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Synergistic effects of HSO_5^- in the gamma radiation driven process for the removal of chlorendic acid: A new alternative for water treatment

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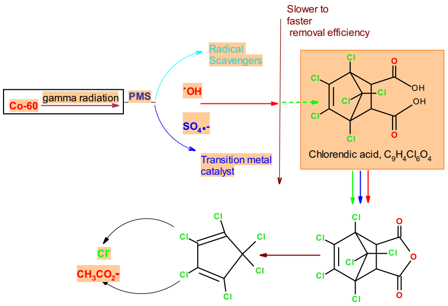
HIGHLIGHTS

- The presence of HSO_5^- with gamma-ray promoted removal efficiency of chlorendic acid.
- The activation of HSO_5^- by gamma-ray and catalyst yield $^{\cdot}OH$ and $SO_4^{\cdot-}$.
- The radical scavengers inhibited the efficiency of $^{\cdot}OH$ and $SO_4^{\cdot-}$.
- Second-order rate constants of chlorendic acid with e_{aq}^- $^{\cdot}OH$, and $SO_4^{\cdot-}$ were determined.
- Degradation pathways were proposed from the nature of identified by-products.

GRAPHICAL ABSTRACT



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ABSTRACT

Removal of chlorendic acid, an emerging water pollutant and potential carcinogenic, was investigated by gamma radiation in the absence and presence of peroxymonosulfate (PMS, HSO_5^-). The removal of chlorendic acid (1.40 μM initial concentration) by gamma radiation was promoted with PMS, i.e., 95% compared to 82% in the absence of PMS, at an absorbed dose of 1000 Gy. The removal of chlorendic acid by gamma-ray/PMS process was due to $^{\cdot}OH$ and $SO_4^{\cdot-}$. Second-order rate constants of 5.90×10^9, 1.75×10^9, and $2.05 \times 10^9\ M^{-1}\ s^{-1}$ for chlorendic acid with e_{aq}^-, $^{\cdot}OH$, and $SO_4^{\cdot-}$, respectively, were determined. The removal efficiency of chlorendic acid was promoted with increasing initial PMS concentration and decreasing initial target contaminant concentration. The removal of chlorendic acid by gamma-ray/PMS was inhibited in the presence of CO_3^{2-}, NO_2^-, *p*-CBA, *m*-TA, and alcohols. The presence of Fe^{2+}, Cu^+, and Fe^{3+} with gamma-ray/PMS promoted removal efficiency of chlorendic acid from 78% to 99, 94, and 89%, respectively, at 592 Gy. The degradation of chlorendic acid by $^{\cdot}OH$ and $SO_4^{\cdot-}$ was found to be initiated at the carboxylate group as could be revealed from nature of the transformation by-products. Nevertheless, this study concluded that gamma-ray/PMS is of practical importance in treatment of natural water containing chlorendic acid, as potential detoxification of chlorendic acid solution can be revealed from 83% loss of chloride ion at 3000 Gy. In addition, gamma-ray/PMS process achieved efficient removal of chlorendic acid even in the presence of commonly found inorganic ions in natural water.

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1. Introduction

Water pollution by xenobiotics is a widespread problem throughout the world and is becoming worst with time due to increased population and consequently increased industrialization and agricultural activities etc. The most important xenobiotics contributing greatly into water pollution and of environmental concern are organochlorine compounds (OCC), characterized by their greater persistency, non-biodegradability, and high toxicity [1]. Due to their greater toxicity, most classes of OCC have been banned, however, some are reported to be still synthesized and used on large scale in different countries of the world [2]. Among these, one important and highly toxic OCC is chlorendic acid (1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-hept-5-ene-2,3-dicarboxylic acid) which is still synthesized and used commercially on large scale in many countries, such as USA and Belgium [3]. The most important uses of chlorendic acid include as a flame retardant in polyurethane foams, wool, resins, paints, piping, in the synthesis of metal organic frameworks, and as an extreme pressure lubricant [4]. The wide spread applications led to extensive use of chlorendic acid. It has been reported that in the years from 1986 to 2002, in the USA, production and import of chlorendic acid totaled 500,000 lb to 10 million pounds [5]. The US Environmental Protection Agency (US EPA) classified chlorendic acid as the most toxic and highly persistent compound [5]. Chlorendic acid can causes irritation in skin and eyes, lung cancer, and gene mutation etc. [3,6]. The wide range applications have resulted in increased contamination of water resources with chlorendic acid [4]. Chlorendic acid also enters into the aquatic environment as a degradation product of cyclodiene pesticides, such as endosulfan. Due to frequent and large scale discharges into aquatic environment as well as greater solubility and persistency in water, chlorendic acid has become a significant threat to public and ecological health [4]. Although highly persistent and toxic, no guidelines are suggested for control of chlorendic acid. The technologies, such as adsorption and biodegradation have been reported inefficient in removal of chlorendic acid from water environment [4]. So there is a need to develop cost effective, efficient, and environmentally friendly technologies that can effectively remove chlorendic acid and other organochlorine compounds from contaminated waters.

Recently advanced oxidation technologies (AOTs) that rely on in situ generation of reactive radicals, such as hydroxyl radical have received considerable attention for effective removal and mineralization of highly toxic, persistent, and recalcitrant emerging water pollutants [7–11]. Hydroxyl radical (HR, $^{\cdot}OH$) with high redox potential of 2.72 V (depending on the experimental conditions) has been reported to be highly reactive and react effectively and non-selectively with organic compounds with a reported second-order rate constant of 10^8–$10^{10}\ M^{-1}\ s^{-1}$ [12]. Recently introduced sulfate radical (SR, $SO_4^{\cdot-}$), having redox potential of 2.5–3.1 V, have received significant attention due to their wide contribution into the efficient removal of organic pollutants [12,13]. On contrary to $^{\cdot}OH$, $SO_4^{\cdot-}$ reacts selectively with most of the organic compounds with a high second-order rate constant of 10^7–$10^{10}\ M^{-1}\ s^{-1}$ [12]. Both $^{\cdot}OH$ and $SO_4^{\cdot-}$ reacts with organic compounds through three different ways, such as addition to unsaturated bond, hydrogen abstraction, and electron abstraction from aromatic ring, double bond, and saturated carbon or carboxylate group [9,12]. As a result, in the present study, removal of chlorendic acid from water environment was investigated by both $^{\cdot}OH$- and $SO_4^{\cdot-}$-AOTs. PMS (HSO_5^-), commonly known as Oxone® and an active component of a triple salt, $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$, was used as a source of $^{\cdot}OH$ and $SO_4^{\cdot-}$ through the activation of gamma radiation and transition metal ions [12]. The high redox potential, 1.82 V, of PMS [14] makes its easier activation by electron from gamma radiation and transition metal ions. The easy electron donating property as well as abundant concentration in natural water make transition metal ions the best option for the activation of PMS and is thus important for potential practical applications [11]. Similarly gamma radiations are predominant precursors of electron and can be effective in the activation of PMS [15,16]. Besides, gamma radiation has been proved to be the most competent, efficient, and environmentally friendly treatment technologies and also recommended by the international agencies for detoxification of pollutants [15,16].

The main aim of the present study is to transform the e_{aq}^- into $^{\cdot}OH$ and $SO_4^{\cdot-}$ by combining PMS with gamma radiation. Although e_{aq}^- is highly reactive species for the removal of halogenated organic compounds, the presence of inorganic ions, such as nitrate and transition metal ions, efficient scavengers of e_{aq}^-, in natural water makes its practical application impossible [15]. Nitrate ion has low reactivity towards $^{\cdot}OH$ and $SO_4^{\cdot-}$ ($k < 1 \times 10^5\ M^{-1}\ s^{-1}$) and therefore, the efficiency of $^{\cdot}OH$ and $SO_4^{\cdot-}$ based AOTs are expected to be independent of this ion. In addition, the presence of transition metal ions could have a positive effect on the efficiency of gamma-ray/PMS process due to their ability to activate PMS through electron transfer mechanism and, hence, dual activation of PMS is possible. Moreover, using relatively higher concentration of PMS could possibly reduce the interference of dissolved oxygen, which hinders the activity of e_{aq}^- based remediation technologies but not of $^{\cdot}OH$ and $SO_4^{\cdot-}$ based remediation technologies. So, in the present study the yield of $^{\cdot}OH$ and $SO_4^{\cdot-}$ from the activation of PMS by gamma radiation and transition metals in the presence of gamma radiation for the treatment of chlorendic acid has been assessed for the first time in the present study. Different radical scavengers and competition kinetic studies were conducted to investigate the yield and performance of $^{\cdot}OH$ and $SO_4^{\cdot-}$ in the removal of chlorendic acid from aqueous solution. The toxicity evaluation and main degradation pathways of the removal of chlorendic acid by $^{\cdot}OH$ and $SO_4^{\cdot-}$ was also examined.

2. Materials and methods

2.1. Materials

Chlorendic acid, chlorendic anhydride and 1,3-cyclopentadiene, 1,2,3,4,5,5-hexachloro (purity ⩾ 99%) were purchased from Supelco (PA, USA). Oxone® (Sigma–Aldrich) was used as the oxidant with gamma radiation in the present study. Other chemicals, i.e., oxetane, *m*-toluic acid (*m*-TA), *p*-chlorobenzoic acid (*p*-CBA), 2-chlorobenzoic acid (2-CBA), 2-butyl alcohol, iso-propyl alcohol, ethanol, methanol, phosphoric acid, sodium sulfate (Na_2SO_4), cuprous chloride (CuCl), sodium nitrite ($NaNO_2$), potassium chloride (KCl), potassium carbonate (K_2CO_3), sodium acetate (CH_3CO_2Na), ferrous sulfate ($FeSO_4{\cdot}7H_2O$), and ferric chloride ($FeCl_3{\cdot}6H_2O$) were purchased from Scharlau. All the chemicals used in the present study were of high purity and used as received. All the solutions were prepared in ultra pure water (resistivity, 18.2 MΩ cm) obtained from Milli-Q® system (Millipore).

2.2. Analysis

The analysis of chlorendic acid, chlorendic anhydride, and 1,3-cyclopentadiene, 1,2,3,4,5,5-hexachloro was carried out using an Agilent 6890 series gas chromatography (GC) equipped with Ni^{63} electron capture detector (ECD) and an HP-5 (5% phenyl methylsiloxane) capillary column (30 m × 0.25 mm I.D., 0.25 μm particle size). Prior to analysis with GC-ECD, the chlorendic acid, chlorendic anhydride, and 1,3-cyclopentadiene,