



Photocatalytic Study of some Common Allergens and Harmful Ingredients used in Everyday Products

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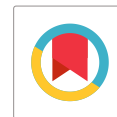
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ABSTRACT

The photocatalytic degradation of allergens such as triclosan on various semiconductor photocatalysts like TiO₂, ZnO, WO₃, Ag/TiO₂ and Pd/TiO₂ and isothiazolin-3-ones on WO₃ in aqueous suspensions under different illumination conditions has been investigated. The degradation of triclosan was monitored by TOC disappearance, carbon dioxide evolution and chloride ion formation. It is shown that TiO₂ exhibited the best photocatalytic efficiency compared to the other catalysts studied. Silver loaded TiO₂ performed better than PdO/TiO₂. The photocatalytic degradation of isothiazolin-3-ones on WO₃ was followed by UV-Vis spectrophotometry, total organic carbon (TOC), Gas chromatography (GC), and High Pressure Liquid Chromatography (HPLC) and Ion Chromatography techniques. The degradation reaction is fast under suntest and then UV lamp, when it is compared to fluorescent lamps. The reaction proceeds faster in the presence of O₂ than in other atmospheric conditions such as air, H₂O₂. The photocatalytic activity of WO₃ is compared with TiO₂ and ZnO. This study proves the viability of photocatalytic degradation of triclosan and isothiazolin-3-ones in an aqueous medium.

Keywords: Allergens; Heterogeneous photocatalysis; Isothiazolin-3-ones; Photodegradation; Titanium dioxide; Tungsten Oxide; Zinc oxide.

1. INTRODUCTION

Semiconductor photocatalysis is a promising technique for environmental cleaning. It can be carried out in various media: gas phase, pure organic liquid phases or aqueous solutions. The most effective functional materials used are nano-sized semiconductor oxides, which found applications in cancer therapy, degradation of pollutants, photothermal catalysis organic synthesis and solar cells (Pastore *et al.* and Ge *et al.*).

Triclosan [5-chloro-2-(2,4-dichlorophenoxy) phenol], is a chlorophenol, suspected of causing cancer in humans. This is one among a broad-spectrum of antibacterial agents, which has been widely used for the last 30 years in soaps, cosmetics, deodorants and other dermatological preparations. Triclosan is also suitable for incorporation into polymers and fibers to give them antibacterial properties. Due to these applications, triclosan reaches wastewater treatment plants and surface waters. Triclosan in several respects is similar to some of the most toxic chemicals, such as dioxin and PCB. The U. S. Environmental Protection agency has registered it as a pesticide, harmful to both man and environment. Triclosan is a relatively stable lipophilic compound and its environmental occurrence has been reported and detected in wastewater, surface water and sediments

(Tixier *et al.* 2002). In a survey for organic wastewater contaminants, triclosan was listed as one of the most frequently detected pollutants and was found in 57.6% of the 139 tested US streams and rivers, suggesting that the contamination is widespread (Kolpin *et al.* 2002). While investigating the occurrence of lipophilic pesticides in Swiss lakes, a team of scientists unexpectedly detected a methylated form of the disinfectant triclosan (Lindstrom *et al.* 2002). It has been found in surface waters with concentrations in the range of about 5-90 ng L⁻¹. Of further concern is the transformation of triclosan into chlorodioxins upon incineration and the influence of UV and sunlight (Latch *et al.* 2003).

Isothiazolin-3-ones are used in household and industrial products such as, metal working fluids, slimicides in cooling tower, paper mills, cutting oils, jet heating fuels and most significantly in cosmetics and toiletries. It is also employed as preservatives for increasing the shelf life of paints. It creates allergic contact dermatitis (Jerschow *et al.* 2001) on some people when it is exposed even at very low concentration. The decomposition of isothiazolin-3-ones is now becoming a significant challenge to environmental chemists, since: (1) its biodegradation is usually very slow requiring several days or weeks; (2) the continued increase in the production and consumption of these products; and (3) the increased consumer resistance against this chemical,

because of the allergic reactions it can cause in humans, when exposed to freshly painted interiors. In spite of all the advantages, employing a strong biocidal agents like triclosan and isothiazolin-3-ones for everyday use is of questionable value in view of its ill effects.

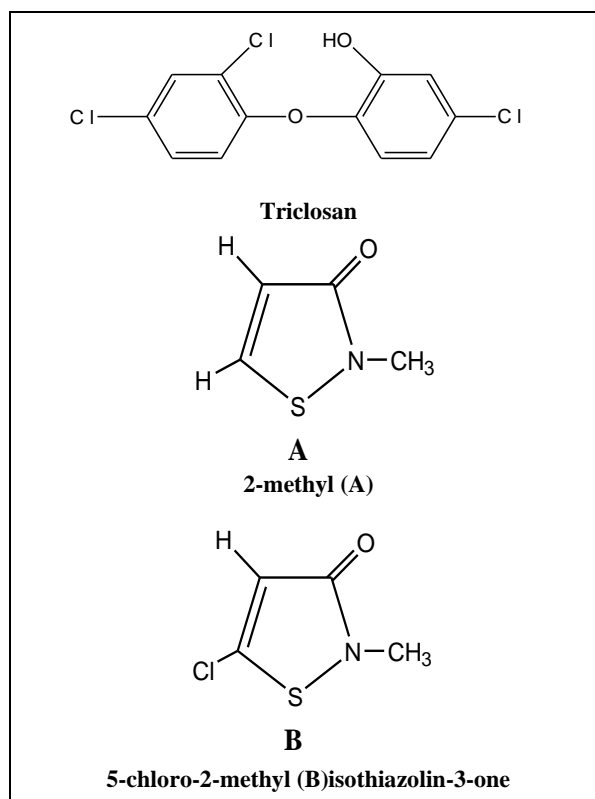
The photocatalytic degradation of toxic organic has been proposed as a viable decontamination process for wastewater and drinking water. The UV activation of a finely divided semiconductor, usually titanium dioxide, in intimate contact with an aqueous solution of pollutants, develops a redox environment capable of oxidizing them into non-toxic substances such as carbon dioxide and water. Basically, the process is initiated by the photogeneration of hole/electron pairs in the semiconductor valence and conduction bands, respectively, upon absorption of UV light with energy equal to or higher than the corresponding band gap (> 3.1 eV for TiO_2 and ZnO , for example). Energized electrons and holes may either recombine, dissipating energy, or be available for redox reactions with electron donor or acceptor species adsorbed on the semiconductor surface. Based on this principle, the degradation of many model compounds has been studied and it has been clearly shown that many organic pollutants present in water can be fully or partially decomposed. Halogenated hydrocarbons, aromatic hydrocarbons, *N*-containing heterocyclics, hydrogensulfide, surfactants and herbicides are among them. Due to the potentially important human health and environmental implications of triclosan and isothiazolin-3-ones, we are reporting the results on its photocatalytic degradation possibilities.

2. EXPERIMENTAL

2.1 Catalysts and Chemicals

Titanium dioxide P25 (80% anatase and 20% rutile, specific surface area $50 \text{ m}^2/\text{g}$) was purchased from Degussa, Germany. ZnO and WO_3 (Merck) were also used as photocatalysts. Triclosan, $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ and AgNO_3 was used as purchased from Aldrich. All the other chemicals were purchased from Fluka. Water used for the preparation of solutions and buffers was purified by Milli-Q system controlled by its resistivity ($\geq 18 \text{ M}\Omega \text{ cm}$).

Isothiazolin-3-ones, commonly known as Kathon has been used in our study, which contains an aqueous solution of 2-methyl-isothiazolin-3-one (MI) and 5-chloro-2-methyl-isothiazolin-3-one (CMI) (1:3 ratio) along with magnesium chloride and magnesium nitrate as stabilizers. It should also be noted that it is this mixture that is widely used in most practical applications, including paints.



Structure of triclosan and isothiazolin-3-one

2.2 Preparation of Metal Loaded Photocatalysts

Loading of palladium oxide on TiO_2 has been carried out by a hydrolysis deposition technique. The required amount of $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ is dissolved in 100 ml HCl (0.1 M). The oxide is added to the solution after raising the solution temperature to 70°C . Under constant stirring at this temperature, the pH of the solution is slowly raised to 10.6 by adding drop-wise 0.1 M NaOH solution over a period of 5-6 h. The suspension is allowed to evaporate to dryness. The resulting powder is heated to 170°C for 18 h, followed by heating at 370°C for another 18 h.

To prepare the Ag-titania samples, 500 mg of TiO_2 is suspended along with 0.1 M glucose and 0.01 M AgNO_3 in 100 ml of water. The dispersion is purged with argon for 20 min before turning on the lamp. After the irradiation, the suspension is centrifuged. The solid is washed and dried in an oven at 150°C .

2.3 Photocatalytic Experiments

All the photocatalysis experiments have been carried out using 20 ml of 1.35×10^{-4} M triclosan along with 50 mg of the catalyst and for isothiazolin-3-ones, 30

ml of 8.75×10^{-4} M isothiazolin-3-ones was used as a suspension along with 100 mg of the catalyst (3.33 g l^{-1}), in a pyrex or a quartz reaction vessel and irradiated using different lamps. The suspension was magnetically stirred during the photolysis. Three millilitres of the homogenized dispersion aliquots were taken at regular intervals, starting from zero time and centrifuged in dark for 20 min using a Biofuge pico superspeed centrifuge at 12,000 rotations per minute.

For simulating different illumination conditions, several types of light sources, such as UV (3.0 mWcm^{-2} ; five 18W Osram lamps; with a spectral range between 340 and 410 nm, where the maximum emission is at 365 nm), suntest (a lamp having a spectrum similar to that of sunlight; 50 mWcm^{-2} total intensity, where the UV is approximately 5%) and fluorescent (2.4 mWcm^{-2} ; white, five 18W lamps; F18W/33 GE model) lamps have been used.

During photocatalytic reaction, the temperature of the dispersions was maintained at 35°C .

2.4 Analyses

UV-Vis spectrophotometric analyses of the solutions have been carried out with a Hewlett-Packard 8452 diode array spectrophotometer. The Total Organic Carbon (TOC) measurements have been performed using a Shimadzu TOC analyzer, model 5000A. This instrument is equipped with an ASI automatic sample injector and it uses potassium phthalate solution as a calibration standard. The evolution of CO_2 from the irradiated samples is monitored by a HRGC 5300 Carlo Erba chromatograph, equipped with a Porapak Q column and Thermal conductivity detector (TCD) in helium carrier gas. For the analysis of ions, a Dionex DX-100 ion chromatograph equipped with an IonPac AS144 column has been used. An aqueous solution of NaHCO_3 (1.0×10^{-3} M) and Na_2CO_3 (3.5×10^{-3} M) served as the eluent at a flow rate of 1 ml/min.

During the photocatalytic experiments, the depletion of triclosan was followed by HPLC on a Varian 9065 system equipped with a Varian 9012Q solvent delivery system, an automatic injector (model 9300) and a Varian Pro Star variable (200-400 nm) diode array detector model 330. All the modules are piloted with the Varian Star 5.5 software for liquid chromatography, using a reverse phase column (Omnispher C18- 5μ , 250 mm, Macherey-Nagel, Switzerland) at room temperature. A mobile phase consisting of acetonitrile-TEA phosphate (70 mM, pH 3.5) 55:45 (v/v) has been used, at a flow rate of 0.4 ml/min. A UV detector set at 230nm performed the detection. For the analyses of isothiazolin-3-ones, a symmetry C8®, $5\mu\text{m}$ column was employed. An eluent containing 12:88 acetonitrile: *o*-phosphoric acid (0.01% in water) mixture was used at a

flow rate of 1 ml min^{-1} . The wavelength of the detector was set at 276 nm.

3. RESULTS & DISCUSSION

3.1 Photocatalytic Degradation of Triclosan

3.1.1 Direct Phototransformation

The photolysis experiments were carried out at natural pH. The UV-visible absorbance peak at 281 nm corresponding to triclosan disappeared within a few minutes of irradiation, indicating the transformation of triclosan to 2,8-dichlorodibenzo-*p*-dioxin (2,8-DCDD) as reported earlier (Latch *et al.* 2003). It is also confirmed by HPLC analysis. The presence of triclosan peak was observed with a retention time of 8 min, with the monitoring wavelength of 230 nm. This peak disappeared after a few minutes of irradiation.

3.1.2 Adsorption

Influence of adsorption on the photocatalyst was studied before irradiating the substrates. With different catalyst it behaves differently, as shown in fig. 1 and 2. An adsorption of 5% triclosan is observed in about 20 minutes on TiO_2 and ZnO where as with the other three catalysts, namely WO_3 , Pd/ TiO_2 and Ag/ TiO_2 , the adsorption was around 4 % during this duration.

3.1.3 Activity of Triclosan on Semiconductor Photocatalysts

TOC elimination curves of the triclosan on various catalysts and lamps are shown in fig. 1 and 2. The results suggest that the TOC disappearance is reasonably fast.

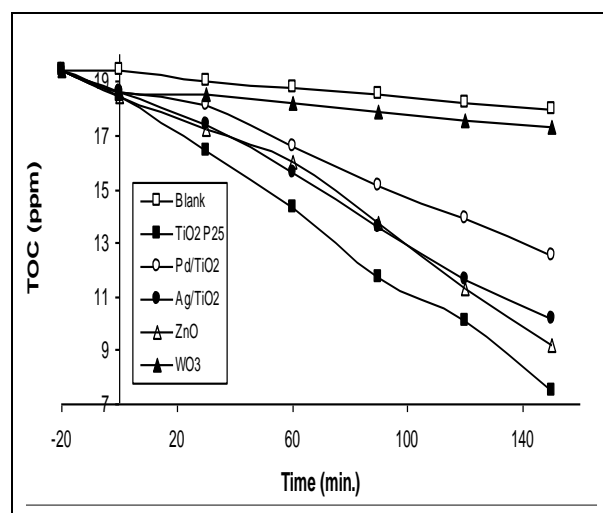


Fig. 1: The change in total organic carbon (TOC) during the photocatalytic degradation of triclosan under UV lamp illumination in air atmosphere [reaction conditions: 50 mg catalyst + 1.35×10^{-4} M triclosan in 20 mL; UV lamp (3 mW cm^{-2})].

Fig 1. shows the TOC decrease as a function of time under UV lamp irradiation with TiO₂, ZnO, WO₃, Pd and Ag loaded TiO₂ catalysts. A dispersion kept in dark for several hours demonstrated that the triclosan gets adsorbed onto titania and ZnO very quickly, within 20 minutes. A blank experiment in the absence of catalyst, but under light, showed no significant degradation of triclosan. As seen from the figure, it appears that the degradation is much faster on TiO₂ compared to the other catalysts.

The results obtained with Suntest lamp, as shown in fig. 2, appear very similar to that of the UV lamp, confirming again the triclosan degradation.

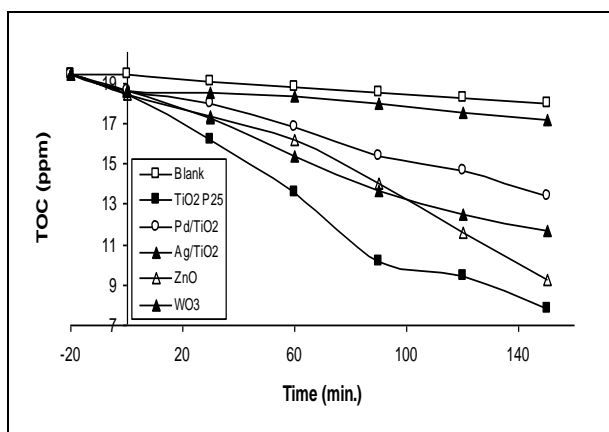


Fig. 2: The change in total organic carbon (TOC) during the photocatalytic degradation of triclosan under suntest illumination in air atmosphere [reaction conditions: 50 mg catalyst + 1.35 x 10⁻⁴ M triclosan in 20 mL, suntest (50 mW cm⁻²)].

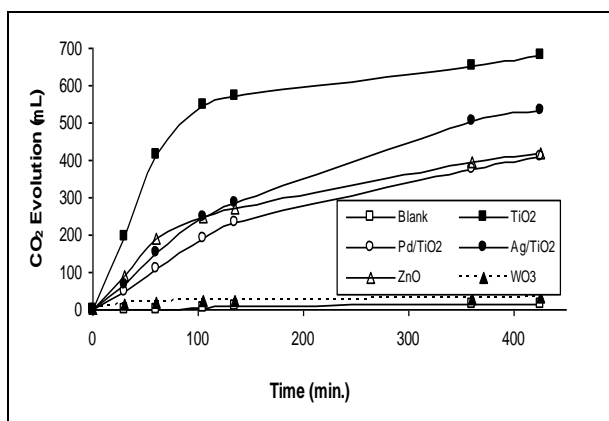


Fig. 3: The evolution of CO₂ (measured in gas phase) during photodegradation of triclosan with the UV lamp in air atmosphere

Fig. 3 and 4 show the amounts of carbon dioxide evolved during the experiment, when different catalysts and lamps were used. As seen from the figures it appears that the evolution rate was more for TiO₂ under both the UV lamp and the Suntest lamp. On ZnO, CO₂ may react to form ZnCO₃. With other catalysts the chemisorption

of CO₂ may be playing an increased role. It was also observed that Ag loaded TiO₂ has shown a better activity than palladium for both the lamps used. Actually it was observed that the Ag loaded TiO₂ catalyst slightly darkens during the irradiation.

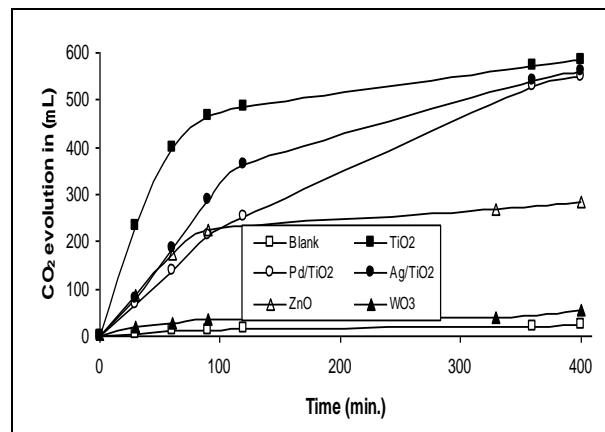


Fig. 4: The evolution of CO₂ (measured in gas phase) during photodegradation of triclosan with the suntest in air atmosphere

3.1.4 Intermediate Product

The formation of phenolic compounds has been identified using HPLC. Phenol and chlorophenol are likely to be formed from the parent compound, during the degradation reaction. The chloride ion evolution data (fig. 5 and 6) suggests the identity of some of the intermediates, which are likely to be formed during the degradation of triclosan. Several other intermediates were also observed as small peaks in HPLC, some of which are thought to be organic acids (acetic acid and formic acid, for example). The formation of these acids is common in the photocatalytic degradation of organic contaminants (Tanaka *et al.* 2000). However, since formic acid is more photocatalytically degradable than acetic acid, a selective formation of formic acid could speed up the triclosan degradation.

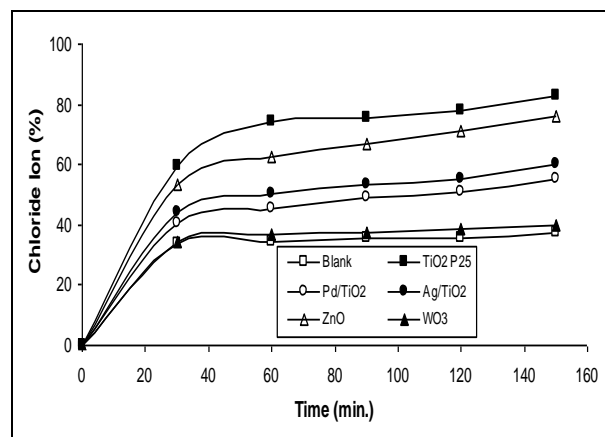


Fig. 5: The chloride ions produced (%) during the degradation of triclosan with the UV lamp in air atmosphere

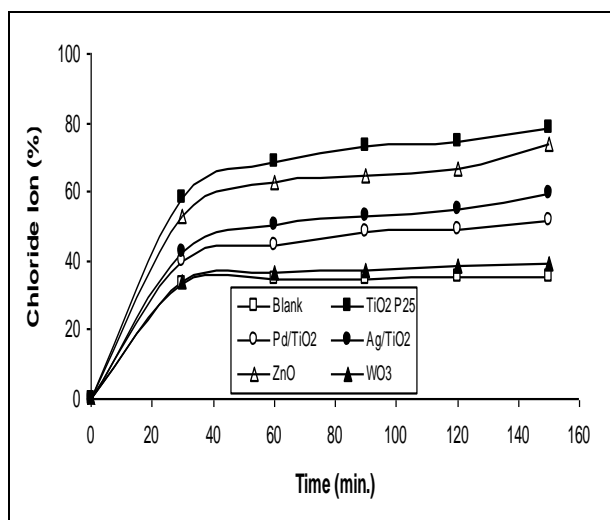


Fig. 6: The chloride ions produced (%) during the degradation of triclosan with the suntest in air atmosphere

3.2 Photocatalytic Degradation of Isothiazolin-3-ones

3.2.1 Activity of Isothiazolin-3-ones on WO_3 Photocatalysts

The photocatalytic degradation of isothiazolin-3-ones was carried out using 100 mg of the WO_3 catalyst in 30 ml solution at their natural pH. The contribution of non-photocatalytic reaction was checked and was found to be absent under our experimental conditions, indicates the responsibility of catalytic sites of WO_3 for the photocatalytic process.

The slowly biodegradable isothiazolin-3-ones were photo-irradiated in the presence of WO_3 in water. The changes in the absorbance of isothiazolin-3-ones as a function of irradiation time are followed by changes in the characteristic absorption peak (274 nm), which indicated the photooxidation of the compound. The natural logarithm of the normalized concentration versus irradiation time showed a good linearity, thus the disappearance of isothiazolin-3-ones in the presence of irradiated semiconductor follows a pseudo-first-order-kinetics.

To understand the role of peroxides and oxygen, the photodegradation reaction was studied under various conditions such as air atmosphere, oxygen, $\text{H}_2\text{O}_2/\text{oxygen}$, $\text{H}_2\text{O}_2/\text{air}$ and different light sources have also been used. The rate for all various reaction conditions is tabulated in table 1. The rate of the degradation increases when we move from air to oxygen atmosphere, indicating the necessity of oxygen for continued and complete destruction. By the added H_2O_2 there was no change in the degradation, may be the catalyst ability to produce H_2O_2 in situ. The degradation is faster in suntest

compared to UV lamp and fluorescent lamps since it emits more energy corresponding to WO_3 absorption maximum.

Table 1. Rates of isothiazolin-3-one degradation reaction in the presence of catalytic WO_3 under various illumination conditions

Lamp	Wt (mg)	Air	O_2	$\text{H}_2\text{O}_2/\text{O}_2$	$\text{H}_2\text{O}_2/\text{Air}$
Rate (X 10^8 M s^{-1})					
Suntest	100	0.66	0.86	0.81	0.62
Fluorescent Lamp	100	0.31	0.40	0.42	0.28
UV Lamp	100	0.63	0.71	0.70	0.58

Lamp Intensity : Suntest (50 mW cm^{-2}), UV lamp (3 mW cm^{-2}), fluorescent lamp (2.4 mW cm^{-2}).

To find out the level of mineralization, the number of carbons remaining in the reaction medium at different time intervals was monitored using TOC analysis. With suspension containing 100 mg of WO_3 , the TOC decreases from 41 to 6 and 8 mg l^{-1} in 140 hours under suntest and UV lamps respectively, whereas under fluorescent lamp it is only up to 39 mg l^{-1} (fig. 7). The opening of the ring in the isothiazolin-3-ones and subsequent splitting to small fragments are responsible for the decrease in TOC. It is, therefore, evident that the suntest is most efficient when the lamp intensities are considered.

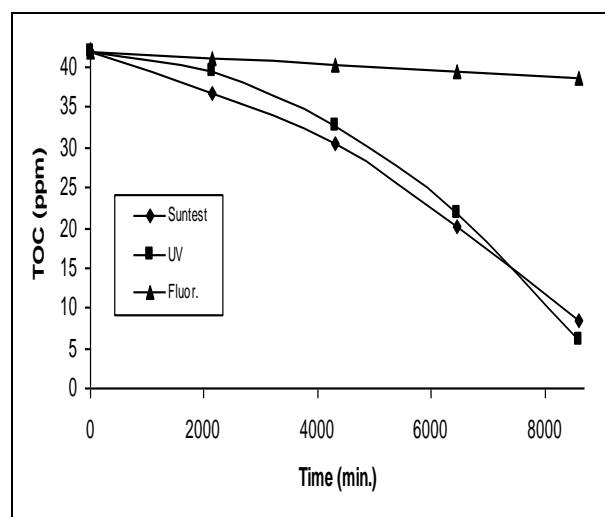


Fig. 7: The change in Total Organic Carbon (TOC) in air atmosphere for WO_3 catalyst reaction under various lamp conditions [reaction conditions: 100 mg catalyst + $8.75 \times 10^{-4} \text{ M}$ isothiazolin-3-ones in 30 mL; suntest (50 mW cm^{-2}), UV lamp (3 mW cm^{-2}), fluorescent lamp (2.4 mW cm^{-2})]

The extent of decomposition of isothiazolin-3-ones was followed by measuring the CO₂ evolution due to the mineralization of the compound. The amount of CO₂ measured as a function of irradiation time for WO₃ assisted reaction for various lamps is shown in fig. 8. Under suntest and UV lamp 2500 μL of CO₂ evolved in 125 hours but it is only less than 500 μL in fluorescent lamp. It was observed that the CO₂ evolution follows first order kinetics in the initial stages followed by a saturation behaviour in the later stages. Such a type of biphasic kinetics was reported in earlier studies. The CO₂ evolution is higher under suntest illumination, compared to other lamps showing the suitability of lamp in bringing the total mineralization.

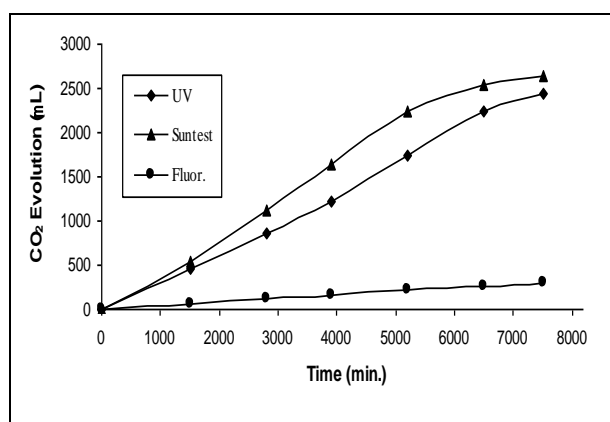


Fig. 8: The evolution of CO₂ (measured in gas phase) during photodegradation of isothiazolin-3-ones for WO₃ reaction in air atmosphere under various lamp conditions

The ionic products formed during the decomposition of isothiazolin-3-ones were analyzed by ion chromatography. Fig. 9 shows the ionic products produced during the WO₃ catalyzed reaction under UV lamp. The formed sulfate and chloride ions during the 120 hr of reaction were determined as 80% and 70 % respectively. For nitrate ions, the measured amounts added up to only 30 %. This variation may be due to the formation of ammonium ions.

HPLC analysis is also useful to follow the course of the reaction. Isothiazolin-3-ones show two peaks correspond to MI and CMI with a retention time of 4.64 and 14.64 min. respectively. The change in the percentage decomposition of two isothiazolin-3-ones, when WO₃ has been used as a catalyst under different lamp conditions is shown in fig. 10. The rates of degradation of MI and CMI are almost equal in all the reactions. It took 200 hr for 80% decomposition under fluorescent lamp, whereas it took only 55-65 hr for UV and suntest lamps.

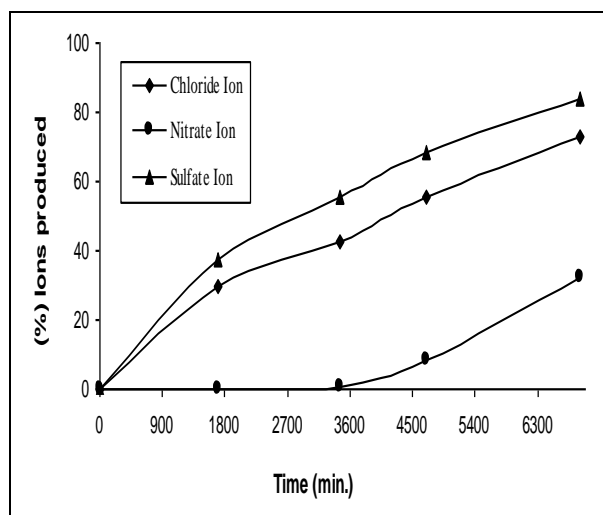


Fig. 9: The anions produced (%) during the photodegradation of isothiazolin-3-ones for WO₃ catalyst reaction using UV lamp in air atmosphere

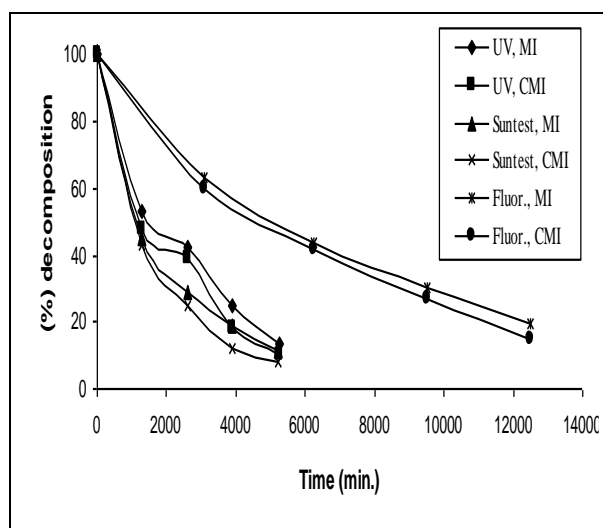


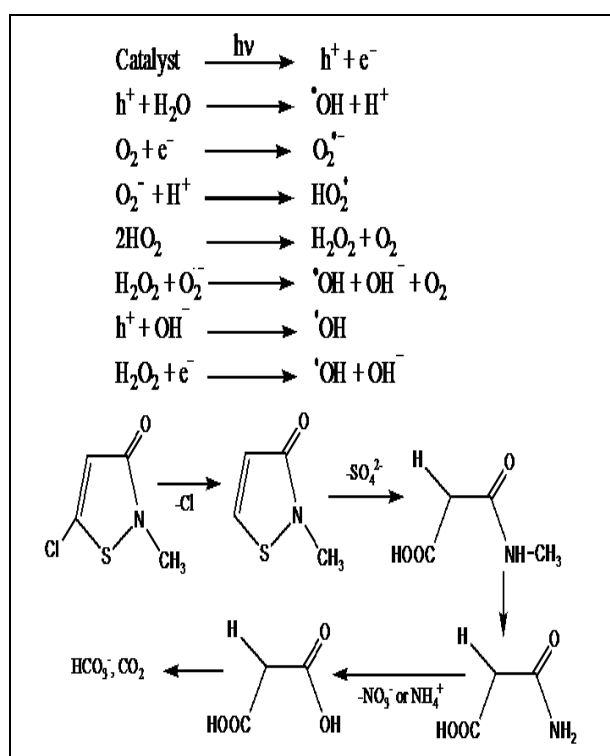
Fig. 10: The % decomposition of 5-chloro-2-methyl- and 2-methyl isothiazolin-3-one, obtained from HPLC profile, for WO₃ catalyst reaction in air atmosphere under various lamp conditions

3.2.2 Mechanism

The photogenerated e⁻ (electrons) and h⁺ (holes) from the photoexcited catalyst induces a series of reactions in the system. It is very well established that in the presence of dissolved O₂, electrons from the photoexcited TiO₂, ZnO and WO₃ produce O₂⁻. This subsequently generates H₂O₂ and OH• radicals (Kormann *et al.* 1988). The H₂O₂ and OH•, produced as a result of these different photoreactions, further facilitate the decomposition and eventually the total mineralization of organic substances such as isothiazolin-3-ones.

SCHEME 1

The degradation of isothiazolin-3-ones proceeds via removal of chloride ion from CMI and ring opening through the nitrogen–sulphur bond. Since S–N bond is an ambiphilic reaction center (Crow *et al.* 1969), electrophilic attack at nitrogen and nucleophilic attack at sulfur are possible. Subsequent hydrolysis and oxidation leads to the formation of amine products, which slowly gets oxidized to CO₂, along with the formation of SO₄²⁻, NO₃⁻ and Cl⁻ ions.



4. CONCLUSIONS

The photocatalytic degradation of triclosan has been proved experimentally over semiconductor photocatalysts. The photocatalytic degradation rate is faster with TiO₂ compared to other semiconductors such as ZnO and WO₃. Among the supported metal photocatalysts, silver showed a better effect than PdO on TiO₂. The UV and the suntest lamps have shown more or less similar results for the photocatalytic degradation of triclosan.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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