# Photocatalytic Degradation of Tributyltin Chloride in Water

Mohammad Reza Reisi*†, Lo Kong Mun and Misni Misran
*Department of Chemistry, Faculty of Science, University of Malaya,*
*Kuala Lumpur-50603, Malaysia*
*E-mail: chemreza2002@yahoo.com*

In this work, photodegradation of tributyltin chloride in water by UV with or without any catalyst, also with different types of $TiO_2$ and with modified catalyst was investigated. The rate equation and rate constant was determined and compared.

**Key Words: Photocatalytic degradation, Tributyltin chloride.**

## INTRODUCTION

The growth of aquatic organisms on vessel hulls creates roughness which gives rise to reduced vessel speed per unit energy consumption. A 10 (μm) increase of the average vessel hull can cause an increase in fuel consumption of about 0.3-1 %. Tributyltin (TBT) based antifouling paints began to use in the early 1970 s[1].

Tributyltins contaminate marine environment and cause problems for marine environment, marine animals and eventually human. Tributyltin pollution in aquatic systems will result in various symptoms on organisms, like thickening of shell and failure of spots in oysters, imposex of *neogastropods* and *gastropods*, reduction of dog whelk population and the retardation of growth in mussels. Imposex was seen in some of the marine animals that are polluted by tributyltin. The dog whelk (*Nucella lapillas*) was often seen at the North Sea coast in Belgium but some years after using tributyltin as antifouling agent, this kind of animals disappeared. This is because of imposex and extinction of females[2-5].

Organotin compounds especially tributyltin compounds are one of the most serious pollutants of sea water There are different approaches to overcome this problem. Many methods were developed for remediation of water from tributyltin chloride. One of the approaches is the degradation of pollution by light.

The average bond energy for Sn-C is about 200 kJ/mol and UV radiation with a wavelength of 290 nm provides energy about 300 kJ/mol. Therefore, by irradiation the organotin compound with UV radiation with suitable wavelength, the Sn-C bond can be cleaved resulting in the formation of di-, mono and inorganic tin compo-unds. However, due to the low range of UV in solar light, using artificial light (UV) with or without catalyst unavoidable. The degradation of tributyltin chloride is gener-ally followed the reaction mechanism where the tributyltin chloride (TBT) will be converted

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† Present Address: Department of Chemistry, University of Isfahan, Isfahan 81746-73441, Iran.

into dibutyltin chloride (DBT) then to monobutyltin chloride (MBT) and finally to inorganic tin species, the loss of an organic groups is accompanied by decreasing toxicity. Hence the more toxic tributyltin chloride is able to degrade into the much less toxic inorganic tin species. This will result in a decrease in the tributyltin chloride pollutant in the environment[6,7].

## EXPERIMENTAL

The chemicals such as tributyltin chloride, hexane, ethyl magnesium bromide, tetrapropyltin, tropolone, Degussa P-25, anatase, rutile and polyoxometallate, $H_3[PMo_{12}O_{40}]X.H_2O$ were commercial chemicals and were used without any purification  Medium pressure mercury lamp (125 W, SAIC India) with emission at UV region 365, 313, 303, 297 and 265 nm was used for photo-reaction. Chromatograms were recorded by using a GC-14A, Shimadzu Gas chromatograph equipped with flame ionization detector and a SGE HT-5 capillary column. For preparation and spiking of the samples in water, a JAC 1505 sonicator (JEIO Tech Korea) was used.

**Photocatalytic procedure:** The tributyltin chloride stock solution was prepared in methanol. Aqueous solution of tributyltin chloride was prepared by spiking an appropriate amount of stock solution in water, followed by sonication and then irradiated by UV radiation for several hours. After that it was extracted by hexane solution containing 0.05 % w/v tropolone and treated with ethyl magnesium bromide under nitrogen atmosphere. The excess Grignard reagent was removed and the resulting mixture was extracted with *n*-hexane. A known amount of tetrapropyltin was added as an internal standard and then the sample was injected into the GC coupled with a FID. The same analytical condition was used for the photodegradation of tributyltin chloride with different types of $TiO_2$ (1 g/L) and also $TiO_2$ mixed with polyoxometallate (0.25 g/L).

The photocatalytic degradation of tributyltin chloride are monitored by gas chromatographic analysis of the product at an interval of 1 h.

## RESULTS AND DISCUSSION

The ratio of the areas under the peaks for tributyltin chloride and internal standard can be calculated and is proportional to the concentration of tributyltin chloride $[C]/[C_o]$ Tables 1 and 2. By plotting $Ln[C]/[C_o]$ *versus* time, a linear relationship (Figs. 1 and 3) is observed. Navio *et al.*[7] had shown that the order for rate of degradation reaction is TBT < DBT << MBT and indicated that first step of degradation is rate determinate step. Thus, by measuring the concentration of tributyltin chloride, the rate equation and rate constant can determined.

Since the rate determining step of photocatalytic degradation of tributyltin chloride is the conversion of tributyltin chloride to dibutyltin dichloride, thus the rate of this step can be measured and report as the rate of reaction, indicating the photodegradation of tributyltin chloride is a first order reaction that follows the modified Langmuir-Hinshelwood equation which is usually adopted by the heterogonous catalyst system[8,9].

TABLE-1
RELATIVE AREA RATIO OF TRYBUTYLTIN CHLORIDE TO INTERNAL
STANDARD WITH DIFFERENT IRRADIATION TIME

| Time (h) | UV | UV + TiO$_2$P$_{25}$ | UV + TiO$_2$ + POM |
|---|---|---|---|
| 0 | 6.9 | 6.9 | 6.9 |
| 2 | – | – | 4.8 |
| 4 | 6.2 | 5.3 | 3.4 |
| 6 | – | – | 2.4 |
| 8 | 5.6 | 4.1 | 1.7 |
| 10 | 5.4 | 3.6 | 1.2 |
| 16 | 4.9 | 2.4 | 0.4 |
| 20 | 4.2 | 1.9 | 0.23 |
| 30 | 3.2 | 1.0 | – |
| 40 | 2.5 | 0.5 | – |
| Rate constant (K) h$^{-1}$ | $2.5 \times 10^{-2}$ | $6.5 \times 10^{-2}$ | $18 \times 10^{-2}$ |

POM = Polyoxometallate.

TABLE-2
RELATIVE AREA RATIO OF TRYBUTYLTIN CHLORIDE TO INTERNAL
STANDARD WITH UV IRRADIATION TIME FOR DIFFERENT KINDS OF TiO$_2$

| Time (h) | UV + TiO$_2$ rutile | UV + P$_{25}$TiO$_2$ | UV + TiO$_2$ anatase |
|---|---|---|---|
| 0 | 6.9 | 6.9 | 6.9 |
| 2 | 5.75 | – | 4.8 |
| 4 | 4.79 | 5.3 | 3.4 |
| 6 | 3.99 | – | 2.4 |
| 8 | 3.33 | 4.1 | 1.7 |
| 10 | 2.77 | 3.6 | 1.2 |
| 16 | 1.60 | 2.4 | 0.4 |
| 20 | 1.12 | 1.9 | 0.23 |
| 30 | 0.45 | 1.0 | – |
| 40 | 0.18 | 0.5 | – |
| Rate constant (K) (h)$^{-1}$ | $9.1 \times 10^{-2}$ | $6.5 \times 10^{-2}$ | $18 \times 10^{-2}$ |
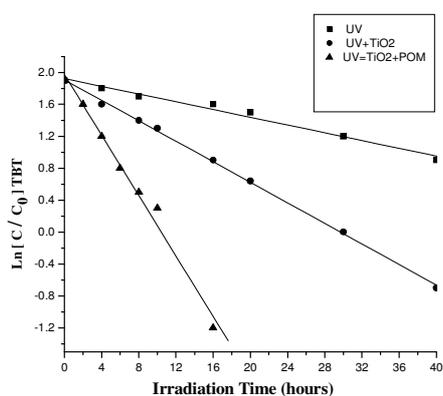


Fig. 1.  Kinetic plot of TBT photodegradation
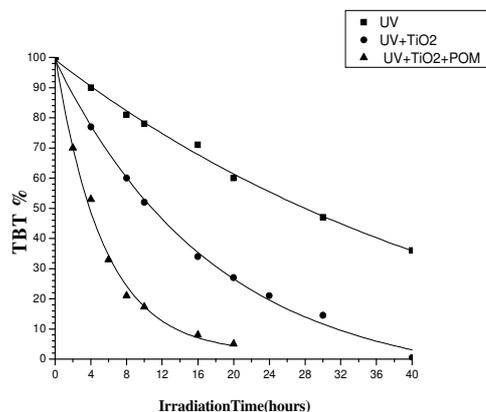


Fig. 2.  Variation of concentration of TBT with different irradiation times
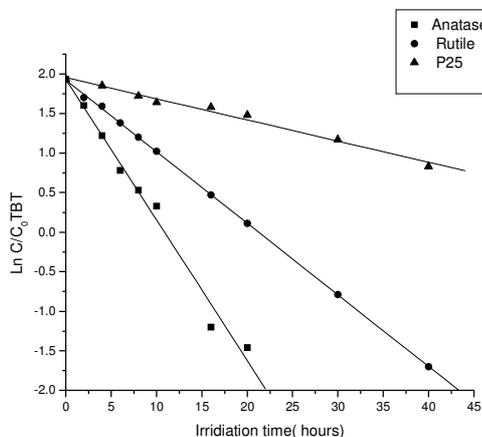
Fig. 3.  Kinetic plot of TBT photodegradation by UV with different types of $TiO_2$
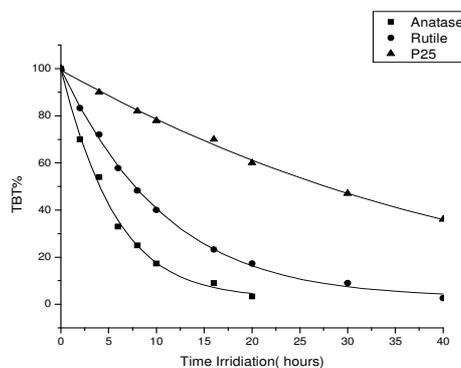
Fig. 4. Variation of TBT concentration with UV irradiations time for different types of $TiO_2$

By dividing the relative area ratio of tributyltin chloride at different intervals to relative area ratio of tributyltin chloride at t = 0 (6.9), the percentage of TBT was calculated. The amount of tributyltin chloride remains after UV irradiation is given in Figs. 2 and 4.

The results showed that in the presence of photosensitized catalyst ($TiO_2$ with POM); the time taken for 95 % of tributyltin chloride to be degraded was 20 h. On the other hand, it takes 40 h for degradation the same percentage of tributyltin chloride if $TiO_2$ was used. In the absence of any $TiO_2$ or catalyst, only 65 % of tributyltin chloride will be degraded after 40 h.

When titanium dioxide ($TiO_2$) absorbs ultraviolet radiation, it will produce pairs of electrons ($e^-$) and holes ($h^+$) due to the excitation of the valence electron of the titanium dioxide by light.

$$TiO_2 + h\nu \rightarrow h^+(VB) + e^-(CB)$$
$$POM + e^- \rightarrow POM^-$$
$$H_2O + h^+ \rightarrow OH^o + H^+$$
$$O_2 + e^- \rightarrow O_2^{o-}$$
$$O_2^{o-} + H^+ \rightarrow HO_2^o$$
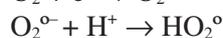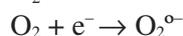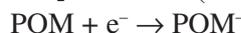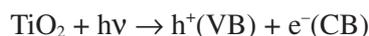
$OH^o$ radicals (hydroxyl) and $HO_2^o$ (hydroperoxide radical) have major impact on pollutant oxidation and degradation as shown below.

$$\text{Organic pollutant} + OH^o \text{ or } HO_2^o \rightarrow CO_2 + H_2O$$

If there is no scavenger, electron and hole recombine and no benefit for photodegradation but in presence of any scavenger such as polyoxometallate (POM), the reaction would proceed and the rate of reaction would increase. The reduced form of polyoxometallate is blue in color and should be easily monitored by visible spectra. Polyoxometallate has been reported and used in some green applications and decontamination of water[10,11].

By comparison of rate constants derived from the three experiments, it was found that the rate of the reaction with UV + $TiO_2$ + polyoxometallate increases seven times relative to rate of reaction using only UV (Table-1). This is probably due to the presence of polyoxometallate, which acts as a scavenger of electrons and prevents the recombination of hole ($h^+$) and electron ($e^-$). The polyoxometallate was reversibly reduced by accepting electron.

Present data showed photocatalaytic activity of anatase > rutile > $P_{25}$ Degussa (Table-2). In general, it is believed that anatase has greater photocatalytic activity than rutile, one can reason that since the anatase phase has a higher Fermi level than the rutile phase by about 0.1 eV, the anatase phase will have lower capacity to absorb oxygen and higher degree of hydroxylation, thus higher number of hydroxyl group on the surface and should have greater photocatalytic activity than the rutile phase. Another substantial difference is that the anatase phase has a wider optical absorbtion gap and may have smaller electron effective mass and hence higher mobility. It has also been reported that the anatase has an indirect band gap whereas rutile has a direct band gap, the indirect band gap will causes further decrease in the recombination of e-h pair. If mobility of $e^-$ and $h^+$ are different the recombination will also decrease[12].

In order to find reproducible results, the use standard $TiO_2$ such as $P_{25}$ Degussa is unavoidable. By using of size quantized semiconductor for increasing photo-efficiencies had been supported by several studies[13].

Degussa $P_{25}$ contain 80 % anatase and 20 % rutile has a remarkable photocatalytic activity than pure anatase. A most important factor is probably the anatase-rutile interface in these two catalysts. The enhanced activity in Degussa $P_{25}$ has been attributed to the efficient electron transfer from rutile to anatase which increase the charge separation and decreasing recombination of electron and hole that is needed for efficient photocatalytic reactions at the particle surfaces.

The common order of photocatalytic activity for $TiO_2$ is $P_{25}$ > anatase > rutile but some exceptions were reported[14]. All parameters such as particle size, surface area, phase, morphology and synergetic effect of mixed phases affect on photo-chemical activity. Present results showed photocatalytic activity of anatas > rutile > $P_{25}$ for photodegradation of tributyltin chloride. This order is similar to the order of decreasing surface area of these catalysts that were reported by suppliers companies.

| $TiO_2$ | Particle size (nm) | Surface area ($m^2$ $g^{-1}$) | Density (g $cm^{-1}$) |
|---|---|---|---|
| $P_{25}$ | 20 | 50 | – |
| Anatase | < 25 | 200-220 | 3.90 |
| Rutile | $10 \times 40$ Diam $\times$ L | 130-190 | 4.17 |

## Conclusion

$TiO_2$ as photocatalyst increases the rate of photodegradation of tributyltin chloride by 2.5 times. Polyoxometallate modifies photocatalytic activity. The rate of the photodegradation with mixed $TiO_2$ and polyoxometallate increases the rate of reaction

seven times relative to rate of reaction when only UV is used and the surface area is a more important factor than structure for photodegradation of tributyltin chloride by $TiO_2$.

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