Regular Article

Quantification of Radicals Generated in a Sonicator

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The hydroxyl radical (OH•) is a powerful oxidant produced as a consequence of cavitation in water. It can react nonspecifically in breaking down persistent organic pollutants in water into their mineral form. It can also recombine to form hydrogen peroxide which is very useful in water treatment. In this study, terephthalic acid (TA) and potassium iodide dosimetry were used to quantify and investigate the behaviour of the generated OH radical in a laboratory scale sonicator. The 2-hydroxyl terephthalic acid (HTA) formed during terephthalic acid dosimetry was determined by optical fibre spectrometer. The production rate of HTA served as a means of evaluating and characterizing the OH• generated over given time in a sonicator. The influence of sonicator power intensity, solution pH and irradiation time upon OH• generation were investigated. Approximately 2.2×10^{-9} M s^{-1} of OH radical was generated during the sonication process. The rate of generation of the OH radicals was established to be independent of the concentration of the initial reactant. Thus, the rate of generation of OH• can be predicted by zero order kinetics in a sonicator.

Keywords: Hydroxyl radical, Hydrogen peroxide, Cavitation, Terephthalic acid, Sonicator, Dosimetry
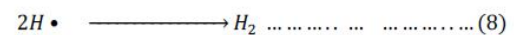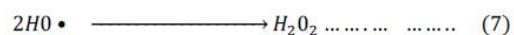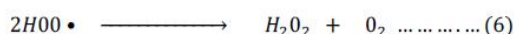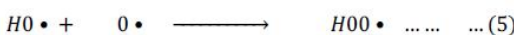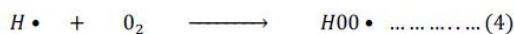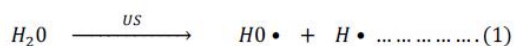
INTRODUCTION

Cavitation is increasingly gaining prominence because of its application in water treatment and its comparative advantage over other types of advanced oxidation processes [1]. Little or no chemicals are needed and the ability to significantly reduce the formation of byproducts as well as microorganisms population makes it a method of choice in water treatment technologies. The OH radicals (OH•) are generated by cavitation through formation, growth and implosion of micro bubbles at an extreme temperature and pressure [2]. The bubbles can be formed as a consequence of alternating rarefaction and compression (acoustic) or change in velocity (hydrodynamic) of pressurized water. The free radicals (HO•, HOO•) formed through thermal dissociation of water and oxygen can either penetrate into water and oxidize dissolved organic compounds or recombine to form hydrogen peroxide [3]. Cavitation is a nonrandomized process which degrades larger molecule faster and it is not affected by the toxicity or biodegradability of the compound [4].

The effective exploitation of the cavitation process depends on understanding the nature, characteristics and reaction mechanism of the OH• generated. Methods such as electron spin resonance [5], emission spectroscopy [6], chemical probes [7] and laser induced fluorescence [8] have been successfully used in the radical identification. Meanwhile, quantification of this radical has been very challenging [9] with most methods depending on the scavenging properties of dosimetry chemicals [10]. The high background noise to signal ratio proved the unsuitability of coumarin-3-carboxylic acid as a probes in fluorescence [11]. Other chemical scavengers such as salicylate and 4-hydroxylbenzoate showed promise but need complex derivatization, sophisticated analytical techniques and expensive equipment [12]. Despite intense research efforts on application of OH• generated in a Sonicator for wastewater treatment, very few publications were able to

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demonstrate the nature and quantity of this radical in acoustic cavitation using terephthalic dosimetry [13,14]. Besides, these publications only focused on application in medical ultrasound field (1 kHz) and there is no reference to the chemical kinetic of OH radical generated [15]. This study uses terephthalic acid dosimetry in the quantification and prediction of the kinetic properties of OH• generated during cavitation in a sonicator operating at 20 kHz and 600 W. The specificity of the terephthalic acid reaction with OH• as well as the simple and inexpensive nature of the method makes it unique. Besides, the hydrogen peroxide generated by the recombination of OH• [16] was investigated using a simple and inexpensive colorimetric determination with potassium iodide [1].

$$H_2O \xrightarrow{US} HO\bullet + H\bullet \dots\dots\dots\dots(1)$$

$$O_2 \xrightarrow{US} 2O\bullet \dots\dots\dots\dots\dots\dots(2)$$

$$HO\bullet + O\bullet \longrightarrow HOO\bullet \dots\dots(3)$$

$$H\bullet + O_2 \longrightarrow HOO\bullet \dots\dots\dots\dots(4)$$

$$HO\bullet + O\bullet \longrightarrow HOO\bullet \dots\dots\dots(5)$$

$$2HOO\bullet \longrightarrow H_2O_2 + O_2 \dots\dots\dots\dots(6)$$

$$2HO\bullet \longrightarrow H_2O_2 \dots\dots\dots\dots\dots(7)$$

$$2H\bullet \longrightarrow H_2 \dots\dots\dots\dots\dots\dots\dots(8)$$

Equations (1)-(8). Generation of reactive species in a Sonicator, US denotes Ultrasonic radiation

MATERIALS AND METHODS

Laboratory based sonicators are branded by many commercial agents. They are handheld or stand mounted devices that operate by converting electric energy to sound energy. The schematic experimental set for cavitation using sonication was as shown in Fig. 1.

Chemical Reagents

The deionized water was obtained from a millipore system (230 V, 50 Hz, 65 W). All the commercially obtained chemical reagents (NaOH, KH_2PO_4, Na_2HPO_4, HCl, NaCl, KCl) were analytical grade and used as received. 2-hydroxyterephthalic acid (97%), potassium iodide (99%), potassium iodate (99%) and terephthalic acid (98%), were obtained from Sigma-Aldrich.

Reactor

The experiments were carried out in a Misonix sonicator (Fig. 1), model S-4000, operating at a fixed frequency of 20 kHz, 600 W maximum with a temperature probe. The temperature was maintained below 10 °C with an ice bath in a plastic container. The intensity of hydroxyl terephthalic acid (HTA) generated as a consequence of OH· reaction with the terephthalic acid (dosimeter) in a sonicator was measured in a spectrofluorometer; Nanolog, i-HR 320 (USA).

Dosimetry Solution

Terephthalic acid (TA) solution (2×10^3 mM) was prepared according to a standard protocol. 332.3 mg TA powder was dissolved in a solution of NaOH (5×10^3 mM) and the volume was made up to 1 Litre with phosphate buffer (pH 7.4) prepared from 198 ml of KH_2PO_4 (1 M) and 802 ml of Na_2HPO_4 (1 M). The solution was stirred for 30 min and refrigerated in the dark at 4 °C to prevent photochemical degradation.

Chemical Dosimetry

200 ml TA solution (2×10^3 mM) was measured into a 250 ml beaker and placed in an ice-water bath and irradiated foran hour using continuous mode sonication (20 Hz, 55 W) at constant temperature (10 °C). An equal volume of the TA solution in an ice-bath beaker was left in the dark (control) and stirred with the aid of a magnetic stirrer for an hour. 2 ml samples were taken from each TA solution separately into a cuvette at 10 min intervals followed by intensity measurement in an optical fibre spectrometer (Nanolog, i-HR 320, USA) set at excitation of 310 nm and emission wavelength of 425 nm. The experiment was repeated in triplicate. The 2-hydroxyl terephthalic acid (HTA) which was formed as a consequence of the reaction between the OH•) radical and TA has peak intensity at wavelength 425 nm. The amount of OH radical generated per unit time was calculated from the linearity obtained in the calibration curve prepared from the standard concentration of
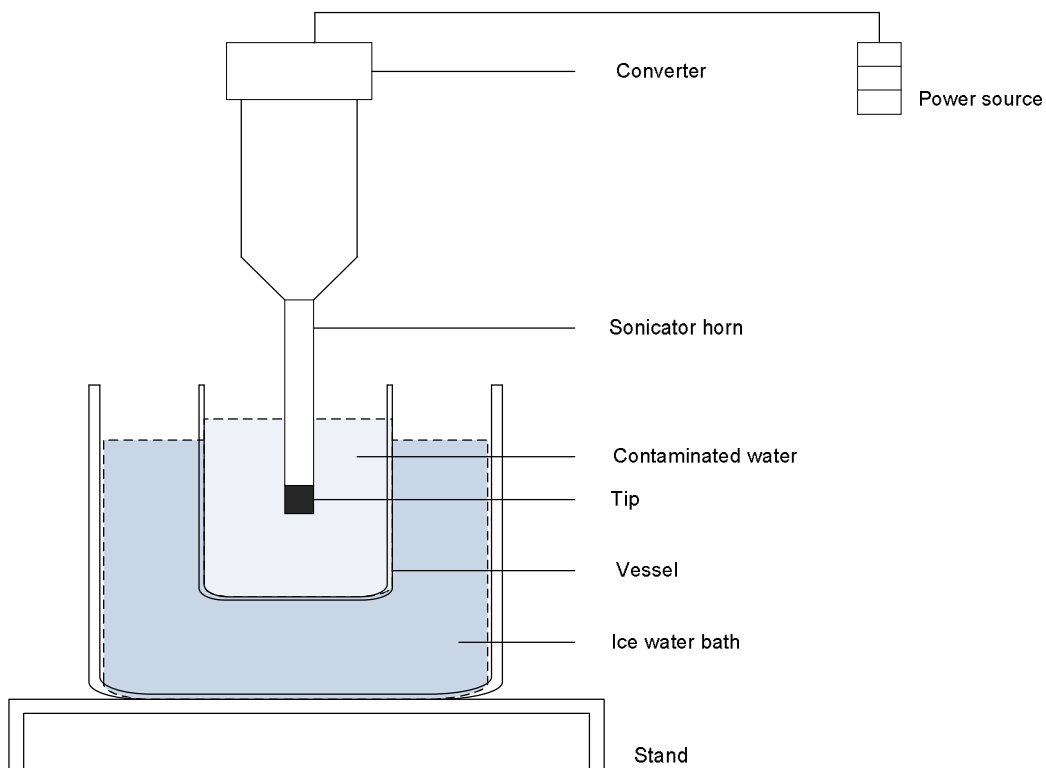
Fig. 1. Experimental set up for sonication.

2-hydroxyl terephthalic acid [3]. A schematic diagram of the experimental reaction between terephthalic acid and the hydroxyl radical is as shown in Fig. 2.

Determination of Hydrogen Peroxide

Hydrogen peroxide was indirectly determined by the iodide method [4]. In the presence of buffer solution (4.8 mM NaOH and 8.3 mM KH_2PO_4) 200 ml of 0.1 M potassium iodide solution was irradiated (20 Hz, 55 W) in the sonicator at a regulated temperature (10 °C). Based on equations (1)-(5), irradiation of aqueous potassium iodide gives the iodine molecule which reacts with excess iodide ion present in the solution to liberate triiodide which absorbs at a wavelength 352 nm. The procedure was repeated in triplicate and a control experiment was set up with an equivalent volume of potassium iodide solution placed in a water bath in the dark. Six separate samples (2 ml) were taken from the experimental set-up at 5 min intervals and added to a quartz cell containing drops of 0.1

M potassium iodide and 0.01 M ammonium heptamolybate. The solution was left to stand for 5 min and the absorbance measured using a spectrophotometer [2] at a wavelength of 352 nm. The calibration was done by measuring the absorbance of known concentrations of potassium iodate (KIO_3).

$$H_2O_2 \ + \ 2I^- \ + \ 2H^+ \longrightarrow I_2 \ + \ 2H_2O \ldots\ldots\ldots\ldots(9)$$

$$HO\bullet \ + \ I^- \longrightarrow I \ + \ HO^- \ldots\ldots\ldots\ldots\ldots\ldots(10)$$

$$I \ + \ I^- \longrightarrow I_2^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

$$2I_2^- \longrightarrow I_2 \ + \ 2I^- \ldots\ldots(12)$$

$$I_2 \ + \ I^- \longrightarrow I_3^- \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots.(13)$$

Equations (9)-(13). Determination of H_2O_2 in a Sonicator
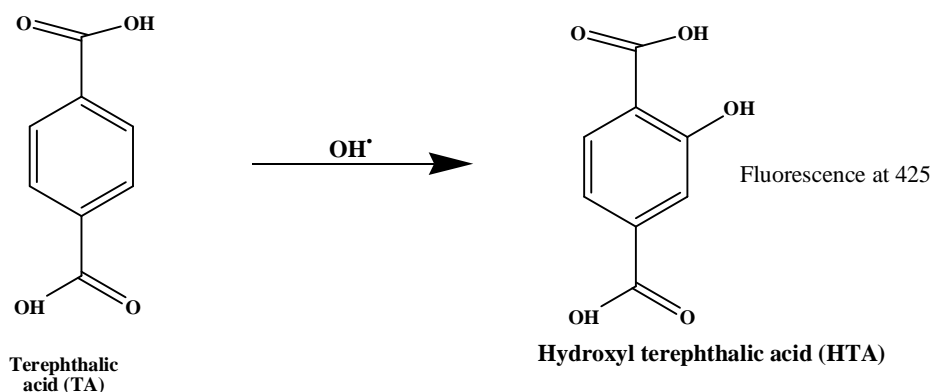
Fig. 2. Schematic reaction for generation of HTA from TA and OH radical.

RESULTS AND DISCUSSION

Quantification of OH Radicals

The uniform increases in fluorescence intensities with respect to time of the TA solutions as measured by the spectrofluorometer were in correspondence to the increases in OH radical productions [5]. The calibration curve for known HTA concentrations was used to determine the amount of OH radical generated (Table 1). The estimated OH radical generated in the sonication system at 55 W, 20 Hz in 200 ml TA solution was approximately 2.2×10^{-9} M s^{-1}. This value is within the range of values (10^{-8}-10^{-10} M s^{-1}) for previous publications on OH radicals generated in cavitation equipments using different methods of measurement [4,6]. Factors such as reactor type, measuring methods and operating conditions are largely responsible for the differences in the reported figures [6]. Apparently, not all the OH radical generated are captured by the TA. It is possible for the radical to recombine and form hydrogen peroxide or be consumed through other partway [7]. However, HTA is the major product and 35% yield has been reported [8]. Besides the quantification of OH radical, TA dosimetery is a very good indicator for the kinetic of OH radical generation.

Kinetics of OH Radical

There is a direct proportionality between the sonication intensity of the TA solution and the amount of OH radicals generated overtime and trapped in the solution [9]. Therefore, a positive correlation exist between the sonication intensity of TA solution and the homogeneous OH radical diffusion in the reaction system as shown by the fluorescence spectral of sonicated TA solution in Fig. 3. The linear relationship between the amount of radicals and the irradiation time in this system (Fig. 4: $R^2 > 0.99$) is an indication of the efficient trapping of the OH radical by terephthalic acid [2]. Consequently, terephthalic acid dosimetry is an ideal method of OH radical quantification [10]. However, the rate of generation of the OH radicals is independent of the concentration of the initial reactant (as shown in Table 1). Zero order kinetic is the general term used for the prediction of a reaction at which the rate remains constant at a uniform change in concentration (increase or decrease) of reactant or product. A unique feature of zero order kinetic is that the substrate (reactant) is usually in excess with respect to the product. The excess reactant (water) in the sonicator undergo cavitation to form hydroxyl and hydrogen radical among many other products (1)-(13) [3]. The rate of generation of OH radical is almost constant (Table 1) despite the multiple incremental amount of radical. Therefore, generation of OH radicals during ultrasonic cavitation under the present experimental condition can be predicted by a zero-order reaction kinetic. Consequently, the concentration of pollutant has no significant effect on the generation of OH radical in a sonicator.

Sonication Intensity

Intensity of sonicator is proportional to vibration amplitude of ultrasonic power source. It can be varied by

Table 1. The Zero Order OH Radical Generation Showing Near Constant Rate of Reaction (55 W, 20 Hz, 2 mM TA Solution in Buffer pH 7.4)

T (s)	Concentration ($M \times 10^{-6}$)	Rate ($M\ s^{-1} \times 10^{-6}$)
600	1.59	0.16
1200	3.13	0.16
1800	4.50	0.15
2400	5.77	0.14
3000	6.81	0.14
3600	7.91	0.13
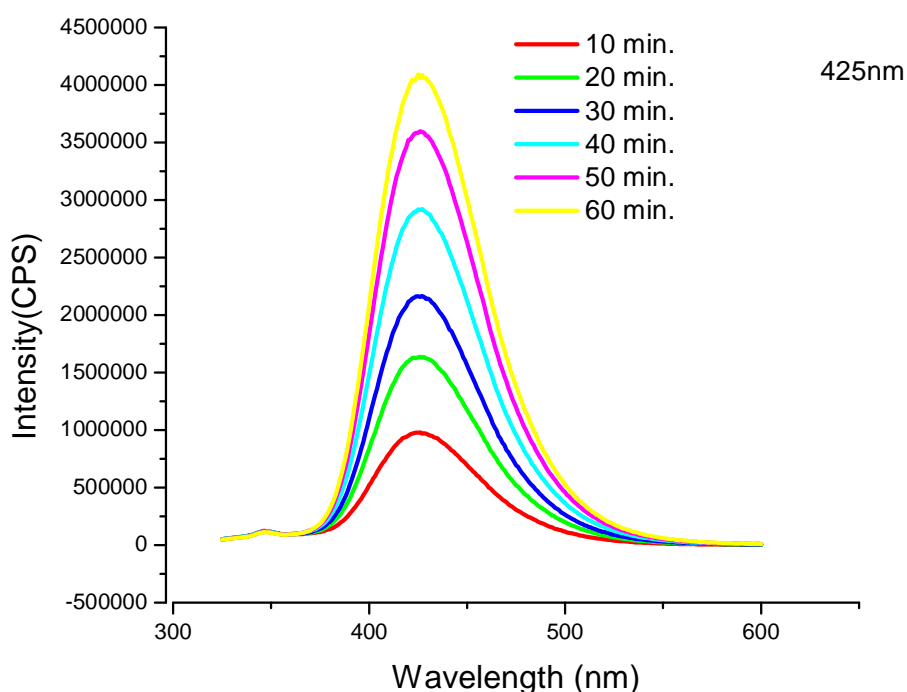
Fig. 3. Fluorescence spectra of sonicated TA solution (2 mM) at different sampling times (55 W, 200 ml TA solution, 20 Hz, phosphate buffer 7.4).

changing the amount (in volume) of the tested liquid at a constant applied power (power density) or by changing the applied power at a constant amount (in volume) of liquid. In this study there was a significant decrease in the cavitation effect as the applied power density decreased due to an increase in the volume of the TA solution at a constant applied power as shown in Fig. 5. Likewise, sonication

intensity increased with an increase in the applied power at a constant volume of the TA solution, (Fig. 6). An increase in power output will lead to an increase in the amplitude of vibration and a corresponding increase in the ultrasonic effect. A high intensity is favorable to viscous liquid because the viscosity of liquid limits the movement of sonicator tip and as a consequence, sonication effect [4].
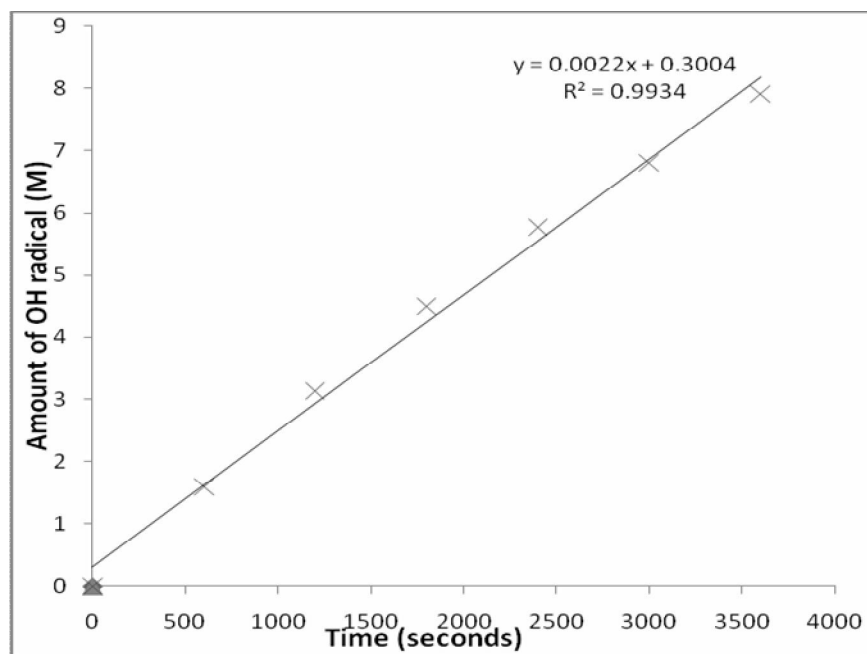
Fig. 4. Homogenous OH radical generation (55 W, 200 ml TA solution, 20 Hz, 2 mM TA solution, phosphate buffer pH 7.4).

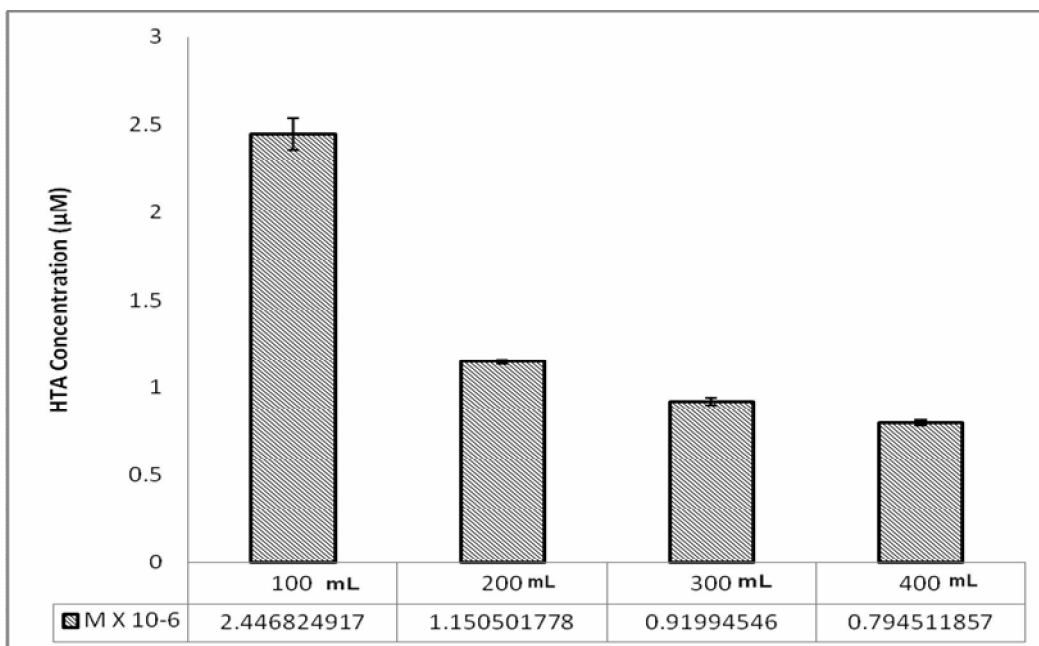|	100 mL	200 mL	300 mL	400 mL
M X 10-6	2.446824917	1.150501778	0.91994546	0.794511857

Fig. 5. Concentration (µM) of generated HTA decrease with increase in volume of the sonicated water (55 W, 20 Hz). Error bars are means +/-standard deviation (× 3).
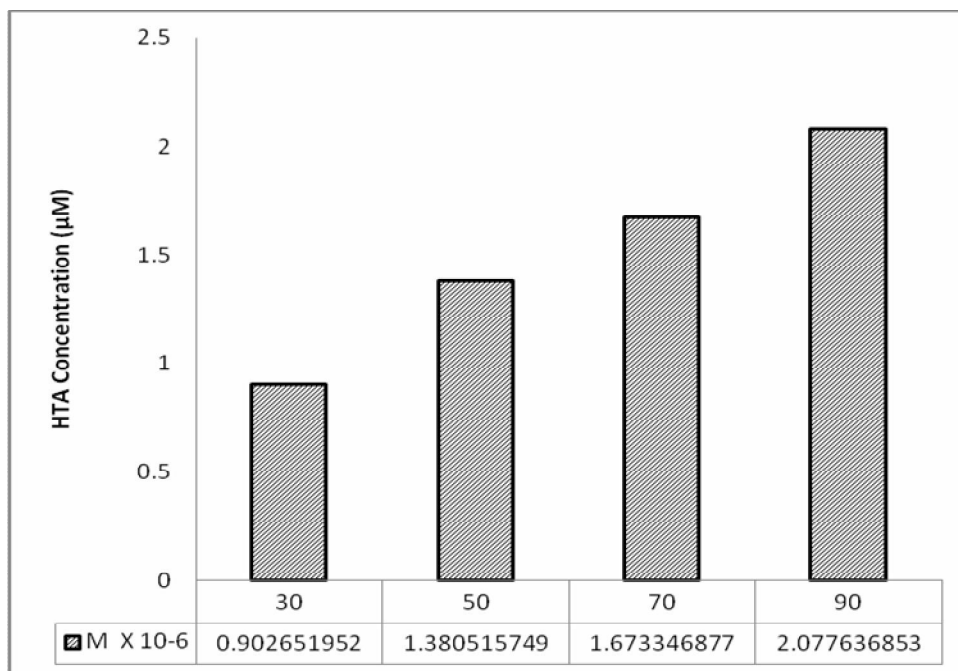
Fig. 6. Concentration of HTA generated in a sonicator increase with irradiation power (30-90 W), Error bars are means +/- standard deviation ($\times$ 3).
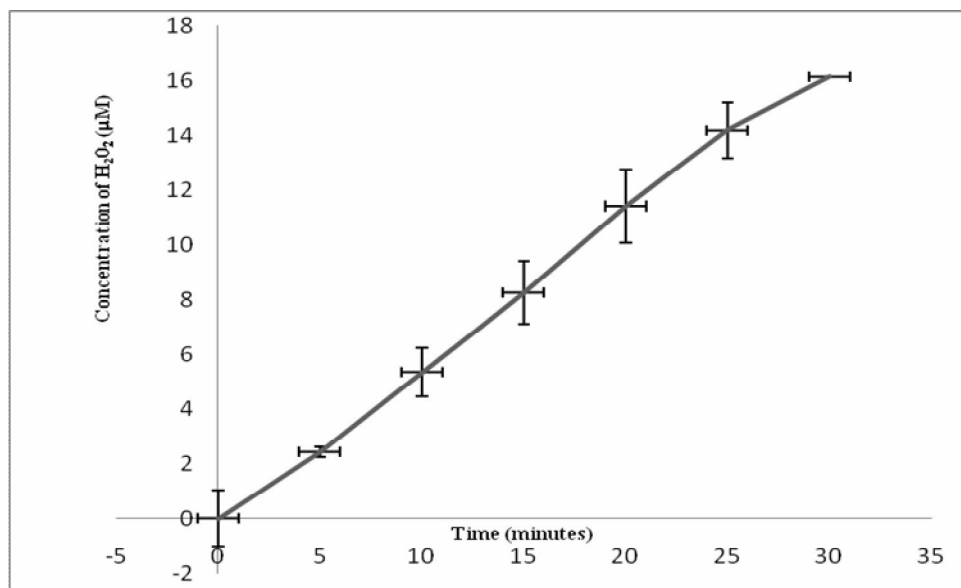

Fig. 7. Concentration of hydrogen peroxide (μM) increases with time (min).
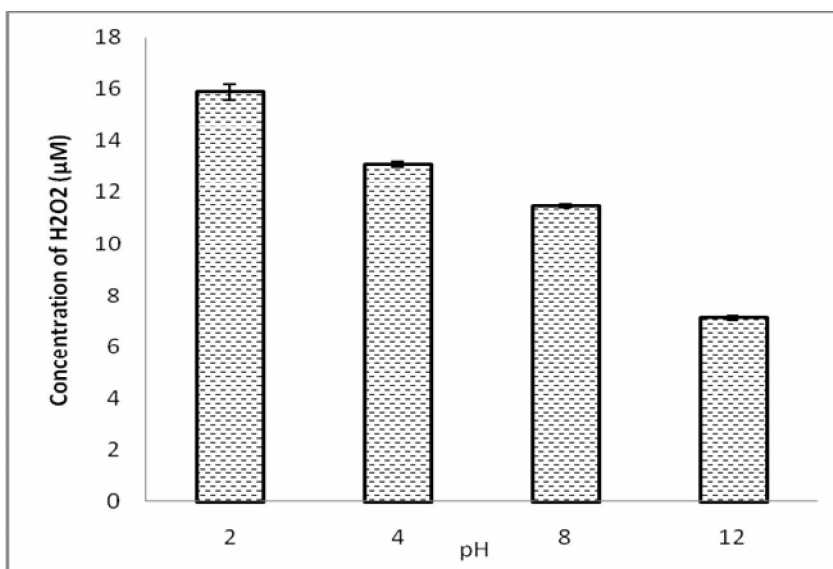
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Fig. 8. Concentration of H_2O_2 generated in a Sonicatorincreases as the solution become more acidic.

However, anoptimum intensity is required to achieve a threshold because a too high intensity value will lead to agitation and damage of the ultrasonic horn [5].

Characteristic of Hydrogen Peroxide (H_2O_2)

OH• in acoustic cavitation can undergo diffusion in the gas-liquid interface and recombine to produce hydrogen peroxide [6]. Identification of hydrogen peroxide formed in a sonicator was done by the hydrogen peroxide indirect monitoring method. The amount of triiodide formed in this reaction is proportional to the quantity of hydrogen peroxide generated in the sonicator system [7]. This was monitored by measuring the absorbance of triiodide ($\lambda_m = 352$) formed as a consequence of hydrogen peroxide reaction with the iodide ion ((9)-(13)). The quantity of hydrogen peroxide generated in the sonicator increase in linear manner with respect to the irradiation time (Fig. 7). The similarity in characteristic of OH radical and hydrogen peroxide is expected because the peroxide was formed as a consequence of recombination of the OH radicals [8].

Effect of pH

pH effect on the generation of OH radical was investigated by the irradiation of potassium iodide solution (55 W, 20 Hz) at pH 2-12. Triiodide liberation in this experiment as monitored by spectrophotometer shows that $H_2O_2$was generation was strongly pH dependent and its production rate increases as the solution become more acidic (Fig. 8). Since the hydrogen peroxide generation is directly proportional to OH radical generation, this is a confirmation of that acidic pH favor the generation of OH radical and consequently the degradation of pollutant in a sonicator. This is further confirmation of pH dependency OH radical production in a sonicator [9].

CONCLUSIONS

Terephthalic acid dosimetry is simple, suitable and efficient method for monitoring the cavitating effect and estimating the generation of the hydroxyl radical in a sonicator. There is a uniform increase ($R^2 > 0.99$) in the amount of generated OH radical with respect to the irradiation time. The rate of generation of the OH radical was established to be independent of the concentration of the initial reactant. Therefore, the generation of OH radical in a sonicator can be predicted by zero order kinetics. Hence, generation of OH radicals in a sonicator cannot be affected by the amount or nature of contaminants in

wastewater treatment application. Besides, high sonication intensity favor generation of OH radical while there was a significant decrease in the amount OH radicals generated as pH increases. The hydrogen peroxide which was produced as a consequence of recombination of the OH radicals was also found to increase linearly with time of irradiation using hydrogen peroxide indirect measurement method. The characteristic of hydrogen peroxide generated in a sonicator practically the same as that of the OH radical.

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