation results in a rapid and effective decomposition of phthalates esters [15], pesticides [16,17] phenols [18], chlorinated compounds [19], and pharmaceuticals [20] in aqueous solution. The main advantage is that the ultrasound process does not require added chemicals, oxidants or catalysts, and does not generate additional waste streams as compared with other processes (ozonation and adsorption). However, the

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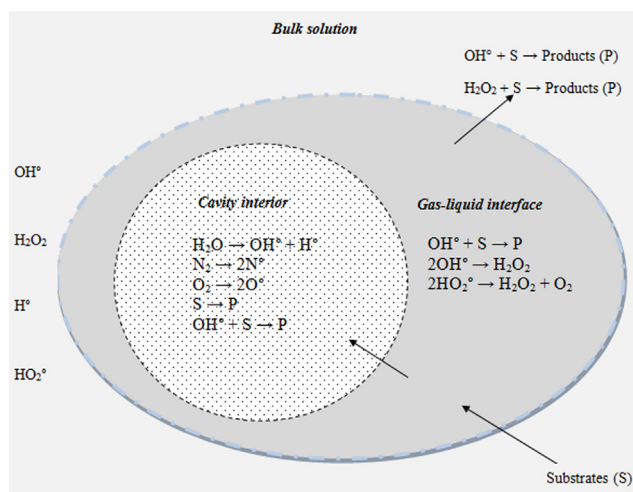


Fig. 1. The reaction zone in the cavitation process [adapted from [9]].

ultrasonic degradation rate is found to be rather slow [21–23]. Several factors, including ultrasonic frequency, solution pH and the addition of hydrogen peroxide, may influence the sonochemical degradation of organic contaminants. Hydrogen peroxide is one of the most effective additives used to enhance sonochemical degradation of organic pollutants. During ultrasound irradiation,  $\text{H}_2\text{O}_2$  can dissociate into hydroxyl radicals, though these have a very short lifetime and tend to combine and form  $\text{H}_2\text{O}_2$ . As hydrogen peroxide present at high concentration can act as a radical scavenger, especially for  $\text{OH}^\bullet$ , it is important to evaluate the optimum concentration of  $\text{H}_2\text{O}_2$ . Unfortunately, this is difficult to do for each compound, because the formation of  $\text{H}_2\text{O}_2$  depends on pollutant types and process parameters [5,21,24,25].

The objective of the work described here was to study the production of hydrogen peroxide in aqueous solution subject to sonication to better understand the sonochemical system. Certain previous studies have investigated the effects of  $\text{H}_2\text{O}_2$  concentration on sonochemical reactions, though only a few experiments have monitored  $\text{H}_2\text{O}_2$  under various input concentrations of  $\text{H}_2\text{O}_2$  and in the presence or absence of target materials [5,21–23]. In contrast, no experiments have hitherto investigated the formation of  $\text{H}_2\text{O}_2$  in tap water. The  $\text{H}_2\text{O}_2$  concentration in the sample containing dibutyl phthalate (DBP) contamination and  $\text{H}_2\text{O}_2$  addition was also not checked. Therefore, the aim of investigation was to study the effect of inorganic and organic substances and the effect of  $\text{H}_2\text{O}_2$  addition on the formation of hydrogen peroxide during ultrasonic irradiation.

## 2. Materials and methods

### 2.1. Chemicals

Reagent grade of sodium hydroxide, potassium biphthalate, and potassium iodide (Chempur, Piekary Śląskie, Poland), as well as ammonium molybdate from POCH (Gliwice, Poland) were used to determine the  $\text{H}_2\text{O}_2$  concentration. Analytical standard of DBP, potassium titanium oxalate were obtained from Sigma-Aldrich (Saint Louis, USA). All reagents were prepared with deionized water, which was made by Purix CNX-100. HCl solution were purchased from POCH. HCl,  $\text{H}_2\text{SO}_4$  and NaOH were used for pH adjustment.  $\text{H}_2\text{O}_2$  solution (30%) was obtained from Chempur.

### 2.2. Apparatus and experimental conditions

Ultrasonic irradiation experiments were conducted on the bench-scale in a reactor comprising an ultrasonic processor, a reactor cell and a water ice bath. The source of ultrasound was a SONOPULS HD 3200

from Bandelin (Berlin, Germany), which is an ultrasonic processor equipped with a 1.3 cm-diameter titanium probe tip. The homogenizer operated at 20 kHz. Irradiation with ultrasonic waves at ultrasonic amplitude of 20, 30 and 50% was applied.

All the experiments were conducted in a 250 ml glass beaker immersed in the ice bath. The reactor was filled with 100 ml of appropriate solutions, i.e. deionized water, deionized water with hydrogen peroxide, tap water, or aqueous DBP solution of the required concentration (0.35 and 1.8  $\mu\text{M/L}$ ). The ultrasonic power was controlled by the panel setting, the sonication probe being dipped 1 cm below the water surface. The  $\text{H}_2\text{O}_2$  concentration in the reaction solution was monitored in the course of the irradiation process (after time 0, 5, 15, 30, 60, 90 min) by iodometric method. All the experiments were duplicated with an observed deviation of less than 5%. For this reason, average values are shown on the graphs. All tests were also conducted at room temperature and pressure. The amount of hydrogen peroxide was also determined using the titanium method (for selected parameters) in order to control the quality of the results. The results did not differ more than 15–20%. Therefore, the iodometric method was carried out for all analyzes.

### 2.3. Analytical methods

#### 2.3.1. Iodometric method

The concentration of  $\text{H}_2\text{O}_2$  generated during sonication was determined using the iodometric method [21,25]. The iodide ion ( $\text{I}^-$ ) reacts with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) to form a triiodide ( $\text{I}_3^-$ ) ion, which absorbs at 352 nm. Sample aliquots (volume: 2.0 ml) from each experiment were mixed in a quartz cuvette containing 0.75 ml of 0.10 M potassium biphthalate and 0.75 ml of a solution containing 0.4 M potassium iodide, 0.06 M sodium hydroxide, and  $10^{-4}$  M ammonium molybdate. The mixed solution (total volume: 3.5 ml) was allowed to stand for 2 min before absorbance was measured using a DR-5000 UV spectrophotometer.

#### 2.3.2. Titanium method

The basis of the method is the formation of a titanium (IV)-peroxide complex in the presence of sulfuric acid. For this purpose, 10 ml of the  $\text{H}_2\text{O}_2$ -containing sample into a 25-ml volumetric flask was collected. 1.0 ml of sulfuric acid (1 + 17) and 1.0 ml of potassium titanium oxalate solution were added and the volume to 25 ml with deionized water was adjusted. The mixed solution was allowed to stand for 5 min before absorbance (at a wavelength of 390 nm) was measured using a DR-5000 UV spectrophotometer.

## 3. Results and discussion

When an aqueous solution is irradiated ultrasonically, OH radicals and H radicals are produced by cavitation. The hydroxyl radical exhibits a high oxidation potential and can oxidize organic substrates directly, causing their degradation or mineralization [1,4,5]. However, hydroxyl radicals have a very short lifetime, and tend to combine with one another to form e.g.  $\text{H}_2\text{O}_2$  [2,3,10]. The production of hydrogen peroxide in the circumstances of different amplitudes of ultrasonic irradiation is as shown in Fig. 2. In the initial phase of the process no difference in concentration of hydrogen peroxide is to be noted, irrespective of the amplitude. However, after 15 min it is clear that hydrogen peroxide production is at a higher level where the ultrasonic amplitude is greater. The greatest production of hydrogen peroxide was found to be associated with higher-amplitude irradiation. An increase in ultrasonic amplitude may increase the number of active cavitation bubbles and the production of hydroxyl radicals. Similar results have been reported in the literature [4,21,24,27,28]. Under ultrasonic irradiation, there is a linear relationship between the  $\text{H}_2\text{O}_2$  concentration generated and irradiation time (Fig. 2). All experiments showed  $R^2$  value greater than 0.9. Previous studies have confirmed that, during

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