



# Influence of inorganic ions and selected emerging contaminants on the degradation of Methylparaben: A sonochemical approach



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## HIGHLIGHTS

- Ultrasound induced degradation of methyl paraben.
- Influence of emerging contaminants triclosan, phthalate and other parabens on the degradation of methyl paraben.
- Influence of common anions on the degradation of methyl paraben.
- Very efficient mineralisation in 90 min of sonolysis with complete removal of COD.
- Degradation mechanism is elucidated.

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## ABSTRACT

The study on the possible pathway of hydroxyl radicals mediated sonolytic degradation of paraben in water is reported. Methylparaben (MPB) which is the most utilized of paraben family is selected as a model emerging pollutant. The influence of common anions and some selected emerging contaminants that may coexist in typical water matrix on the degradation pattern is analyzed alongside. Among the anions, carbonate presents a negative influence which is attributed to the competition for OH radical. Some emerging contaminants also showed negative impact on degradation as was clear from HPLC data. The intermediates, analyzed by LC–Q–TOF–MS include hydroxylated and hydrolytic products. Three major steps (aromatic hydroxylation, hydroxylation at the ester chain and hydrolysis) are proposed to involve in the reaction of OH radical with MPB which ultimately leads to mineralization. The intensity of formation and decay of mono and dihydroxy products of MPB in the presence of additives have also been evaluated. COD analysis indicates a percentage reduction of 98% at 90 min of sonolysis and further increase in the degradation time resulted complete mineralization, which became evident from the mass spectrometric data. MTT assay revealed considerable decrease in the potential cytotoxicity.

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## 1. Introduction

Water pollution arising from emerging contaminants such as pharmaceuticals and Personal Care Products (PPCPs), Persistent Organic Pollutants (POPs), Endocrine Disrupting Chemicals (EDCs)

and their metabolites are of major concern [1–3]. Many of the compounds that fall under the category of EDCs are deliberately added to food stuffs, medicines and cosmetics for their recognized properties. Not that the use of these compounds can be avoided, as some of them are most needed for medical and agricultural purposes. It then sounds proper to adapt a technological solution that will be economically sound without enhancing the possible toxic byproducts.

Parabens, once considered being a safest preservative, is now listed under endocrine disrupting chemicals [4]. They are alkyl esters of *p*-hydroxybenzoic acid and are extensively used as preservatives in personal care products, pharmaceuticals, food products and beverages [5–7]. Among the various parabens, methylparaben

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(MPB) is the most widely used preservative in the commercial applications. The study of Rastogi et al. showed the prevalence of MPB in cosmetic products as high compared to other parabens [8]. In commercial applications MPB is used singly or in combinations. It can be metabolized to the acid form which would then be excreted through urine. But its hydrophobic character may favor its accumulation in body fats. A recent finding of paraben in its native form in certain tumor cells appears to be quite alarming [9]. The occurrence of parabens (singly or in combinations) in cosmetic products along with certain ingredients like ethanol paves its way to the body and may promote the formation of higher parabens (butylparaben), the known estrogenic compounds [10,11]. All these compounds (MPB, its metabolite hydroxybenzoic acid and other higher chain parabens) are equally accountable for the estrogenic activity.

The wastewater from domestic, hospitals and/or municipal that contaminate the fresh water bodies might carry large load of contaminants which coexist and lead to cross reactions. The way out from this problem is the development and establishment of more effective and efficient treatment technologies. Advanced oxidation process (AOPs) is perhaps the best choice if one desires to go for the complete mineralization of the organic component. The process is also advantageous in terms of fast reaction and non selective oxidation of pollutants by hydroxyl radicals ( $\bullet\text{OH}$ ) [12]. OH mediated degradation pathways have already been worked out for parabens [13–17]. One of the recent additions is the photocatalytic degradation of propylparaben by Fang et al. [18]. A TOC removal percentage of about 75% was reported. This means a complete mineralization of the paraben is not attained from the above study. Furthermore, the influence of inorganic ions and the emerging contaminants (ECs) that are likely to impede the degradation pathway was not investigated so far.

Sonochemical reactions have been successfully employed for the degradation of various pollutants [19–21]. It is yet another route which utilizes  $\bullet\text{OH}$  for the degradation. In sonolysis complete mineralization of organic pollutants is expected within a short span of time. However, this degradation protocol has not been attempted so far for the possible mineralization of parabens. In this manuscript we report the study of the sonochemical degradation of methylparaben as a model compound. Primarily various operational parameters such as frequency, power density and pH on the sonolytic degradation are optimized. Further the degradation efficiency of MPB under different cross reacting systems such as inorganic ions (chloride, sulfate, nitrate and carbonate) and selected ECs (propylparaben (PP), diethyl phthalate (DEP), benzoic acid (BA) and triclosan (TRI)) are studied. A detailed end product analysis has been carried out using high resolution mass spectrometric technique (LC–Q–TOF–MS) in order to elucidate a feasible mechanism for the degradation process. The cytotoxicity evaluation at different stages of degradation has also been carried out.

## 2. Experimental

### 2.1. Materials

Methylparaben (99% purity), propylparaben, diethyl phthalate, benzoic acid and triclosan from Sigma–Aldrich and analytical grade NaCl,  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaNO}_3$  and acetonitrile from Merck India Pvt., Ltd., were used for this study. The solutions were prepared using ultrapure water (18.2 M $\Omega$  cm).

### 2.2. Sonolytic degradation and analysis

The experiments were carried out in a sonoreactor consisting of an ultrasound transducer (L3 ELAC Nautik) powered by an Allied Signal R/F generator and a double-walled cylindrical glass reactor.

The concentration of MPB during the reaction was estimated using HPLC (Shimadzu prominence UFLC, LC 20 AD) with diode array detector (SPD-M20 A). Liquid Chromatography Quadrupole Time of Flight Mass Spectrometry (LC–Q–TOF–MS, Waters Xevo G2 Q TOF with electrospray ionization (ESI) technique) was used to identify the intermediate products. The Chemical Oxygen Demand (COD) reduction was analyzed by using standard dichromate method. Details of the experimental analysis are provided in the Supporting information (SI).

### 2.3. Cytotoxicity assessment

The cytotoxicity of MPB was evaluated by a 3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyltetrazolium bromide (MTT) colorimetric assay using EZ COUNT™ MTT CELL ASSAY KIT (SI).

## 3. Results and discussion

### 3.1. Effect of frequency

The sonolytic degradation of MPB was carried (1.52 ppm) at a constant power density of 22.75 Wml<sup>-1</sup>. The degradation study was performed at four different frequencies (200 kHz, 350 kHz, 620 kHz and 1 MHz), for a period of 90 min. The respective results are presented in Fig. 1A. The maximum degradation rate was observed at 350 kHz followed by 620 kHz, 1000 kHz and 200 kHz. The first order rate constants for the reactions were 0.03299 min<sup>-1</sup>, 0.08534 min<sup>-1</sup>, 0.07747 min<sup>-1</sup> and 0.05063 min<sup>-1</sup>, respectively, for the frequency 200 kHz, 350 kHz, 620 kHz and 1 MHz.

In sonolysis there are certain parameters dependent on the ultrasonic frequency that controls the degradation efficiency. The most important being the number and size of bubbles, and the availability of OH in the interface and bulk liquid region [22]. Finding an optimum frequency is critical where all these parameters correlate. The increase in applied frequency enhances the availability of OH but at the same time results in a reduction of the resonant size of the bubble [23]. In the present system 350 kHz seems to be the most suitable frequency. At the lower frequency of 200 kHz, the availability of number of bubbles and acoustic cycles will be relatively less agreeing with the observed lower rate of degradation. The increase in applied frequency to 350 kHz, results in larger number of bubbles and hence an increase in the surface area to volume ratio [24]. But with further increase in the frequency the resonant size starts to decrease. This causes a reduction of the released temperature during cavitation collapse though the number of available bubble increases and eventually, leads to lower production of OH [25]. These arguments agree with the observed lower degradation rate at 620 kHz and 1 MHz.

### 3.2. Effect of power density

In order to optimize the power density, the sonolytic degradation was carried out at 20 W, 50 W and 80 W at a frequency of 350 kHz. The power densities of these applied powers were initially determined and are 7, 22.75 and 40.25 Wml<sup>-1</sup>, respectively. The complete degradation pattern and the first order nature of the degradation are given in Fig. 1. As the power increases, the degradation rate increases. The calculated values of rate constants are 0.03094, 0.08534 min<sup>-1</sup> and 0.13836 min<sup>-1</sup> with respect to the increasing order of power density. The applied power increases the bubble formation by lowering the threshold limit of cavitation [26]. The resonant radius of the bubble and hence the energy of collapse increases resulting in higher degradation at 40.25 Wml<sup>-1</sup>.

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