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Studies on oxidative radiolysis of ibuprofen in presence of potassium persulfate

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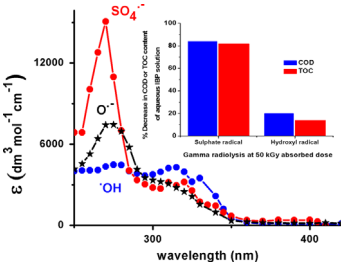
HIGHLIGHTS

- The radiolysis of aqueous solution of Ibuprofen (IBP) was investigated.
- The COD and TOC content decreased significantly in presence of $K_2S_2O_8$.
- Pulse radiolysis studies revealed the mechanism of mineralization of IBP.
- The presence of $K_2S_2O_8$ increased the efficiency of gamma radiolysis.

GRAPHICAL ABSTRACT



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ABSTRACT

The radiolysis of ibuprofen (IBP), a model pharmaceutical compound, was studied by gamma irradiation in an aqueous solution in the presence and absence of potassium persulfate ($K_2S_2O_8$). The extent of mineralization was investigated by measuring the UV–visible spectra, decrease in the chemical oxygen demand (COD) and the total organic carbon (TOC) content of aqueous IBP solution at different doses. The gamma radiolysis, in the presence of $K_2S_2O_8$, required much lesser dose compared to in the absence of $K_2S_2O_8$ for the same extent of mineralization of aqueous IBP solution. The pulse radiolysis of IBP was carried out under different radiolytic conditions to understand the mechanism of efficient mineralization of IBP during gamma radiolysis in the presence of $K_2S_2O_8$. It was found that unlike $^{\bullet}OH$ radical, $SO_4^{\bullet-}$ radical preferentially produces benzyl type of radicals via the formation of the benzene radical cation. The results concluded that the gamma radiolysis in presence of $K_2S_2O_8$ could be one of the efficient advanced oxidation processes for degradation of pharmaceutical compounds present in the aqueous solution.

1. Introduction

The presence of emerging pollutants has become a major environmental concern worldwide. This has resulted in the scarcity of fresh water, which has resulted in further scarcity due to the discharge of these contaminants into the ecosystem. These contaminants pose new challenges as they do not respond to practiced or available treatment facilities. During the last several years, pharmaceutically active compounds have become a subject of great interest to environmental researchers worldwide (Hao et al., 2007; Ziylan and Ince, 2011; Bu et al., 2013). Water pollution due to pharmaceuticals can be attributed to several sources, such as effluents from pharmaceutical industries, unethical disposal of expired or surplus medicines into sewage systems, excretion from human and animal bodies *etc.* (Perez-Estrada et al., 2001; Espulgas et al., 2007; Trovo et al., 2008). The non-steroidal anti-inflammatory drugs (NSAIDs), including analgesics are among the most prevailing groups of pharmaceutical contaminants (Cleuvers, 2004).

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Ibuprofen (IBP) is one of the most widely used NASIDs being found in water. It is widely administered for rheumatic disorder, fever and to reduce pain (Connors et al., 2013). There have been some implications of long-term effects from IBP on the ecosystem. Firstly, it is a persistent pollutant as it is not completely destroyed in a municipal water treatment plant (Fent et al., 2006; Mendez-Arriaga et al., 2008). Secondly, it adversely affects several aquatic plants and fungal species (Zuccato et al., 2006; Brown et al., 2007; Connors et al., 2013). Most importantly, it has been reported that IBP present in drinking water along with other environmental pharmaceuticals might impede cell proliferation in human embryonic cells (Schnell et al., 2009). Recently, a study by World Health Organization reported IBP as the leading contaminant among other pharmaceuticals *viz.* Erythromycin, Bleomycin *etc.* present in aquatic environment in United Kingdom (Connors et al., 2013).

Advanced oxidation processes (AOPs), involving the reaction of hydroxyl radicals ($^{\bullet}OH$), are emerging as an efficient technique for complete destruction of organic compounds by oxidation with minimized generation of sludge, secondary waste and toxic intermediates (Andreozzi et al., 1999). Recent studies involving different AOP's *viz.* UV/peroxodisulfate, catalytic decomposition of persulfate *etc.* (Gimeno et al., 2009; Peternel et al., 2010) utilized sulfate radical anion ($SO_4^{\bullet -}$) for degradation of non-biodegradable contaminants, including dyes, pharmaceuticals and other specific pollutants. The high energy ionizing irradiation is one of the promising AOPs, which can effectively degrade a wide variety of dyes and organic pollutants in aqueous solution by $^{\bullet}OH$ radical produced in situ by the radiolysis of water. The simple operation, least requirements of additional chemicals, insensitivity to color and suspended solids in the effluent and most importantly, significant reduction of sludge generation encourage radiation technology to be a step ahead compared to other oxidation techniques.

The different AOPs, *viz.* photocatalysis with semiconductor materials, photo-Fenton, gamma-irradiation, sono-photocatalysis *etc.* have been extensively investigated for the treatment of IBP in water/waste water (Méndez-Arriaga et al., 2010; Illes et al., 2013; Ramasundaram et al., 2013; Michael et al., 2014), where authors have reported on the degradation of IBP that $^{\bullet}OH$ radical attacks either on the aromatic ring or to the side chains. However, to the best of our knowledge, no systematic study on the efficient degradation of IBP during gamma radiolysis in the presence of potassium persulfate ($K_2S_2O_8$) has been reported. The present work is focused on the systematic investigation of the efficacies of two AOPs, *viz.* gamma radiolysis in presence and also in absence of $K_2S_2O_8$ for mineralization of IBP. The pulse radiolysis (PR) experiment was carried out under different radiolytic conditions to understand the mechanism of efficient mineralization of IBP during gamma radiolysis in the presence of $K_2S_2O_8$.

2. Experimental

2.1. Chemicals

IBP, $K_2S_2O_8$, *tert*-butanol were purchased from Sigma-Aldrich and used as such without further purification. All other chemicals used were purchased locally and were of highest purity.

2.2. Instruments and analytical procedures

Steady state radiolysis of aqueous solution of IBP was carried out using a ^{60}Co gamma radiation chamber GC-5000 supplied by M/s. BRIT Mumbai, having a dose rate of 1.3 kGy h^{-1} as determined by using Fricke dosimetry [$G(Fe^{3+})=15.6$ $(100\ eV)^{-1}$]. PR experiments were performed with 7 MeV linear electron accelerator with a pulse duration of 500 ns. Dose per pulse was measured using an aerated aqueous solution of thiocyanate taking $(G\varepsilon)=2.6\times10^{-4}$ m^2 J^{-1} at 475 nm (Buxton and Stuart, 1995). Chemical oxygen demand (COD), total organic carbon (TOC) content and dissolved oxygen (DO) concentration of the solutions were measured by using a Spectroquant® Pharo 300 COD/TOC analyzer and DO meter PCD650, respectively.

3. Results and discussion

3.1. Mineralization of aqueous IBP solution

3.1.1. The variation of COD and TOC on gamma irradiation of aqueous IBP solution

COD determines the amount of oxygen required to fully oxidize organic matter into carbon dioxide using a strong oxidizing agent such as $K_2Cr_2O_7$. Thus in the studied case, COD indirectly determines the amount of organic compounds present in the aqueous solution. The mineralization of IBP in aqueous solution on gamma irradiation can also be studied by TOC measurement (Suzuki et al., 1975). Gamma irradiation of 1×10^{-3} mol dm^{-3} aqueous solutions of IBP was carried out for different absorbed doses at pH ~7 and (%) decrease in COD and TOC of aqueous IBP solution with absorbed doses have been shown in Fig. 1. It clearly shows that decreases in COD and TOC were ~20% and ~14%, respectively, for an absorbed dose of 50 kGy and no further significant decrease in COD or TOC was observed at doses greater than 50 kGy.

Radiolysis of water in the pH range 3–11 produces primary radiolytic species and among these hydrated electron (e_{aq}^-), hydroxyl radical ($^{\bullet}OH$) and hydrogen atom ($H^{\bullet}$) are three main reactive intermediates. The G values [species $(100\ eV)^{-1}$] of the intermediates are given below (Getoff, 2002)

$G(e_{aq}^-)=2.7$; $G(^{\bullet}OH)=2.7$; $G(H^{\bullet})=0.6$

During the radiolysis of aqueous IBP solution under atmospheric condition, e_{aq}^- and $H^{\bullet}$ mainly react with the dissolved oxygen producing superoxide radical anion ($O_2^{\bullet -}$) and perhydroxyl radical ($HO_2^{\bullet}$), respectively, whereas, oxidizing species $^{\bullet}OH$ preferentially reacts with IBP. However, as shown above, gamma radiolysis alone cannot effectively mineralize aqueous IBP solution. Therefore, an alternative AOP was investigated to increase the radiolytic mineralization efficacy of IBP.

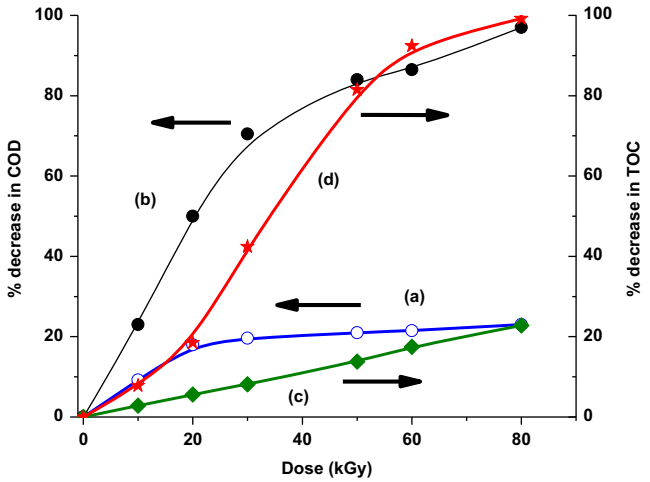

Fig. 1. % decrease in COD (a) and (b) and TOC (c) and (d) in absence (a) and (c) and presence (b) and (d) of $K_2S_2O_8$ during gamma radiolysis of IBP as a function of absorbed dose.