

Effect of surfactant on TiO₂/UV mediated heterogeneous photocatalytic degradation of DDT in contaminated water

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ABSTRACT

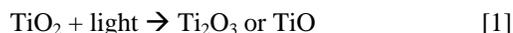
In the present study we describe the TiO₂/UV mediated heterogeneous photocatalytic treatment of 4,4-Dichloro-Diphenyl-1,1,1-Trichloroethane (DDT) contaminated water and the effect of surfactant (Surfox) on this process. A novel photocatalytic system is designed, made by TiO₂ coated tubular glass in a photoreactor with UV light illumination. The photo catalytic degradation was observed to be very fast and the treatment time was reduced to 40 min which is much faster compared to the biodegradation of the pollutants. After this study we conclude that the best result for the degradation is found to be at 200ml/min air flow, CMC (critical micelle concentration) and above CMC of the surfactant. The surfactant concentration does not inhibit the generation of free radicals involved in pesticides photocatalytic degradation.

Key words: TiO₂, photocatalysis, DDT, Surfactant

1. INTRODUCTION

Photocatalysis is a photocatalytic reaction simultaneously involving oxidation from photogenerated holes and reduction from photogenerated electrons on a semiconductor surface.^[1] From 1970 photocatalytic oxidation has been studied as a method to degrade toxic substances. Since 1980 it has been explored as an effective method for treatment of toxic and polluted water.^[2] Recently heterogeneous photocatalytic oxidation is becoming popular due to its fast degradation time. Various metal oxides have been explored as photocatalysts but the catalyst that has got a great deal of attention from scientist is titanium dioxide (TiO₂) due to its various applications such as self cleaning, self sterilizing and anti fogging surfaces. The coatings are extensively used for water and air purification due to its environmental friendly surface treatment.^[3] Titania is partially reduced during illumination with sunlight in the presence of an organic compound.

For TiO₂, the reaction proposed was:



Different supports systems have been designed for the immobilization of titanium dioxide (TiO₂), Some of the studies have reported its immobilization on activated carbon for photo degradation of organic pollutant^[4,5] Some papers have reported the immobilization on different substrates like glass, quartz and stainless steel.^[6]

Semiconductor when illuminated by photons of energy higher or equal to the band gap of the semiconductor, photo electrons and photoholes are created. Several factors that govern the kinetics of the photo catalysis are: the mass of catalyst, the wavelength, the initial concentration of the reactant, the radiant flux, and the temperature.^[7] The toxic effects from the use of pesticides are of great concern to the environment. The pesticides containers are not treated according to the Mexican normativity and hence increase the pollutant levels in the environment. 4, 4-Dichloro-Diphenyl-1, 1, 1-Trichloroethane (DDT) is an organochloride pesticide that is of moderate mammalian toxicity which is cumulative in nature. DDT mainly affects the central, peripheral nervous systems, and the liver. Nausea, diarrhoea, increased liver enzyme activity, irritation of the eyes, nose and throat are other mild effects of its exposure.^[8]

The use of surfactants increases the pesticides removal from the containers that can be degraded through remediation by photocatalysis. By various studies we know that surface acting agents are organic compounds that are amphiphilic in nature which reduces the interfacial tension between oil and water by absorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates forming vesicles and micelles.

In the present study we describe the TiO₂/UV mediated heterogeneous photocatalytic treatment of DDT contaminated water and the effect of surfactant (Surfox) on the process.

1. EXPERIMENTAL DETAILS

2.1 Reagents

All the reagents (Ethanol, acetone and DI water) used were of analytical grade and the solvents of HPLC grade. The TiO₂ powder Degussa P25 was used for the coating of the substrate. Methanol and dichloromethane was provided by Bardick and Jackson of HPLC grade. Hexane was provided by Honeywell of HPLC grade.

2.2 TiO₂ nanoparticle coating

TiO₂ nanoparticle coating was done on the glass substrate. Sonic cleaning was done for the substrate by immersing it in distilled water, ethanol, acetone, and deionized water for 20 min respectively. The tubular glass substrate was dried in air and kept safely away from the environment. The glass substrate was coated by sonicating the substrate in a suspension of TiO₂ in methanol (5% w/v). The TiO₂ films were dried in air. The coated samples were annealed at 450°C for 1 hr in air to achieve cohesion and adhesion of the particles to the substrate. The cycle was repeated to get a homogenous film on the substrate.

2.3 Photocatalytic treatment

A novel photocatalytic system (Fig 1) was designed, having TiO₂ coated tubular glass in the photoreactor with UV light.

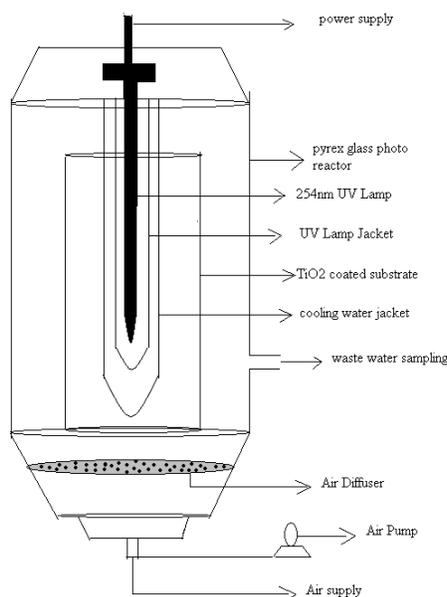


Figure 1. Photocatalytic reactor designed for the treatment of DDT contaminated water.

A light source for UV illumination at 254 nm was placed to illuminate the TiO₂ coated glass substrate. A double cylindrical jacket of quartz was made around the UV lamp to maintain the temperature of the system at 25°C. Prior to every treatment, the system was bubbled with air in closed chamber to establish an adsorption/desorption equilibrium.

We proposed an experimental design to check the effects of surfactant concentration and airflows. The conditions that were analyzed are shown in Table 1. We established different controls to check the effects of UV, surfactant and TiO₂ coating.

Table 1. Conditions for photocatalytic treatments of contaminated water.

Treatment	Airflow [ml/min]	Surfactant concentration [mg/L]
1	200	0.01
2	200	0.05
3	300	0.01
4	300	0.05
Controls		
5	UV + DDT + TiO ₂ coated substrate	
6	UV + DDT + Surfactant	
7	UV + DDT	
8	UV + Surfactant	

2.4 Characterization methods

2.4.1 Scanning electron microscopy

The TiO₂ coating made on glass substrate was scanned with JEOL JSM – 740IF Field emission scanning electron microscopy.

2.4.2 Lucigenin assay for superoxide

The accumulation of superoxide in treated water was measured by lucigenin-dependent chemiluminescence. The assay was done in a total volume of 1 ml by placing 0.1 ml of sample and 0.1 ml of lucigenin in 0.8 ml of Gly-NaOH buffer (pH 9.0) containing 1 mm EDTA and 1 mm sodium salicylate. The chemiluminescence was detected by luminometer, which detects real-time luminosity. [9]

2.4.3 Gas chromatography

The pesticide degraded water was analyzed by VARIAN CP-3380 gas chromatograph equipped with split less electron capture detector. The injector port temperature was at 200°C and nitrogen which served as the carrier gas with a flow rate of 1.5ml/min. Chromatographic separation was accomplished with capillary column CD Sil. 5CB (Varian, 15m x 0.25mm x

0.25mm film thickness). The temperature program used was 80°C for 1 min with an increase rate of 20°C/min reaching the final temperature of 200°C for 8min. The detector temperature was set at 300°C. A PC interfaced to the Gas Chromatograph using Galaxie Workstation was used for data acquisition and processing. The samples that were obtained were extracted by dichloromethane and 1µl of sample was injected in hexane.

3. RESULT AND DISCUSSION

The TiO₂ coating which was done on the glass substrate were analysed by SEM and the thin films were observed at 5.0kV, X100,000 and WD 3.0mm which was found to be homogenous with a size less than 50nm. (Fig. 2)

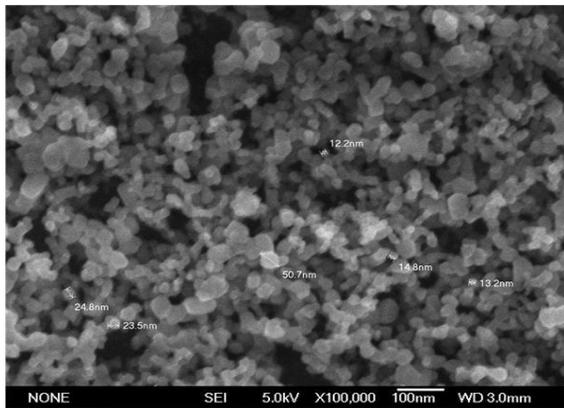


Figure 2. SEM image for the TiO₂ coated glass substrate.

Photocatalysis lead to the oxidation and degradation of the DDT contaminated water. The use of air bubbles helps to maintain the dissolved oxygen concentration at the surface of the photocatalyst particles, potentially increasing the overall activity. [12]

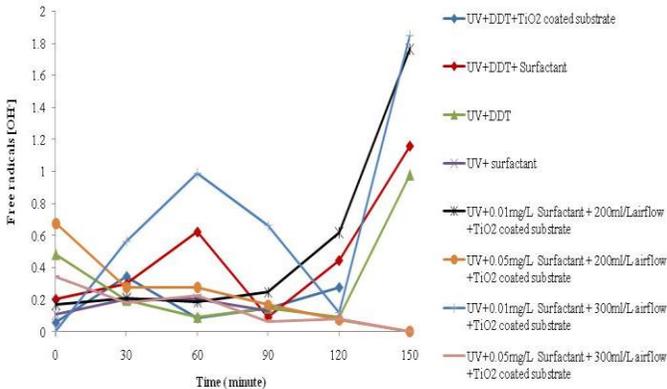


Figure 3. Free radicals in the photocatalytic treatments.

The TiO₂/UV condition leads to the oxidation of organic compounds by free radicals and direct oxidation by holes generated on the surface of the photocatalyst. [12] which was observed in the control (UV + DDT + TiO₂ coated substrate) that had a higher generation of free radicals.

The presence of surfactant does not inhibit the generation of free radicals (Fig.3) whereas the concentration of the surfactant showed a statistical significant effect (P<0.05) in the formation of reactive species, which showed higher generation at low level of surfactant.

The photocatalytic degradation of DDT was confirmed by gas chromatography, since 1,1-dichloro2,2-bis(p-chlorophenyl) ethylene (DDE) a metabolite of DDT degradation was detected in a very short time of treatment. The results showed a positive effect of surfactant in DDT degradation.

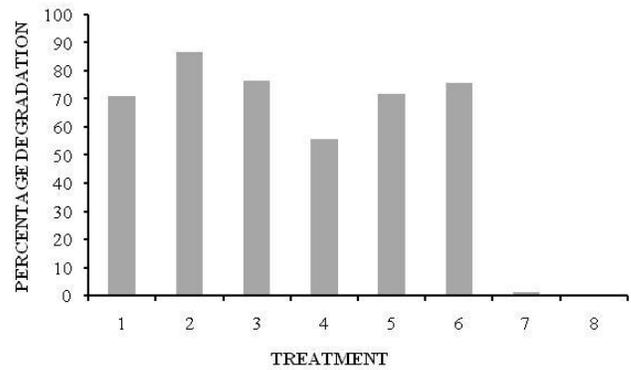


Figure 4. Degradation percentage of total DDT in treatments

In all the conditions with different airflows and surfactant concentrations we observed a degradation of more than 50% (Treatment 1 to 4). On comparing all the percentage degradation for different conditions we found that there was no degradation in seventh treatment having just UV and DDT whereas the fifth treatment with UV, DDT and the TiO₂ coated substrate showed a degradation of 71.67% which suggest that the degradation of DDT is due to the photo redox reactions taking place in the system, however, the degradation rate in this treatment was slower.

Solubilization is a micellar phenomenon, which depends on the CMC of the surfactant .The solubility is very low at concentration below CMC of the surfactant but rises once the CMC has been reached, so this phenomenon is an important factor in solubilizing the toxic agents. [11]

The highest total percentage degradation observed was 86.67% at 0.05mg/L surfactant concentration and 200mL/min, with 44.04% degradation of DDE. (Fig.5)

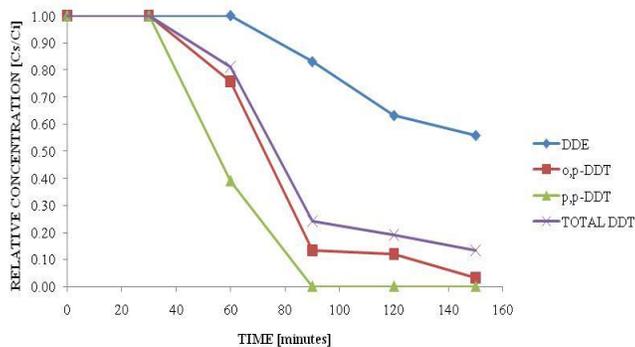


Figure 5. Photodegradation kinetics for DDT above CMC (0.05mg/L) of surfactant.

At surfactant CMC (0.01mg/L) we found the degradation to be 71.14% with no DDE degradation. (Fig. 6)

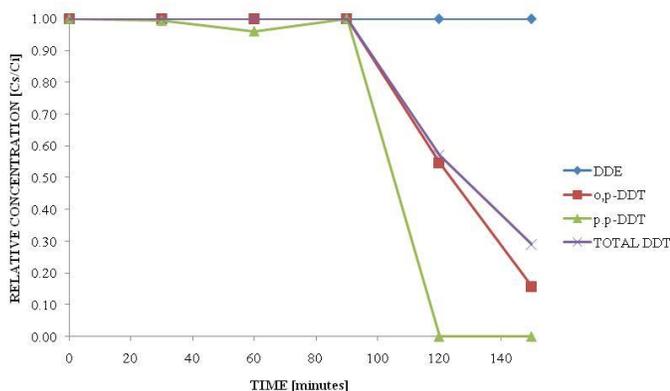


Figure 6. Photodegradation kinetics for DDT at CMC (0.01mg/L) of surfactant.

This can explain the higher degradation in the treatment having surfactant above CMC, which normally water-insoluble substances like DDT shows. Specifically, in this study the surfactant used generates unstable residues which when reacts with organic compounds, degrades to water and oxygen.

4. CONCLUSIONS

After this study we conclude that the best result for the degradation was found to be at 200ml/min air flow and the concentration of surfactant influences the degradation of DDT. The best concentration which can be used for the photocatalysis is at CMC and above the CMC. This surfactant concentration does not inhibit the generation of free radicals involved in pesticides photocatalytic degradation and the degradation time is reduced to 40 minutes for o,p-DDT, p,p-DDT, and to 60 minutes for DDE.

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