# Decomposition of Anionic Sodium Dodecylbenzene Sulfonate by UV/TiO$_2$ and UV/H$_2$O$_2$ Processes a- Comparison of Reaction Rates

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**ABSTRACT:** *Anionic DBS surfactant can be photodegraded in a TiO$_2$ dispersion and H$_2$O$_2$ solution under an Hg-lamp (15W) UV illumination or solar exposure. Degradation process has been monitored through cleavage of aromatic moiety. Degradation of the detergent was small when the photolysis was carried out in the absence of TiO$_2$ and H$_2$O$_2$ and it was negligible in the absence of light. Most of the curves representing the semi-log of pollutant concentration versus time were nearly linear, suggesting first order reactions. In the UV/TiO$_2$ process, the extent of surfactant degradation was found to be influenced by the TiO$_2$ loading, initial detergent concentration, agitation rate, temperature and initial pH. The UV peroxided degradation of the anionic detergent (DBS) by the UV/H$_2$O$_2$ process is more effective than UV/TiO$_2$ process making it a promissable method for desrtoying the aquatic pollutants. A combination of UV and Solar light is used, degradation of DBS it is more effective than UV/ H$_2$O$_2$ process.*

**KEYWORDS:** *Dodecylbenzene sulfonate, Hydrogen peroxide, Photocatalytic mineralization, Photooxidation, Titanium dioxide, Photodegradation*

## INTRODUCTION

Environmental pollution by surfactants is a highly serious ecological problem. Various surfactants are widely used in households, industrially and in other fields. The amount of liquid concentrated detergents produced in 1991 was 3.4 million ton in the USA, 3.9 million ton in Western Europe, and 0.6 million ton in Japan. The production will continue to increase in the near future. Unfortunately, some surfactants are not easily bio-degraded by bacteria, and so accumulate and persist in nature for long periods and become one of many direct causes of water pollution. Thus, in the case of sodium n-

dodecylbenzene sulfonate (DBS), the decomposition requires a period of two days while branched isomers of DBS are not biodegraded even after a week of exposure to bacteria [1,2].

Recent developments in the domain of chemical water treatment have led to the utilization of improved catalytic and photochemical degradation procedures for organic compounds dissolved or dispersed in aquatic media. These are generally referred to as "advanced oxidation processes", (AOP) [3].

In the UV/TiO$_2$ process, the adsorption of surfactants

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on the TiO$_2$ surface, the generation of OH radicals at the TiO$_2$/H$_2$O interface, the mineralization of the surfactants to CO$_2$, and the intermediate formation of peroxides and aldehydes have all been examined in previous studies (2). With attention to the intermediate formation of peroxides and aldehydes and the NMR spectra of DBS for different irradiation times a catalyzed photodegradation mechanism is suggested [4].

The other system is UV/H$_2$O$_2$ process. Hydrogen peroxide is also an effective oxidizing agent for UV catalyzed reactions. It can be stored for use according to process demand and is readily mixed with water. Absorption of UV photons by hydrogen peroxide dissociates it into hydroxyl radicals that attack organic molecules by abstracting hydrogen atoms or by adding to double bonds. Under suitable operating conditions, the final products are water, CO$_2$ and low molecular weight aliphatic acids [5]. In this paper, we report the photooxidative degradation of DBS in UV/TiO$_2$ system (with a particular emphasis on process variables), UV/H$_2$O$_2$ system and the combination of this two systems.

## MATERIALS AND METHODS

Anionic detergent containing DBS was obtained from Paxan company, Tehran, Iran. TiO$_2$, HClO$_4$ and NaOH obtained from Merck (Darmestadt, Germany) and H$_2$O$_2$ obtained from Kiankaveh company. Doubly distilled water was used. The experimental investigation was performed using a batch photoreaction system. For the batch system, a mixture or solution containing a known concentration of DBS(50ppm) and H$_2$O$_2$ or TiO$_2$ and or both was prepared and the suspensions were allowed to equilibrate for 30min in the dark then 100ml from solution or suspension prepared was transferred to a 500ml Pyrex reactor. The pH was kept constant at the desired levels with NaOH and HClO$_4$ solution by manual adjusting. The solution temperatures can were adjusted by a thermostatic device, then Pyrex reactor on a magnetic stirring device or laboratory jack was illuminated with a UV lamp(15W). After an appropriate illumination time, the suspension or solution was sampled. The concentration of surfactant in each treated sample was measured by UV spectroscopy (absorption of aromatic moieties, 196-224nm) and the use of a calibration curve (Fig. 1) [1]. By this method percent of DBS degradation can obtained at different time intervals. The percent degraded (x) is given by :

$$X = \frac{C_0 - C}{C_0} \times 100$$

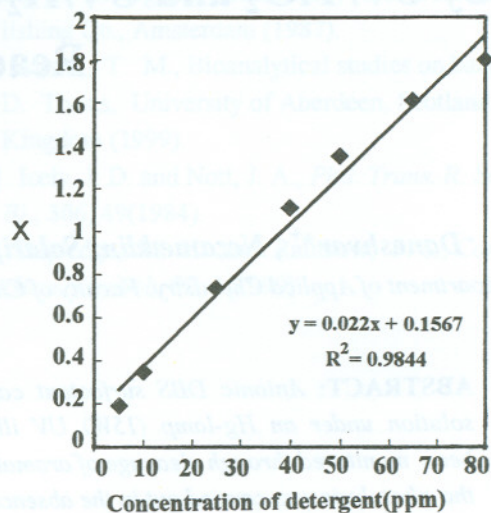where C$_0$ = initial concentration of DBS and C = concentration of DBS at time t.



Fig.1: Calibration Curve in Wavelength 196 nm

## RESULTS AND DISCUSSION

### Effect of Process Variables in UV/TiO$_2$ Process

### Effect of UV Illumination Time

The photodegradation of DBS with TiO$_2$ as a function of irradiation time is illustrated in Fig. 2. The decomposition of DBS increases with time and attains a constant level in 4.5hr. Decomposition rate of DBS is rapid
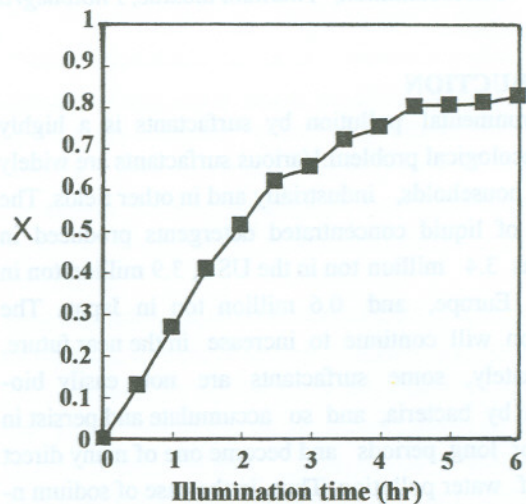


Fig. 2: Effect of illumination time in decomposition of DBS in UV/TiO$_2$ process. T = 302K, pH= 6.9, [DBS]$_o$= 50 ppm, TiO$_2$= 50 ppm, without agitation

in the initial stages of illumination and gradually decreases with time. The logC(DBS) versus time of illumination plots for DBS are linear suggesting that the photodegradation reaction approximately follows first-order kinetics. The rate constants(k) were estimated from the slope of the logC(DBS) versus time plots; while $t_{0.5}$ value were deduced from 0.693/k. It was found that the average k and $t_{0.5}$ values of DBS in UV/TiO$_2$ process without optimization the conditions were 0.006 min$^{-1}$ and 115 min, respectively.

## Effect of UV Irradiation in Presence of TiO$_2$ Particles

The effect of UV irradiation in presence of TiO$_2$ particles in decomposition of DBS is illustrated in Fig. 3. Decomposition of DBS was small when photolysis was carried out in the absence of TiO$_2$ (direct photolysis) and negligible in the absence of light. With both TiO$_2$ and UV illumination present, DBS was found to be more effectively degraded than its decomposition UV irradiation alone. Experimental results show that only about 75% of DBS was decomposed after 6hr of direct photolysis while about 82% of DBS was decomposed after 4.5hr of illumination in the presence of 50ppm TiO$_2$. Because in UV/TiO$_2$ photocatalysis, as illustrated in Fig. 4, is unique among advanced oxidation processes in that simultaneous reduction and oxidation reactions can occur
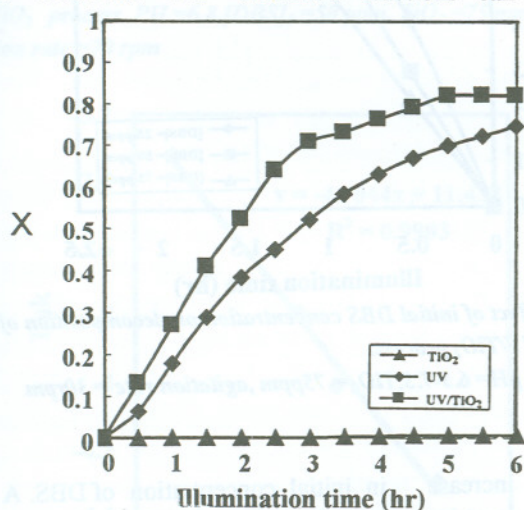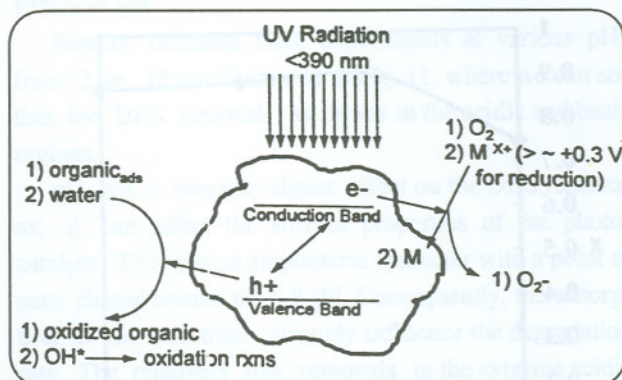


*Fig.4: Schematic of the reactions at the surface of illuminated TiO$_2$ (Madden and Datye et al., 1997).*

on TiO$_2$ particles. The band gap of anatase TiO$_2$ is 3.2 ev; therefore, excitation by UV radiation of wavelength 390nm or less produces electron(e$^-$)- hole(h$^+$) pairs. The holes at the TiO$_2$ valence band, having an oxidation potential of + 2.6V vs normal hydrogen electrode (NHE) at pH=7, can migrate to the catalyst surface and either (a) oxidize an adsorbed species directly by direct hole oxidation,(b) oxidize water or hydroxide to produce hydroxyl radicals, which then proceed to oxidize other species. The electrons migrate to the surface to take part in the reduction reactions [6].

## Effect of Agitation Rate

The percent of DBS removal increases with increasing agitation rates up to 30 rpm and thereafter remains almost constant (Fig.5). When agitation rate is smaller than 30 rpm, the process is controlled by diffusion rate of the particles to the surface. Above this rate, the system changes to kinetic control.

## Effect of TiO$_2$ Amount

Effect the amount of TiO$_2$ on the DBS removal for this reactor was studied, Figures 6 and 7. The removal increases with increasing the amount of TiO$_2$, approaching a limiting value at the loading of about 75ppm for solutions containing about 50ppm DBS. The gradual decrease in the removals at higher loadings is thought to occur due to increased turbidity (less UV penetration & lower photoactivation) even though increased suspension loadings provide more active sites. Thus the loading of photocatalyst should be a compromise between these two
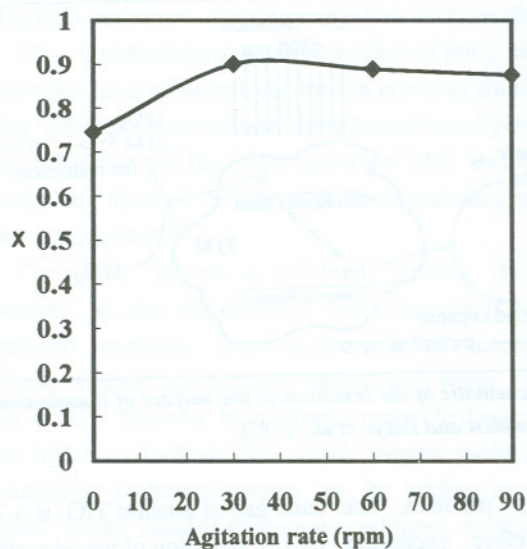


*Fig.3: Effect of UV irradiation and TiO$_2$ particles in decomposition of DBS. T=302K, pH=7,[DBS]$_0$=50ppm, TiO$_2$=50ppm, without agitation*

*Fig.5: Effect of agitation rates on decomposition of DBS in UV/TiO$_2$ process.  T=305K, pH=6.82, [DBS]$_0$=50 ppm, TiO$_2$= 50 ppm, illumination time = 4 hr*



*Fig.6: Effect of TiO$_2$ amount on decomposition of DBS. T= 305K, pH=6.5-7.5, [DBS]$_0$ = 50ppm, agitation rate = 30rpm*
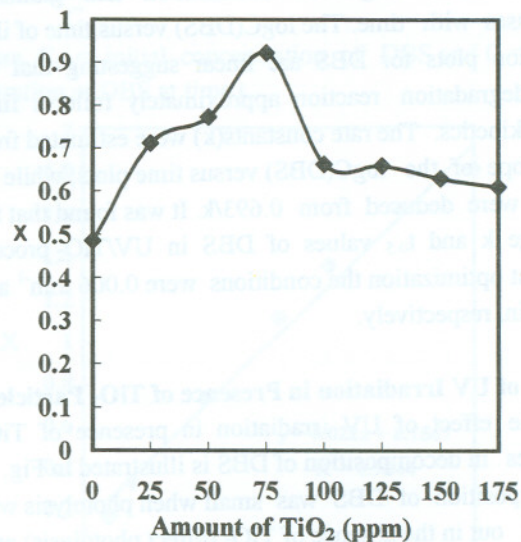
*Fig.7: Effect of TiO$_2$ amount on decomposition of DBS after 2.5hr of illumination time, refer to Fig.6 for experimental details.*
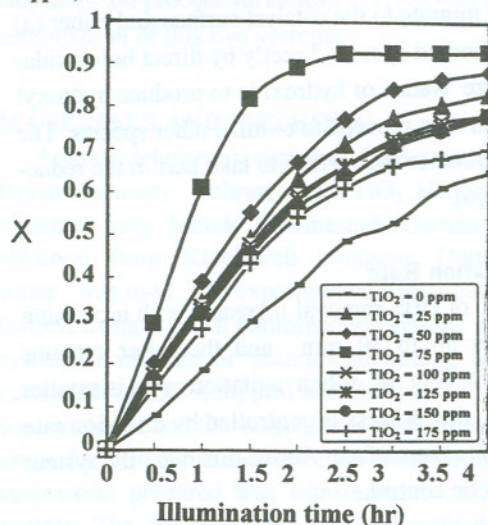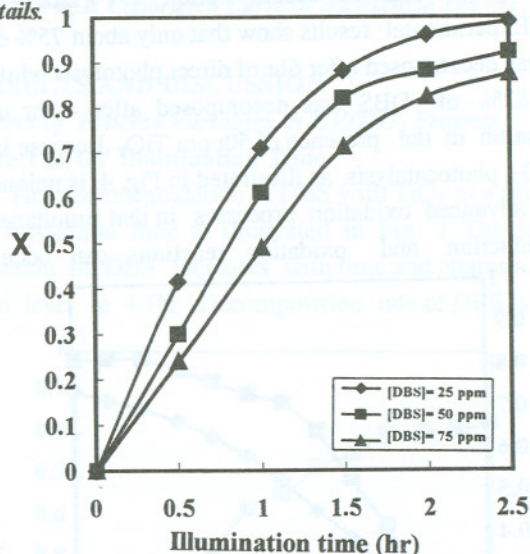


*Fig.8: Effect of initial DBS concentration on decomposition of DBS in UV/TiO$_2$ process.*
*T =305K, pH= 6.5-7.5, TiO$_2$= 75ppm , agitation rate = 30rpm*

opposing effects and depend on the initial concentration of the pollutant to be degraded [7].

### Effect of Initial DBS Concentration

Fig. 8 shows the increase of  DBS removal  as a function of time for the experiments conducted at different initial concentrations of DBS. From the plot, it can be  seen that the photodegradation of DBS decrease

with the increase    in initial concentration of DBS. A plausible explanation  of this behavior can be the follow-ing: as the initial  concentration increases, more organic substances  are adsorbed on the surface of TiO$_2$ but when the intensity of  light and illumination time are constant; the ˙OH   formed on the surface of TiO$_2$ is constant and,

the relative number of $^\bullet$OH attacking DBS decreases, and the photodegradation efficiency decreases [8].

### Effect of Temperature

Fig. 9 shows the removal percent of DBS versus time for the experiments conducted at different temperatures, where a progressive influence can clearly be observed. The apparent energy of activation obtained from the Arrhenius plot (Fig.10) is 39.1 kJmol$^{-1}$.
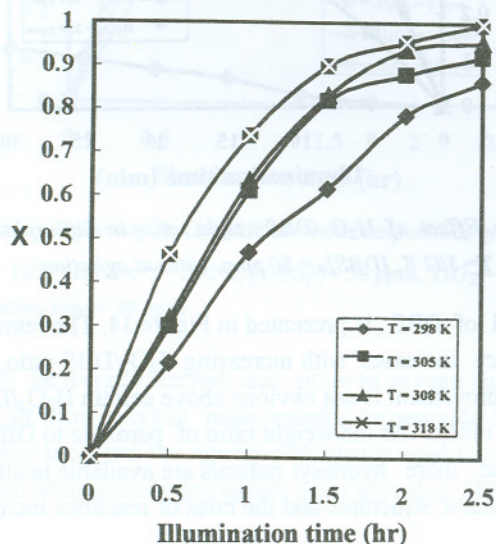
Fig.9: *Effect of temperature on decomposition of DBS in UV/ TiO$_2$ process. PH =6.8,[DBS]$_0$ =50 ppm, TiO$_2$ =75 ppm, agitation rate =30 rpm*
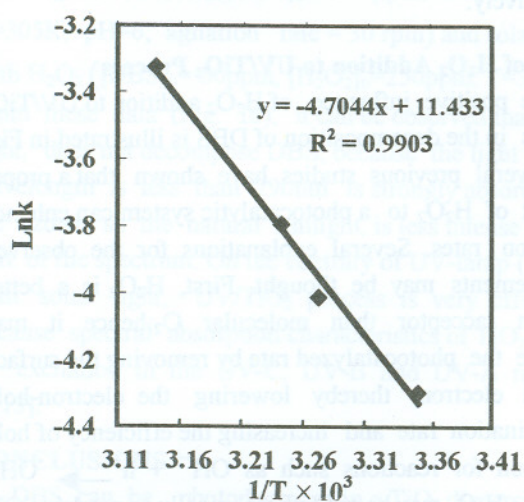
Fig.10: *Arrhenius plot for decomposition of DBS on irradiated TiO$_2$*

### Effect of pH

Results obtained from experiments at various pHs from 2 to 12 are illustrated in Fig. 11, where we can see that the DBS removal is lower in the acidic and basic regions.

pH has a stronger direct effect on the DBS removal as; it can affect the surface properties of the photo-catalyst. TiO$_2$ has an amphoteric character with a point of zero charge around pH 6.8 [9]. Consequently, the adsorption of the substrate strongly influence the degradation rate. The relatively low removals in the extreme acidic region may be attributed to the competition of ClO$_4^-$ with the substrate, H$_2$O and O$_2$ for adsorption on TiO$_2$ [10].
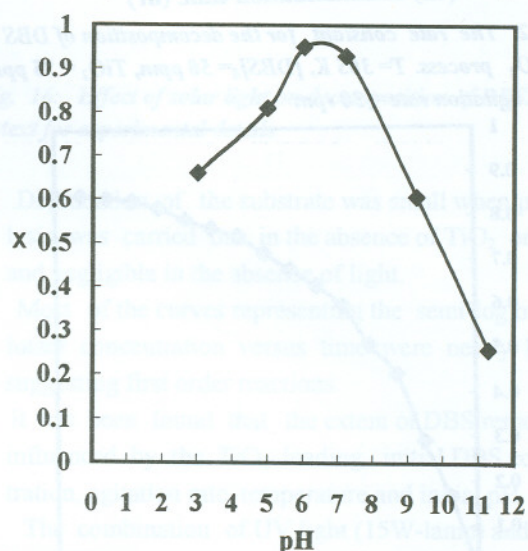
Fig. 11: *Effect of pH on decomposition of DBS in UV/TiO$_2$ process. T= 350 K, [DBS]$_0$ = 50 ppm, TiO$_2$ = 75 ppm, agitation rate = 30 rpm, illumination time = 2.5 hr*

Under the optimum conditions decomposition of DBS ( TiO$_2$ =75ppm,pH=6,T=305K and agitation rate=30 rpm) during UV/TiO$_2$ process accurs with average k and t$_{0.5}$ values in the order were 0.02 min$^{-1}$ and 33.5 min respectively, Fig. (12).

### UV/H$_2$O$_2$ Process

### Effect of Illumination Time of UV Irradiation

The photodegradation of DBS with UV/H$_2$O$_2$ process at H$_2$O$_2$/DBS weight ratio 1:1 as a function of irradiation time, is illustrated in Fig. 13. The decomposition of DBS increases with time and attains constant level in 75 min. Quantitative conversion of the substrate in a compa-
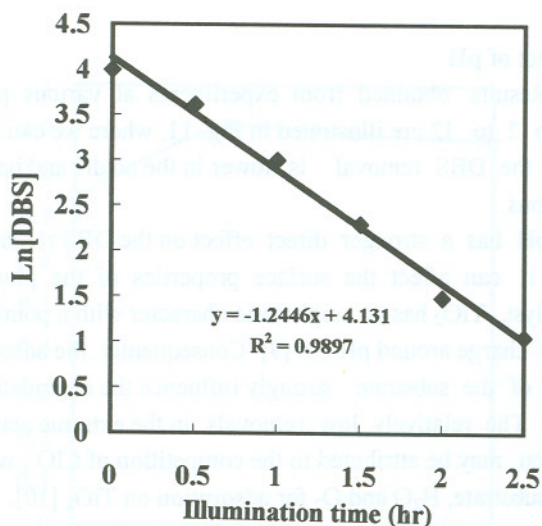
Fig. 12: The rate constant for the decomposition of DBS in UV/TiO₂ process. T= 305 K, [DBS]₀= 50 ppm, TiO₂ = 75 ppm, pH= 6, agitation rate = 30 rpm
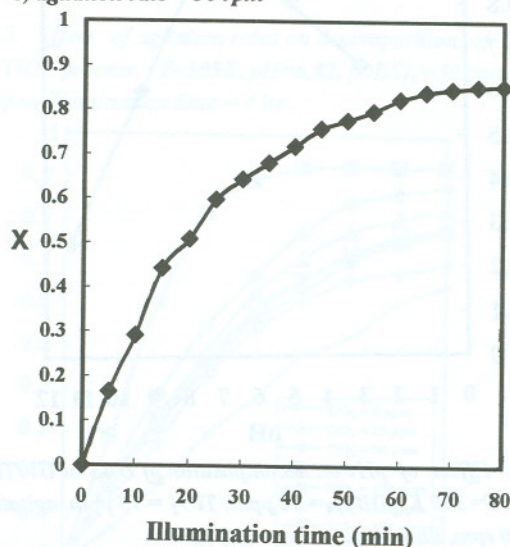


Fig. 13: Effect of illumination time in decomposition of DBS in UV/TiO₂ process. T= 302 K, [DBS]₀= 50 ppm, [H₂O₂]=50 ppm, without agitation

ratively shorter time was realized with higher concentrations of the oxidant ($H_2O_2$), mainly due to the powerful oxidative action of the hydroxyl radical which is formed from hydrogen peroxide by photolysis [11]. The combination of hydrogen peroxide and UV light is much more effective than combination of $TiO_2$ and UV light in destroying DBS.

## Effect of H₂O₂/DBS Weight Ratios

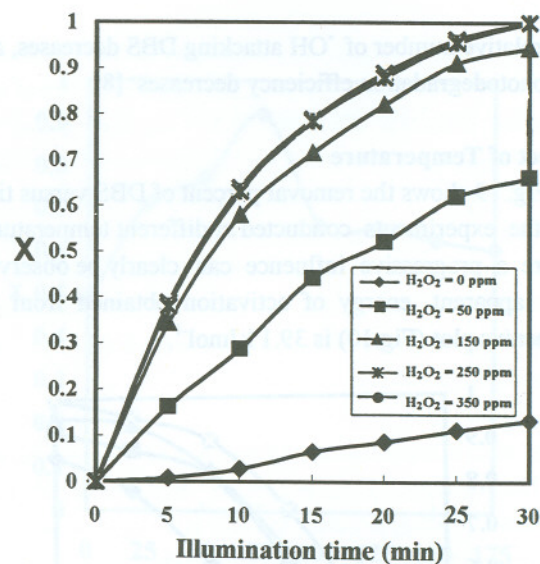The effect of hydrogen peroxide concentration on the



Fig. 14: Effect of $H_2O_2$/DBS weight ratios in decomposition of DBS. T= 302 K, [DBS]₀ = 50 ppm, without agitation

removal of DBS is presented in Figure 14. The removal efficiency increases with increasing $H_2O_2$/DBS ratio, but the improvement is not obvious above certain $H_2O_2$/DBS weight ratios. As the weight ratio of peroxide to DBS is increased, more hydroxyl radicals are available to attack the aromatic structures and the rates of reactions increase [5].

For decomposition of DBS in $H_2O_2$/DBS at a weight ratio of 5:1 by the UV/$H_2O_2$ process the average k and $t_{0.5}$ values in the order were 0.132 $min^{-1}$ and 5.2 min. respectively.

## Effect of H₂O₂ Addition to UV/TiO₂ Process

The positive influence of $H_2O_2$ addition to UV/TiO₂ process in the decomposition of DBS is illustrated in Fig. 15. Several previous studies have shown that a proper amount of $H_2O_2$ to a photocatalytic system can enhance oxidation rates. Several explanations for the observed enhancements may be thought. First, $H_2O_2$ is a better electron acceptor than molecular $O_2$; hence it may increase the photocatalyzed rate by removing the surface trapped electron, thereby lowering the electron-hole recombination rate and increasing the efficiency of hole utilization for reactions such as $OH^- + h^+ \longrightarrow {}^{\cdot}OH$. Second, $H_2O_2$ may be split photolytically to produce $^{\cdot}OH$ directly, as cited in studies of homogenous photooxidation using UV/$H_2O_2$. Third, the solution phase may at
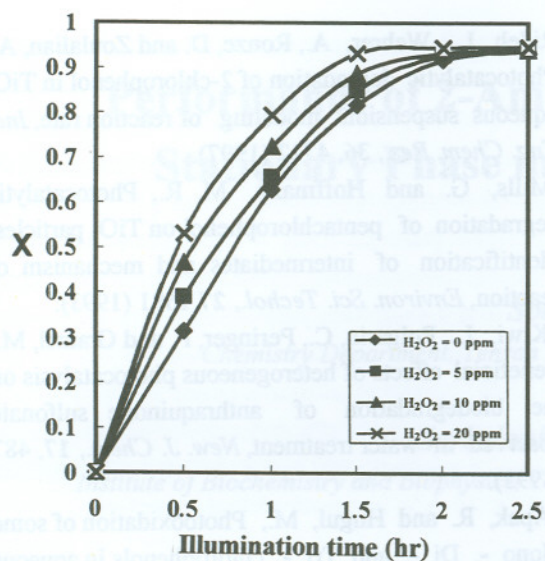
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*Fig. 15: Effect of $H_2O_2$ addition in decomposition of DBS in UV/ $TiO_2$ process. T= 302 K, $[DBS]_0$= 50 ppm, $TiO_2$= 75 ppm, agitation rate = 30 rpm*

times be oxygen starved, due either to oxygen consumption or slow oxygen mass transfer; or peroxide addition thereby increases the rate toward what it would have been had an adequate oxygen supply been provided [12].

**Effect of Solar Light**

Experiments were performed to study the decomposition of DBS only with solar light ($[DBS]_0$ = 50 ppm), solar light with $TiO_2$($[DBS]_0$ = 50ppm, $TiO_2$= 75 ppm, T=305K, pH=6, agitation rate = 30 rpm) and solar light with $H_2O_2$ ($[DBS]_0$= 50ppm, $[H_2O_2]_0$=250ppm, T=301K). From these data (Fig. 16), it can be observed that solar light, does not decompose DBS, because the light whose wavelength is less than 290nm is strongly absorbed by the ozone, so the natural sunlight, is less intense in this part of the spectrum. On the contrary of UV-lamp (15W), with solar light, UV/$TiO_2$ process is very effective, because spectral absorption characteristics of $TiO_2$ allow its excitation in the UV-C, UV-B and UV-A regions [3,13].

**CONCLUSIONS**

1. DBS can be photodegraded in a $TiO_2$ dispersion in presence of $H_2O_2$ alone or under illumination with a UV-lamp(15W) or solar exposure.
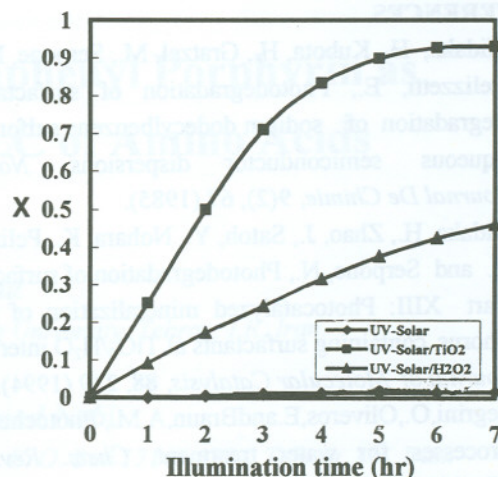


*Fig. 16: Effect of solar light on decomposition of DBS. Refer to text for experimental details*

2. Degradation of the substrate was small when photolysis was carried out in the absence of $TiO_2$ or $H_2O_2$ and negligible in the absence of light.

3. Most of the curves representing the semi-log of pollutant concentration versus time were nearly linear, suggesting first order reactions.

4. It has been found that the extent of DBS removal is influenced by the $TiO_2$ loading, initial DBS concentration, agitation rate, temperature and initial pH.

5. The combination of UV light (15W-lamp) and $H_2O_2$ was effective in destroying of DBS ,so that, the pseudo rate constant was up to 6.5 times ($H_2O_2$ / DBS weight ratio 5:1) than UV light plus $TiO_2$ (optimum condition).

6. A proper addition of $H_2O_2$ to a photocatalytic system (UV/$TiO_2$) can enhance oxidation rates.

7. The combinator UV-lamp (15W) and solar radiation in the , UV/$TiO_2$ process is the most effective.

**Acknowledgments**

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