

# Rapid photocatalytic degradation of flufenacet and cyflufenamid in aquatic ecosystem by direct sunlight

Saranya B. R.<sup>1</sup>, Sathiyarayanan V.<sup>2</sup> & Maheswari S. T.<sup>3</sup>

<sup>1,3</sup>Department of Analytical Chemistry, International Institute of Biotechnology and Toxicology (IIBAT), Padappai, Chennai, Tamil Nadu - 601 301, India.

E-mail: [maheswariraja@yahoo.com](mailto:maheswariraja@yahoo.com), [bsaranyareddy9@gmail.com](mailto:bsaranyareddy9@gmail.com)

<sup>2</sup> Department of Chemistry, B.S.Abdur Rahman Crescent Institute of Science and Technology, Vandalur, Chennai, Tamilnadu state -600 048, India.

## Abstract:

*Photocatalytic (ZLT, air and solar radiation) degradation of flufenacet and cyflufenamid in aquatic ecosystem by direct sunlight were studied. Lanthanum ion doped nano TiO<sub>2</sub> (LnP) encapsulated in NaY Zeolite pores (1:10) (ZLnp) and then impregnated in Polystyrene film (ZLT) catalyst was synthesized. Catalyst characterization was done by SEM-EDX, TEM and AFM. Results revealed the successful loading of Lanthanum ion doped nano TiO<sub>2</sub> (LnP) inside NaY Zeolite cages. The photocatalytic conditions were carried out at a concentration of 20 mg L<sup>-1</sup> of pesticide, with 0.01M of H<sub>2</sub>O<sub>2</sub> and catalytic amount of 500 mg L<sup>-1</sup> of ZLT under stirred conditions. Based on the results, ZLT showed 40% and 60% degradation of the Flufenacet and Cyflufenamid after 5 hours. Same film models were used in presence of Zebrafish (Danio rerio) and optimized ratio yielded good results. Upon observation the present investigation also revealed that the synthesized catalyst was reusable successfully for six times without any loss in catalytic activity. So, from the above results it was proved that ZLT is an efficient ecofriendly catalyst for the degradation of flufenacet and cyflufenamid in aquatic ecosystem by direct sunlight.*

## Keywords

*Lanthanum ion; NaY Zeolite; Polystyrene film; Photocatalytic degradation; Flufenacet; Cyflufenamid.*

## 1. Introduction

Photocatalysis with the aid of semiconductors has been extensively used worldwide to find solutions to the environmental related problems. The photocatalytic decomposition of the pollutants in waste water is the emerging trends in the green chemistry (Abdullah et al., 1990; Conningham et al., 1994; Fox et al., 1994; Greem and Rudham, 1993; Mattews, 1988a, 1988b, 1990; Ollis and Al-Ekabi,

1993; Sabate et al., 1991, 1992; Serpone and Pelizzetti, 1989; Xu and Chen, 1990). Busca et al., 2008 has reported the removal of many hazardous, toxic, organic pollutants using the effective catalyst from the environment and particularly from waste water. Nano structured materials has proven their key role and got attractive interest for the researchers in the recent years due to their chemical and physical properties and also due to their electron transport properties. Nanocrystalline TiO<sub>2</sub> is a well-known semiconductor with photocatalytic activities and has great potential for environmental applications (Chauhan et al., 2012; Hao et al., 2007; Robichaud et al., 2009; Zou et al., 2013). On the other hand, fast charge carrier recombination and low interfacial charge-transfer rates difficulties were the main drawbacks of using bare TiO<sub>2</sub> (Okte and Yilmaz, 2009). In order to overcome these problems nano-heterogeneous photocatalysis is an advanced oxidation process (AOP) that has been the subject of a huge amount of studies related to water cleaning and disinfection in recent years (Joo et al., 2013; Nezamzadeh-Ejhieh and Zabihi- Mobarakeh, 2014; Suri et al., 2012). Many other researchers have reported the differences in the catalytic activity of TiO<sub>2</sub> with different types of doping metals (Jamalluddin and Abdullah, 2011; Song et al., 2011; Wang et al., 2009). Among various dopants, the lanthanide element have been used as dopant since they are known to increase the catalyst surface area by decreasing crystallite size and the adsorption of the organic reactants by forming complexes via their f-orbitals with various organic Lewis bases, as well as to suppress electron-hole recombination rates due to the presence of Ti<sup>3+</sup> defects at the Ln<sup>3+</sup>-TiO<sub>2</sub> interface (Li et al., 2005; Ranjit et al., 2001; Sibin et al., 2002; Zhang et al., 2004). Doping with La exhibits effective photocatalytic activity for the degradation of organic pollutants under visible light irradiation (Ando et al., 2009; Liqiang et al., 2004; Wu et al., 2006; Zhao et al., 2011). The recycling of nano particles is troublesome and costly in order to solve this problem, researchers have used zeolite as hosts to fix semiconductors because it have

applications in many technological fields such as catalysis and wastewater treatment (Breck, 1974; Katzer, 1977; Rabo, 1976). Encapsulation of  $\text{TiO}_2$  into zeolite was first introduced by Krueger et al. (1990), Liu et al. (1992 and 1993). Unlike other amorphous adsorbents, the zeolites have unique uniform pores and channel sizes (3–8 Å), which provide selective exclusion of molecules or ions. Thus, the zeolites have been used as hosts to entrap nano-sized semiconductors. In this study we have synthesized lanthanum ions doped  $\text{TiO}_2$  encapsulated in Na Y zeolite cages and which was further impregnated in polystyrene film and characterized the film by SEM-EDX, TEM and AFM. Its application was performed by using Flufenacet and Cyflufenamid model pollutants for photocatalytic degradation experiments in aquatic ecosystem.

Flufenacet is an herbicide used as pre-emergence to control annual grasses and some broadleaf weeds in a variety of crops. It displays relatively high solubility in water (56 mg/L) and is particularly stable against photolysis (Pest Management Regulatory Agency, 2003). Its chemical stability along with its mobility enables this herbicide to cause contamination of the ground water via leaching through soil as well as surface water supplies via dissolved run-off and/or erosion (US EPA Pesticide Fact Sheet, 1998). Cyflufenamid is a fungicide used to control powdery mildew on vegetables, fruits and outdoor landscaped and nursery ornamentals. It was classified as “not readily biodegradable” according to a standard test (OECD 301/B) of ready biodegradability following incubation with an activated sludge inoculum (Conclusion on pesticide peer review regarding the risk assessment of the active substance cyflufenamid, 2009). Based on environmental fate properties and its mobility it leads to ground water contamination. It has potential to bioaccumulate in aquatic organisms also toxic to fish and fresh water invertebrates (New Active Ingredient Review July 2012). As the literature regarding these pesticides was limited we had referred the regulatory data as reference. Hence, we developed an effective detoxification method for eliminating these pesticides from water. In addition to the detoxification of flufenacet and cyflufenamid we also here report the fish (*Danio rerio*) acute toxicity of flufenacet, Cyflufenamid during degradation.

## 2. Materials and methods

Titanium tetraisopropoxide (97%) – Aldrich, Ammonia solution (25%) – Merck Limited, Mumbai, 2-propanol (99.5%) – Merck Limited, Mumbai, Lanthanum (III) nitrate (98%) – Alfa aesar, Methanol (99.9%) – Himedia, Dichloromethane (99.5%) – Merck Limited, Mumbai, Tetrahydrofuron (99%) –

Merck Limited, Mumbai, Hydrogen peroxide (30%) – Merck Limited, Mumbai, Acetonitrile (99.9%) – Merck Limited, Mumbai, Hydrogen chloride (35%) – Merck Limited, Mumbai, Polystyrene – Sigma Aldrich, USA.

### 2.1 Physical measurements

The Scanning Electron Micrographs (SEM) of sample was recorded using F E I Quanta FEG 200 High Resolution Scanning Electron Microscope. The Transmission Electron Micrographs (TEM) of samples was recorded using F E I Quanta FEG 200 High Resolution Transmission Electron Microscope (HRTEM). The Atomic Force Micrographs (AFM) of samples was recorded using Agilent Pico LE Scanning Probe Microscope. ICP-OES analysis was performed on a Perkin-Elmer Optima 2000 DV model. Evaporation of was done by using Buchi rotavapour. Mack pharmatech Oven is used for drying of sample. The quantification of residues of pesticides flufenacet and cyflufenamid was done by Shimadzu prominence High Performance Liquid Chromatograph equipped with two pumps (model LC-20AT), oven (CTO-20A), Ultra Violet detector (SPD-20A), and a C18 reverse phase column (25 cm length x 4.6 mm i.d x 5  $\mu$  particle size, Phenomenex). Eluent was a mixture of acetonitrile and water (80:20 v/v) with 1.0 mL/min flow rate, oven temperature 40°C, detection was at 235 nm with an injection volume of 20  $\mu$ L. The peak of flufenacet and cyflufenamid was eluted at 4.9 and 6.0 minutes.

### 2.2 Preparation of film

#### 2.2.1 Preparation of nano particle $\text{TiO}_2$ (np)

$\text{TiO}_2$  powder was prepared by a sol-gel process (Siwinska-Stefanska et al., 2014), in which sol was prepared by mixing titanium tetraisopropoxide (TTIP), 2-propanol, and ammonia at room temperature. 10 cm<sup>3</sup> (0.036 mol) of titanium tetraisopropoxide was dissolved in 80 cm<sup>3</sup> (0.82 mol) of 2-propanol in a round bottom flask and homogenized by stirring for 10 minutes. To the above mentioned mixture 10 ml of ammonia solution was added gradually at a rate of 1 cm<sup>3</sup>/min. The solution changed from being clear to appearing as a white precipitate. After 1 hour stirring 2-propanol was evaporated by buchi rotavapour. At the terminal stage, the sample was dried by convection at 105 °C for 18 h. The sample was then calcined at 600 °C for 2 h.

#### 2.2.2 Preparation of lanthanum ions doped $\text{TiO}_2$ nano particle (Lnp)

1 g (np) was taken in a round bottomed flask containing 20 ml of 2-propanol and was kept over the magnetic stirrer for stirring for about 10 minutes. To the above mentioned mixture 200 mg of Lanthanum (III) nitrate was added and stirred for five hours. The 2-propanol was evaporated by buchi rotavapour. At the terminal stage, the sample was dried by convection at 105 °C for 18 h. The sample was then calcined at 600 °C for 2 h.

### 2.2.3 Preparation of lanthanum ion doped TiO<sub>2</sub> nano particle encapsulation in NaY Zeolite (ZLnp)

500 mg of zeolite was taken in 100 ml round bottom flask containing 30 ml methanol and the mixture was sonicated for 10 minutes. To the above mentioned mixture 50 mg of lanthanum doped nano particles (Lnp) was added and sonicated for 5 hours. Methanol was then evaporated using buchi rotavapour. The residual methanol was removed by drying in the oven at 105 °C for 3 hours.

### 2.2.4 Preparation of ZLnp impregnated polystyrene film (ZLT)

Thin film polystyrene was impregnated with ZLnp by adding 200 mg ZLnp to a 5 % polystyrene in a tetrahydrofuron solution (Saranya et al., 2016). The above mentioned mixture was sonicated for 20 minutes. An aliquot of above mixture was then spread on a uniform smooth surface and the solvent was evaporated in the oven at 50°C for 2 hours. The same procedure was employed without the addition of ZLnp for the preparation of bare polystyrene film.

## 2.3 Design of Degradation experimental Procedure

The selective photocatalytic degradation activities were investigated by employing the catalyst. A total of 4 aquariums tanks sized (60 x 30 x 45cm, lbh) filled with 10 L of water were used for the studies. The aquarium tanks were aerated and nine Zebra fishes (*Danio rerio*) were taken in each aquarium. The first aquarium contained 20 ppm of pesticide solution, ZLT 0.1g and 20 mM of H<sub>2</sub>O<sub>2</sub> added dropwise. The second aquarium contained 20 ppm of pesticide solution and 20 mM of H<sub>2</sub>O<sub>2</sub> added dropwise. The third aquarium was used as a control, without ZLT, pesticide, and of H<sub>2</sub>O<sub>2</sub>. The fourth aquarium contained 20 ppm of pesticide solution, ZLT 0.1g and 20 mM of H<sub>2</sub>O<sub>2</sub> added dropwise in the absence of fish. All fishes were fed with Pinar Yem at a concentration of 1 % of their body mass per day. All the four aquariums were kept under direct sunlight with stirred conditions. The course of

pesticide degradation was monitored at the regular intervals and the pattern of degradation was analyzed using HPLC method.

## 3. Results and discussion

### 3.1 Scanning Electron Microscopy

The SEM images of the ZLT indicated the encapsulation of ZLnp in the bare polystyrene film Figure. 1(a) shows the SEM image at 5µm with 15,000 magnification and Figure. 1(b) shows the SEM image at 5µm with 20,000 magnifications. This confirms that Lnp was preserved inside the cages of the zeolite pores without the leaching of Lnp and protected by the polystyrene film. The EDX spectrum of ZLT shows the presence of different elements on the surface of catalyst such as C, Si, O, Ti, and La. Hence, it was believed that the existence of signals attributed to the elements in these samples indicated the success of metals loading during the preparation method. Carbon is the element of Polystyrene film; Silicon and Oxygen are the main elements of zeolite frame work. In Figure. 2 Titanium and Lanthanum was successfully encapsulated inside the supercages of the zeolite.

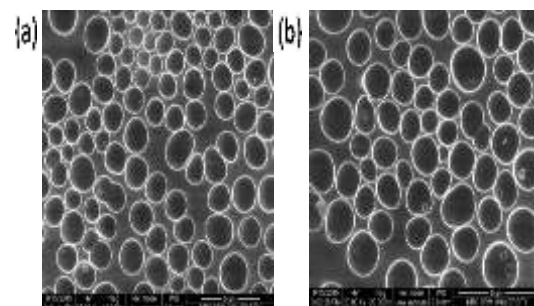


Figure. 1 (a) FE-SEM analysis image at 5µm with 15,000 magnification of ZLT (b) FE-SEM analysis image at 5µm with 20,000 magnification of ZLT

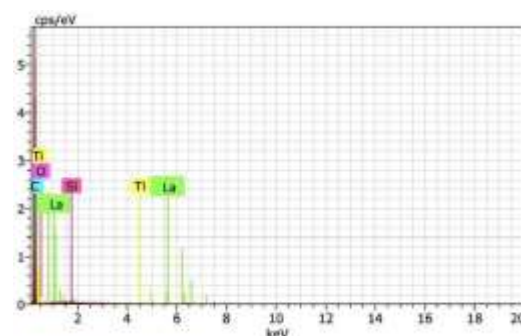


Figure. 2 SEM-EDX Spectrum of ZLT

### 3.2 Transmission Electron Microscopy



### (TEM)

The TEM imaging was carried out for lanthanum ion doped TiO<sub>2</sub> nano particles encapsulated in zeolite impregnated in polystyrene film to examine the metal positions of Ti and La with respect to zeolite structure. Figure. 3 represents the TEM image at different magnifications, were dark and light spots observed on the outer and inner side of the nanoporous structure. The light spots exist between lattice plan of zeolite ascribed to TiO<sub>2</sub> clusters and dark spots at the outer edges ascribe La. Since La has higher molecular weight than Ti. The image shows more dark spots than light due to overlapping of metals with the matrix of zeolite. Similar results have been reported by Atheel Hassan Alwash et al. (2013).

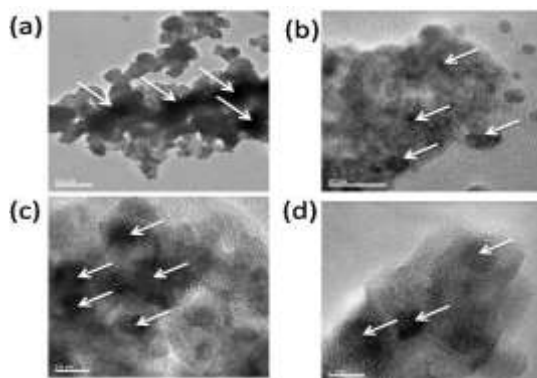


Figure. 3 (a) Tem image of catalyst at 0.2 μm (b) Tem image of catalyst at 20 nm (c) Tem image of catalyst at 10 nm (d) Tem image of catalyst at 5 nm

### 3.3 Atomic Force Microscopy (AFM)

AFM surface analysis requires close consideration since many factors can lead to erroneous results such as the presence of deformation, presence of artifacts in the image due to the tip and/or contamination. The choice of operating mode – no contact or contact – is among these important factors. In contact mode, the probe is placed in contact with the surface; in this case, the force between the tip and the sample can cause irreversible damage to the polymer film (Brushan et al., 2003). Thus, it is suitable to use only the non-contact mode, since in the non-contact mode the tip is placed very close to, but not in contact with, the sample (Brushan et al., 2003). Figure. 4 shows AFM images of polystyrene film, area analyzed was 2 μm × 2 μm. It can be seen on the surface of the images the topography of the polymer is fairly regular (Figure. 4a). The image with a profile (Figure. 4c) was traced in the roughness, which shows a RMS value of 0.8946 in the surface topography of the polystyrene film impregnated with Lnp. These high rough and porous surfaces of La-doped TiO<sub>2</sub> are beneficial to enhance the

Photocatalytic activity for the degradations of organic pollutants present in aqueous solution (Abou-Helal and Seeber, 2002).

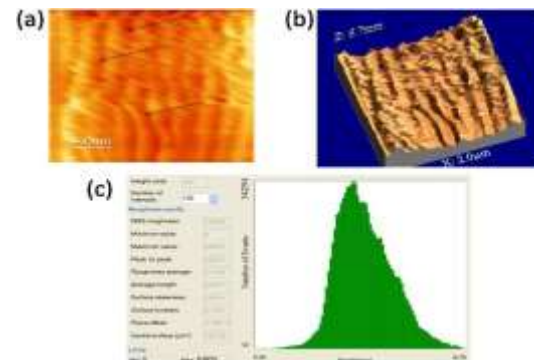


Figure. 4 (a) Two dimensional image of catalyst at 400nm (b) Three dimensional image of catalyst (c) Roughness image of the catalyst

### 3.4 Catalytic Activity

The photocatalytic activity of the newly fabricated ZLT was conducted in aquatic system for the degradation of pesticide flufenacet and cyflufenamid in the presence of Zebra fish. There was a constant decrease in the both the pesticides concentration during every interval of the sample collection. The HPLC analysis shown in Figure. 5 and Figure. 6 revealed the photocatalytic degradation pattern of pesticide flufenacet and cyflufenamid. The influence of the catalyst was studied by comparison of the experiment with and without ZLT in the tank under identical conditions. A sluggish degradation profile was observed for the sample intervals and also the pesticide flufenacet and cyflufenamid concentration existed more than 90 %, even after two days. Catalyst reproducibility was estimated by conducting the experiment with presence of catalyst for six replicates. Concordance was achieved for the reproducibility experiments. In addition to its reusability, the catalyst was also easily recoverable under all conditions; even after more than three cycles it was reused without any degeneration. Assessment of fish acute toxicity of catalyst was conducted with high amount of catalyst loaded in the tank in presence of Zebra fishes for a week and found no visible abnormalities such as loss of equilibrium, swimming behavior, respiratory function, and pigmentations as per OECD Guideline No. 203. In addition, leaching of the impregnated zeolite was tested by soaking the ZLT in the 0.1M Hydrochloric acid for 2 hours at 40°C. The collected samples were analyzed in ICP-OES which showed less the 0.01 ppm of silica and 0.0003 ppm of Titanium in solution. Therefore the toxicity of the

metal was decreased due to its excellent encapsulation during the fabrication process. The DT<sub>50</sub> values of pesticides flufenacet and cyflufenamid were 3.17 and 2.48 hours shown in Table 1 and Table 2. The influence of hydrogen peroxide showed no significant decrease of DT<sub>50</sub> value but in presence of catalyst with a dropwise addition of the hydrogen peroxide yielded very rapid degradation of 40% and 60% of the Flufenacet and Cyflufenamid after 5 hours. Further, any abnormalities and mortality to fish was assessed and was observed during and even after the completion of the experiment, all the fishes were alive and active. Upon observation of fishes even after a month of completion of experiment the same result was noticed.

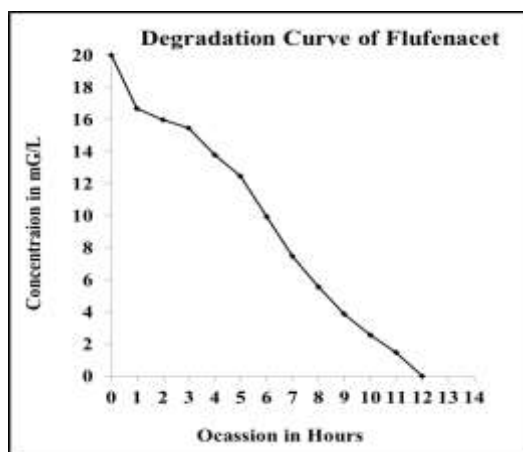


Figure. 5 Degradation curve of Flufenacet

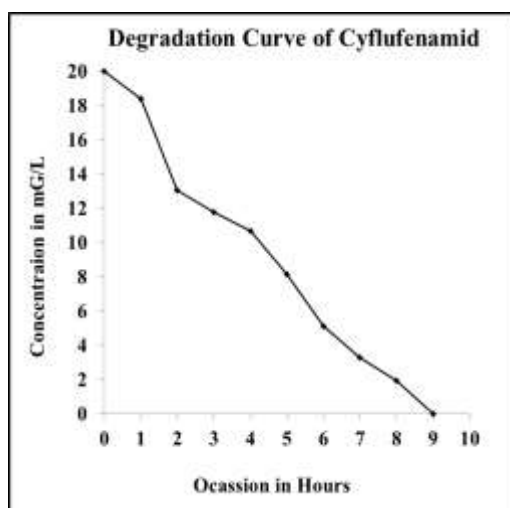


Figure. 6 Degradation curve of Cyflufenamid

Table 1. DT<sub>50</sub> values of Flufenacet

Hours	Concentration (Mg/L)	Log of Concentration
0	20.000	1.3010
1	16.682	1.2222
2	15.958	1.2030
3	15.472	1.1896
4	13.793	1.1397
5	12.467	1.0958
6	9.932	0.9970
7	7.477	0.8737
8	5.561	0.7451
9	3.868	0.5875
10	2.553	0.4070
11	1.485	0.1718
12	0.000	0.0000
<b>Slope</b>		<b>-0.0951</b>
<b>DT<sub>50</sub></b>		<b>3.17 h</b>

Table 2. DT<sub>50</sub> values of Cyflufenamid

Hours	Concentration (Mg/L)	Log of Concentration
0	20.000	1.3010
1	18.390	1.2646
2	13.062	1.1160
3	11.786	1.0714
4	10.691	1.0290
5	8.138	0.9105
6	5.120	0.7093
7	3.287	0.5168
8	1.923	0.2841
9	0.000	0.0000
<b>Slope</b>		<b>-0.1214</b>
<b>DT<sub>50</sub></b>		<b>2.48 h</b>

#### 4. Conclusion

The novelty of the present investigation concludes that the synthesized catalyst has greater impact on the serious pollutant such as pesticide residue. It was also found that the ZLT acted as a heterogeneous catalyst, which is an efficient catalyst for the Photo catalytic degradation of pesticides flufenacet and cyflufenamid under direct sunlight for aquatic system with stirred condition. Excellent reproducible results were obtained when tested for the catalyst reusability. The observed DT<sub>50</sub> values were 3.17 and 2.48 hours for flufenacet and cyflufenamid in presence of catalyst. We also made an attempt to demonstrate the fish acute toxicity of Catalyst as per the OECD Guideline No. 203. Based on the results of our study, it could be concluded that ZLT is non-toxic and as well as toxicity reducing species of pesticides flufenacet and cyflufenamid to aquatic species.

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