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Potentiation of hydrogen peroxide mediated water decontamination using thioglycolic acid

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ABSTRACT

There is an increasing interest in the development of metal-free catalysts for hydrogen peroxide (H_2O_2) based water decontamination. Thiols are well known reductants and react with oxidants via electron transfer mechanism. However, the effect of thiols on H_2O_2 based degradation remains uninvestigated. Herein, we reveal the potential of thiols such as thioglycolic acid (TGA), cysteine and glutathione to enhance H_2O_2 based degradation. The pseudo first order decolorization rate (k_1) of Methylene Blue (MB) by H_2O_2 alone was $1.0 \times 10^{-4}\,min^{-1}$, however, in the presence of thiols such as GSH, Cys and TGA, k_1 of MB by H_2O_2 was increased to $26.9 \times 10^{-4}\,min^{-1}$, $265.3 \times 10^{-4}\,min^{-1}$, and $940.4 \times 10^{-4}\,min^{-1}$, respectively. Furthermore, we demonstrate that TGA can drastically enhance H_2O_2 based oxidation for decolorizing a variety of dyes and to inactive bacteria as well. Nitroblue tetrazolium (NBT) assay revealed that the superoxide anion radical as primary reactive oxygen species in TGA/H_2O_2 oxidation system.

1. Introduction

Hydrogen peroxide (H_2O_2) has been recognized as "green oxidant" owing to its desirable properties such as environmental friendliness and non-toxic nature [1]. H_2O_2 is a widely used oxidant in environmental, health, food and industrial sectors [1–8]. Importantly, the only by-product of H_2O_2 mediated oxidation is water unlike chlorine based oxidizing agents that generate environmentally harmful byproducts [1–3,9,11]. Therefore, H_2O_2 has received enormous interest in emerging water treatment technologies such as advanced oxidation processes to degrade organic and microbial pollutants [2,3].

Potentiating H_2O_2 mediated degradation of contaminants is a subject of great environmental significance. Physical routes such as ultraviolet radiation [9], ultrasound [10], microwave [11] and heat treatment [12] and chemical routes such as metal catalysis [2] and non-metal catalysis [13–16] have been used to enhance H_2O_2 mediated degradation. However, major drawbacks of physical routes are the requirement of specialized reactor, expensive and difficult to implement in large scale. On the other hand, chemical routes are relatively less expensive and easy to implement. Nevertheless, in metal catalysis, the use of copper, chromium, manganese, iron etc., in homogeneous or heterogeneous form [2] may lead to secondary pollution and metal toxicity and require a post treatment process for the removal of these metals [14].

Alternatively, non-metal catalysed H_2O_2 mediated degradation is free from metal toxicity. Therefore, it is important to develop efficient metal-free catalysed H_2O_2 mediated degradation of organic contaminants. However, only limited studies are available in this direction [13–16]. Non-metal compounds that catalyse H_2O_2 mediated degradation include quinones, halogenated quinones, activated carbon, and reducing agents such as ascorbate [13–16]. Recently, it was demonstrated that hydroxylamine, widely used reducing agent, was also useful to potentiate H_2O_2 based oxidation [14]. It is important to note that thiol containing compounds are also good reducing agents [17]. However, the effect of thiol containing compounds on H_2O_2 based degradation of contaminants remains uninvestigated. Here, we aim to address this gap by studying the effect of addition of some representative thiols such as glutathione, cysteine and thioglycolic acid on H_2O_2 mediated water decontamination.

We choose dyes as principal model organic pollutants because they are released in the effluents of many industrial sectors such as textiles, paper, printing, leather, etc., and constitute a great burden for environment [18]. Importantly, because of their high molar absorption co-efficient and wide absorption in visible region of electromagnetic radiation, they produce highly colored water even when present in micromolar concentrations. For example, some common dyes such as Methylene blue (MB), Methyl orange (MO), and Rhodamine B (RhB) absorb visible light in the range of 350–580, 450–600 and 500–710 nm, respectively. In a dye contaminated water body, much of the natural sunlight which is essential for photosynthesis is masked by these dye

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contaminants, thereby detrimentally affecting natural aquatic system [18]. Generally, both organic and bacterial contaminants co-exist in polluted water. Water polluted with bacteria has serious health consequences and it is important to inactivate bacteria. Therefore, we choose *E. coli* as a surrogate bacterium to study the effect of thiols on H_2O_2 based disinfection of bacterial contaminants.

2. Experimental

2.1. Chemicals and reagents

Hydrogen peroxide (30% w/v), Thioglycolic acid Terephthalic acid, Hydrochloric acid (32%), and Nitroblue tetrazolium dichloride (NBT) were analytical grade purchased from Merck. Nutrient Agar, Luria-Bertani broth were purchased from HiMedia Pvt Ltd, India, Methylene Blue, Methyl Orange, Rhodamine B, and Malachite Green were of analytical reagent grade purchased from S.D Fine Chemicals Ltd., India. All the solutions, buffers and aqueous reagents were freshly prepared with deionized (D.I) water (resistivity 18.21 MΩ.cm) from the Millipore system. Stock solutions of dyes (2.5 mM), TGA (100 mM) and H_2O_2 (100 mM) were freshly prepared. All glasswares were washed carefully with dilute aqua regia and rinsed thoroughly with D.I water to avoid trace contamination of metal ions.

2.2. Dye degradation studies

Dyes were selected as model organic pollutants because they had strong absorption at visible light region that is favorable in two ways: (i) easy spectrophotometric monitoring and, (ii) negligible spectral interference due to the presence of other analytes in reaction mixture. It should be noted that TGA and hydrogen peroxide (H_2O_2) shows no absorption in the visible light region. Reactions were carried out in a borosilicate reaction vessel (7 × 9.5 cm) in dark conditions at ambient temperature (293 ± 3 K) under constant magnetic stirring. Degradation of dyes by TGA/H_2O_2 system was carried out by adding 5 ml of TGA stock solution to deionized water (80 ml). The pH was adjusted to desired value by adding 0.1 N HCl or 0.1 N NaOH. To this, 2.5 ml of dye stock solution was added, and the volume was adjusted to 95 ml. The degradation was initiated by adding 5 ml of H_2O_2 stock solution. The concentration of the reagents in this reaction mixture (100 ml) is as follows: [TGA] = 5 mM; [dyes] = 25 μM and [H_2O_2] = 5 mM. For control experiments i.e., TGA alone and H_2O_2 alone, similar protocol was followed except that instead of TGA or H_2O_2 5 ml D.I water was added. 1 ml of sample was withdrawn at desired time interval and the absorption at 664 nm, 618 nm, 464 nm and 554 nm for dyes MB, MG, MO and RhB, respectively was recorded using Shimadzu UV–vis spectrophotometer; version 1700. Pseudo first order decay rate constant (k_1 min^{-1}) and half-life ($t_{1/2}$, min) values for dye decolorization were determined from the slope of linear plot obtained from the log of ratio of concentration at specific time (C) to initial concentration (C_0). Total organic carbon was measured using a Shimadzu TOC-V_{CSN} analyzer. The procedure for TOC analysis was similar to that used for spectroscopic analysis of dye decolorization as mentioned above.

2.3. Determination of hydroxyl radical and superoxide anion radical

Detection of ·OH in Fe(II)/TGA/H_2O_2 and Fe(II)/H_2O_2 system using terapthalic acid (TA) as probe compound [19] was carried out by a protocol similar to degradation of dyes as mentioned above except for the modification that instead of MB, TA was added. The reaction was initiated by adding H_2O_2 and the fluorescence at 425 nm was recorded at desired time intervals using Gen 5 Version 2.08.13 Fluorescence plate reader, Biotek instruments.

Detection of superoxide anion radical was carried out using nitroblue tetrazolium dichloride (NBT) as probe compound [20]. This assay was carried out by a protocol similar to TA assay mentioned above. The generation of superoxide anion radical was followed spectrophotometrically by monitoring absorbance at 550 nm at desired intervals.

2.4. Microbiological assays

Bacterial strain, Gram negative bacteria *Escherichia coli* (NCIM 2345), were cultured in LB medium using an orbital shaker set at 100 rpm, 37 °C for 12 h. Cells (at log phase) were harvested by centrifugation at 4000 R.P.M for 15 min and washed twice with sterile D.I water. A bacterial stock solution of ~10^8 colony forming units (CFU) mL^{-1} was prepared by suspending cell pellet in an appropriate volume of phosphate buffer (100 mM, pH 5). Disinfection of bacteria by TGA/H_2O_2, TGA alone and H_2O_2 alone was carried out under sterile conditions in laminar air flow following the same procedure as mentioned above for dye degradation studies (mentioned above) except that, instead of dye stock solution, appropriate volume of bacterial stock solution was added to the reaction mixture. The initial cell concentration for bacterial inactivation studies was fixed at ~10^6 CFU ml^{-1}. Enumeration of bacterial cells was carried out by spread plate technique (Standard Method 9215C). Cell concentration before and after treatment (at specific time intervals) was determined by counting colonies after serial dilution and spread plating 0.1 ml of sample on NB agar plates, followed by incubation for 12 h at 37 °C. The accuracy of this procedure is 2 CFU ml^{-1}. Pseudo first order bacterial inactivation rate constant (k_2 min^{-1}) and half life ($t_{1/2}$, hour) values for *E. coli* inactivation were determined from the slope of linear plot obtained from the log of ratio of *E. coli* concentration at specific time (N) to initial concentration (N_0). Experimental procedure for reduction of Cr (VI) ion was carried out as outlined by Wang et al. [21] by adopting the same protocol used for MB degradation except that Cr(VI) stock solution was added instead of MB stock solution.

3. Results and discussion

3.1. Effect of TGA on decolourization of dyes by H_2O_2

The decolorization rate (k_1) of MB by H_2O_2 alone was 1.0 ± 0.004 × 10^{-4} min^{-1} (Fig. 1, Table 1). Interestingly, in the presence of thiols such as GSH, Cys and TGA, k_1 of MB by H_2O_2 was dramatically enhanced to 26.9 ± 0.053 × 10^{-4} min^{-1}, 265.3 ± 0.064 × 10^{-4} min^{-1}, and 940.4 ± 40.06 × 10^{-4} min^{-1}, respectively (Fig. 1, Table 1). From these results, it is evident that thiols

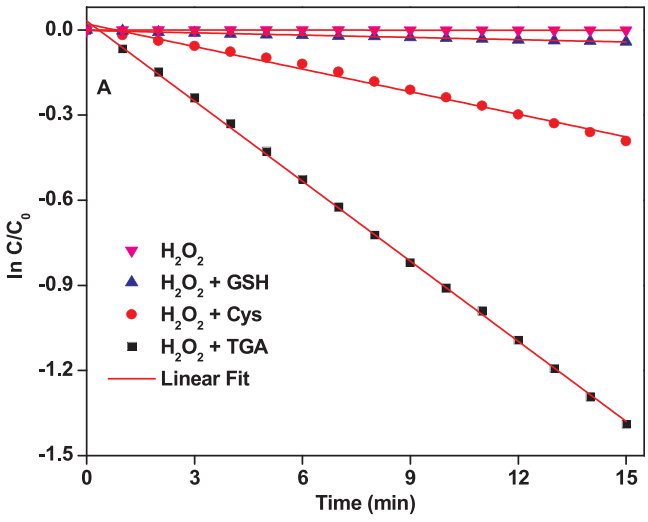

Fig. 1. Decolourisation kinetics of MB by H_2O_2 and H_2O_2 in presence of GSH or Cys or TGA. [MB] = 25 μM; [TGA] = [Cys] = [GSH] = 5 mM; [H_2O_2] = 5 mM; pH = 3.