

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/341264997>

# Application of Nanopillars–TiO<sub>2</sub> Thin Films in the Photocatalytic Degradation of Methyl Parathion from Aqueous Solution

Article · January 2018

CITATIONS

0

READS

87

3 authors, including:



**Chhakchhuak Lalhriatpuia**  
Pachhunga University College

14 PUBLICATIONS 268 CITATIONS

[SEE PROFILE](#)



**K. Vanlaldinpuia**  
Pachhunga University College

21 PUBLICATIONS 197 CITATIONS

[SEE PROFILE](#)

# Application of Nanopillars-TiO<sub>2</sub> Thin Films in the Photocatalytic Degradation of Methyl Parathion from Aqueous Solution

C. Lalhriatpuia<sup>1\*</sup>, Thanhmingliana<sup>1</sup>, K. Vanlaldinpuia<sup>1</sup>

<sup>1</sup>Department of Chemistry, Pachhunga University College, Aizawl-796001, Mizoram, India.

Correspondence Author: Email: [clhpuia@gmail.com](mailto:clhpuia@gmail.com)

## Abstract

The photocatalytic activity of Nanopillars-TiO<sub>2</sub> thin films S1 (without PEG) and S2 (with PEG) was assessed in the degradation of Methyl Parathion (MPT) from aqueous solution under batch reactor operations. The thin films were characterized by the XRD, SEM, AFM and BET analytical methods. Results showed that pH 6.0 was an optimum pH for the photocatalytic degradation of MPT using the UV light and lower initial pollutant concentration greatly favoured the MPT degradation using the thin films. The time dependence photocatalytic degradation of MPT was demonstrated with the pseudo-first-order rate kinetics. Overall degradation efficacy was in the order: S2 > S1 > UV. Study was further extended with total organic carbon measurement using the TOC (Total Organic Carbon) analysis. This demonstrated an apparent mineralization of MPT from aqueous solutions.

**Key words:** Methyl Parathion, Nanopillars-TiO<sub>2</sub>, Thin films, Photocatalyst, Kinetics

## INTRODUCTION

The contamination of aquatic environment by pesticides residues and their metabolites posed a serious concern due to their strong recalcitrant, high persistency and ecotoxicity [1]. Parathion and other pesticides are reported to be Endocrine disrupting Chemicals (EDCs) which alters the functioning of endocrine system, hence, caused adverse health effect [2]. Methyl parathion (MPT) (O, O- dimethyl O- 4-nitrophenyl phosphorothioate) is one of the most common organophosphorus pesticides and insecticides. It has neurotoxicological properties which inhibit the activity of acetylcholinesterase (AChE) in the nervous systems of both humans and insects [3]. Various methods were employed in the remediation of such contaminated water however; they show different issues related to the subsequent environmental concerns or high input cost of the treatment process. [4]. Advanced oxidation process (AOP) based on heterogeneous TiO<sub>2</sub> photocatalysis is found to be one of efficient and environment friendly treatment process for various wastewater treatment strategies. The photo-generated electron-hole pairs (e<sup>-</sup>/h<sup>+</sup>) enables the oxidation and reduction of pollutant adsorbed onto the surface of TiO<sub>2</sub>. The e<sup>-</sup> and h<sup>+</sup> leads to the formation of radical species viz., hydroxyl radical (•OH) and peroxide radical (O<sub>2</sub><sup>•-</sup>). The redox potential of •OH radical is relatively very high (E<sup>o</sup> = 2.80 V) which enables efficient oxidation of even stable organic compounds/species from aqueous solutions [5]. It was demonstrated that the use of TiO<sub>2</sub> nanoparticles or nanocomposites greatly hindered the

separation of catalyst once operation is completed and hence, the further use of catalyst is restricted in successive operations. Moreover, the reactivity of photo-catalyst is greatly hampered with the shadowing effect of the particles. Therefore, the present study intent to immobilized thin films of TiO<sub>2</sub> particles on a glass substrate using the sol-gel template method and further it was employed in the photocatalytic degradation of Methyl Parathion (MPT) from aqueous solutions.

## MATERIALS AND METHODS

### Chemical and materials

The chemicals used for the experiments were of AR/GR grade. Stock solution of MPT (25.0 mg/L) was prepared in purified water. Further, the required experimental concentration was obtained by the successive dilution of stock solution. The UV-Visible Spectrophotometer (Thermo Fisher Scientific, Model: Evolution 201) was used for quantitative determination by measuring the change in concentration at a fixed wavelength of 277 nm. The TOC Analyzer (Shimadzu, Japan; Model: TOC-VCPH/CPN) was fully employed to obtain the total organic carbon content data for the study of mineralization of the organic compounds.

### Methodology

#### Preparation of nano TiO<sub>2</sub> thin films

Nanopillars-TiO<sub>2</sub> thin films were obtained on borosilicate glass disk with and without PEG as template using sol-gel dip coating method. The detailed preparation process was described elsewhere [6-7] and also described briefly here. Two types of nano-TiO<sub>2</sub> (T1 and T2) sol solutions were obtained using the sol-gel synthetic route. T1 was prepared by dissolving titanium isopropoxide (TISP) as precursor in acetyl-acetone (AcAc). Ethanol (EtOH), acetic acid (AcOH) and distilled water (H<sub>2</sub>O) were added drop by drop to this solution to start hydrolysis and condensation reactions. The solution was stirred vigorously for 2 h and then it was sonicated for 30 min. The obtained sol was aged for 1 day prior to use it for the thin film preparation or immobilization. The molar ratios of these chemicals: TISP: AcAc: EtOH: AcOH: H<sub>2</sub>O was taken as 1: 1.3:40:0.9:12.5, respectively. A similar process was used to prepare titania (T2) but added with 2.0 g of Poly(ethylene glycol) (PEG) (average molecular weight 8000) maintaining the previous molar ratios of precursors.

A previously cleaned and dried borosilicate circular glass disk (2.3 cm diameter and 0.5 mm thickness) was dipped in to the transparent orange colour T1 and T2 sol solutions, separately and were kept it (in vertical position) for 1 h. It was then removed slowly and kept in air at room temperature for 12 h. A very thin film of TiO<sub>2</sub> formed on the substrates and was dried first at 100 °C for 1 h and subsequently annealed at 500 °C for 3 h in an electric furnace (Nabertherm; Model No. LT/15/12/P330, Germany). The dipping process was repeated for three times for both solutions in order to obtain a homogeneous thin film. The nanopillars- TiO<sub>2</sub> thin films obtained, S1 (TiO<sub>2</sub> film without PEG) and S2 (TiO<sub>2</sub> film with PEG) were stored in a closed and dry container under dark condition.

### Characterization of thin films

Surface morphology of thin films was observed by scanning electron microscope (Model FE-SEM SU-70, Hitachi, Japan). Atomic Force Microscopy (AFM) measurements were carried in the non-contact mode, using XE-100 apparatus from Park Systems (2011) having sharp tips (>8 nm tip radius; PPP-NCHR type from NanosensorsTM). The topographical 3D AFM images were taken over the area of 10×10µm<sup>2</sup>. X-ray diffraction (XRD) data was collected by X-ray diffraction machine i.e., PANalytical, Netherland (Model X'Pert PRO MPD) and the diffraction data was recorded at the scan rate of 0.034 of 2θ illumination and at an applied voltage of 45 kV with a measured current 35 mA. The Cu K<sub>α</sub> radiation was employed having wavelength of 1.5418 Å. The BET specific area was obtained using the Protech Korea BET surface area Analyzer (Model ASAP 2020).

### Photocatalytic degradation studies

Photocatalytic degradation of MPT was carried out under batch reactor experimentation. The detailed reactor set up was described elsewhere [7]. The pollutant concentration was analysed with a UV-Vis spectrophotometer at certain time interval up to 2 h. Initially, blank experiments were performed under UV irradiation without TiO<sub>2</sub> photocatalyst for comparison.

## RESULTS AND DISCUSSION

### Characterization of thin films

XRD data collected for the S1 and S2 samples were shown in the Fig. 1 or elsewhere [7]. The characteristics peaks obtained for the samples S1 and S2 at 2θ values of 25.39, 37.84, 48.14, 53.44 and 54.59 of 25.39, 37.84, 48.14, 53.44 and 54.59 were assigned to the TiO<sub>2</sub> anatase phase [7]. The average particle size of the TiO<sub>2</sub> using Debye–Scherrer equation [6] for S1 and S2 catalysts were found to be 25.4 and 21.9 nm, respectively. This further reiterated that the S1 and S2 comprised with Nanosized, possibly the Nanopillars- TiO<sub>2</sub>, are evenly distributed on the substrate surface.

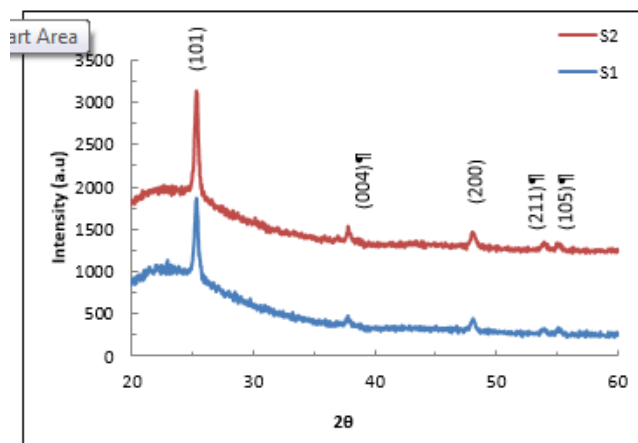


Figure 1. X-ray diffraction pattern for the S1 and S2 thin films [7].

The SEM images of S1 and S2 were shown in Fig. 2 and also presented previously [7]. It was observed that the S1 catalyst contained Nanosized pillars of TiO<sub>2</sub> which were very evenly distributed and forming a thin film onto the substrate surface with an average size of less than 15 nm. However, the S2 sample was more disordered and possessed with several cracks on the surface. The particles of TiO<sub>2</sub> were also, at places, aggregated.

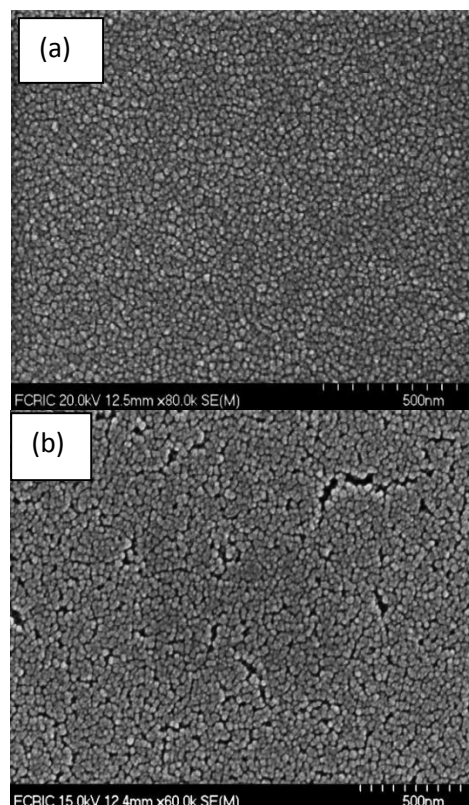
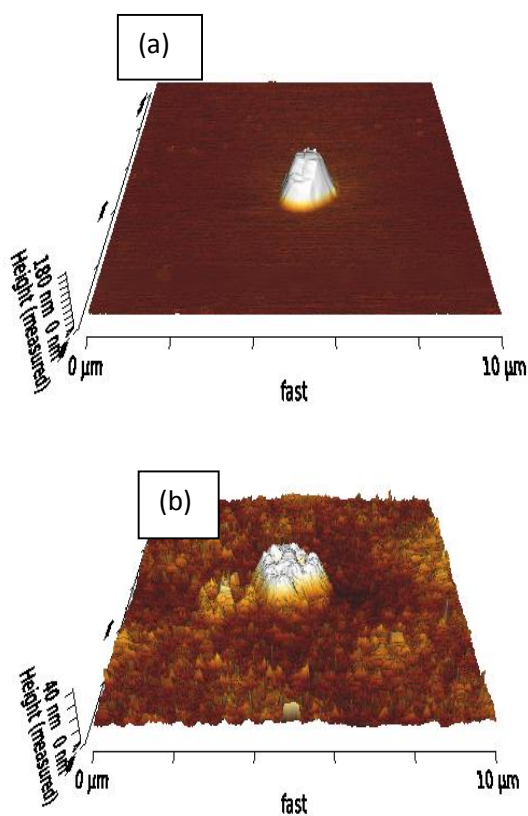


Figure 2. FE-SEM images of the thin films (a) S1; and (b) S2 [7].

The 3D AFM images of S1 and S2 samples were shown in Fig. 3, or elsewhere [6]. It was observed that S1 was composed with homogeneous distribution of nanopillars-TiO<sub>2</sub>

with optically smooth surface. However, a non-uniform distribution of particles was observed with S2 catalyst. Further, the average height of the pillars was found to be 180 and 40 nm respectively for the S1 and S2 samples. Moreover, the average roughness (Ra) and root mean square roughness (Rq) parameters for S1 and S2 samples were calculated and found to be 3.523, 14.06 nm and 2.708, 4.668 nm, respectively.



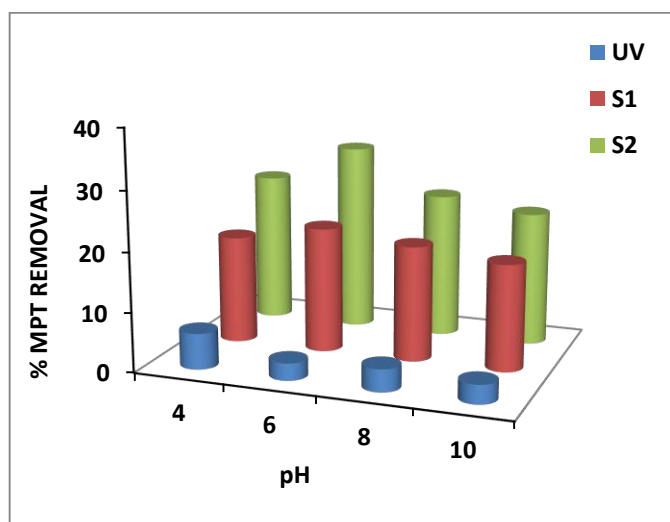
**Figure 3.** 3D AFM images of S1 and S2 samples at the scale of  $10 \times 10 \mu\text{m}^2$  [6].

The BET specific surface area of S1 and S2 catalyst were found to be 5.217 and 1.420  $\text{m}^2/\text{g}$ , respectively [7]. Similarly, the pore size was found to be 7.77 and 4.16 nm for the samples S1 and S2, respectively. Since, the Scherrer diameter indicated that the particle diameter was in the order of 21–29 nm. Therefore, it was assumed that a regular network was obtained on the substrate surface and, possibly, the titania was forming a Nanopillars on the substrate with a maximum size of 30 nm. It was also observed that although the specific surface area of the S2 catalyst was less than S1 sample however, the meso-pore size was decreased significantly. This enhances the possibility of the pollutants to trap within the pores and show a better catalytic activity.

### Photocatalytic degradation of MPT

#### Effect of pH in the degradation of MPT

The pH dependence degradation of MPT was presented in Fig. 4. The Figure clearly demonstrated that the percentage of MPT removal was increased until pH 6.0, beyond which it started to decrease even up to pH 10.0. This suggested that an optimum pH 6.0 could be an appropriate pH for better performance of photocatalyst. Further, the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of the thin films (S1 and S2) was found to be 6.9 [6]. It was assumed that the  $\text{TiO}_2$  surface was remained positively charged in acidic media ( $\text{pH} < 6.9$ ) and negatively charged in alkaline solutions ( $\text{pH} > 6.9$ ). On the other hand, the acid dissociation constant ( $\text{pK}_a$ ) of MPT was reported to be 7.15 [8]. Similar results were reported for the degradation of MPT employed suspension of titanium dioxide (degussa P25) [9]. In contrast, previously it was found that the MPT was degraded with higher rate at alkaline solution using the sonocatalytic degradation employing nano sized rutile  $\text{TiO}_2$  [10].

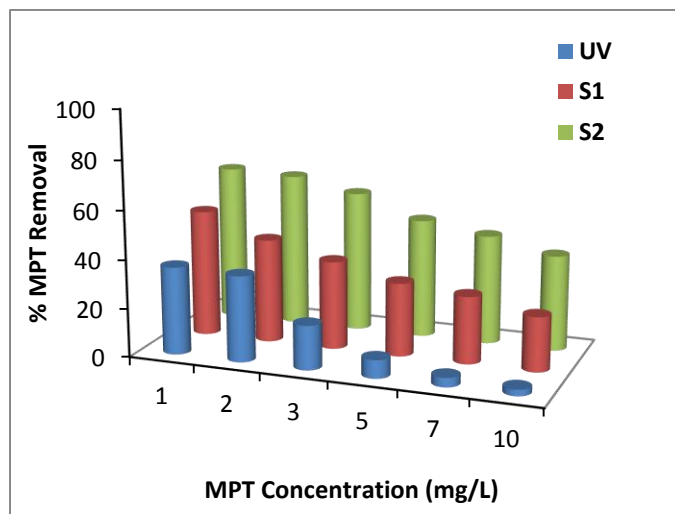


**Figure 4.** Effect of pH in the Photocatalytic degradation of Methyl Parathion using UV, S1 and S2. MPT Initial concentration: 10.0 mg/L

#### Effect of MPT concentration

The effect of pollutant concentration was studied at varied MPT concentrations, 1.0 to 10.0 mg/L at pH 6.0. The results obtained were presented as percent removal as a function of initial MPT concentration and returned in Fig. 5. The percent degradation of MPT was increased from 39.2 to 64.10% (with S2), from 22.2 to 52.0% (with S1) and 2.6 to 36.0% (with UV only) by decreasing the MPT concentration from 10.0 to 1.0 mg/L, respectively. These results further indicated that the thin films S1 and S2 showed significantly higher photocatalytic activity in the degradation of MPT from aqueous solutions compared to the UV only irradiated samples. Furthermore, the PEG template thin film S2 sample had more enhanced photocatalytic activity than the S1 samples, since more MPT molecules were effectively trapped

inside the small mesopores provided by the catalyst surface, and hence, effectively oxidized by the reactive species.



**Figure 5.** Effect of concentration in the photocatalytic degradation of Methyl Parathion using UV, S1 and S2.

#### Photocatalytic Degradation Kinetics of MPT

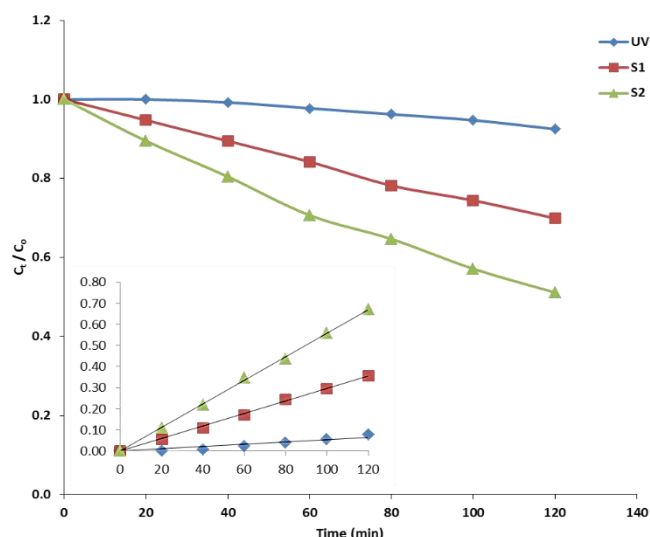
The photo-catalytic degradation kinetics of MPT was presented graphically in Fig. 6. The change in  $C_t/C_0$  values (where  $C_0$  is the initial concentration of MPT and  $C_t$  is the concentration of MPT at time 't') were taken as a function of time. A sharp decrease in degradation of MPT was observed in presence of thin films S1 and S2 after the 2 h UV irradiation. At the end of 2 h irradiation the  $C_t/C_0$  values were found to be 0.92, 0.70 and 0.51 for the UV only, S1 and S2 samples, respectively. A significant lower value of  $C_t/C_0$  obtained using the S2 sample compared to the S1 sample confirmed the affinity of the pollutant towards the thin film (S2) surface with enhanced photo-catalytic degradation of MPT at the surface. The kinetics of the MPT degradation was represented using the known pseudo-first-order rate equation (Eq. (2)):

$$r = -\frac{d[MPT]}{dt} = k_{app} [k_{photolysis} + k_{photocatalysis}] [MPT] = k_{app} [MPT] \quad (2)$$

where  $[MPT]$  represents the concentration of pollutant and  $k_{app}$  is the pseudo-first-order rate constant. It is obvious that the  $k_{app}$  depends on the concentration of MPT. Integration of Eq. (2) with the extreme conditions, i.e., at  $t=0$  the  $[MPT]=C_0$ . Eq. (2) resulted in Eq. (3):

$$LN\left(\frac{C_0}{C_t}\right) = k_{app} \cdot t \quad (3)$$

Straight lines were drawn between the  $LN(C_0/C_t)$  against time 't'. The results obtained were presented graphically in figure 6 (inset) for the MPT photocatalytic degradation (Initial concentration of MPT: 5.0 mg/L and pH: 6.0). Moreover, the pseudo-first-order rate constants were evaluated at different concentrations using the UV, S1 and S2 samples and results were returned in Table 1. It was evident that the apparent pseudo-first-order rate constant values were decreasing with increased in the concentration of MPT. Therefore, the lower initial concentration of MPT was found to be efficient in the photo-catalytic degradation using the thin films. Similarly, the S2 sample was found to be more efficient comparing to the S1 samples which indicated the potential use of template synthesis of thin films using the PEG as filler media. On the other hand, UV only showed very slow and almost negligible degradation of MPT compared with S1 and S2 samples.



**Figure 6.** Photocatalytic degradation of MPT as a function of time using thin films. MPT concentration: 5.0 mg/L; pH: 6.0 at Temperature: 25±1°C.

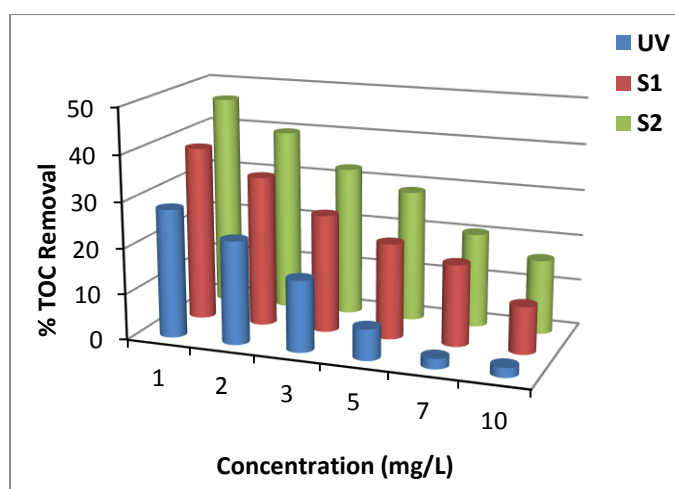
**Table 1.** Kinetic data obtained in the photo-catalytic degradation of Methyl Parathion using UV, S1 and S2.

	Pseudo-first order rate constant as ( $K_{app} \times 10^{-3}$ )/min					
	[Initial concentration of Methyl Parathion (mg/L)]					
	1.0	2.0	3.0	5.0	7.0	10.0
UV only	3.8 (0.963)	3.5 (0.974)	1.6 (0.979)	0.5 (0.8857)	0.3 (0.986)	0.2 (0.989)
S1	5.8 (0.9992)	4.6 (0.994)	3.9 (0.998)	3.0 (0.998)	2.7 (0.995)	2.1 (0.996)
S2	8.6 (0.993)	8.2 (0.998)	7.3 (0.998)	5.6 (0.999)	4.9 (0.998)	4.0 (0.997)

\*R<sup>2</sup> values are given in parenthesis.

### Mineralization of MPT

The mineralization of MPT was studied varying the pollutant concentration from 1.0 to 10.0 mg/L at constant pH 6.0 using UV only, S1 and S2 photocatalyst. Percent of TOC removal as a function of MPT concentration after 2 h irradiation was presented graphically in Fig. 7. The results showed that increasing the concentration of MPT from 1.0 to 10.0 mg/L the percent of TOC removal was decreased from 46.4 to 16.2% (using S2 thin films) and 38.1 to 10.3% (using S1 thin films) and 28.0 to 2.1% (UV only). It is interesting to note that a partial mineralization was achieved using the thin films. Further, similar to the concentration dependence study, the S2 thin film showed significantly higher efficiency compared with S1 and UV only irradiation.



**Figure 7.** Percent TOC removal of methyl parathion as a function of MPT concentration in the photo-catalytic degradation using UV, S1, S2 thin films.

### CONCLUSION

The Nanopillars-TiO<sub>2</sub> photocatalysts were immobilized on the borosilicate glass disk using the sol-gel synthetic method with (S1) and without (S2) PEG (polyethylene glycol) as template to obtain thin films. The thin films were well characterized with the XRD, SEM, AFM and BET analytical methods. XRD data revealed that the S1 and S2 sample contained anatase phase of Nanopillars-TiO<sub>2</sub>. SEM images showed fine grains of TiO<sub>2</sub> were evenly distributed on the substrate and forming a uniform thin layer of TiO<sub>2</sub> particles for S1 sample. Whereas S2 sample possessed relatively disordered surface structure which has several micro-cracks on the surface. AFM analytical data showed that the mean pillar size of TiO<sub>2</sub> particles was Ca 180 and 40 nm respectively for the S1 and S2 samples. Moreover, the average roughness (Ra) and root mean square roughness (Rq) were found to be 3.523, 14.06 nm and 2.708, 4.668 nm, respectively for S1 and S2 samples. Similarly, BET surface area for the S1 and S2 thin films were found to be 5.217 and 1.420 m<sup>2</sup>/g, with the pore size 7.77 and 4.16 nm, respectively.

Furthermore, catalysts were fully employed in the efficient

photocatalytic degradation of a potential pesticide Methyl Parathion from aqueous solutions. Relatively, very high degradation occurred at pH 6.0, which was slightly decreased at higher pH conditions. Low MPT initial concentration favored greatly the efficiency of photocatalyst in the percent degradation of MPT. The degradation process followed pseudo-first-order rate kinetics. Overall the S1 and S2 thin films showed very high percent degradation of MPT compared to the photolysis. S2 showed relatively higher photocatalytic efficiency compared to the S1 photocatalyst. Similarly, the mineralization of this pollutant increased with decreasing the pesticide concentration. The study conducted by using the thin films provide additional advantages with easy separation of catalyst as well as diminishing the shadowing effects commonly occurred with the TiO<sub>2</sub> powder or granules suppressing the catalytic activity and enabled the S1 and S2 thin films to be potential and cost effective photocatalyst which could possess greater practical or industrial applicability.

### REFERENCE

- [1] Affam, A.C., Chaudhuri, M., 2013, "Degradation of pesticides chlorpyrifos, cypermethrin and chlorothalonil in aqueous solution by TiO<sub>2</sub> photocatalysis." *J. Environ. Manage.*, 130, pp. 160 - 165.
- [2] Mnif, W., Hassine, A.I.H., Bouaziz, A., Bartegi, A., Thomas, O., Roig, B., 2011, "Effect of endocrine disruptor pesticides: a review," *Int. J. Environ. Res. Public Health*, 8, pp. 2265–2303.
- [3] Yen, J., Donerly, S., Levin, E.D., Linney, E.A., 2011, "Differential acetylcholinesterase inhibition of chlorpyrifos, diazinon and parathion in larval zebrafish." *Neurotoxicol. Teratol.*, 33, pp. 735–741.
- [4] Pankaj N. Patil, P.N., Gogate, P.R., 2012, "Degradation of methyl parathion using hydrodynamic cavitation: Effect of operating parameters and intensification using additives." *Sep. Purif. Technol.*, 95, pp. 172–179.
- [5] Fujishima, A., Zhang, X., Tryk, D.A., 2008, "TiO<sub>2</sub> photocatalysis and related surface phenomena." *Surf. Sci. Rep.*, 63, pp. 515–582.
- [6] C. Lalhriatpuia, Tiwari, D., Tiwari, A., Lee, S.M., 2015, "Immobilized Nanopillars-TiO<sub>2</sub> in the efficient removal of micro-pollutants from aqueous solutions: Physico-chemical studies." *Chem. Eng. J.*, 281, pp. 782–792.
- [7] Tiwari, D., C. Lalhriatpuia, Lalmunsiam, Lee, S.M., Kong, S.H., 2015, "Efficient application of nano-TiO<sub>2</sub> thin films in the photocatalytic removal of Alizarin Yellow from aqueous solutions." *Appl. Surf. Sci.*, 353, pp. 275–283.
- [8] Wolfe, N.L., 1980, "Organophosphate and organophosphorothionate esters: Application of linear free energy relationships to estimate hydrolysis

rate constants for use in environmental fate assessment, *Chemosphere*, 9, pp. 571-579.

- [9] Moctezuma, E., Leyva, E., Palestino, G., de Lasa, H., 2007, "Photocatalytic degradation of methyl parathion: Reaction pathways and intermediate reaction products." *J. Photochem. Photobiol. A: Chem.*, 186, pp. 71-84.
- [10] Wang, J., Pan, Z., Zhang, Z., Zhang, X., Wen, F., Ma, T., Jiang, Y., Wang, L., Xu, L., Kang, P., 2006, "Sonocatalytic degradation of methyl parathion in the presence of nanometer and ordinary anatase titanium dioxide catalysts and comparison of their sonocatalytic abilities." *Ultrason. Sonochem.*, 13, pp. 493-500.