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Journal of Photochemistry and Photobiology A: Chemistry 167 (2004) 11–16

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Studies on photo-degradation of thionine in the presence of uranyl ion and H_2O_2

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Received 25 November 2003; received in revised form 27 January 2004; accepted 19 March 2004

Abstract

Highly oxidizing nature of electronically excited uranyl ion has been utilized to degrade thionine dye with the aim of developing a new methodology for degradation of organic pollutants/waste. In this connection, photo-degradation of thionine has been studied under different conditions. It was found that in $HClO_4$ medium photo-degradation is faster than in H_2SO_4 medium on photolysis with 254 nm light. Experiments with visible light irradiation of the same system were studied in the presence of H_2O_2. In the presence of H_2O_2, hydroxyl radicals formed during oxidation of U(IV)/U(V) were found to enhance the rate of photo-degradation.

Keywords: Excited uranyl ion; Photo-degradation; Thionine

1. Introduction

With growing world population and industrialization, pollution of ground/surface water and air has become a major problem. Conventional plants for waste treatment are often not sufficient for taking care of this problem [1,2]. In recent years, advanced oxidation processes are being increasingly applied for destruction of pollutants [3,4] These include photochemical oxidation systems, viz. UV/H_2O_2 [5], UV/O_3 [6], and semiconductor photocatalysis [7–9] as well as photo-fenton processes [10]. UV combined with ozonation has also been tried for destruction of hazardous chemicals. Photolysis of ozone in water forms hydrogen peroxide, which reacts with ozone to form hydroxyl radicals [11]. Combination of H_2O_2 with UV-radiation to produce highly reactive OH radicals is an emerging technology. Studies have shown that the radiation intensity and the concentration of H_2O_2 have to be optimized to degrade pollutants effectively [5]. Semiconductors such as TiO_2, ZnO, Fe_2O_3, CdS, etc. can act as sensitizers for light induced redox processes due to their electronic structure, which is characterized by a filled valence band and an empty conduction band [12]. TiO_2 has proven to be the most suitable for widespread environmental applications [13]. The hole formed in the valence band on light absorption is strongly oxidizing in nature.

It is known that in acid solutions, uranyl displays a complex system of weak bands ($\varepsilon \sim 10\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$) between 330 and 500 nm and a monotonously increasing absorption at decreasing wavelengths [14]. The absorption spectra of the uranyl complexes are essentially ligand field bands determined by the O–U–O field. In H_2SO_4 medium, the λ_{max} is at 419 nm. Absorption maximum as well as extinction coefficient depends on the type of acid as well as acid concentration. Electronically excited uranyl ion is a strong oxidant ($E_0 = 2.6$ V versus NHE in acid solutions) [14,15] and is generally reduced by a variety of organic and inorganic substrates unless only energy transfer takes place in a quenching process [16]. Photochemical reduction of uranyl ions using organic compounds as reductants has been subject of many investigations [17,18]. In addition to electron transfer, its reaction with organic compounds can also be by H-abstraction mechanism:

$$^*UO_2^{2+} + RR'CHOH \rightarrow UO_2^{+} + RR'C^{\bullet}OH + H^{+} \qquad (1)$$

U(V) species disproportionates giving U(IV) and U(VI) while the organic radical gets transformed into an aldehyde or a ketone. Photo-physical and photochemical processes involved in the photo-reduction of U(VI) have been extensively studied [19]. Recently, Nagaishi et al. [20] have

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doi:10.1016/j.jphotochem.2004.03.027

studied photo-reduction of the uranyl ion by alcohols in acidic solutions and ϕ(U(IV)), and quenching constants were determined. Photochemically formed U(IV) has also been considered as a reductant for plutonium(IV) to overcome the problems arising due to high salt content when Fe(II) is used as a reductant in the 'PUREX' process. U(IV) and U(V) get oxidized to U(VI) by oxygen. H_2O_2 can also oxidize U(IV) and U(V) species as below:

$$U^{4+} + H_2O_2 + H_2O \rightarrow UO_2{}^{+} + OH + 3H^{+} \tag{2}$$

$$UO_2{}^{+} + H_2O_2 \rightarrow UO_2{}^{2+} + OH + OH^{-} \tag{3}$$

Hydroxyl radicals (OH) generated in above reactions can react with U(IV) or any other reactive additive present in the system. Compared to electron transfer reactions of excited U(VI), OH can undergo different type of reactions which can help in the degradation process.

In the present study, we have tried to make use of the oxidizing nature of excited U(VI) and the generation of OH radicals in the reaction of U(IV)/U(V) with H_2O_2 to cause the degradation of a thiazine dye, viz. thionine.

2. Experimental details

2.1. Preparation of uranyl sulphate solution

An amount of 0.1 mol dm^{-3} of uranyl sulphate solution in 0.5 mol dm^{-3} sulphuric acid was prepared by taking 3.58 g of uranyl oxalate in about 70 ml of distilled water to which 10 ml of concentrated HNO_3 was added. The solution was slowly heated and then boiled during which uranyl oxalate was decomposed. The solution volume was brought to about one-fifth of its initial volume. It was again boiled in presence of nitric acid and evaporated almost to dryness. To the residue, 2.8 ml of concentrated sulphuric acid was added along with some amount of water and the solution was brought to boiling whereby nitrate was converted into sulphate. After cooling, the solution was transferred quantitatively into a 100 ml volumetric flask and made up to the mark with distilled water.

2.2. Preparation of uranyl perchlorate solution

To prepare 0.1 mol dm^{-3} of uranyl perchlorate solution in 1 mol dm^{-3} perchloric acid medium, initially 3.58 g of uranyl oxalate was treated with HNO_3 twice as described in Section 2.1. The dried mass of uranyl nitrate was then treated with 10 ml of perchloric acid (60%, w/v) and some amount of water. The solution was brought to boiling whereby nitrate was converted into perchlorate. The whole solution was transferred quantitatively in a 100 ml volumetric flask and volume made up with the required amount of distilled water.

2.3. Photo-irradiation

Solutions containing uranyl ion and thionine in sulphuric acid/perchloric acid medium were taken in a 1 cm × 1 cm quartz cell and irradiated with 254 nm light using Rayonet photo-reactor under various conditions. Light flux was determined to be 5×10^{15} photons cm^{-2} s^{-1} using potassium ferrioxalate actinometry. Solutions containing uranyl ion, thionine and H_2O_2 were also irradiated in a 25 ml beaker kept under a 100 W tungsten filament lamp. To calculate the intensity of light absorbed by then uranyl solution, 10 ml of solution containing 0.02 mol dm^{-3} uranyl sulphate and 0.005 mol dm^{-3} oxalic acid were irradiated with tungsten filament lamp for different time duration (150 and 300 min). Concentration of the residual oxalic acid was estimated by titration against standardized $KMnO_4$ solution. Light intensity absorbed by the above solution was calculated to be 7×10^{14} photons s^{-1}, taking quantum yield for oxalic acid decomposition as 0.5.

Absorption spectra were recorded using U-2001 Hitachi spectrophotometer and fluorescence quenching experiments were carried out using F-4010 Hitachi fluorescence spectrophotometer.

3. Results and discussions

3.1. Photolysis of uranyl sulphate and thionine solutions

Absorption spectra of the solutions containing 0.01 mol dm^{-3} uranyl sulphate and 10^{-5} mol dm^{-3} thionine in 0.05 mol dm^{-3} H_2SO_4 irradiated with 254 nm light using Rayonet photo-reactor for various time durations are given in Fig. 1. Absorbance of the solution (A_t) at 599 nm was also recorded after each irradiation. Fig. 2 shows the plot of absorbance at 599 nm versus irradiation time which was found to be exponential in nature. The plot of $\ln A_t$ versus time of irradiation was found to be linear indicating that degradation of thionine follows first-order kinetics and the rate constant for the above first-order degradation reaction (k_1) was found to be 0.04318 min^{-1} from the slope of the above plot. It has to be noticed that this first-order rate constant is function of available light intensity. Also, quantum yield for degradation will depend on the available thionine concentration. During photolysis, steady concentration of excited uranyl species is generated. The reaction between excited uranyl ion and thionine thus obeys pseudo first-order kinetics with respect to thionine concentration. Mechanism for thionine degradation can be as follows:

$$UO_2{}^{2+} + h\nu \rightarrow {}^*UO_2{}^{2+} \tag{4}$$

$${}^*UO_2{}^{2+} \rightarrow UO_2{}^{2+} + \text{heat} \tag{5}$$

$${}^*UO_2{}^{2+} + TH^{+} \rightarrow {}^*[UO_2{}^{2+} \cdots TH^{+}] \tag{6}$$

$${}^*[UO_2{}^{2+} \cdots TH^{+}] \rightarrow UO_2{}^{2+} + TH^{+} \tag{7}$$

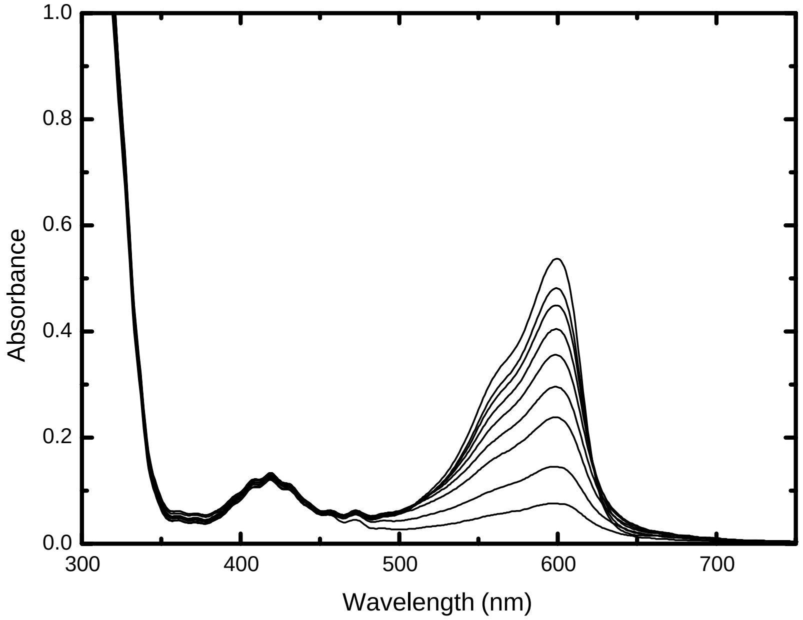

Fig. 1. Absorption spectra of solutions containing 10^{-5} mol dm^{-3} thionine and 0.01 mol dm^{-3} uranyl sulphate in 0.05 mol dm^{-3} H_2SO_4 at various time of irradiation (0, 3, 6, 12, 18, 24, 36, 48 and 60 min).

$$[{}^*UO_2{}^{2+} \cdots TH^+] \rightarrow UO_2{}^+ + \text{semioxidized thionine } (TH^{\bullet 2+}) \quad (8)$$

In aqueous solutions, thionine gets oxidized by one electron oxidants such as azidyl ($N_3{}^\bullet$) and $Br_2{}^{\bullet-}$ radicals quite efficiently [21]. It is expected that excited uranyl ions having potential of 2.6 V versus NHE should also undergo facile electron transfer reaction. The semioxidized thionine species subsequently undergoes decay to give products.

$$2TH^{\bullet 2+} \rightarrow \text{products} \quad (9)$$

Photolysis of a 10^{-5} mol dm^{-3} thionine solution in 0.05 mol dm^{-3} H_2SO_4 medium with 254 nm light led to very little degradation (6%) in 30 min. In this case only thionine absorbs light. Thus, in the case of a solution containing uranyl ions and thionine, direct degradation of thionine will be less than 6%, as most of the 254 nm light will be absorbed by $UO_2{}^{2+}$ due to its higher concentration and high ε at this particular wavelength.

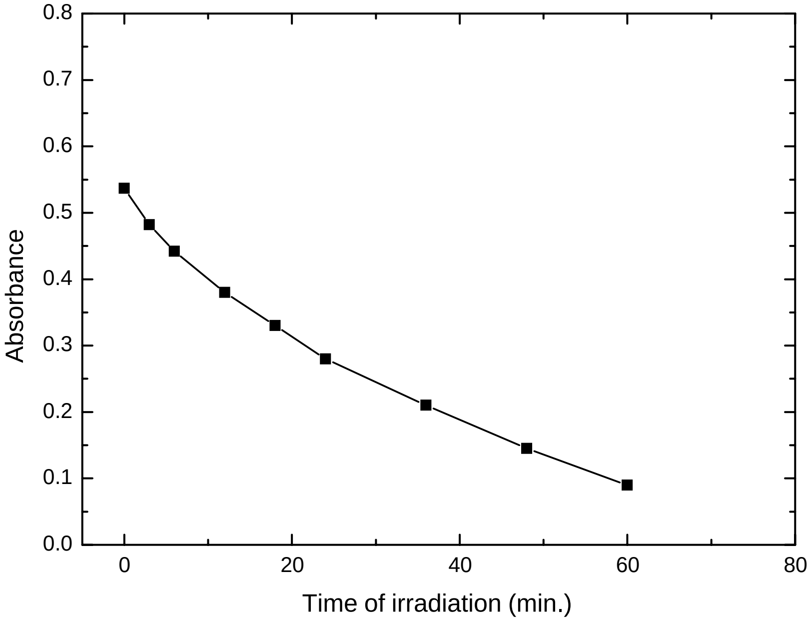

Fig. 2. Plot of absorbance of thionine at 599 nm as a function of time of irradiation of solutions containing 10^{-5} mol dm^{-3} thionine and 0.01 mol dm^{-3} uranyl sulphate in 0.05 mol dm^{-3} H_2SO_4.

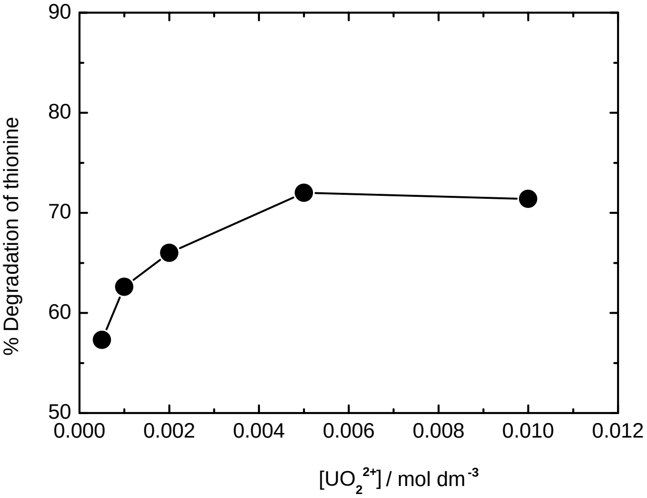

Fig. 3. Percent degradation of thionine as a function of uranyl ion concentration in 0.05 mol dm^{-3} H_2SO_4 and 10^{-5} mol dm^{-3} thionine.

To study the effect of concentration of uranyl sulphate on the degradation of thionine, experiments were carried out at different concentrations of uranyl sulphate at a fixed concentration of thionine (10^{-5} mol dm^{-3}) in 0.05 mol dm^{-3} H_2SO_4 medium. It was observed that on increasing uranyl ion concentration from 0.0005 to 0.005 mol dm^{-3}, the extent of degradation of thionine (for a fixed time of 30 min irradiation) reached a plateau of around 73%. After that, further increase in the concentration of uranyl ion does not lead to any increase in the extent of degradation of thionine rather it shows a decrease as shown in Fig. 3. This can be due to the fact that initial increase in the concentration of uranyl ion leads to increase in excited uranyl ion concentration due to increased absorbance at 254 nm. As absorbance value exceeds 2, more and more of the available light is getting absorbed near the walls of the quartz cell rather than reaching the interior of the solution.

To observe the effect of O_2 on the extent of degradation of thionine, O_2 saturated solutions containing 0.01 mol dm^{-3} uranyl sulphate and 10^{-5} mol dm^{-3} thionine in 0.05 mol dm^{-3} H_2SO_4 medium were employed. Photolysis with 254 nm light gave a higher degradation (83%) of thionine after 30 min irradiation as compared to 72% in aerated solutions. Enhanced degradation of thionine can be attributed to faster reoxidation of UO_2^+ species by O_2 and as well as to the reaction of O_2 with intermediates formed in the process.

Effect of concentration of thionine on the photo-degradation was studied. For this purpose, experiments were performed using different concentrations of thionine, viz. 0.5×10^{-5}, 1.0×10^{-5}, 2.0×10^{-5} and 3.0×10^{-5} mol dm^{-3} keeping uranyl sulphate concentration same (0.01 mol dm^{-3}) and the extent of degradation of thionine was found to be 85, 71, 48 and 37%, respectively. In terms of amount of thionine degraded, there is increase in degradation with increasing thionine concentration. As thionine concentration increases, more of excited uranyl ions react with thionine.

Irradiation of a solution containing 0.01 mol dm^{-3} uranyl sulphate and 2×10^{-5} mol dm^{-3} thionine in 0.05 mol dm^{-3} H_2SO_4 produces an oxidized product of thionine which on prolonged irradiation further degrades to simpler molecules.

3.2. Photolysis of thionine in presence of uranyl perchlorate

The type of experiments described in Section 3.1 were also performed in 0.1 mol dm^{-3} perchloric acid medium. The absorption spectra of the irradiated solution were recorded in 200–700 nm region. It was seen that the degradation of thionine is much faster in $HClO_4$ medium as compared to that in 0.05 mol dm^{-3} H_2SO_4 medium. In 10^{-5} mol dm^{-3} thionine containing solutions, nearly 77% degradation takes place in 5 min of photolysis. From the plot of $\ln A_t$ versus time of irradiation, rate constant for the first-order degradation reaction (k_1) was found to be 0.3575 min^{-1}. Faster degradation in perchloric acid can be due to the availability of free uranyl ions in the perchloric acid medium.

After 20 min irradiation of a solution containing 0.01 mol dm^{-3} UO_2^{2+} and 3×10^{-5} mol dm^{-3} thionine in 0.1 mol dm^{-3} perchloric acid medium with 254 nm light, the thionine absorption at 599 nm almost disappears the absorption in 530 nm region does not undergo much change as compared to the initial absorbance. This shows that the initial product formed on oxidation of thionine absorbs light in 530 nm region. The spectrum of this species (Fig. 4) was generated by taking a difference spectrum of 0.01 mol dm^{-3} UO_2^{2+} in 0.1 mol dm^{-3} $HClO_4$ and the above mentioned irradiated solution when the 599 nm absorption of thionine almost approaches zero. It may be mentioned here that in H_2SO_4 medium also an absorption spectrum, which can be ascribed to initial oxidation product, was generated.

3.3. Photolysis of thionine in presence of uranyl sulphate and H_2O_2

Solutions containing 0.01 mol dm^{-3} uranyl sulphate, 10^{-5} mol dm^{-3} thionine and 0.07 mol dm^{-3} H_2O_2 in 0.05 mol dm^{-3} H_2SO_4 were irradiated with a 100 W tungsten filament lamp for various time durations. Absorption spectra of the solutions were recorded in 200–700 nm region after each irradiation (Fig. 5). Absorption at 599 nm (A_t) was also recorded and plotted against the time of irradiation and from the plot of $\ln A_t$ versus time of irradiation, rate constant for the above first-order degradation reaction (k_1) was found to be 0.0163 min^{-1}. In this case, it was observed that a decrease in thionine absorption at 599 nm is also accompanied by a decrease in absorption at 530 nm. This shows that the intermediate product formed during degradation of thionine in the absence of H_2O_2 is not formed in the presence of H_2O_2. The reason for this

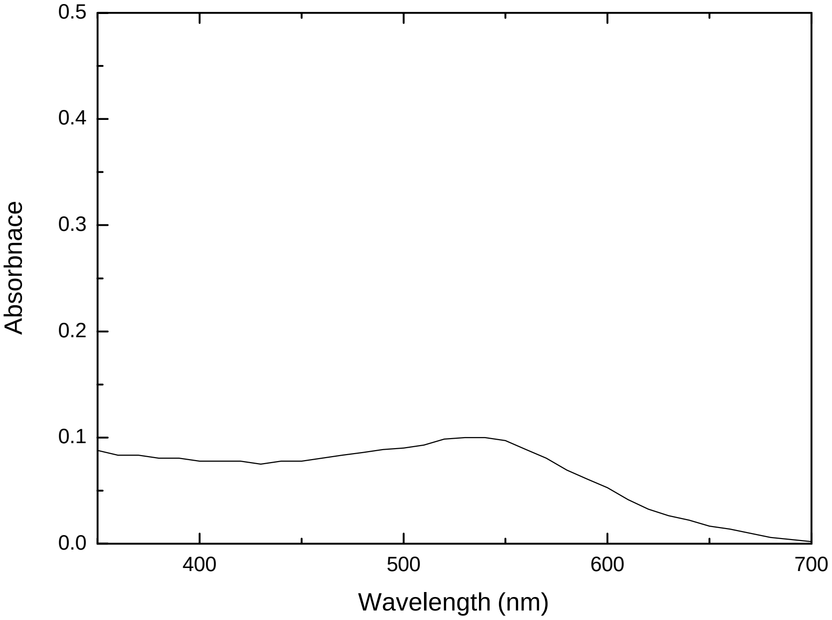

Fig. 4. Absorption spectrum of degradation product formed after 20 min of photo-irradiation of 3×10^{-5} mol dm^{-3} thionine, 0.01 mol dm^{-3} uranyl in 0.1 mol dm^{-3} $HClO_4$.

can be that in the absence of H_2O_2 oxidation of thionine takes place only through excited uranyl ions, whereas in the presence of H_2O_2, reaction of hydroxyl radicals in addition to those of excited uranyl ion can give different products. It has been reported that in pulse radiolysis of thionine in aqueous solutions, OH radicals radicals are reacting with thionine not exclusively by electron transfer [21]. To calculate quantum yield for thionine degradation, a solution containing 0.02 mol dm^{-3} uranyl sulphate, 0.07 mol dm^{-3} H_2O_2 and 2×10^{-5} mol dm^{-3} thionine in 0.05 mol dm^{-3} H_2SO_4 was also irradiated for 5 min with tungsten filament lamp. The quantum yield for thionine degradation in this solution was found to be 0.052 and it has to be mentioned that it refers to the initial stage of degradation.

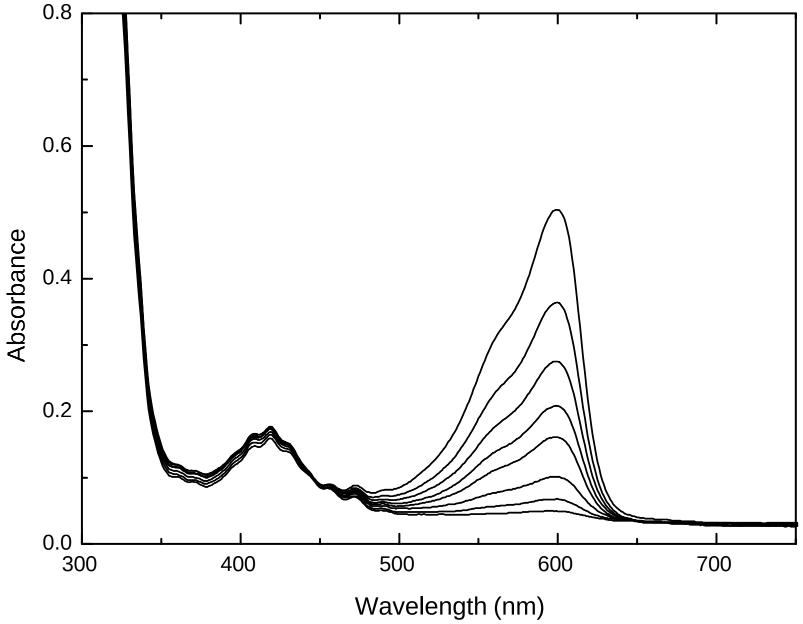

Fig. 5. Absorption spectra of solutions containing 10^{-5} mol dm^{-3} thionine, 0.01 mol dm^{-3} uranyl sulphate and 0.07 mol dm^{-3} H_2O_2 in 0.05 mol dm^{-3} H_2SO_4 at various time of irradiation.

3.4. Fluorescence quenching study of uranyl ions and thionine

Excited UO_2^{2+} species ($\lambda_{exc} = 419$ nm) gives luminescence with peaks at around 494, 515 and 539 nm in 0.1 mol dm^{-3} H_2SO_4 medium. In the presence of thionine, these peak intensities were found to decrease due to the reactions of excited UO_2^{2+} species with thionine. Experiments were performed in presence of 1.0, 2.0 and 3.0×10^{-5} mol dm^{-3} thionine and 0.01 mol dm^{-3} uranyl sulphate solution and the corresponding luminescence values were recorded. Ratios of initial light intensity (I_0) and emitted light intensity (I) were plotted against the concentrations of thionine. The Stern–Volmer constant (K_{SV}) was found to be 10^4 dm^3 mol^{-1}. Taking a value of 1.7 μs for uranyl excited state life time, one obtains a quenching constant of about 6×10^9 dm^3 mol^{-1} s^{-1} showing that thionine is reacting with excited uranyl ion quite efficiently.

4. Conclusions

It is found that photolysis of thionine in presence of uranyl ion leads to its degradation. Photo-degradation of thionine is much faster in $HClO_4$ medium than in H_2SO_4 medium which has been ascribed to availability of free uranyl ion in $HClO_4$. Photolysis with visible light of the thionine–uranyl system carried out in the presence of H_2O_2 suggests that in presence of H_2O_2, hydroxyl radicals formed by way of its reactions with U(V)/U(IV) enhance the rate of photo-degradation. The intermediate formed from thionine in the presence of only uranyl solutions is not formed when H_2O_2 is present in the system.

Acknowledgements

The authors are thankful to Dr. T. Mukherjee, Associate Director Chemistry Group, BARC, for his keen interest and support for this work.

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