Short communication

Fenton-enhanced γ-radiolysis of cyanuric acid

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Abstract

Degradation of cyanuric acid (OOOT), a stable end product of oxidative decomposition of atrazine, is investigated in a combined field of gamma radiolysis and fenton reaction. The reaction of hydroxyl radical ($^\bullet$OH) at pH 6 was carried out by irradiating N_2O saturated aqueous solutions containing OOOT (1×10^{-3} mol dm^{-3}), and this resulted only a marginal degradation (20%). However, when the same reaction was carried out in the presence of varying concentrations of ferrous sulfate ((5–10) $\times 10^{-5}$ mol dm^{-3}), the decay of OOOT has been enhanced to more than 80%. This decay followed a first order kinetics. Nearly similar effects were observed with another triazine derivative, 2,4-dioxohexahydro-1,3,5-triazine (DHT). Two major reaction mechanisms are proposed for the enhanced decay of OOOT. The formation of unstable hydroxyl radical adducts from the reaction of $^\bullet$OH which is the result of gamma radiolysis and the Fenton reaction (resulting from the reaction of the added Fe(II) and of the H_2O_2 from the radiolysis of water), is proposed as the first mechanism. The second mechanism, which is likely the major contributor to degradation, is proposed as the reaction of a nucleophilic adduct, Fe(II)OOH, which could directly react with the electron deficient triazine ring. It is highlighted that such degradation reactions must be explored for the complete degradation of the byproducts of the oxidative decomposition of atrazine.
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1. Introduction

Efficient technologies are required for the complete destruction of hazardous organic chemicals that pollute drinking water. The major contaminants, which persist in water and cause many ecological problems include pesticides, herbicides, dyes, detergents and a wide variety of industrial effluents. The conventional methods used for the removal of these pollutants from drinking water such as flocculation, filtration, sterilization, reverse osmosis and adsorption on activated carbon are inadequate to degrade the stable aromatic ring. Direct photo-degradation under sunlight or biodegradation has little effect on most of these pollutants and those with sufficient solubility in water are capable of penetrating deep into soil and hence into ground water. Advanced oxidation processes (AOPs) are gaining lot of importance as these have proved to be highly efficient in degrading organic pollutants [1–5]. These processes involve the genera-tion of a highly reactive oxidizing agent, the hydroxyl radical ($^\bullet$OH), in relatively high steady state concentration, which can react non-selectively with most of the organic compounds at almost diffusion controlled rate. Such reactions result in either their complete mineralization into inorganic products or their conversion into non-toxic compounds. Radiolysis of water using ionizing radiations [1], sonolysis of water [2], TiO$_2$/UV [3], H_2O_2/UV, O_3/UV [4], Fenton reaction and photo-Fenton reaction [5] are the major AOPs that generate $^\bullet$OH in the solution state and are currently of interest for the degradation of several organic pollutants.

Among the various AOPs, radiation chemical method can be considered as a potential technique in understanding the fundamental reactions that lead to aromatic degradation, as it allows to create a selective oxidizing or reducing condition in the solution state [1,6,7]. The oxidizing condition is attributed to the reaction of $^\bullet$OH and the reducing condition to the hydrated electron (e_{aq}^-) and hydrogen atom (H$^\bullet$). In situ generation of $^\bullet$OH as well as a variety of other free radicals are possible in the radiolysis of water [7] (reaction (1)):

$$H_2O \xrightarrow{} {}^\bullet OH, H^\bullet, e_{aq}^-, H_2, H_2O_2, H_3O^+ \tag{1}$$
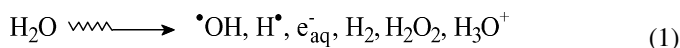
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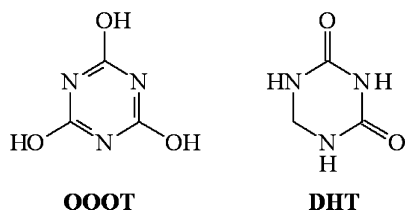 *E-mail address:* CT-Aravindakumar@rocketmail.com
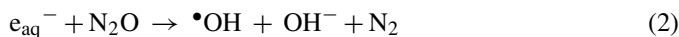(C.T. Aravindakumar).

Fig. 1. Structures of cyanuric acid (OOOT), and 2,4-dioxohexahydro-1,3,5-triazine (DHT).

A totally oxidizing condition can be obtained by saturating the solution with N_2O which converts e_{aq}^- into $^\bullet OH$ (reaction (2)) thereby doubling the yield of $^\bullet OH$:

$$e_{aq}^- + N_2O \rightarrow \, ^\bullet OH + OH^- + N_2 \tag{2}$$

Fenton reaction is another method to generate $^\bullet OH$ via the oxidation of Fe(II) by H_2O_2 [5,8] (reaction (3)):

$$Fe^{2+} (aq) + H_2O_2 (aq) \rightarrow Fe^{3+} (aq) + \, ^\bullet OH + OH^- \tag{3}$$
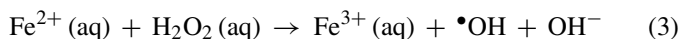
Triazine herbicides are commonly used to control broad leaf and grass weeds in corn and other crops [9]. Atrazine is the most widely used among this class of compounds. Almost all triazines have their $\lambda_{max} \leq 250$ nm and hence cannot be directly photolysed by exposure to sunlight. Decontamination processes using microorganisms like bacteria are relatively very slow and therefore, it is almost inefficient in the case of triazines. They can persist in soil resulting in the contamination of drinking water. Similar to other pollutants the conventional methods used for the decontamination of wastewater are not effective in the case of triazines and hence more work is being concentrated for the development of new technologies for their complete degradation. There are several reports on the degradation of triazine derivatives using different AOPs [10–16]. It is seen in all these reports that only a transformation of the atrazine to a relatively less toxic cyanuric acid can be achieved. On the other hand, $^\bullet OH$ has only little reactivity with cyanuric acid. The aromatic ring of OOOT remains intact even after prolonged treatment with $^\bullet OH$ and hence its degradation is a major challenge. In the present study, we have investigated the degradation of cyanuric acid (OOOT) in a combined field of gamma radiolysis and fenton reaction. The results obtained were very promising and these will be presented in this report. In addition to cyanuric acid, 2,4-dioxohexahydro-1,3,5-triazine (DHT) was also used for the study. The structures of these compounds are shown in Fig. 1.

2. Methods and materials

The selected triazines, OOOT (98%) and DHT (99%) were purchased from Aldrich chemical Co., USA and were used as received. Ferrous sulfate was obtained from E. Merck India Ltd., Mumbai. The initial concentration of triazines was kept at 10^{-3} mol dm^{-3} in all experiments and the concentrations of Fe(II) were varied from 10^{-5} to 10^{-3} mol dm^{-3}. γ-Radiolysis was carried out in a ^{60}Co-γ-chamber. The dose rate, determined using ceric sulfate dosimetry, was about 80 Gy min^{-1} [6]. The degradations of the parent triazines at each stage of irradiation were monitored using a Shimadzu (model LC 10AS)

high performance liquid chromatograph (HPLC) coupled with a UV–vis detector (SPD 10A). Triply distilled water was used as the mobile phase for DHT and OOOT in a 25 cm, Supelcosil 5C-18 column at a flow rate of 1 ml min^{-1} for all analyses. All experiments and analyses were performed at least twice and obtained a very good reproducibility.

3. Results and discussion

The reaction of $^\bullet OH$ with OOOT was carried out at pH 6 by irradiating N_2O saturated aqueous solutions containing OOOT $(1 \times 10^{-3}$ mol dm$^{-3})$. As expected, only a very marginal degradation of OOOT (about 20%) is obtained even after prolonged irradiation (Fig. 2). However, when the same reaction was carried out in the presence of ferrous sulfate $(5 \times 10^{-5}$ mol dm$^{-3})$ the decay of OOOT has been enhanced and after about an absorbed radiation of 8000 Gy, more than 70% of OOOT was disappeared (Fig. 2). The same trend followed when the concentration of ferrous sulfate was up to about 10^{-4} mol dm^{-3} and about 80% OOOT was disappeared. When the decay of its concentration was plotted on a logarithmic scale against the time of irradiation, a clear first order nature is observed and the first order rate constants were calculated from these plots. These first order rates are plotted against the concentration of Fe(II) in Fig. 3. It can be seen that the dependence is linear. However, this linearity was observed only up to a concentration of Fe(II) as 10^{-4} mol dm^{-3} above which this follows a saturation point (data not shown). Similar experiments were carried out using another triazine, DHT, which is known to have high reactivity with hydroxyl radical [16]. Radiolysis in the absence of Fe(II) showed a complete degradation after about 7000 Gy (Fig. 4). However, when the irradiation was carried out in the presence of Fe(II), a complete degradation was attained within 2000 Gy.

$^\bullet OH$ reacts non-selectively with most of the organic compounds and its reaction with many of the aromatic compounds is diffusion controlled [17]. The pattern of reaction of $^\bullet OH$ with a number of triazine derivatives is reasonably well documented
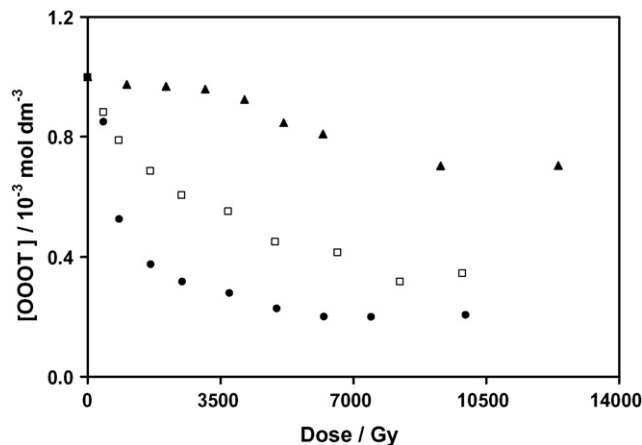

Fig. 2. Degradation profile of cyanuric acid: gamma radioysis of N_2O saturated aqueous solutions containing $(10^{-3}$ mol dm$^{-3})$ (▲), in the presence of Fe(II) $(5 \times 10^{-5}$ mol dm$^{-3})$ (□) and Fe(II) $(10^{-4}$ mol dm$^{-3})$ (●).
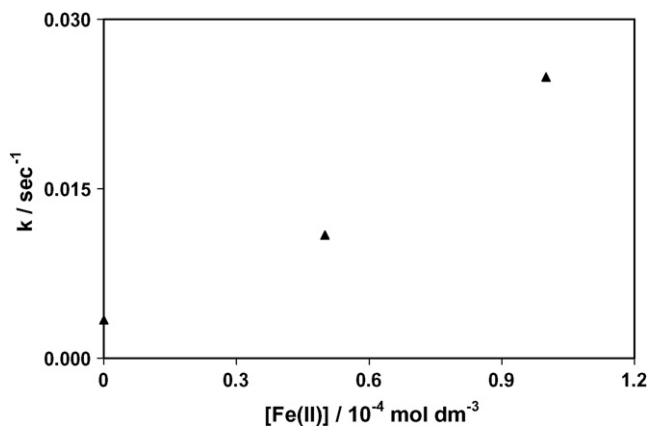
Fig. 3. Dependence of the first order rate constant of degradation of cyanuric acid on the concentration of Fe(II).

[11,15,16]. $^{\bullet}$OH undergoes either addition or hydrogen abstraction reaction with atrazine [15,16]. It was also shown that the major end product of oxidation of atrazine by $^{\bullet}$OH is cyanuric acid (OOOT) [17]. The poor efficiency of $^{\bullet}$OH to degrade OOOT can be understood from Fig. 1. Even after prolonged irradiation for more than 8000 Gy, only less than 30% is degraded. The poor reactivity can be justified due to the electron affinic nature of $^{\bullet}$OH and the electron deficient triazine ring. On the other hand, though very slow, $^{\bullet}$OH reacts with OOOT as at least 30% OOOT is degraded after about a radiation dose of 8000 Gy. It can be reasonably assumed that $^{\bullet}$OH undergoes addition reaction with OOOT based on the earlier understanding that $^{\bullet}$OH reacts with many of the triazine ring by addition [11,15,17].

As can be seen from reaction (1) that in addition to the formation of free radicals, some amount of hydrogen peroxide (H_2O_2) is also formed during radiolysis of water. It is therefore obvious that addition of Fe(II) in the solution under irradiation will evoke a Fenton reaction as shown in reaction (3). This will definitely produce more $^{\bullet}$OH. However, the yield of H_2O_2 is only about 13% of the total yield of $^{\bullet}$OH. This calculation is made on the basis of G-values which is defined as the number of species produced or destroyed on absorption of 100 eV radia-
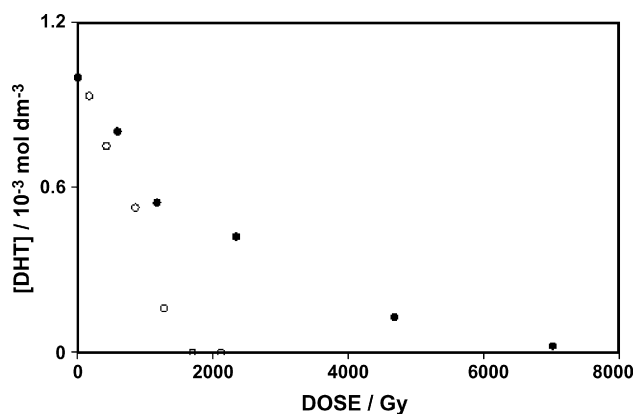

Fig. 4. Degradation profile of 2,4-dioxohexahydro-1,3,5-triazine (DHT): gamma radiolysis of N_2O saturated aqueous solutions containing DHT (10^{-3} mol dm^{-3}) ($\bullet$) and in the presence of Fe(II) (5×10^{-5} mol dm^{-3}) ($\bigcirc$).

tion energy and this can be expressed in SI unit by multiplying with 1.036×10^{-7} mol J^{-1} [6,7]. According to this, the G-value of $^{\bullet}$OH and e_{aq}^{-} are about 2.8×10^{-7} mol J^{-1}, and of H_2O_2 is 0.72×10^{-7} mol J^{-1}. Since e_{aq}^{-} is quantitatively converted into $^{\bullet}$OH according to the reaction (2), the total yield of $^{\bullet}$OH in N_2O saturated solution is assumed as 5.6×10^{-7} mol J^{-1}. Therefore, the additional yield of $^{\bullet}$OH resulting from the Fenton reaction during the radiolysis of water is only about 13%. Such a nominal increase in the yield of $^{\bullet}$OH is not expected to contribute to a large extent in the degradation of OOOT. The main reason for this conclusion is that the percentage of degradation should be proportional to the yield of $^{\bullet}$OH, if the degradation is initiated wholly by $^{\bullet}$OH. In the present case, the increase in the percentage of degradation is about 60% and hence is not really proportional to the yield of $^{\bullet}$OH. Under these circumstances, a number of other reasons must be considered. The intermediate radicals from the addition reaction of $^{\bullet}$OH would lead to both oxidizing and reducing radicals [15]. During Fenton reaction, both Fe(II) and Fe(III) will be present in the reaction mixture (see reaction (3)). The oxidizing and reducing intermediate radicals which otherwise would have undergone a recombination reaction, must react with the reducing Fe(II) and the oxidizing Fe(III). Such reactions were well documented in the case of a number of other organic compounds [18,19]. In these reactions, a clear difference between the gamma radiolysis in N_2O saturated solutions and dark Fenton reaction was reported [18,19]. The explanations given in the case of OOOT are equally valid in the case of the degradation of DHT (Fig. 4). DHT is already degradable on its reaction with $^{\bullet}$OH. However, this is definitely enhanced in the presence of Fe(II) in the reaction mixture as can be seen from Fig. 4. The degradation has already attained a saturation limit with 5×10^{-5} mol dm^{-3}. This concept of combination of the reaction of $^{\bullet}$OH from the gamma radiolysis and of $^{\bullet}$OH derived from Fenton reaction along with the oxidation and reduction of the intermediate radicals by Fe(II) and Fe(III), of course, would enhance the efficiency of degradation of both OOOT and DHT, but cannot be accountable for the increased efficiency of degradation to such a large extent in the case of OOOT.

In order to account for the high efficiency of the degradation of OOOT, another reaction channel for Fenton reaction is considered for the present case, in addition to the addition reaction of $^{\bullet}$OH. It is reported in Fenton reaction of organic substrates that in addition to the hydroxylated products which include the oxidized and reduced products due to the presence of Fe(II) and Fe(III) as discussed above (Scheme 1), a number of other products whose reaction mechanism can not be explained on the basis of the reactions of free $^{\bullet}$OH in solution state [20]. The possibility of another dominant species was demonstrated by Sawyer et al. in a Fenton reaction [20]. This is from a highly stabilized Fe(II) complex such as [(EDTA)Fe(II)OOH + H_3O^+] which is a nucleophile and can easily react with organic substrate. Therefore, under our experimental conditions, it is highly probable that such a nucleophilic adduct [Fe(II)OOH], can directly react with OOOT which may act as a better degrading agent compared to $^{\bullet}$OH. Being a nucleophile, this adduct can have a better reactivity with electron deficient triazine ring.
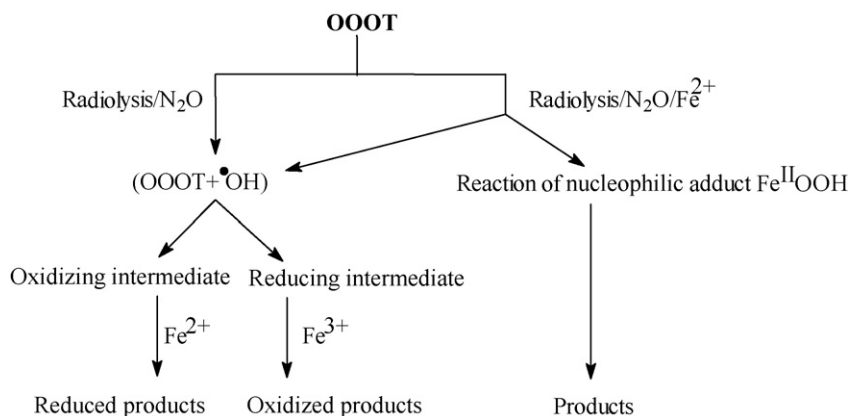
OOOT

Radiolysis/N$_2$O Radiolysis/N$_2$O/Fe^{2+}

(OOOT+$^{\bullet}$OH) Reaction of nucleophilic adduct Fe^{II}OOH

Oxidizing intermediate Reducing intermediate

Fe^{2+} Fe^{3+}

Reduced products Oxidized products Products

Scheme 1. Degradation pattern of cyanuric acid (OOOT) on gamma radiolysis and in the combined field of gamma radiolysis and Fenton reaction.

4. Conclusion

Cyauric acid possesses only a weak toxicity compared to atrazine. The major concern in the detoxification of aromatic compounds in solution state is to get effective degradation reaction in the ring. This is the main reason why advanced oxidation processes gained tremendous importance. While using such methodology, the conversion from one form to other form will only reduce toxicity, but it will not completely degrade the aromatic ring. The present work is the first step in the achievement of multiple reactions with aromatic ring and hence it is important and interesting. Furthermore, the combined effect from two reaction channels in the complete conversion of an aromatic ring is highlighted. The observation of the degradation of OOOT in the combined field of radiation and Fenton reaction is certainly a promising methodology for its efficient degradation, particularly when the highly reactive $^{\bullet}$OH has little effect. The combined effect of ultrasound and photolysis had only shown a cumulative effect in an early study with atrazine and cyanuric acid [21]. Therefore, the present method for the nearly complete transformation of OOOT is particularly interesting. The identification of the final reaction products from the various reaction channels merits further study, and this is currently in progress in our laboratory.

Acknowledgement

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