Photocatalytic Degradation of Herbicide Orthosulfamuron using Zinc Oxide Nanoparticles in Water

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ABSTRACT
In the present study, the Photocatalysis of Orthosulfamuron, a new class of sulfonyl urea herbicide was investigated using ZnO nanoparticles in different buffer solutions of pH ranging from 4 to 9. In this study, optimum concentration of the catalyst, initial concentration of the orthosulfamuron and effect of pH of the buffer solution were studied under direct sunlight. The ZnO nanoparticles were synthesized by sol-gel process and characterized by using SEM, XRD and FT-IR. A commercial formulation of the herbicide having the active strength of 50% was used for the experiment. The rate of reaction followed pseudo first-order kinetics in water. The rate of reaction was 12 folds higher when compared to photolysis. The DT₅₀ values of orthosulfamuron with ZnO nanoparticles in different buffer solution were 6.42, 21.68 and 35.22 hours, respectively. The optimum concentration of nanoparticles to decontamination of orthosulfamuron was observed at 100 mg L⁻¹ and the initial concentration of the orthosulfamuron used in the photocatalysis is 10 mg L⁻¹. The fastest degradation of herbicide orthosulfamuron was observed in pH 4 buffer solution. The degradation products formed during the photocatalysis were identified by using LC-MS/MS which were N-(4,6-dimethoxypyrimidin-2-yl) urea, 2-dimethyl carbamoyl phenyl sulf amic acid and 1-(4-hydroxy-6-methoxypyrimidin-2-yl)-3-[2-(dimethylcarbamoyl) phenyl]sulfamoyl urea.

Key words: Catalyst, Degradation, Herbicide, Nano particles, Optimum.

INTRODUCTION
Contamination of surface water due to the extensive use of crop protection chemicals in agriculture is a major public health hazard issue. Herbicide residues are likely to get transferred to aquatic reservoirs by surface runoff and leaching. In Agriculture production, pesticides are widely used throughout the world against weeds, pests and fungi to protect the plants. Therefore, the pesticide residues mostly desecrated in soils, ground water and drinking water. In water, the organic chemicals found as pollutants which may come from domestic or industrial sources must be detoxified or decontaminated before entering into the environment. To achieve the acceptable drinking water quality, the pollutants require treatment that was found in ground and surface water. Linder et al. (1995). The combination of Heterogeneous catalysis with solar technologies is mostly used the technique in photocatlytic decontamination process in waste water treatment Zhang et al. (1994). There is a major chance to improve the decontamination of polluted water of the toxic chemicals using nanosize semiconductors by photocatalytic degradation, Cheng et al. (2014), Nouri et al. (2014). In Current the days, researchers faced the important challenges are pollutant-free air, water. To achieve this challenge, researchers design new materials by using solar energy is the main source. By using ZnO and TiO₂ for the application of photocatalysis using solar energy an extensive work carried out due to their high stability, suitable bandgap and photocatalysis efficiencies O’Regan and Grätzel (1991), Hoffmann et al. (1995), Barbé et al. (1997). In the field and laboratory studies, the organic compounds such as pesticides, herbicides, carboxylic acid, phenols, aldehydes, alcohols were destroyed photcatalytically. In this process of photo catalysis, the hazardous organic chemicals can degrade into simple mineral acids, water and carbon dioxide, Ahmed and Ollis, (1984). Therefore, there is a need to develop low-cost, effective, robust methods to decontaminate the water before they enter into the environment or human health is in endangering. Now a day’s application of solar chemistry is very relevant, especially in a chemical reaction caused by the catalyst or a reactant absorbed by solar photons in photochemical process and Advanced Oxidation Process (AOP) has quite useful. Vela et al. (2017). In most of the present studies, ZnO and TiO₂ have been used widely and reported as the best catalysts in the application of photocatalysis due to thier optical properties and in the visible region, they are showing much better quantum efficiency, Chong et al. (2010). In both the acidic and basic medium ZnO and TiO₂ completely mineralize the organic pollutants due to their high chemical stability, high oxidation...
efficiency, low toxicity, more abundant in nature and low in cost. Due to these reasons, ZnO and TiO₂ are widely used in the applications of photocatalysis, Saleh and Djaja (2014). At room temperature, ZnO has 60 MeV of excitation binding energy, wide and direct band gap of 3.37 eV at 300 K due to these properties it is a more promising II-VI semiconductor Ozug et al. (2005). The ZnO has the same bandgap energy as TiO₂. In aqueous solutions, some of the studies showed that ZnO has better or equal efficiency to TiO₂ in the photodegradation of dyes, Dindar and Icli (2001); So, in heterogeneous catalysis, ZnO can be used as a suitable alternative to TiO₂. Tan et al. (2011). Orthosulfamuron, 1-(4, 6-dimethoxypyrimidin-2-yl)-3-[2-(dimethylcarbamoyl)] phenylsulfamoyl] urea is a systemic herbicide belongs to the sulfonylurea class of herbicide. It is a post-emergence herbicide of annual and perennial broad leaves weeds, sedges and barnyard grass, in dry and water-seeded and transplanted rice, Pesticide manual, (2012). Orthosulfamuron exhibits “low mobility” and it belongs class II herbicide. The mode of action of this compound is, it inhibits the plant enzyme acetolactate synthase, which is also known as acetyloxyxy acid synthase. Inhibition of this enzyme blocks branch-chain amino acid biosynthesis of valine, leucine and isoleucine involved in plant growth processes leading to the death of the plant. According to standard test (OECD 301/ B) of biodegradability with an activated sludge inoculum, it was classified as “not a readily biodegradable” compound, EFSA Journal (2014). Its solubility is high if the water pH is increased. The solubility at different pH was (26.2 mg/L (pH-4), 629 mg/L (pH-7) and 38.9 g/L (pH-8.5) at 20°C). The compound is stable against the photolysis, OECD Guidelines, (1992). Its solubility, chemical stability and mobility facilitate this herbicide to cause contamination of the groundwater. The literature availability of this herbicide was limited, so we had referred the regulatory data as a reference. So we had developed a decontamination method of Orthosulfamuron by using ZnO/ Na₂S₂O₃ as a catalyst in different water media for eliminating the residues from water. Also the initial concentration herbicide, the optimum amount of catalyst used for the decontamination, effect of pH and reusability of the catalyst in the photo catalysis was studied.

MATERIALS AND METHODS

Materials

The present experiment was conducted at Department of Analytical Chemistry, International Institute of Biotechnology and Toxicology (IIBAT) in the period of March 2017 to June 2017. Orthosulfamuron (purity 99.73%), analytical reference standard was pursed from Sigma- Aldrich (USA) and herbicide formulation were purchased from the local market. All the solutions used in the study are reagent grade and used without further purification. Acetonitrile, Sodium peroxidisulfate, Potassium biphthalate and Sodium phosphate dibasic, Potassium phosphate monobasic, Sodium tetra borate and orthophosphoric acid, Zinc acetate dehydrate, Triethanol amine, Ethanol and ammonium hydroxide was obtained from the Merck India Limited, Mumbai. Double distilled water was used to prepare all the solutions. Stock solutions (1000 mg L⁻¹) of the pesticide standard were prepared in acetonitrile protected from light and stored at 5°C. A pesticide intermediate stock solution was prepared by dilution in the same solvent to obtain a concentration of 10 mg L⁻¹.

Experimental Procedures

Preparation of ZnO nano particles

ZnO nano particles were prepared in sol gel process Vafee and Ghamsari (2007). In this 20 mL of double distilled water was taken in to a 100 mL beaker and 30 mL of triethanolamine (TEA) was taken, to this ethanol was added drop wise (2 mL) with continuous stirring results a homogeneous solution (Solution-I). A 0.5 M Zinc acetate di hydrate solution was prepared by adding 5.42 g of Zinc acetate in 50 mL of water subjected to continuous stirring to get a homogeneous solution (Solution-II). Now, these two solutions were mixed in a 500 mL beaker and ammonium hydroxide was added with continuous stirring and heating for 20 minutes. The resulting solution is in the form of a yellow colored gel. Then the gel was washed 5-7 times with water and dried in a hot air oven at a temperature of about 200°C for 8 hours. The obtained powder was calcinated at 700°C for four hours.

Preparation of pH buffer solutions

pH 4 -

A buffer solution of pH 4.0 was prepared by adding 8 g of potassium dihydrogen phosphate in water and diluted to 1 literacy. The pH was adjusted to 4.0 using potassium dihydrogen phosphate.

pH 7 -

A buffer solution of pH 7.0 was prepared by adding 6.3g of disodium hydrogen ortho phosphate and 5.0 g of potassium dihydrogen phosphate by dissolving in water and diluted to 1 liter. The pH of the buffer was adjusted with disodium hydrogen ortho phosphate and potassium dihydrogen phosphate.

pH 9 -

A buffer solution of pH 9.0 was prepared by adding 12.5 g of boric acid and 15.0 g potassium chloride by dissolving in water and diluted to 1 liter. The pH was adjusted to 9.0 using sodium hydroxide.

Instrumental

Agilent 1290 series High Performance Liquid Chromatography equipped with a DAD detector with Phenomenex C18 of 4.6 mm i.d. and 250 mm length was used for the quantification of residues of orthosulfamuron. The λₘₐₓ 254nm. The mobile phase used for the elution was a mixture of 650 ml acetonitrile and 350 ml of 0.1% of ortho phosphoric acid in Milli- Q water. The used flow rate was 0.5 mL min⁻¹, the injection volume was 10 µl. The orthosulfamuron was eluted at 7.1 minutes retention time, respectively.
Characterization of ZnO particles
The synthesized ZnO nano particles were characterized using various techniques to check the morphology and crystalline nature of the obtained nano particles using SEM, XRD and FT-IR.

Photocatalysis
The photocatalytic experiment of orthosulfamuron in water was studied by spiking orthosulfamuron 50% WG formulation at 10 µg mL\(^{-1}\). The study was conducted under direct sunlight in the presence/absence of the catalyst from March to June 2017. The intensity of the light during the study was noted as 22500-178400 LUX and temperature was 25 to 44\(^\circ\)C. The experiment was conducted in Milli-Q water and three different buffers of pH 4.0, 7.0 and 9.0. Two sets of spiked concentration are prepared for the studies. To one set of samples, the catalyst (ZnO/Na\(_2\)S\(_2\)O\(_8\)) was added and the other set was studied without the addition of the catalyst. To attain the adsorption equilibrium and uniform distribution of the catalyst/ Oxidant particles, the solutions were sonicated (75 Hz) in the dark for about 20 min before exposure to sunlight. The samples were collected at the beginning of the experiment and regular time intervals up to 120 hours. The sample suspensions were centrifuged using Beckman cooling centrifuge at 10000 rotations per minute at 2\(^\circ\)C. The supernant was transferred into the amber-colored Vials. After centrifuging the remaining ZnO nano particles were dried at 100\(^\circ\)C and used for the catalyst reusability study following the above procedure.

Reusability of the Catalyst
To check the reusability of the catalyst, the catalyst was separated through centrifugation and dried at 100\(^\circ\)C for 4 hours. With the freshly prepared herbicide solution, the recovered catalyst was used to check the efficiency of the catalyst in batch mode for several runs. The conditions which were used for the photocatalysis, were also followed for the reusability test. The degradation efficiency of the catalyst and photocatalytic stability of the ZnO nano particles were calculated from the following equation, Kitture \(et\ al\). (2011).

\[
\ln \left( \frac{m}{m_0} \right) = -Kt
\]

Where

- \(m_0\) is the efficiency of degradation during the first use,
- \(m\) is the catalyst efficiency after fifth run (t),
- \(K\) is the decay constant.

RESULTS AND DISCUSSION
Characterization of ZnO nano particles
Scanning electron microscopy (SEM)
To study the morphological properties of the ZnO nano particles, the SEM technique was used. From the SEM image Fig 1, it can be clearly seen that the ZnO nano particles are in homogeneous shape and size. From the SEM images observed that the ZnO nano particles were having the needle like morphology with size 50-80 nm in diameter. From the literature, it was revealed that as compared to spherical structures, needles or rod-like structures exhibit more photocatalytic activity, Zheng \(et\ al\). (2007), Wan \(et\ al\). (2005).

X-ray diffraction technique (XRD)
The synthesized ZnO nano particles were characterized by using X-ray diffraction technique (XRD). There are evidences and good agreement between standard diffraction peaks and the obtained peaks, which reveal that the ZnO synthesis method was successfully done. From the below Fig it was revealed that diffraction peaks which are narrow and more intensive shows good crystalline nature of the ZnO and at the bottom, the broadening peaks were indicating that the crystalline sizes are very small, El Saeed \(et\ al\). (2015). The graph was shown in Fig 2.

Fourier Transformation infrared spectroscopy (FT-IR)
Fig 3 shows the FT-IR spectra of the ZnO nano particle where the scanning range was 400-4000 cm\(^{-1}\). The spectra exhibit a strong Zn-O stretching bond at 557.43 cm\(^{-1}\) and stretching was observed at 3428 cm\(^{-1}\) corresponds to O-H Stretching bond. The above results are reliable with the literature values.

Effect of Light Source on the degradation of the Orthosulfamuron
To study the degradation of the Orthosulfamuron, the studies were conducted in the dark, under direct sunlight irradiation.

![SEM Images of the ZnO nano particles.](image-url)
Photocatalytic Degradation of Herbicide Orthosulfamuron using Zinc Oxide Nanoparticles in Water

with and without ZnO nano particles, under direct sunlight irradiation with ZnO nano particles and oxidant. It was observed that under direct sunlight with catalyst orthosulfamuron degraded 90% in 100 hours in pH 9 buffer solution. In the case of dark and without catalysts under direct sunlight, the half-life of orthosulfamuron was nearly one month. This clearly indicates the importance of the process of the photocatalytic degradation of this herbicide. The observations were presented in Fig 4.

**Effect of the Catalyst amount on decontamination of the orthosulfamuron**

The study was conducted to establish the optimum amount of catalyst required to decontaminate the residues. From the results it was established that the optimum concentration to decontaminate the residues as 100 mg L$^{-1}$ of ZnO nanoparticles. The gradual increase in the efficiency of the catalyst was observed when the concentration of the catalyst was ranged from 10, 20, 50, 100 and 150 mg L$^{-1}$. The level...
Photocatalytic Degradation of Herbicide Orthosulfamuron using Zinc Oxide Nanoparticles in Water

of decontamination was increased up to 100 mg L\(^{-1}\) thereafter efficiency of catalyst was decreased. An increase in the load of the catalyst may show two opposite effects. One is on the surface of the particles it creates the high number of active sites available for the adsorption and on the other hand, the catalyst particles may disperse the higher amount of light. Therefore these particles are unable to generate electron-hole pairs. On the other hand, through collision, the activated ZnO nano particles were deactivated. From the above observations, the amount of catalyst was kept constant at 100 mg L\(^{-1}\) for all photocatalysis experiments. The graphical representation was presented in Fig 5.

**Effect of initial concentration of the compound on photocatalysis reaction**

Also, by using photocatalysis, the effect of the initial concentration of the herbicide was studied at 2 mg L\(^{-1}\) to 50 mg L\(^{-1}\) in pH 9 buffer solution. The results are presented in Fig 6. From the results, the rate of the photocatalysis was decreased while increasing the initial concentration of the compound. In the photocatalysis of orthosulfamuron, in the presence of ZnO nano particles, it can be concluded that while increasing the initial concentration of the compound, there is a decrease in the photo degradation. It can be explained that while increasing the orthosulfamuron concentration, more and more herbicide molecules were adsorbed on the surface of the ZnO nano particles it leads to the inhibition effect of the reaction of herbicide molecules with holes or hydroxyl radicles, due to the short of direct contact between herbicide molecules with catalyst, Daneshvar et al. (2008) leads to the decrease in the rate of the reaction. So, the initial concentration of the compound optimized for the photocatalysis reaction was 10mg L\(^{-1}\). The initial degradation of Orthosulfamuron in the presence of catalyst follows pseudo-first order reaction.

**Effect of pH on decontamination of the herbicide Orthosulfamuron**

The one of the most important parameter in the photocatalysis to remove the residues of herbicides is the pH of the solution. The photocatalysis was studied in three different buffer solutions of pH 4, 7 and 9. The catalyst amount used is 100 mg L\(^{-1}\) and the concentration of the test solution is 10mg L\(^{-1}\) was added into each test vessel and irradiated under sunlight. The samples were collected and injected at predetermined intervals. From the above results,
the most degradation of the Orthosulfamuron was observed at pH value 4.0. The surface of semiconductor is positively charged below its Pzc value, when its Pzc value exceeds, the surface of the semiconductor is negatively charged. ZnO zero point charge is 9.0 Tomasevic et al. (2009) above this value the surface of the ZnO is negatively charged. While increasing the pH of the solution, it is noticed that hydroxyl radicals were scavenged rapidly and inhibits the photocatalysis reaction Davis and Huang (1989). In this photocatalysis clearly indicates that the degradation was processed via OH radicals.

**Photocatalysis**

The degradation of the herbicide orthosulfamuron was studied in different pH buffer solutions with and without catalyst and oxidant (Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}) under direct sunlight. The results were given in Table 1-3 and the degradation curves were presented in Fig 7. The half-life values without the ZnO nanoparticles were observed 3.19, 23.36 and 29.27 days in pH 4, 7 and 9 buffers respectively. The Dt\textsubscript{50} values with the ZnO nanoparticles were 6.42, 21.68 and 35.22 hours.

**Table 1:** DT\textsubscript{50} and DT\textsubscript{90} values of Orthosulfamuron in pH 4 buffer using ZnO/Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}.

| Sampling occasion (Hours) | Concentration (mg L\textsuperscript{-1}) | Log of Concentration |
|---------------------------|------------------------------------------|----------------------|
| 0                         | 9.99                                     | 0.999                |
| 1                         | 9.53                                     | 0.979                |
| 5                         | 7.06                                     | 0.849                |
| 20                        | 5.11                                     | 0.708                |
| 25                        | 2.25                                     | 0.352                |
| 44                        | 0.26                                     | -0.585               |
| 50                        | 0.03                                     | -1.523               |
| 70                        | 0.00                                     | 0.000                |

*Slope -0.045
DT\textsubscript{50} 6.42 h
DT\textsubscript{90} 21.31 h

*Mean of three replicates.
respectively. The fastest degradation observed in pH 4 buffer solutions. So it indicates that the fastest degradation was observed in the photocatalysis process (half life is in hours) than the photolysis process (half life is in days).

**Reusability of the Catalyst**

The reusability of the catalyst was examined by performing the photocatalysis study in a batch mode. The study was performed with 100 mg L\(^{-1}\) of ZnO nano particles with 10 mg L\(^{-1}\) of herbicide concentration. The results were presented in Fig 8. From the graph, it can be explained that the change in the degradation efficiency of the ZnO nano particles from the initial experiment to after five repeated runs were 95.6-92.1% very minor change (3.5%) in the efficiency was observed after the five successive runs.

**CONCLUSION**

Zinc Oxide nanoparticles were successfully synthesized by Sol-gel method, characterized and used in the photocatalysis reaction as a photo catalyst. Orthosulfamuron was taken as a model herbicide for decontamination. The Synthesized ZnO particles were having the size of 50-60 nm and needle like in shape. The characterization was done by SEM, XRD and FT-IR. The rate of the reaction was followed by pseudo-first order kinetics. The optimum amount of catalyst used for the decontamination was 100 mg L\(^{-1}\) and the initial concentration of the compound used was 10mg L\(^{-1}\) and the highest degradation efficiency was observed at pH 4. The effect of the light source was studied. From the results, it was observed that UV-Vis/ZnO/Oxidant (Na\(_2\)S\(_2\)O\(_8\)) shows maximum photo degradation among the others. The complete mineralization of the orthosulfamuron was observed at 120 h of irradiation in pH 9 buffer solution. It was possible to identify the three major metabolites by using LC-MS/MS. To reduce the toxicity of the parent herbicide the degradation process and the degradation path way could be a useful source of information to decontamination. In the groundwater...
containing orthosulfamuron, the photocatalytic degradation is a useful method for the decontamination, removal and complete mineralization of the residues.

**Discloser Statement**

No potential conflict of interest was reported by authors.

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**REFERENCES**

Ahmed, S. and Ollis, D.F. (1984). Solar assisted catalytic decomposition of the chlorinated hydrocarbons trichloroethylene and trichloromethane. Solar Energy. 32(5): 597-601.

Barbe, C.J., Arendse, F., Comte, P. (1997). Nanocrystalline titanium oxide electrodes for photovoltaic applications. Journal of the American Ceramic Society. 3157-3171.

Cheng, C., Amini, A., Zhu, C., Xu, Z., Song, H. and Wang, N. (2014). Enhanced photocatalytic performance of TiO$_2$-ZnO hybrid nanostructures. Scientific Reports. 4.

Chong, M.N., Jin, B., Chow, C.W., Saint, C. (2010). Recent developments in Photocatalytic water treatment technology: a review. Water Research. 44: 2997-3027.

Danheshvar, N., Aber, S., Seyed Dorraji, M.S., Khatae, A.R., Rasoulifard, M.H. (2008). Preparation and Investigation of Photocatalytic Properties of ZnO Nanocrystals: Effect of Operational Parameters and Kinetic Study. Int. J. Chem. Biomol. Eng. 1: 24-29.

Davis, A.P. and Huang, C.P. (1989). The removal of phenols from water by a Photocatalytic Oxidation Process. Wat. Sci. Tech. 21: 455-464.

Dindar S. and Icli (2001). Unusual photoactivity of Zinc Oxide irradiated by Concentrated Sunlight. Journal of photochemistry and photobiology A: Chem. 140: 263-268.

El Saeed A.M., El-Fattah M.A., Azzam A.M. (2015). Synthesis of ZnO nanoparticles and studying its influence on the antimicrobial, anticorrosion and mechanical behavior of polyurethane composite for surface coating. Dyes Pigments. 121: 282-289.

Gilliom, R.J., Hoffmann, M.R., Martin, S.T., Choi, W. and Bahnmann, D.W. (1995). Environmental applications of semiconductors for photocatalysis. Chemical Reviews. 95: 69-96.

Kitture, R., Koppikar, S.J., Ghanekar, R., Kale, S.N. (2011). Catlyst efficiency, photostability and reusability study of ZnO nanoparticles in Visible light for dye degradation. Journal of Physics and Chemistry of Solids. 72: 60-66.

Linder M., B. Bahnmann, B. Hirtheandw Griebler (1995). Solar water detoxification: Novel TiO$_2$ powders as highly active photocatalysts. Solar Engineering. 1: 399-408.

MacBean C. (2012). The Pesticide Manual, 16th ed. Hampshire; UK: British Crop Production Council.

Mendez-Arriaga, F., Esplugas, S., Gimenez J. (2008). Photocatalytic degradation of non-steroidal anti-inflammatory drugs with TiO$_2$ and simulated solar irradiation. Water Res. 42: 585-594.

Nasrabadi, T., Bidhendi, G.N., Karbassi, A., Grathwohl, P., Mehradadi, N., (2011). Impact of major organophosphate pesticides used in agriculture to surface water and sediment quality (Southern Caspian Sea basin, Haraz River). Environ. Earth. Sci. 63: 873-883.

Neppolian, B., Choi, H.C., Sakhthivel, S., Arabindo, B., Murugesan, V (2002). Solar/UVinduced photocatalytic degradation of three commercial textile dyes. J. Hazard. Mater. 89: 303-317.

Nouri, H., Habibi-Yangieh A. (2014). Microwave assisted method for preparation of Zn$_x$-Zn$_{1-x}$O nanomaterials and their activities for photodegradation of methylene blue. Advanced Powder Technology. 25(3): 1016-1025.

O’Regan, B. and Gratzel, M. (1991). A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO$_2$ films. Nature. 353: 737-740.

OECD Guidelines for Testing of Chemicals (No. 301, Adopted: 17th July 1992). Ready Biodegradability. 1-62.

Ozgur O., Alivov Y.A., Liu C., Teke A., Reschikov M.A., Dogan S., Avrutin V., Cho S.J. and Morkoc H. (2005). A Comprehensive review of ZnO materials and Devices. Journal of Applied Physics. 98. 043101; https://doi.org/10.1063/1.1992666.

Saleh, R. and Djaia, N.F. (2014). UV light photocatalytic degradation of organic dyes with Fe-doped ZnO nanoparticles. Superlattices and microstructures. 74: 217-233.

Tan T.K., Khiew, P.S., Chu, Radiman S., Abi-Shukor R., Huang N.M. and H.N. Lim (2011). Photodegradation of Phenol Red in the Presence of ZnO Nanoparticles. World Acad. Sci. Eng. Technol. 5: 613-618.

Tomasevic, A., Daja, J., Petrovic, S., Kiss, E.E., Mijin, D. (2009). A Study of the Photocatalytic Degradation of Methomyl by UV Light. Chemical Industry and Chemical Engineering Quarterly. 15(1): 17-19.

United States Environmental Protection Agency (2014). Washington, D.C. 20460; PPDB Ref IR 5878.

Vafaee, M. and Ghamsari, M.S. (2007). Preparation and Characterization of ZnO nanoparticles by a novel sol-gel route. Materials Letters. 61: 3265-3268.

Veia, N., Perez-Lucas, G., Fenoll, J. and Navarro, S. (2017). Recent Overview on the Abatement of Pesticide residues in Water by Photocatalytic treatment Using TiO$_2$. Intech Open Science.

Wan, Q., Wang, T.H., Zhao, J.C. (2005). Enhanced photocatalytic activity of ZnO nanotetrapods. Appl. Phys. Lett. 87: 083105-083107.

Zhang Y., Crittenden, J.C., Hand, D.W. and Perram, D.L. (1994). Fixed-bed photocatalysis for solar decontamination of water. Environmental Science Technology. 28: 435442.

Zheng, Y., Chen, C., Zhan, Y, Lin, X., Zheng, Q., Wei, K., Zhu, J., Zhu, Y. (2007). Luminescence and Photocatalytic activity of ZnO nanocrystals: Correlation between Structure and Property. Inorg. Chem. 46: 6675-6682.