Journal of Molecular Catalysis A: Chemical 414 (2016) 116–121

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Persulfate assisted photo-catalytic abatement of cetirizine hydrochloride from aqueous waste: Biodegradability and toxicity analysis

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ARTICLE INFO

Article history:
Received 7 September 2015
Received in revised form
23 December 2015
Accepted 27 December 2015
Available online 13 January 2016

Keywords:
Cetirizine dihydrochloride
Sulfate radicals
Hydroxyl
Toxicity
Mineralization

ABSTRACT

The present work aims at demonstrating the application of UV/$S_2O_8^{2-}$ system successfully for degradation of cetirizine dihydrochloride (CTZ) from aqueous waste. More than 95% CTZ was degraded within 90 min of UV irradiation. The degradation kinetics followed a pseudo-first order kinetics at all the experimental conditions studied. The studied process enhanced the biodegradability, BOD_5/COD ratio from 0.15 to 1.94 of the aqueous wastewater. Acute toxicity test using *Photobacterium phosphoreum* showed that the degradation products are less toxic than the initial toxicity levels of CTZ. The sulfate radical generated from the photochemical decomposition of $S_2O_8^{2-}$ shows that UV/$S_2O_8^{2-}$ system is a kinetically favorable process in removing cetirizine hydrochloride from aqueous waste along with reduction of toxicity.

1. Introduction

Many pharmaceuticals have been recently found in surface waters (rivers, lakes, back-waters, sea, etc.) as a result of large concentration of these recalcitrant organic compounds present and incompetent removal at the wastewater treatment plants (WWTP) [1,2]. The presence of such pharmaceutical compounds have gained much attention because they are related to abnormal physiological processes in the reproduction cycle, development of antibiotic resistant bacterias and enhanced toxicity of mixture of chemicals [3,4]. Many researchers are finding out ways to understand the adverse effect of these pharmaceutical compounds on the ecological systems and many other studies are devoted to develop efficient treatment technologies to achieve the complete removals of these drugs from waters and wastewaters [5]. It has been very well reported that physiological and biological treatment units are inefficient in removal of these pharmaceuticals and thus more effective ways of deactivating and eliminating this class of organics from water are being devised [6].

One of the promising oxidation methods devised for the removal of these non-biodegradable compounds are advanced oxidation processes (AOP's). AOP are mainly based on generation of highly reactive hydroxyl radicals (HR) have gained a lot of interest for the degradation of pharmaceutical compounds by photocatalysis [7–9], ozonation [10,11], electrochemical oxidation [12,13], wet air oxidation [14–16] and combination of oxidants [1]. Although hydroxyl radicals are highly reactive species, the complex water matrix containing dissolved organic matter (DOM) and carbonate/bicarbonate anions are major scavengers of HR and thus limit its practical applications [17]. In order to overcome this limitation of HR, sulfate radical anion ($SO_4^{-\bullet}$, SR) has been regarded as an alternative to HR although very few studies have been reported for their usage. SR is a strong one-electron oxidant and is more selective in activity as compared to HR [18,19]. SR are generated by photochemical activation of peroxymonosulfate or peroxydisulfate anions to yield one HR and one SR in the former case whereas two SR in the latter.

In the present study, the degradation of cetirizine dihydrochloride (CTZ) has been attempted. CTZ has been reported in variable concentration in Indian subcontinent [20] in the range up to 1400 μ/L in the effluent stream collected from the wastewater treatment plant near Hyderabad [21,22]. Cetirizine dihydrochloride append to the piperazine class of second generation antihistamines used in the treatment of allergies, hay fever, angioedema and urticaria. Chemical name of cetirizine dihydrochloride is 2-(2-(4-(4-chlorophenyl) phenylmethyl) piperazin-1-yl) ethoxy) acetic

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http://dx.doi.org/10.1016/j.molcata.2015.12.021
1381-1169/

acid dihydrochloride [23]. To the best of our knowledge, there have been no reports on the degradation of cetirizine dihydrochloride by any advanced oxidation processes. Thus, the major objectives of the present work were the following: (i) to investigate the application of SR over HR for degradation of CTZ; (ii) to optimize the various parameters for degradation of CTZ using UV/PMS system; (iii) to study the biodegradability and toxicity assessment of the process.

2. Materials and methods

2.1. Materials

Cetirizine dihydrochloride ($C_{21}H_{25}ClN_2O_3{\cdot}2HCl$; M.W. 461.81 g/mol, 98% purity) was obtained from Sigma–Aldrich. Potassium peroxymonosulfate (triple potassium salt, $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$, also known as oxone), sodium hydroxide, hydrogen peroxide (H_2O_2), hydrochloric acid were obtained from SD Fine Chemicals Pvt. Ltd. Methanol, Acetonitrile and ortho-Phosphoric acid were all HPLC grade and obtained from Thomas Baker. All the chemical obtained were used without further purification. Mili-Q de-ionised water was used for all the experiments. The secondary effluent was obtained from the inlet stream of Common Effluent Treatment Plant (CETP) for treatment of effluents generated by industrial units in ROHA MIDC industrial area.

2.2. Experimental

All experiments were carried out in a laboratory photochemical reactor obtained from Lelesil Innovative Systems. The schematic diagram of the experimental set-up is shown in Fig. 1. It consists of a variable speed magnetically stirred 1 L glass reactor combined with a cylindrical quartz double jacketed photoreactor. A 250 W HPMV UV Lamp (200–400 nm) is inserted into the quartz reactor which has an water cooling arrangement. The quartx tube was then inserted into the glass reactor. There are two ports to the reactor, one for air inlet and other one for sampling periodically. The reaction volume of 500 mL was fixed and aqueous solutions of CTZ and solid peroxymonosulfate (PMS) was charged into the reactor and samples were withdrawn periodically for analysis.

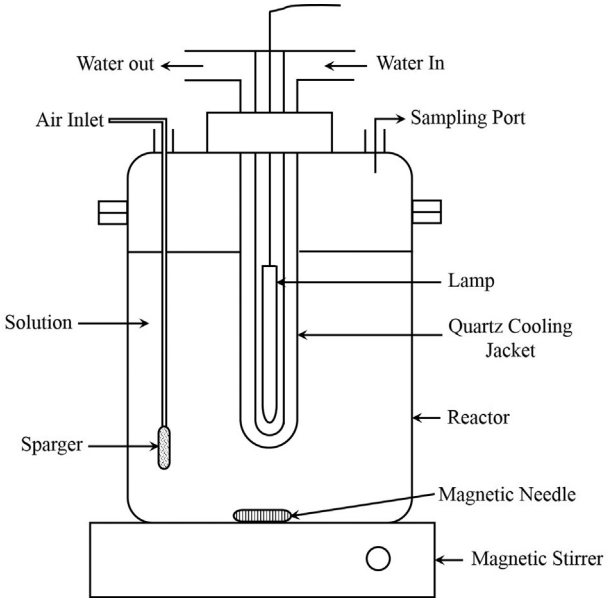

Fig. 1. Schematic of the experimental set-up employed in the present study.

2.3. Analytical methods

CTZ concentration was monitored on a reversed-phase high performance liquid chromatography (HPLC) equipped with a C18 Phenomenex-Gemini column with mobile phase acetonitrile: water(adjusted at pH 3.0 using phosphoric acid) (70:30, % v/v) at a flow rate of 1.0 mL/min on a Thermo scientific UHPLC with a VWD detector at a wavelength of 230 nm. The mineralization profile with respect to Total organic carbon (TOC) was analysed using a SHIMADZU TOC Series L, TOC analyser working on the photo-catalytic principle. A five day biological oxygen demand (BOD_5) was carried as per the Standard Methods for the examination of Water and Wastewater, 20th ed. APHA. The dissolved oxygen content and chemical oxygen demand (COD) analysis was carried out using COD thermometer (HI839800) and multiparameter bench photometer (HI83099), Hanna instruments Pvt. Ltd. All the pH measurements were made on benchtop pH meter (Model EQ-621, Equiptronics).

2.4. Acute toxicity test

The acute toxicity assay for CTZ degradation study was carried out by using the procedure reported by Wang et al. [24] with a slight modification. The marine luminescent bacteria *Photobacterium phosphoreum* (*Vibrio fischeri* 5269; Deposited by Microexpress, Goa (2008) MTCC 1738, ATCC 7744, NCIMB 1281) obtained from NCIM Pune, was used to acute Toxicity assay of the CTZ samples before and after UV irradiation. The cultivation of luminescent bacteria and toxicity evaluation procedure were according to ISO 11348-7 standard protocol [25]. The solution sample was adjusted to pH 7. Samples taken at different time were exposed to *Vibrio fischeri* for a period of 5 min and the change in the luminescence was measured by a LS-110 Luminance Meter (Konica Minolta). Toxicity is expressed as the % inhibition, is the ratio of change in luminescence intensity as per the following Eq. (1)

$$\%inhibition = \frac{L_o - L_t}{L_o} \times 100 \quad (1)$$

where L_o is the luminescence intensity of the solution at time, $t = 0$ min and L_t at time, $t = 5$ min. To ensure the accuracy, experiments were carried out in duplicate.

3. Results and discussion

3.1. Effect of UV irradiation and peroxomonosulfate on abatement of cetirizine hydrochloride

The results of the CTZ degradation due to photolysis, UV/$S_2O_8^{2-}$, $S_2O_8^{2-}$ alone and UV/H_2O_2 is shown in Fig. 2 for an initial CTZ concentration 100 mg/L, 3 mM H_2O_2 and 0.01 mM $S_2O_8^{2-}$. In all the system, the degradation followed a pseudo first order kinetics. Within 60 min, CTZ degradation reached 5%, 15% and 99% in photolysis, UV/$S_2O_8^{2-}$, $S_2O_8^{2-}$ alone and UV/H_2O_2 respectively and their rate constant were as follows: 2.5×10^{-3} (r_2 0.9563), 6×10^{-2} (r_2 0.9758), 6×10^{-4} (r_2 0.9763) and 4.9×10^{-4} (r_2 0.9263) respectively.

The major mechanism is photolysis is UV irradiation which leads to decomposition but its a very slow process. Persulfate system also shows some degradation as they form sulfate radicals when thermally activated but in the present case the degradation was carried out at constant room temperature (28 °C). Persulfate is a very strong oxidant (redox potential = 2.01 V) but oxidation process without any activating agent is slow. However, in presence of UV irradiation, $S_2O_8^{2-}$ gets concerted to two powerful $SO_4^{-\bullet}$ radical ions with a quantum yield one. Thus, in UV/$S_2O_8^{2-}$, photochemical activation