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Application of La Doped Copper Oxide Nanoparticles as Photocatalytic for the Decontamination of Imidacloprid and Bifenthrin Pesticide Residues in Water

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A B S T R A C T

Lanthanum doped with copper oxide nanoparticles with size ranging from 20 to 100 nm and 10 µm length were prepared by reacting copper nitrate with Lanthanum oxide. The structure of the nanoparticles was confirmed by scanning electron microscope (SEM) analysis. Photocatalytic activity of the insecticides imidacloprid and bifenthrin was investigated. The decontamination effect of catalyst on the residues of imidacloprid and bifenthrin in water was evaluated in three different buffer solutions (pH 4.0, 7.0 and 9.0). The catalytic reaction was measured under direct sunlight at two different concentration levels of Imidacloprid and Bifenthrin. The optimum concentration of catalyst (lanthanum doped copper-oxide) required for the decontamination was found to be 0.05 g/L. Residues were quantified by ultra-fast High-Performance liquid chromatography method (UHPLC-PDA). Parameters, DT_{50} and DT_{90} were calculated from the dissipation data. The rate of the reaction showed first order kinetics in water. The addition of Lanthanum doped with copper oxide nanoparticles contributed to significant photocatalytic dissipation of residues. Complete mineralization of the residues was confirmed by the ultra-fast high-performance liquid chromatography. The method has the limit of quantification 0.01 mg/L in water.

***Key words*:** DT_{50} and DT_{90}, La doped CuO nanoparticles, Photolysis, SEM, UHPLC

Pesticides are widely used in agriculture to bring down the pest infestations in the field eventually leading to environmental contamination. Presence of agrochemical residues in water reservoirs and other environmental strata leads to environmental contamination and poses risk to the living organisms. Imidacloprid ((NE)-N-[1-[(6-chloropyridin-3-yl)methyl] imidazolidin-2-ylidene]nitramide); neonicotinoid and Bifenthrin ((2-methyl-3-phenylphenyl)methyl3-[(Z)-2-chloro-3,3,3-trifluoroprop-1-enyl]-2,2 dimethylcyclopropane-1-carboxylate;insecticide) is generally used as combinational insecticide (Imidacloprid 20% (w/w) + Bifenthrin 8% (w/w) SL) for the control of broad spectrum of sucking pests in agriculture. Many reports are published for the determination of residues of imidacloprid in water and other environmental substrates including the application of Zinc as a photocatalytic agent for the decontamination of residues [1]. Photocatalytic degradation of imidacloprid in water was evaluated with heterogeneous catalysis and homogeneous catalysis under direct sunlight and UV irradiation. The semiconductor oxides are found to be the most effective in photocatalysis of residues of organophosphate pesticides. The catalytic activity of Ferrous, Zinc oxide, Copper oxide on several pesticides and other environmental contaminants are widely reported by different researchers [2-8]. The copper oxide (group II -VI) behaves as semiconductor with optical properties. The utility of copper oxide nanoparticles is reported in gas sensors, magnetic storage media, photo conductivity and photocatalytic reactions. The photocatalytic activity of lanthanum doped copper oxide nanoparticles was evaluated on the pesticide residues (Imidacloprid and Bifenthrin) in the current study [9].

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MATERIALS AND METHODS

Analytical reference standards of imidacloprid purity 99.90% and bifenthrin purity 99.54% were purchased from Sigma Aldrich, Bangalore, India. The soluble concentrate (SL) formulation of combination insecticide was purchased. Water was collected from the Milli Q water purification system (Millipore SAS). Acetonitrile, copper nitrate, ammonia solution and triethyl amine supplied by Merck life sciences private limited. The other chemicals used are analytical grade reagents.

Analytical instrument

The Agilent-1260 Infinity II, Ultra High-Performance Liquid Chromatography (UHPLC) equipped with a PDA detector was used for the identification and quantification of residues of Imidacloprid and Bifenthrin. The chromatographic conditions are used, Zorbax C8, 250 mm length × 4.6 mm i.d × 5 µm, mobile phase mixture of acetonitrile and 0.1% orthphosphoric acid and 10 µL injection volume with flow rate of 1.0 mL/min. The retention times of Imidacloprid and Bifenthrin observed were 3.1 and 5.3 minutes respectively.

Preparation of lanthanum doped with copper oxide nanoparticles

La doped copper oxide nanoparticles were prepared by chemical precipitation method. The lanthanum oxide, copper nitrate and ammonia solutions were prepared separately and taken in three-different burettes. The solutions were allowed to drop continuously into a conical flask containing 100 mL of distilled water placed on a magnetic stirrer with magnetic bead for vigorous mixing to form the precipitate. The precipitate thus obtained was taken out and filtered with buckner funnel, washed with distilled water thrice. Few drops of triethyl amine was used for neutralization. The precipitate was later washed with acetone and transferred to a clean and dried silica crucible placed in a hot air oven set at 80 °C for 1 hour. It was later placed in a pre-heated muffle furnace set at 250 °C for two hours. Coffee brown color powder was obtained at the end of reaction showing the completion of lanthanum doped copper oxide nanoparticles. It was confirmed by scanning electron microscope (SEM), Energy Dispersive Spectrum (EDS) and FT-IR and UV Spectra. The details are presented in (Fig 1-4).

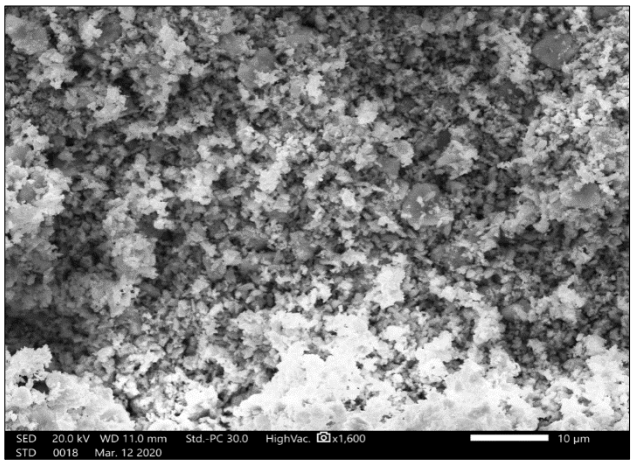

Fig 1 Scanning electron microscope of La doped copper oxide nanoparticles (20-100 nm)

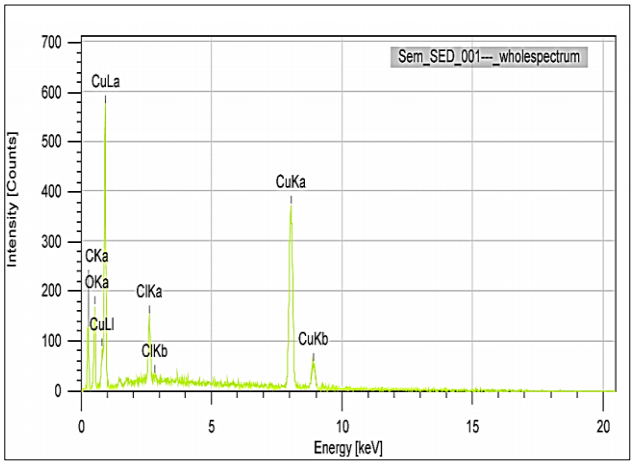

Fig 2 Energy dispersive spectrum analysis of La doped copper oxide nanoparticles

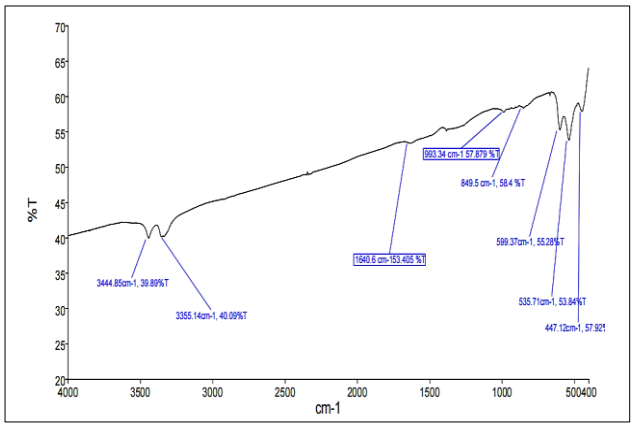

Fig 3 FT-IR spectrum of La doped copper oxide nanoparticles

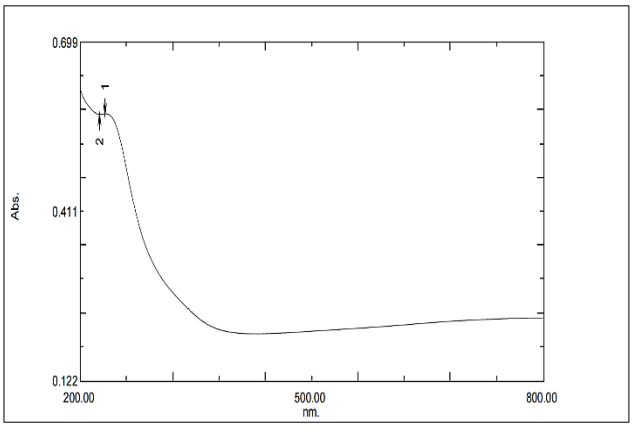

Fig 4 UV-Vis spectrum of La doped copper oxide nanoparticles

Photocatalysis

The photocatalytic effect of La doped copper-oxide on residues of Imidacloprid and Bifenthrin insecticides in water was evaluated on two different concentrations of combinational insecticide formulation (Imidacloprid 20% (w/w) + Bifenthrin 8% (w/w) SL) at 1.0 and 2.0 mg/L. The study was conducted in Milli Q water and in three different buffer solutions, pH 4.0, 7.0 and 9.0 without and with catalyst (Lanthanum doped copper oxide nanoparticles) under direct sunlight. The temperature of the water samples during the study period was found between 27 to 42 °C. The intensity of sunlight was measured during the exposure. The graphical representation was shown in the (Fig 5). At designated time intervals, the samples were collected, centrifuged using cooling centrifuge set at 10000 RPM for 5 minutes, filtered using 0.2-micron filter and stored in amber-coloured bottles. All the samples were stored in dark (~ 4 °C) before injecting in to UHPLC. The concentration of La doped copper-oxide used was 0.05 g/L.

RESULTS AND DISCUSSION

Photolysis of pesticides without catalyst

The photolysis of Imidacloprid and Bifenthrin insecticide in different pH water conditions and milli q water under the influence of direct sunlight without catalyst was evaluated. The study showed that the compounds degraded to below detectable levels within 10 days in milli Q water, acidic

buffer (pH-4.0) and neutral buffer (pH-7.0). The degradation of Imidacloprid and Bifenthrin was found rapid in basic buffer (pH-9.0) with below detectable level within 5 days. The details are presented in the (Table 1).

Table 1 Photolysis of imidacloprid and bifenthrin under direct sunlight in milli Q water, pH-4.00, pH-7.00 and pH-9.00 buffer solutions (Without catalyst)

Tested dose	Imidacloprid		Bifenthrin		Tested dose	Imidacloprid		Bifenthrin	
	T_1: 0.2 mg/L	T_2: 0.4 mg/L	T_1: 0.08 mg/L	T_2: 0.17 mg/L		T_1: 0.2 mg/L	T_2: 0.4 mg/L	T_1: 0.08 mg/L	T_2: 0.17 mg/L
Sampling occasions (Days)	Dissipation of residues in milli Q water (mg/L)				Sampling occasions (Days)	Dissipation of residues in acidic buffer (mg/L)			
0	0.20	0.39	0.08	0.17	0	0.20	0.39	0.08	0.17
1	0.17	0.36	0.07	0.16	1	0.16	0.34	0.07	0.15
3	0.13	0.26	0.05	0.14	3	0.12	0.23	0.05	0.13
5	0.09	0.13	0.03	0.12	5	0.1	0.13	0.03	0.10
7	0.05	0.09	<LOQ	0.08	7	0.04	0.08	<LOQ	0.07
10	<LOQ	<LOQ	<LOQ	<LOQ	10	<LOQ	<LOQ	<LOQ	<LOQ
15	<LOQ	<LOQ	<LOQ	<LOQ	15	<LOQ	<LOQ	<LOQ	<LOQ
Dissipation of residues in neutral buffer (mg/L)					Dissipation of residues in basic buffer (mg/L)				
0	0.20	0.40	0.08	0.17	0	0.19	0.39	0.08	0.17
1	0.18	0.35	0.07	0.15	1	0.14	0.28	0.05	0.10
3	0.14	0.24	0.04	0.14	3	0.08	0.17	0.02	0.05
5	0.08	0.12	0.02	0.11	5	<LOQ	<LOQ	<LOQ	<LOQ
7	0.03	0.09	<LOQ	0.06	7	<LOQ	<LOQ	<LOQ	<LOQ
10	<LOQ	<LOQ	<LOQ	<LOQ	10	<LOQ	<LOQ	<LOQ	<LOQ
15	<LOQ	<LOQ	<LOQ	<LOQ	15	<LOQ	<LOQ	<LOQ	<LOQ

Photolysis of pesticides with catalyst

The photolysis of insecticides in presence of La doped copper oxide under the influence of direct sunlight and different buffer solutions and milli Q water was evaluated. The details are presented in the (Table 2) and representative chromatograms are presented in the (Fig 6-7). The adsorption of insecticides on the catalyst was quantified in water at designated time intervals. The increase in amount of catalyst (tested concentrations ranged from 0.02 to 0.2 g/L) enhanced the degradation of pesticide residues with equilibrium attained at 0.05 g/L. The DT_{50} and DT_{90} values are calculated from the dissipation data of insecticides. From the study, it was observed that the reaction was influenced by change in pH. The reaction was found slow at lower pH while dissipation was found rapid with alkaline pH. When compared with imidacloprid the dissipation of bifenthrin is more rapid in basic solution. Further it was observed that in the water and buffer solutions after the addition of lanthanum doped copper oxide nanoparticles as catalyst enhanced the degradation of insecticide. The influence of the aeration in decontamination of residues was presented in (Table 3). The DT_{50} and DT_{90} values were calculated using the following formula:

$$DT_{50} = \ln 2/(k) \text{ and } DT_{90} = \ln 10/(k)$$

Where “k” is slope of the curve obtained from the dissipation data

Table 2 Photolysis of imidacloprid and bifenthrin under direct sunlight in milli Q water, pH-4.00, pH-7.00 and pH-9.00 buffers solution (With catalyst)

Tested dose	Imidacloprid		Bifenthrin		Tested dose	Imidacloprid		Bifenthrin	
	T_1: 0.2 mg/L	T_2: 0.4 mg/L	T_1: 0.08 mg/L	T_2: 0.17 mg/L		T_1: 0.2 mg/L	T_2: 0.4 mg/L	T_1: 0.08 mg/L	T_2: 0.17 mg/L
Sampling occasions (Hours)	Dissipation of residues in milli Q water (mg/L)				Sampling occasions (Hours)	Dissipation of residues in acidic buffer (mg/L)			
0	0.20	0.40	0.08	0.17	0	0.20	0.40	0.08	0.17
1	0.18	0.38	0.07	0.16	1	0.17	0.37	0.07	0.16
3	0.16	0.35	0.05	0.14	3	0.15	0.33	0.05	0.14
5	0.14	0.24	0.03	0.12	5	0.13	0.22	0.03	0.12
7	0.11	0.15	<LOQ	0.07	7	0.09	0.12	<LOQ	0.07
10	0.06	0.11	<LOQ	<LOQ	10	0.05	0.09	<LOQ	<LOQ
24	<LOQ	<LOQ	<LOQ	<LOQ	24	<LOQ	<LOQ	<LOQ	<LOQ
Dissipation of residues in neutral buffer (mg/L)					Dissipation of residues in basic buffer (mg/L)				
0	0.20	0.40	0.08	0.17	0	0.19	0.39	0.08	0.17
1	0.18	0.38	0.07	0.16	1	0.16	0.25	0.06	0.12
3	0.16	0.34	0.05	0.15	3	0.14	0.21	0.03	0.07
5	0.14	0.24	0.04	0.13	5	0.11	0.17	<LOQ	<LOQ
7	0.10	0.14	0.02	0.09	7	0.08	0.11	<LOQ	<LOQ
10	0.06	0.11	<LOQ	<LOQ	10	<LOQ	<LOQ	<LOQ	<LOQ
24	<LOQ	<LOQ	<LOQ	<LOQ	24	<LOQ	<LOQ	<LOQ	<LOQ

Table 3 DT_{50} and DT_{90} values of imidacloprid and bifenthrin in water at different pH conditions with and without catalyst

Insecticide	Milli Q water		Acidic buffer (pH-4.00)		Neutral buffer (pH-7.00)		Basic buffer (pH-9.00)	
	DT_{50} in days (Without catalyst)							
	T_1	T_2	T_1	T_2	T_1	T_2	T_1	T_2
Imidacloprid	3.63	3.12	3.36	3.00	2.66	3.06	2.41	2.54
Bifenthrin	3.55	6.85	3.55	5.69	2.45	5.14	1.50	1.74
	DT_{90} in days (Without catalyst)							
Imidacloprid	12.06	10.36	11.16	9.95	8.83	10.15	8.02	8.44
Bifenthrin	11.78	22.75	11.78	18.89	8.15	17.06	4.99	5.77
Insecticide	Milli Q water		Acidic Buffer (pH-4.00)		Neutral Buffer (pH-7.00)		Basic Buffer (pH-9.00)	
	DT_{50} in hours (With catalyst)							
	T_1	T_2	T_1	T_2	T_1	T_2	T_1	T_2
Imidacloprid	6.18	4.98	5.29	4.28	5.99	4.91	5.93	4.37
Bifenthrin	3.55	5.94	3.55	5.15	3.71	6.17	19.71	14.52
	DT_{90} in hours (With catalyst)							
Imidacloprid	20.52	16.55	17.57	14.23	19.89	16.31	2.10	2.37
Bifenthrin	11.78	19.47	11.78	17.12	12.32	20.49	6.98	7.89

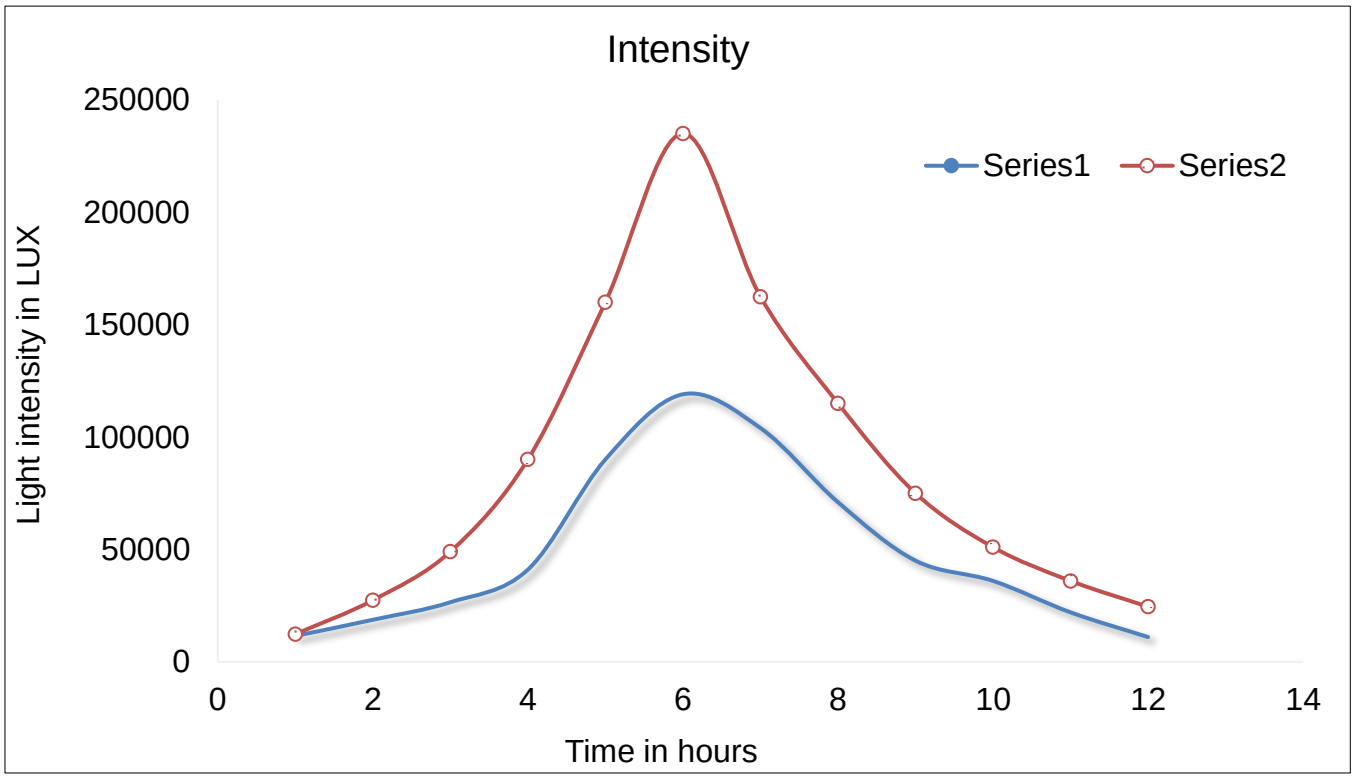

Fig 5 Intensity of light during the study period

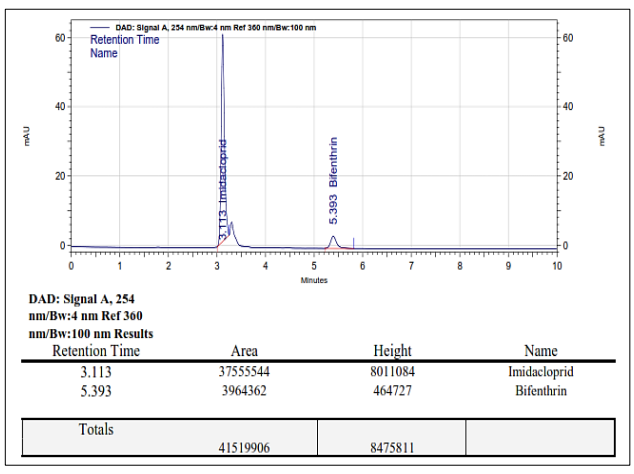

Fig 6 Representative chromatogram of 0th day sample analysis without catalyst

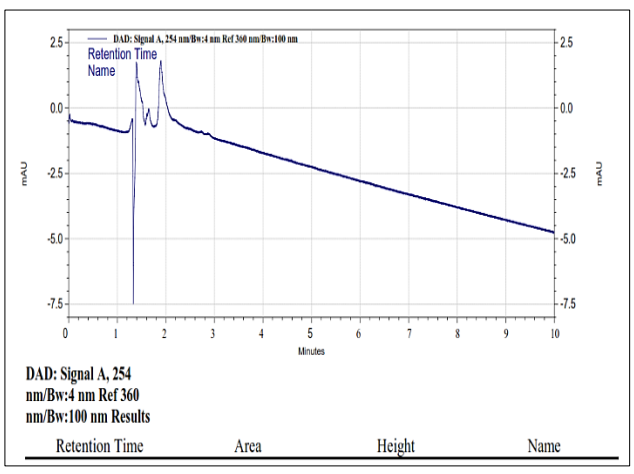

Fig 7 Representative chromatogram of 15th day sample analysis without catalyst

CONCLUSION

The photocatalytic degradation of residues of Imidacloprid and Bifenthrin clearly indicates that the sunlight photolysis was influenced by the addition of the lanthanum doped copper oxide nanoparticles as catalyst. The La doped CuO nanoparticles were observed to be an excellent decontaminating catalyst in different water samples. The basic pH significantly enhanced degradation of pesticides. The lanthanum doped copper oxide nanoparticles was characterized by SEM, EDS, FT-IR and UV-Vis. The compound was identified and quantified by UHPLC-PDA detection. The present study with La doped CuO nanoparticles was found to be effective catalyst in photo catalytic degradation.

LITERATURE CITED

1. Daraghmeh A, Shraim A, Abulhaj S, Sansour R, Ng JC. 2007. Imidacloprid residues in fruits, vegetables and water samples from Palestine. *Environ Geochem Health* 29(1): 45-50.
2. Denet E, Espina-Benitez MB, Pitault I, Thierry, Pollet, Didier Blaha, Marie-Alexandrine Bolzinger, Veronica Rodriguez, Nava, Stéphanie Briançon. 2020. Metal oxide nanoparticles for the decontamination of toxic chemical and biological compounds. DOI: https://doi.org/10.1016/j.ijpharm.2020.119373.
3. Varughese G, Rini V, Suraj SP, Usha KT. 2014. Characterization and optical studies of copper oxide nanostructures doped with lanthanum ions. DOI: .2478/adms-2014-0021.
4. Mehdi Shirzad-Siboni, Ahmad Jonidi-Jafari, Mahdi Farzadkia, Ali Esrafifili, Mitra Gholami. 2016. Enhancement of photocatalytic activity of Cu-doped ZnO nanorods for the degradation of an insecticide: Kinetics and reaction pathways. *Journal of Environmental Management*. 22 October.
5. Nageswara Rao T, Benarji Patrudu, Basaveswara Rao MV, Apparao K. 2016. Degradation study of benalaxyl fungicide residues in different pH waters using ferrous doped titanium dioxide nanoparticles. *Analytical Chemistry: An Indian Journal*. July 25.
6. Prashanthi Y, Rao TN, Sridhar V, Naidu TM. 2016. Photo catalytic applications of zinc oxide nanorods for the analysis of chlorimuron herbicide residues in water by LC-MS/MS. 5(4).
7. Sathiyanarayanan S, Ravi PE, Ramesh A. 2009. Applications of zinc oxide nanorods as photocatalyst for the decontamination of imidacloprid and spirotetramat residues in water. *The Open Catalysis Journal* 2: 24-32.
8. Khan SH, Suriyaprabha R, Pathak B, Fulekar MH. 2015. Photocatalytic degradation of organophosphate pesticides (Chlorpyrifos) using synthesized zinc oxide nanoparticle by membrane filtration reactor under UV irradiation. *Front Nanosci Nanotech*.
9. Rao TN, Patrudu TB, Basaveswara Rao MV, Apparao K, Rao NK. 2016. Photo catalytic applications of ferrous doped titanium dioxide nanoparticles in dissipation kinetics of tricyclazole fungicide residues in different pH waters under direct sunlight. *OSR Journal of Environmental Science, Toxicology and Food Technology* 10(6): 109-115.