

## Photocatalytic Oxidation of Surfactant Hexadecyltrimethyl-Ammonium Bromide in Aqueous Diluted Solutions

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**Abstract:** The photo catalytic oxidation of Surfactant Hexadecyltrimethyl-ammonium bromide in aqueous diluted solution has been investigated. Compressed air was used as oxidant and the temperature was maintained at 25-30°C. Effect of UV rays alone and in combination of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and titanium dioxide (TiO<sub>2</sub>) on Hexadecyltrimethyl-ammonium bromide (C<sub>19</sub>H<sub>42</sub>NBr) was recorded. Finally, from HPLC and IR analysis the intermediates products have been detected prior to the total Hexadecyltrimethyl-ammoniumbromide mineralization.

**Key words:** Catalytic degradation • Kinetic studies • Degradation of Hexadecyltrimethyl-ammoniumbromide  
• Photolysis of Hexadecyltrimethyl-ammoniumbromide

### INTRODUCTION

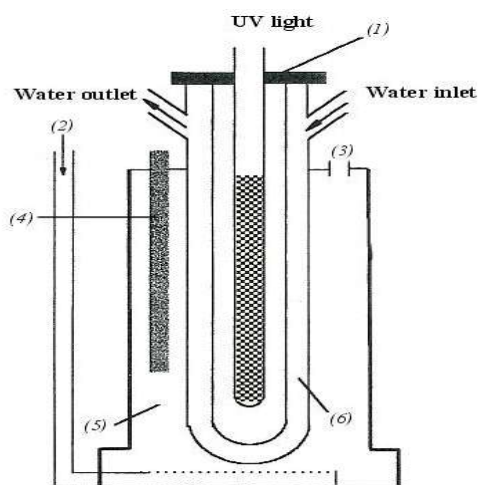
The photo catalytic degradation (PCD) process is gaining importance in the area of effluent treatment, especially for wastewater containing small amounts of refractory organic substances [1, 4]. The process has several advantages over competing processes. These are (i) complete mineralization, (ii) no waste disposal problem, (iii) low cost and (iv) mild temperature and pressure conditions are necessary. Surfactants (surface-active agents) can be anionic, amphoteric, polymeric and non-ionic. They are held in industries such as agro-chemical, mining and oilfield. Surfactants have a hydrophilic head which attaches to water and a hydrophobic side of the molecule that avoids water. The hydrophobic part of the molecule is also free to attach to grease, fat, or oil on the surface

Heterogeneous photo catalysis is a well-known technology to solve the problem of water pollution [1, 2]. Even in the nuclear industry, during decontamination of protective wears and contaminated materials, detergents are employed to bring down the level of radioactive contamination to within safe limits. However, the surfactant present in these wastes interferes with the chemical treatment process, reducing the decontamination [3]. Although surfactants have been studied in complex water soil systems [4, 5], the effects are not well understood.

Different methods have been used to destroy and reduce the levels of organic pollutants including treatment with activate sludge [6], Clinical oxidation [7], biological oxidation [8], thermal degradation, ionization, sono-chemical and photo-oxidation with ultraviolet radiation [9-14].

The present experiments were conducted using surfactants as a model on account of the possible contamination of the environment by surfactants arising from the widespread use of soaps and detergents [15], of low biodegradability [16] and the inhibiting effect to the biodegradation of some other pollutants [17]. The surfactant used was hexadecyltrimethyl-ammonium bromide (C<sub>19</sub>H<sub>42</sub>NBr), which is a cationic surfactant with a chemical formula of CH<sub>3</sub> (CH<sub>2</sub>)<sub>15</sub>NBr (CH<sub>3</sub>)<sub>3</sub>. It has a molecular weight of 364.45 and is known as Cetrimonium bromide with abbreviations such as HTAB, CTAB and CTABr.

It has been demonstrated [18, 19] that various parameters have an effect on the degradation rate of compounds. A few degradation kinetic expressions of different compounds have been reported in the literature. In this study, Hexadecyltrimethyl-ammonium bromide (C<sub>19</sub>H<sub>42</sub>NBr) was chosen as the model compound. The effects of the initial pollutant concentration, light intensity, initial concentration of H<sub>2</sub>O<sub>2</sub>, catalyst concentration, pH value of the suspension and temperature on the degradation rate of C<sub>19</sub>H<sub>42</sub>NBr were studied. The catalyst was titanium dioxide (TiO<sub>2</sub>).



1. UV Probe                      2. Inlet  
3. Outlet                         4. Thermometer  
5. Reaction Chamber         6. Cooling Jacket

Fig. 1: Schematic illustration of the photolytic cell system

**Experimental:** The photolytic cell system used (Figure 1) consists of a UV probe (1) surrounded by a reaction chamber (5). Compressed air was used as the oxidant in the photolysis and is supplied through the inlet (2) and an exit through the outlet (3). The temperature in the system was measured by thermometer (4) and the reaction chamber was maintained at 25-30°C by a water cooling jacket (6) which surrounded the UV probe.

All the chemicals were analytical grade and were purchased from Fisher Scientific. The titanium dioxide (Degussa P.25) was predominately anatase (80% anatase and 20% rutile) as shown by x-Rays diffraction. All other chemicals used in this work were at least of reagent grade and were used as received.

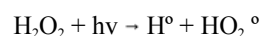
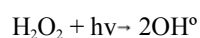
The effects of UV source, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and titanium dioxide ( $\text{TiO}_2$ ) on the degradation of  $\text{C}_{19}\text{H}_{42}\text{NBr}$  were studied. The effect of the UV source on the degradation of  $\text{C}_{19}\text{H}_{42}\text{NBr}$  was examined using a 150W and 400W UV probe. 50ppm of  $\text{C}_{19}\text{H}_{42}\text{NBr}$  and  $5 \text{ cm}^3\text{dm}^{-3}$  of  $\text{H}_2\text{O}_2$  were prepared. The same procedure was applied for the preparation of the concentration of  $\text{H}_2\text{O}_2$  ( $10 \text{ cm}^3\text{dm}^{-3}$ ).

The degradation was followed by using another catalyst, namely  $\text{TiO}_2$  and as in  $\text{H}_2\text{O}_2$ , the same procedure and method was applied. The analysis of  $\text{C}_{19}\text{H}_{42}\text{NBr}$  was carried out by using High performance liquid Chromatography (HPLC) and Infrared (IR) Spectroscopy.

## RESULTS AND DISCUSSION

The photo decomposition of Hexadecyltrimethylammonium bromide ( $\text{C}_{19}\text{H}_{42}\text{NBr}$ ) in the presence of  $\text{H}_2\text{O}_2$  or in the presence of catalyst ( $\text{TiO}_2$ ) was studied.

It has been observed as shown in Table 1 that in the presence of UV radiation or catalyst only, a small decrease in the concentration of  $\text{C}_{19}\text{H}_{42}\text{NBr}$  is observed. However,  $\text{C}_{19}\text{H}_{42}\text{NBr}$  is degraded rapidly in the presence of  $\text{H}_2\text{O}_2$ ,  $\text{TiO}_2$  and irradiation. The photolysis of the solutions gives OH radicals as primary photoproducts together with small amounts of  $\text{HO}_2$  radicals [20].



Under these conditions, irradiated  $\text{C}_{19}\text{H}_{42}\text{NBr}$  forms a triplet state that reacts with  $\text{H}_2\text{O}_2$ .

In the presence of  $\text{TiO}_2$ ,  $\text{H}_2\text{O}_2$  and UV radiation (Table 1), a greater decomposition of  $\text{C}_{19}\text{H}_{42}\text{NBr}$  is observed. Therefore, careful study of this degradation process is important. The primary step in the photodegradation process is certainly the adsorption of  $\text{H}_2\text{O}_2$  onto the catalyst surface, which leads to adsorbed  $\text{OH}^\circ$  radicals.

Table 1: Effect of  $\text{H}_2\text{O}_2$  and  $\text{TiO}_2$  on the degradation of Hexadecyltrimethyl- ammonium bromide ( $\text{C}_{19}\text{H}_{42}\text{NBr}$ )

Degradation of $\text{C}_{19}\text{H}_{42}\text{NBr}$ (%)						
Time (h)	No catalyst	$\text{H}_2\text{O}_2$ (5cm <sup>3</sup> dm <sup>-3</sup> )	$\text{H}_2\text{O}_2$ (10 cm <sup>3</sup> dm <sup>-3</sup> )	$\text{TiO}_2$ (1g dm <sup>-3</sup> )	$\text{TiO}_2$ (2g dm <sup>-3</sup> )	$\text{H}_2\text{O}_2$ (5cm <sup>3</sup> dm <sup>-3</sup> )+ $\text{TiO}_2$ (1g dm <sup>-3</sup> )
2	10.2	19.8	25.1	17.6	24.1	40.1
4	20.8	39.5	50.0	39.5	48.0	78.4
6	45.1	62.6	74.9	62.6	71.9	99.9
8	60.3	82.7	99.8	82.7	95.8	99.9

Table 2: Effect of UV source on the degradation of Hexadecyltrimethyl- ammonium Bromide ( $\text{C}_{19}\text{H}_{42}\text{NBr}$ )

Degradation of $\text{C}_{19}\text{H}_{42}\text{NBr}$ (%)		
Time (h)	150W Lamp	400W Lamp
2	7.7	10.2
4	12.9	20.8
6	21.5	45.1
8	32.7	60.3

$C_{19}H_{42}NBr$  will be attacked by hydroxyl radicals formed in the above equation to generate organic radicals or other intermediates. Eventually, all the parent compound and intermediates will be oxidized to  $CO_2$  with an overall reaction stoichiometry.

The catalytic stability of the  $TiO_2$  sample was tested with fresh Hexadecyltrimethyl-ammonium bromide. Up to three consecutive cycles were performed to test the long-term stability of  $TiO_2$ . After each cycle (8 h), fresh Hexadecyltrimethyl-ammonium bromide was added; the catalyst was washed with distilled water and was reused in the following cycle. Soluble  $TiO_2$  was determined by inductively coupled plasma-mass spectrometry (ICP-MS). The results show that there is no catalyst deactivation during the reaction, but slight catalyst leaching. The copper analysed in the solution after hexadecyltrimethyl-ammonium bromide mineralization represents less than 1% of the total  $TiO_2$  content of the catalyst.

UV-visible absorption investigation was carried out. A series of UV-visible spectra of an irradiated solution containing  $TiO_2$  and  $H_2O_2$  were recorded in the 200–500 nm range at increasing reaction times, in order to monitor the gradual disappearance of pollutants. These spectra, which are not reported here for the sake of brevity, show that the characteristic absorptions of Hexadecyltrimethyl-ammonium bromide almost disappear after 8h of irradiation with the appearance of new bands in the range 400–500 nm during the photodegradation process. The presence of these bands gradually decreases at increasing reaction times, suggesting the formation and subsequent destruction of intermediate compounds.

HPLC results have been reported to show the formation of organic acids. The formation of organic acids during Hexadecyltrimethyl-ammonium bromide degradation has been reported to be due to hydroxylation of this compound. The Table 2 shows that by increasing the intensity of UV source, the degradation percentage of Hexadecyltrimethyl- ammoniumbromide ( $C_{19}H_{42}NBr$ ) also increases.

The results described are on the degradation of  $C_{19}H_{42}NBr$  with different types of catalysts and concentrations. By the addition of  $H_2O_2$  as an oxidant and  $TiO_2$  as a heterogeneous catalyst, the results showed that there is an increase in degradation percentage (Table 1).

Experiment with  $H_2O_2$  on  $C_{19}H_{42}NBr$  was determined by adding different volumes (5 and  $10\text{cm}^3\text{dm}^{-3}$ ) of  $H_2O_2$  solution to a solution containing the same initial concentration of  $C_{19}H_{42}NBr$ . The addition of  $5\text{cm}^3\text{dm}^{-3}$  of

$H_2O_2$  increased the extent of degradation of  $C_{19}H_{42}NBr$  and further increases the concentration of  $H_2O_2$  ( $10\text{cm}^3\text{dm}^{-3}$ ) increases even more.

Heterogeneous photo-catalysis using semiconductor particles of titanium dioxide ( $TiO_2$ ) on the degradation of  $C_{19}H_{42}NBr$  was determined by adding different volumes (1 and  $2\text{gdm}^{-3}$ ) of  $TiO_2$  to a solution containing the same initial concentration of  $C_{19}H_{42}NBr$ . The results show that the addition of  $1\text{gdm}^{-3}$  of  $TiO_2$  increases the initial degradation of  $C_{19}H_{42}NBr$  which is further improved if 2 grams are used.

## CONCLUSION

It can be concluded that the photo-catalytic system can be used for the degradation of organic pollutants. The rate of degradation of  $C_{19}H_{42}NBr$  varies according to the type and volume of a catalyst compared to the absence of catalysts. The level of degradation on  $C_{19}H_{42}NBr$  was recorded with varying levels of  $H_2O_2$  and  $TiO_2$ .

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