



Photocatalytic degradation of pesticide phorate using zinc oxide nanoparticles

Niranjani R,* Anchana Devi C

PG & Research, Department of Biotechnology, Women's Christian College, Chennai, Tamil Nadu, India

Abstract

Phorate is a highly toxic organophosphate pesticide used commonly in most of the developing countries. These pesticides are commonly washed away and mixed up in the water bodies leading to reduction in water quality and fatal consequences in the aquatic system. The application of nanoscale particles in pollution control is an emerging technology. It is considered more efficient because of its low cost and simplicity. The present study has been planned to investigate the photocatalytic action of chemically synthesized zinc oxide nanoparticles. The results showed that phorate was rapidly degraded by zinc oxide nanoparticles under solar light and the physico chemical properties of the water sample before and after treatment were studied. Maximum degradation of phorate zinc oxide nanoparticles were obtained after 120 minutes, which was measured photometrically at 350nm.

Keywords: zinc oxide nanoparticles, phorate, photocatalytic degradation and SEM

1. Introduction

Pesticides are used for destroying insects which affects the crops. They work by attracting; seducing and destroying the pest. They are also known as crop protection products, which protect plants from weeds or insects. Targeted pesticides include insects, pathogens and microbes that may cause disease or are vectors of diseases. As per Food and Agricultural Organization (FAO), pesticides are any substances or complex of substances intended for preventing, destroying or controlling any pest including vectors of animal diseases. Also used as substances applied to crops either before or after harvest to protect the commodity during storage or transport.

Pesticides can be classified based on their chemical structure (organic, inorganic or biological). Chemical insecticide families include organochlorines, organophosphates and carbamates. Organochlorine pesticides operate by disrupting the sodium/potassium balance of the nerve fibre. Their use has been replaced by organophosphate and carbamates because of their potential to bioaccumulate. Later two operate by inhibiting the enzyme acetylcholinesterase. Organophosphates are quite toxic to vertebrates.

Recent studies investigated degradation of these pesticides and surfactants using nanotechnology. Nanoparticles are particles between 1 and 100 nanometers in size. Nanotechnology uses these nano sized materials. They exist in various morphologies such as sheet, spherical, tubes etc., (Colvin, 1994) [6] Nanoparticle research is an area of an immense interest because of its wide application over biomedicine, electronic and environmental fields. Nanoparticles are used because of their small size, orientation and physical properties which are reported to alter the properties of materials to which they contact. Nanoparticles can be synthesized by physical, chemical or biological approaches. (Klaus *et al.* 1999) [11] In this study, Zinc oxide nanoparticle are of interest due to the reasons that they are effective low cost metal oxide, which is

used as a replacement for titanium oxide. This semiconductor nanoparticle has various unique properties. ZnO nanoparticles are potential enhancer of yield and growth of field crop. Various studies have been done with ZnO nanoparticles to be used as a photocatalyst in photo degradation. (Saber A *et al.*, 2011; Sahithya K and Nilanjanna D., 2015) [14, 15] In present study, zinc oxide nanoparticles are synthesized by simple solution based approaches. In chemistry, photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. For the purpose of degradation of organic pollutants in water titanium oxide and zinc oxides are used as the photocatalyst. Various water treatment techniques are employed for the removal of harmful contaminants such as pesticides in water, which may lead to various illnesses in man and many other organisms in the ecosystems. Photocatalytic degradation of contaminants uses a semiconductor such as titanium oxide or zinc oxide nanoparticles, When semiconductors are exposed to sunlight, electrons from the valence bond jumps to conduction band which improves their catalytic property and aids in breakdown of toxic chemical compounds such as pesticides and reduces their toxic nature there by improving the quality of life in aquatic systems.

2. Materials and methods

2.1 Sample collection

500ml of Sample water was collected and stored in sterile bottles and transported to the laboratory and kept at room temperature for further analysis. Pesticide phorate was commercially purchased from Ashok seed, T-Nagar, Chennai and stored in room temperature.

2.2 Physico Chemical analysis

2.2.1 Colour

The colour of the phorate contaminated water was observed with naked eye and recorded.

2.2.2 pH

The pH of the contaminated water was measured using portable field digital pH meter.

2.2.3 Acidity (Ritu mahajan, et al. 2010) [13]

100ml of water samples was taken in a clean conical flasks. To this varying concentration of phorate (0.01, 0.02, 0.03, 0.04, 0.05mg) was added. Few drops of phenolphthalein were added to each flask. The mixture was then titrated against 0.1N sodium hydroxide until pink color appears. Acidity of water with varying concentrations of phorate was estimated using the formula:

$$\text{Acidity} = \frac{\text{Volume of 0.1N NaOH}}{\text{Volume of sample}} \times 1000$$

2.2.4 Alkalinity

Alkalinity was determined by the procedure of Trivedy and Goel (1986) [17]. 5 g of Chemical Methyl orange was taken in 100 ml of distilled water. 0.5 g of Phenolphthalein was taken in 50 ml of ethanol and 50 ml of distilled water added. 3 ml of H₂SO₄ was added into 1 L of distilled water. 50 ml of sample was taken in a conical flask. 5 drops of Phenolphthalein was added into it and the values noted.

2.2.5 Chemical oxygen demand (COD): (Ritu mahajan, et al. 2010) [13].

50 ml of water samples was taken in conical flasks. To this varying concentrations of phorate (0.01, 0.02, 0.03, 0.04, 0.05mg) was added. 5ml of 0.1N potassium permanganate was added to the water sample and kept in water bath for one hour. The flask was allowed to cool to room temperature then 5ml of 1% potassium iodide was added followed by 10ml of 2M sulphuric acid. The mixture was titrated against 0.1N sodium thiosulfate until pale yellow colour appears. Then 1ml of 1% starch was added and again titrated against sodium thiosulfate until blue colour disappears.

Formula

$$\text{COD (mg/L)} = \frac{8 \times C \times (B-C)}{S}$$

2.2.6 Total Suspended Solids: (Ritu mahajan, et al. 2010) [13].

The water samples mixed with phorate (0.01, 0.02, 0.03, 0.04, 0.05mg) were filtered on a pre-weighed filter paper. The filtered paper was dried at 103 – 105°C in oven and TSS contents, expressed in mass per volume of sample filtered (mg/L). TSS was determined by the following formula.

$$\text{TSS} = \frac{\text{initial weight of filter paper} - \text{final weight of filter paper} \times 1000}{\text{Volume of the sample}}$$

2.2.7 Total Dissolved Solids: (Ritu mahajan, et al., 2010) [13].

The TDS of the water samples were determined by the gravimetric method. After filtration for TSS analysis, the filtrate was heated in oven at above 100°C until all the water was completely evaporated. The remaining mass of the residue represents the amount of TDS in a sample. TDS is calculated using the formula:

$$\text{TDS} = \frac{W_2 - W_1 \times 1000}{V}$$

2.3 Synthesis of Zinc oxide nanoparticles

20 ml of 0.1M zinc nitrate was taken in a beaker and heated at 55°C. 10ml of 0.2M sodium hydroxide solution was added drop wise to the solution and kept under continuous stirring for 30 minutes. (Asthana s et al, 2014) [1]

2.4 Characterization of Nanoparticles

2.4.1 UV-Vis spectrophotometer

The samples were observed under UV-Vis spectrophotometer for its maximum absorbance and wavelength to record the UV-visible absorption spectra of the samples and confirm the reduction of zinc nitrate. Instrument used for this study is UV double beam Spectrophotometer model U-2900.

2.4.2 Scanning Electron Microscopy

The morphology of the zinc oxide samples were characterized by scanning electron microscope (SEM)-Hitachi S-4800 model.

2.4.3 Fourier Transform Infrared Spectrum

FT-IR is a technique which uses a mathematical process to convert raw material into data spectrum. It gives the absorption or emission spectrum of the material in all physical states. It measures how well the material absorbs light at various wavelengths. This can be used to identify specific compounds present in the material. Instrument used for this study is of Spectrum two model of series 96905.

2.5 Catalytic degradation (Asthana. S et al. 2014) [1]

100ml of water sample with 0.05mg of phorate were taken in a conical flasks. 3ml of synthesized ZnO nanoparticles were added to the flask. It was exposed to sunlight for photocatalytic degradation process. Degradation using zinc oxide was visually observed and Optical Density (O.D) was measured using UV-Vis spectrometer at 350nm. (Hariharan C, 2006) [8].

3. Results and Discussion

3.1 Sample collection

500ml of Sample water for this study was collected near Acharapakkam, Chennai, Tamilnadu, India. The Sample pesticide Phorate was purchased from Ashok seed, T-Nagar, Chennai. (Figure. 1)

Composition of the purchased pesticide:

- Phorate technical -10% w/w
- Water soluble encapsulating film containing material -1%
- Other ingredients -89%
- Total - 100%



Fig 1: Pesticide Phorate

3.2 Physico Chemical properties of water

Table 1: Physicochemical properties of the collected water sample.

Sample concentration (mg of phorate/100mL water)	0.01	0.02	0.03	0.04	0.05
pH	7.1	7.4	7.5	7.7	7.8
Colour	Grey	Grey	Grey	Grey	Light black
Alkalinity (N)	5	10	15	25	35
Acidity(N)	5	5	10	15	15
TDS (mg/L)	5	10	15	25	35
TSS (mg/L)	0.4	1.0	1.7	2.0	2.7
COD (mg/L)	1.23	2.72	3.36	3.52	3.84

3.2.1 Colour

The colour of the water varies with the concentration of contamination with phorate. The unfit colour of contaminated water is reduced after treatment. The water contaminated with phorate was blackish and turbid with suspended particles.

3.2.2 pH

pH of contaminated water was measured immediately after the addition of phorate at varying concentrations using pH meter. pH was between the range of 7.1 to 7.8 which showed slight alkalinity. pH was positively correlated with electrical conductance and total alkalinity (Gupta 2009) [7]. The photosynthetic activity of the contaminated water is ultimately reduced, the carbon dioxide and bicarbonates assimilation are greatly responsible for increase in pH.

3.2.3 Alkalinity & Acidity

Alkalinity estimation was done titrimetrically against 0.1N HCl. This estimation shows the normality of the contaminated water ranged between 5N to 15N. Acidity of phorate contaminated water was estimated against 0.1N NaOH. It was estimated to be in the range of 5N to 25N. Alkalinity and pH affect the toxicity of substances present in the water. The alkalinity of water may be caused due to OH⁻, CO₃²⁻, HCO₃⁻ ions. It reflects the capacity of contaminated water to neutralize acids, and is not potable. The present water sample is slightly alkaline which is expected to not to completely neutralize the acidic content of the contaminated water sample. Most of the acidic nature of the sample increases with increase in concentration of the phorate content.

3.2.4 Total Dissolved Solids

Total dissolved solids are the total amount of mobile charged ions, including minerals, salts or metal dissolved in a given volume of water in mg/L. TDSs are composed mainly of bicarbonates, chlorides, carbonates, phosphates, and nitrates of calcium, magnesium, sodium, and potassium; manganese; salt; and other particles. TDS in contaminated water was measured to be in the range of 5 to 35 mg/L. Higher amounts of TDS was measured in 0.05mg of phorate contaminated water which is the highest concentration used in this study. TDS of potable should not exceed 500 mg/lit. It is directly related to the potability of water and affects everything that is present in the aquatic system and also those use the water. (Mahananda *et al.* 2010) [12].

3.2.5 Total Suspended Solids

Amount of TSS was measured in contaminated water and was found to be in the range of 0.4 to 2.7mg/L. Phorate itself had large amount of suspended particles which were insoluble in water and found as sediments when left undisturbed. The TSS increased with increase in concentration of Phorate. The commercially purchased phorate contained insoluble salts which contributed to the factor.

3.2.6 Chemical oxygen demand

The COD determination is a measure of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant. COD specifies the toxicity of the contaminated water. COD for the contaminated water in this study was measured to be in the range from 1.23 to 3.84mg/L. The high levels of COD in the water sample indicate the release of material with high chemical oxygen demand and impact the sustainability of the aquatic system. While determining COD, oxygen demand value is useful in specifying toxic condition and presence of biologically resistant substances. COD reflects the common measures of pollutant organic material present in water. In this study, addition of Phorate had contributed to the increase in COD in dose dependent manner.

Physicochemical parameters of wastewater were done to study the components and nature of the contaminated water to be treated. pH, color, TDS and TSS of waste water varied based on the concentration of contaminants present in the water. COD of waste water was measured to be higher due to their high level of contamination (Table 1). The findings of the study correlated with the work carried out by Benit. N and Stella. R.A., 2015 [5] in which pH of the waste water was in the range of 6.3 to 7.3. The amount of TDS was about 409.5 to 1505.7 ppm and maximum COD value was 602.9mg/L.

4. Synthesize of Zinc oxide nanoparticles

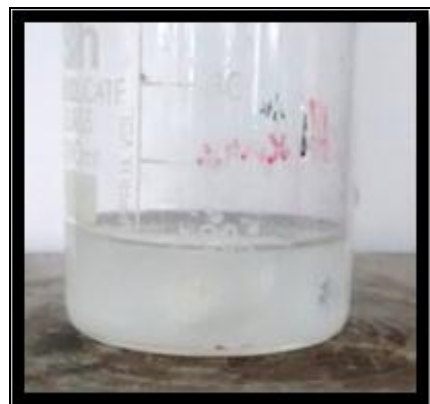


Fig 2: Synthesis of Zinc nanoparticles

Zinc oxide nanoparticles were synthesized by chemical method (Alessio. B *et al.* 2008) [2] Continuous stirring in magnetic stirrer for about 30 minutes resulted in pale white colour solution with white colored precipitate. Thus preparation of the nanoparticle was confirmed and subjected to further analysis to characterize the nanoparticles. The formation of white colour precipitate was also reported in the

work carried out by Asthana. S., 2014 [1] where zinc nitrate and sodium hydroxide were used for the synthesis. (Figure 2).

4.1 Characterization of Nanoparticles

4.1.1 UV-VIS spectrophotometer

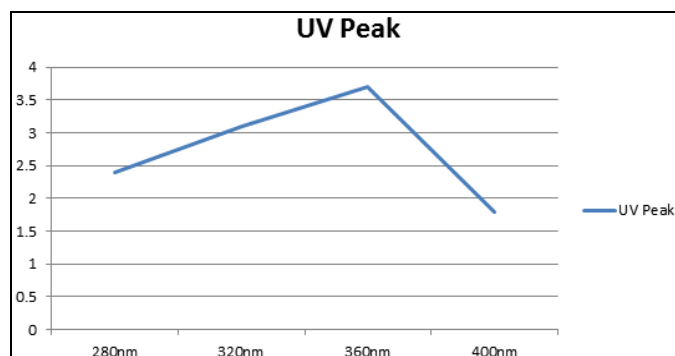


Fig 3: UV-VIS spectrophotometer reading of Zinc oxide nanoparticles

The size of the nanoparticles plays an important role in changing the entire properties of materials. Thus, size evolution of semiconducting nanoparticles becomes very essential to explore the properties of the materials. UV-visible absorption spectroscopy is widely being used technique to examine the optical properties of nanosized particles. It exhibits a strong absorption band at about 360 nm. (Figure 3) The absorption peak of synthesized nanoparticles was correlated with the study of Jin Y.D *et al.* 2000 [10] which showed a maximum peak at 355nm.

4.1.2 FTIR of Zinc Oxide nanoparticle

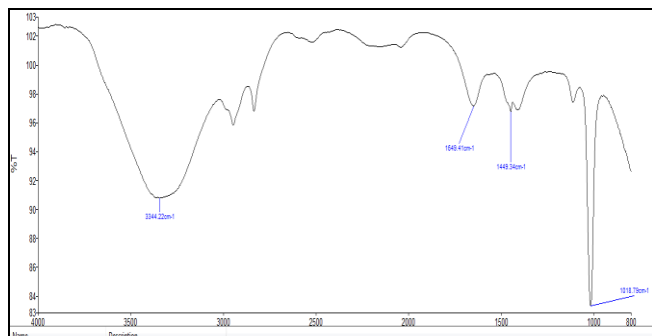


Fig 4: FT –IR spectra of synthesized Zinc Oxide nanoparticles

Table 1

Spectrum range	Bond
3344.22 cm ⁻¹	O-H
1649.41 cm ⁻¹	C=O
1449.34 cm ⁻¹	C-O
1018.79 cm ⁻¹	C-N

From this FTIR we can also observe that increasing the annealing temperature sharpens of the characteristic peaks for metal oxide, suggesting that, the crystalline nature of ZnO increases on increasing the calcination temperature (Figure 4). Broad bands were observed at 3344.22cm⁻¹ which corresponds to hydroxyl group (OH group). The peaks in the range of

1400-1600cm⁻¹ corresponds to the C=O bonds two bands were observed at that range of 1649cm⁻¹and 1449cm⁻¹. The bands correlated to metal oxide bond (ZnO). FT-IR was recorded for the known sample which exhibited capping agent and reducing agent for the Zinc oxide nanoparticles correlated with the finding published by Thirunavukarasu. C., 2016 [16].

4.1.3 Scanning Electron Microscope

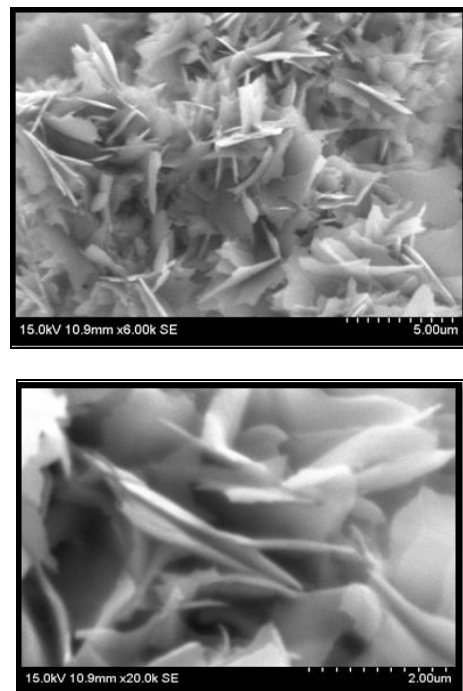


Fig 5 a-b: SEM images of ZnO nanoparticles

Figure 5 Clearly shows the SEM morphology of the synthesized nano ZnO particles at different calcining temperatures. It demonstrates clearly the formation of platted flake ZnO nanoparticles, formed with the calcination temperature. (Zhong LW, 2004) [18] The nano-sized ZnO flakes are 2 to 5 nm. The low-resolution image (Figure 5a) confirms that the flakes were synthesized in very large quantity; and the high-resolution image (Figure 5b) of the synthesized flakes reveals that the products have uniform flake shape which was correlated with results of the study of Jia, X *et al.* 2011 [9], in which the prepared nanoparticles were confirmed to have nanosheets of thickness 10-20 nm.

5. Photocatalytic Degradation of Phorate

Maximum concentration of 0.05mg was selected for this study. Water and nanoparticles were mixed in the ratio of 20ml: 3ml. Phorate present in contaminated water was catalytically degraded using zinc oxide nanoparticles when exposed to Solar light. Colour change was observed within 10 minutes, due to the addition of zinc oxide nanoparticle which acts as a semiconductor on exposure to solar light. Figure 6 shows colour change of contaminated water with zinc oxide nanoparticles at 0, 10, 30 and 120 minutes. Clear solutions with lesser suspended particles were obtained under sunlight after 120 minutes. (Fig 6d). The treated water was then subjected to analyze physico-chemical properties (Behnajady

MA *et al.* 2009)^[4].

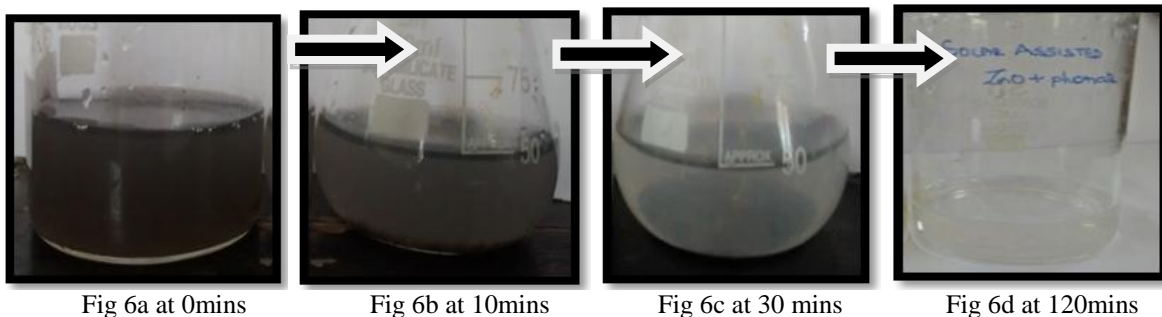


Fig 6: shows the Photocatalytic degradation of Phorate under solar light.

Table 2: shows Optical Density of Phorate treated water (in nm)

Sample	Optical Density of Phorate treated water (in nm)							
	5mins	10mins	15mins	20mins	25mins	30mins	60mins	120mins
Water sample treated with ZnO nanoparticles	0.632	0.521	0.421	0.392	0.341	0.301	0.101	0.029

The gradual decrease in the OD range after the treatment of water sample with zinc oxide nanoparticles was observed (Table 2), which correlated with the study of Asthana. *S et al.* 2014^[1] which showed total degradation of the pesticide within 120 minutes on treatment with zinc oxide nanoparticles (Figure 6). The nanostructures of metal oxide zinc oxide (ZnO) acts as semiconductors. It can be an attractive and cost effective way of water purification as it is capable of removing chemical as well as biological contaminants. The interesting aspect of photocatalysis is the other than being cost effective is its potential utilization of sunlight, which could allow energy efficient treatment even in remote locations. (Baruah, *S et al.* 2009)^[3].

6. Physico-chemical properties of contaminated water after treatment

Table 3: Physico chemical properties of water before and after treatment

Analysis	Untreated water sample	Treated with ZnO nanoparticle - Solar
Colour	Blackish	Nearly transparent
Alkalinity	35N	5N
Acidity	10N	5N
TSS(mg/L)	0.27	0.31
TDS(mg/L)	35	10
COD(mg/L)	3.8	0.8

The physico-chemical properties of both untreated and treated water were compared (Table 3). Most of the physico-chemical parameters of untreated waste water are beyond permissible limits which makes the water not suitable for consumption. The level of COD, alkalinity, acidity and TDS was reported to be decreased after treatment. TSS amount was increased as the suspended particles were visibly more when compared to untreated water. This shows improvement in the quality of water after treatment using ZnO nanoparticles.

7. Conclusion

The present study shows the chemical synthesise of zinc oxide

nanoparticles. The characterization of the nanoparticles included UV, SEM and FTIR. The synthesized nanoparticles were found to possess sheet shape. The physico chemical characteristics such as pH, colour, alkalinity, acidity and COD of the phorate contaminated water were studied. The degradation of phorate using zinc oxide nanoparticles was investigated under solar light. The physico chemical parameters were also observed to be improved after treatment. Thus, this study shows that semiconductor nanoparticle ZnO exhibits excellent photocatalytic activity in removing contaminants. Innovative uses of nanotechnology, using catalysts and exploiting unique properties of nanomaterials are capable of making an impact in reducing the pollution and water treatment. The availability of safe drinking water in developing countries has become a major challenge. This cheap and safe technology is a promising factor in near future for recovery of contaminated water bodies and making potable water available readily.

8. References

1. Asthana S, Pal S, Sharma M. Solar assisted nanoZnO photocatalytic mineralization- The green technique for the degradation of detergents. *IJCPA*. 2014; 1(3):141-147.
2. Alessio B, Maximillian D, Pierandrea LN, Piero B. Synthesis and characterization of zinc oxide nanoparticles: Application to textiles as UV-Absorbers *J Nanopart. Re*. 2008; 10(4):679-689.
3. Baruah S, Dutta J. Nanotechnology applications in pollution sensing and degradation in agriculture. *Environ. Chem. Lett*. 2009; 7:191-204.
4. Behnajady MA, Modirshala N, Shokri M, Zeininezhad A, Zamani HA. Enhancement photocatalytic activity of ZnO nanoparticles by silver doping with optimization of photodeposition method parameters, *JESHT*. 2009; 44(7):666-672.
5. Benit N, Stella Roslin A. Physicochemical properties of wastewater collected from different sewage sources, *International Journal of Innovative Science, Engineering & Technology*. 2015; 2(11):691-696.
6. Colvin VLS, Alivisatos A. Light emitting diodes made

- from Cadmium Selenide nanocrystals and a semiconducting polymer, *Nature*. 1994; 370:354-357.
7. Gupta, DP, Sunita, Saharan JP. Physicochemical Analysis of Ground Water of Selected Area of Kaithal City (Haryana) India, *Researcher*. 2009; 1(2):1-5.
 8. Hariharan C. Photocatalytic degradation of organic contaminants in water by ZnO nanoparticles, *Appl. Catal. A*. 2006; 304:55-61.
 9. Jia X, Fan H, Afzaal M, Wu X, O'Brien P. Solid state synthesis of tin-doped ZnO at room temperature: Characterization and its enhanced gas sensing and photocatalytic properties, *Journal of Hazardous Materials*. 2011; 193:194-199.
 10. Jin YD, Yang JP, Heremans PL. Single-layer organic light-emitting diode with 2.0% external quantum efficiency prepared by spin-coating. *Chemical Physics Letters*. 2000; 320(5-6):387-392.
 11. Klaus TJ, Olsson E. Silver based crystalline nanoparticles: microbially fabricated. *Proceeding of nation academy of sciences USA*. 1999; 96:13611-13614.
 12. Mahananda MR, Mohanty BP, Behera Mahananda MR. Physico – chemical analysis of surface and ground water of Bargarh district, Orissa, India. *IJRRAS*. 2010; 2:26-30.
 13. Ritu mahajan, Jitendar Sharma, Mahajan RK. *Practical manual of biotechnology*, Vayu education of India, New Delhi, 2010.
 14. Saber A, Rsul MG, Hashib MA. Influence of parameters on the heterogenous photocatalytic degradation of pesticides and phenol contaminants in wastewater. *Journal of environment management*. 2011; 92(2):311-330.
 15. Sahithya K, Nilanjanna D. Remediation of pesticides using nanomaterial: An overview. *International journal of Chem. Tech. Research*. 2015; 8(8):86-91.
 16. Thirunavukkarasu C, Archana R, Sharmila S, Janarthanan B, Chandrasekaran J. Preparation and characterization of ZnO nanoparticles using *Moringa oleifera* extract by green synthesis method, *Asian Journal of Phytomedicine and Clinical Research*. 2016; 4(3):121-132.
 17. Trivedy RK, Goel PK. *Chemical and biological methods for water pollution studies*, Environmental Publication, Karad, Maharashtra, 1986.
 18. Zhong LW. Zinc oxide nanostructures: growth, properties and applications, *Journal of physics condensed matter*. 2004; 16:829-858.