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Investigation of Photocatalytic Degradation of Diuron, Flufenacet and Cyflufenamid in Natural Waters

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ABSTRACT

The pesticides which were used in agricultural applications and the residues enters surface waters, creates environmental and health concerns. Thus, use of photo reactive catalyst has shown promise for contaminant control and surface water remediation. However, investigation has been done on impact of photolytic as well as photocatalytic degradation process of pesticides diuron, flufenacet and cyflufenamid respectively with the natural waters. Physico chemical characteristics, microbial count was investigated for the samples collected from three locations. Results signify the selectivity and the effectiveness of the catalyst. The impact of bacteria was less on the degradation of pesticides.

***Key words*:** Photocatalysis, Diuron, Flufenacet, Cyflufenamid, Natural waters

Among the various organic substances, which were known as water pollutants, pesticides are a major pollution sources for both underground and surface waters [1]. Photocatalytic oxidation is considered as one of the promising technologies for the elimination of toxic organic pollutants. Investigations on the photocatalytic oxidation of pesticides in aqueous media irradiated by UV radiation have been a rapidly growing field of research [2]. Now a days interest has been focused on the use of semiconductor materials as photocatalysts for the removal of organic and inorganic species from aqueous [3]. One of the most effective methods for elimination of many hazardous, toxic, organic pollutants from the environment and particularly from wastewater is their photocatalytic degradation in the presence of catalyst particles [4]. Photocatalytic degradation holds promise for dealing with aquatic contamination [5-11]. The photocatalytic degradation of some pesticides was studied in different natural waters (sea, river and lake) as well as in distilled water under natural sunlight and simulated irradiation [12-13]. In the present work, we studied Photocatalytic degradation of pesticides diuron, flufenacet and cyflufenamid in different natural waters – Impact of bacteria on degradation. The aim of this work was to check the influence of the catalyst in the degradation of pesticides in natural waters and the impact of bacteria on the degradation of pesticides.

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MATERIALS AND METHODS

Materials

Experiments were performed with the catalyst "Lanthanum ions doped TiO_2 nanoparticles encapsulated NaY zeolite impregnated in polystyrene film" synthesized by Saranya *et al*. [14]. Acetonitrile of purity 99.9% supplied by Merck limited, Mumbai. Hydrogen peroxide (30%) supplied by Merck limited, Mumbai. Hi media Nutrient agar (Peptone - 5g/L, HM Peptone B - 1.5g/L, Yeast extract - 1.5g/L, Sodium chloride - 5g/L, Agar - 15.0 g/L). Deionized water - 1000 mL.

Instrument and apparatus

The pH of the all the samples were measured by pH using Hanna digital pH meter. conductivity was measured using Cyberscan CON11-Eutech conductivity meter, dissolved oxygen by using Hanna-HI 9146 dissolved oxygen meter, Metrohm ion chromatography was used to analyze ions such as NO_3^-, SO_4^{-2}, PO_4^{-3}, SO_4^+, Cl^-, Na^+, K^+. Media and water samples of 3 lakes were sterilized by using Autoclave of model LAC 3. Addition of samples into petri-plates was done in Laminar air flow chamber of model ASH – 1200 F to maintain aseptic condition. Magnetic stirrer of model Spinit Flat Type – Tarson 4050 was used to mix the media Cyclo mixer of model CM – 101 was used to mix the sample Incubator of model LSI 2 was used for incubation of agar plates. The quantification of residues of pesticides

diuron, flufenacet and cyflufenamid respectively were done by Shimadzu prominence High Performance Liquid Chromatography equipped with two pumps (model LC-20AT), oven (CTO-20A), Ultra Violet detector (SPD-20A), and a C18 reverse phase column (25 cm length × 4.6 mm i.d × 5 µ 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 µL. The peak of diuron, flufenacet and cyflufenamid respectively were eluted at 4.6, 4.9 and 6.0 minutes respectively.

Methods

Collection of water sample

Water samples were collected in pre-washed polyethylene bottles from three locations Puzhal (Tamil Nadu) Latitude: 13.1667°N; Longitude: 80.1715°E), Kolavai (Tamil Nadu) Latitude: 12.7104°N; Longitude: 79.9892°E) and Madurantakam lake (Tamil Nadu) Latitude: 12.5245°N; Longitude: 79.8717°E). The total amounts of collected waters were separated to two equal aliquots for un-sterilization and sterilization process.

Physico - chemical properties of natural water

Analyzed physical-chemical properties of natural water such as colour by visual appearance, pH using Hanna digital pH meter, conductivity using Cyberscan CON11-Eutech conductivity meter, dissolved oxygen by using Hanna-HI 9146 dissolved oxygen meter, total hardness estimation by EDTA method [15], total organic carbon (TOC) by titration method [16], Metrohm ion chromatography was used to analyze ions such as NO_3^-, SO_4^{-2}, PO_4^{-3}, SO_4^+, Cl^-, Na^+, K^+. The collected water samples were analyzed for the pesticide residues using LC-MS/MS technique with the respective mass transition.

Sterilization of samples collected

Test vessels and all the water samples collected from three different lakes were labeled and sterilized using autoclave at about 15 lb/in^2 for 15 minutes.

Sample preparation and application

A total of 36 aquarium tanks sized (60 × 30 × 45cm, lbh) 12 for each location respectively were used for the experiment. Six aquariums were used for sterile and six aquariums were used for unsterile water samples. Three aquarium tanks contained 5 L of unsterile water, 20 mg/L of selected pesticides (diuron, flufenacet and cyflufenamid) in each tank respectively and 0.01M of H_2O_2 added dropwise. Three aquarium tanks contained 5 L of sterile water, 20 mg/L of selected pesticides in each tank respectively and 0.01M of H_2O_2 added dropwise. Three aquarium tanks contained 5 L of unsterile water, 20 mg/L of selected pesticides in each tank respectively, ZLT 100 mg/L and 0.01M of H_2O_2 added dropwise. Three aquarium tanks 5 L of sterile water, 20 mg/L of selected pesticides in each tank respectively, ZLT 100 mg/L and 0.01M of H_2O_2 added dropwise. All the aquariums were kept under direct sunlight in unstirred condition. The course of the degradation was monitored at the regular intervals and the pattern of degradation was analyzed using HPLC method.

Impact of bacteria on pesticide degradation

Pesticide's degradation in natural waters was done under unsterile and sterile condition, to find the impact of bacteria on degradation of pesticides and also to determine the efficiency of catalyst. Sterility check was done for initial and final hour samples.

Preparation of culture medium - Nutrient agar (NA) composition (As per imedia container)

Required quantity of nutrient agar medium (28 g/L) was prepared by weighing known quantity of nutrient agar medium and made up with deionized water. The media pH was adjusted to 7.44 and after pH adjustment the media was sterilized using autoclave at about 15 lb/in^2 for 15 minutes. Inoculation and Incubation of Culture - Technique Used: Serial Dilution and Pour Plate Method [17].

Sterility check was performed for samples mentioned with codes in (Table 1). Test system was treated with sterile (autoclaved) and unsterile (collected water as such) water collected from 3 different places during the study. Single set of sample dilutions were prepared for the test. One mL of sample was taken and mixed with 9 mL of sterile deionized water (10^{-1} dilution) water and thoroughly mixed using the cyclo mixer. One mL of the suspension thus obtained was further diluted into a test tube containing 9 mL of sterile distilled water (10^{-2} dilutions) and serially diluted up to 10^{-3} dilutions.

One mL of suspension from 10^{-1} to 10^{-3} dilutions was taken out using a micropipette and transferred into sterilized Petri-plates aseptically, using laminar air flow. Approximately 20 mL of sterilized nutrient agar medium was uniformly poured in to Petri-plates and gently rotated the plates for uniform mixing of sample with the medium under laminar airflow and allowed to solidify. After solidification, all the agar plates were incubated in an incubator (inverted position). Triplicates were maintained for test samples and for control (medium alone), two replications were maintained. These plates were labeled with the inoculation date and were kept inverted position in the incubator at 35 ± 2°C for two days. After incubation, all the Petri-plates were enumerated for microbial contaminants. The number of colonies was calculated by following formula:

$$\text{No. of colonies count per g/mL} = \frac{\text{No. of colonies in agar plate (Avg. of replication plates)}}{\text{Volume of culture suspension plated}} \times \text{Dilution factor}$$

Table 1 Sample details with codes

Location	Diuron	Flufenacet	Cyflufenamid
Puzhal	1a	1b	1c
Kolavai	2a	2b	2c
Madurantakam	3a	3b	3c

Water samples results

Physico-chemical results of collected water samples were mentioned in (Table 2).

Photolytic degradation (without catalyst)

Experiments were made in order to know the photolytic degradation of selected pesticides in natural waters collected from different lakes under unsterile and sterile conditions. The DT_{50} results were presented in (Table 3) which indicates very slow mineralization of selected pesticides in both unsterile and sterile natural waters of three different locations. The dissipation graphs were presented in (Fig 1-3).

Table 2 Physico-chemical results of different natural waters

Physical properties						
Water sample	Colour	pH	Conductivity (µs cm^{-1})	Dissolved Oxygen	Total hardness	Total organic carbon
Puzhal	Colourless	7.9	250	85	308	1.44
Kolavai	Slightly pale yellow	5.9	241	80	374	1.63
Madurantakam	Slightly pale green	6.2	238	87	205	1.15

Chemical properties							
Water sample	NO_3^- (mg/L)	SO_4^{-2} (mg/L)	PO_4^{-3} (mg/L)	SO_4^+ (mg/L)	Cl^- (mg/L)	Na^+ (mg/L)	K^+ (mg/L)
Puzhal	60	12	0.05	0.52	280	150	15
Kolavai	42	60	0.08	0.18	320	210	32
Madurantakam	12	5	0.01	0.13	50	20	4

Table 3 DT_{50} results of photolytic degradation of pesticides

Pesticide	Puzhal		Kolavai		Madurantakam	
	Unsterile (Hours)	Sterile (Hours)	Unsterile (Hours)	Sterile (Hours)	Unsterile (Hours)	Sterile (Hours)
Diuron	1178.75	1225.19	1191.61	1284.71	1163.57	1207.97
Flufenacet	1935.44	1989.91	1963.68	1984.28	1960.01	1974.23
Cyflufenamid	1606.23	1638.77	1614.35	1678.69	1546.38	1628.44

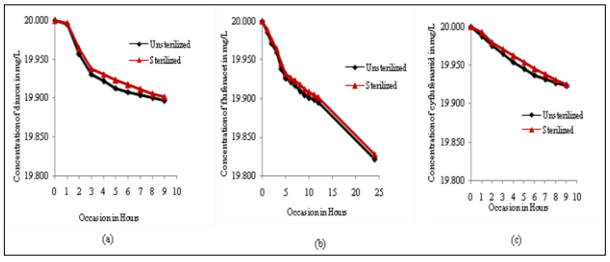


Fig 1 Dissipation graph of (a) Diuron; (b) Flufenacet; (c) Cyflufenamid in Puzhal lake samples

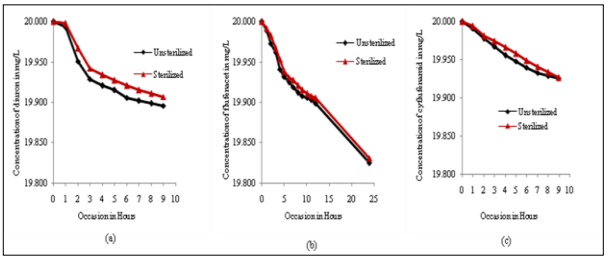


Fig 2 Dissipation graph of (a) Diuron; (b) Flufenacet; (c) Cyflufenamid in Kolavai lake samples

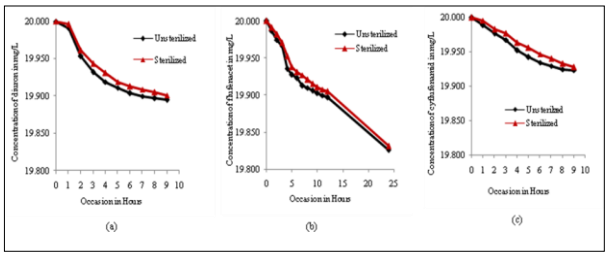


Fig 3 Dissipation curve of (a) Diuron; (b) Flufenacet; (c) Cyflufenamid in Madurantakam lake samples

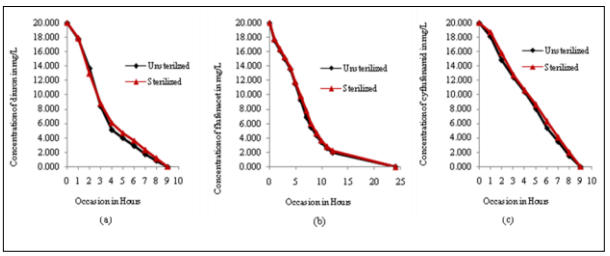


Fig 4 Dissipation graph of (a) Diuron; (b) Flufenacet; (c) Cyflufenamid in Puzhal lake samples

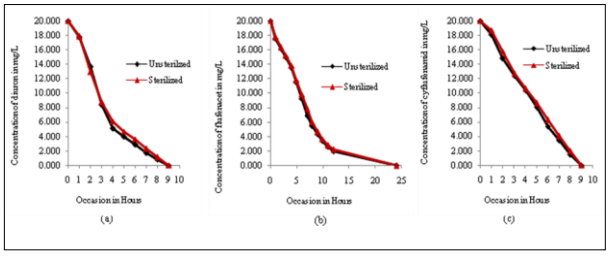


Fig 5 Dissipation graph of (a) Diuron; (b) Flufenacet; (c) Cyflufenamid in Kolavai lake samples

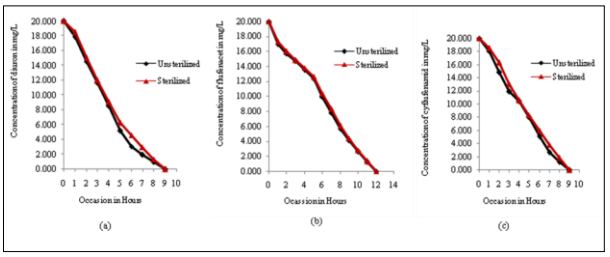


Fig 6 Dissipation graph of (a) Diuron; (b) Flufenacet; (c) Cyflufenamid in Madurantakam

Photocatalytic degradation

The photocatalytic degradation of selected pesticides was studied in natural waters collected from different lakes under unsterile and sterile conditions. The DT_{50} results were presented in (Table 4). From the results it was observed that the presence of catalyst shows the enhanced degradation of selected pesticides in three location water samples. Pronounced degradation of selected pesticides observed in presence of catalyst which were acknowledge from the DT_{50} values. The higher efficiency of photocatalytic degradation was observed when compared with photolytic degradation of pesticides. The dissipation graphs were presented in (Fig 4-6).

Table 4 DT_{50} results of photocatalytic degradation of pesticides

Pesticide	Puzhal		Kolavai		Madurantakam	
	Unsterile (Hours)	Sterile (Hours)	Unsterile (Hours)	Sterile (Hours)	Unsterile (Hours)	Sterile (Hours)
Diuron	1.68	1.96	1.76	1.98	1.83	2.16
Flufenacet	3.06	3.82	3.52	3.69	3.12	3.22
Cyflufenamid	2.12	2.36	2.32	2.56	2.13	2.48

Table 5 Bacterial count data of unsterile initial hour samples

Dilution factor	Mean No. of microbial / bacterial pathogenic colonies*								
	1a	1b	1c	2a	2b	2c	3a	3b	3c
10^{-1}	252	181	165	247	201	154	215	181	149
10^{-2}	185	136	125	180	101	54	183	132	118
10^{-3}	8.67	7.33	6.33	7.33	5.00	1.67	61.33	69.00	87.33
Dilution factor	No. of colonies/mL ($\times 10^3$)*								
10^{-1}	2.52	1.81	1.65	2.47	2.01	1.54	2.15	1.81	1.49
10^{-2}	18.50	13.57	12.53	18.03	10.07	5.43	18.27	13.23	11.77
10^{-3}	8.67	7.33	6.33	7.33	5.00	1.67	61.33	69.00	87.33
Total	29.69	22.71	20.52	27.84	17.08	8.64	81.75	84.04	100.59
Mean	9.90	7.57	6.84	9.28	5.69	2.88	10.21	7.52	6.63

*Mean of three replicates

Table 6 Bacterial count data of unsterile final hour samples

Dilution factor	Mean No. of microbial / bacterial pathogenic colonies*								
	1a	1b	1c	2a	2b	2c	3a	3b	3c
10^{-1}	253	160	165	248	197	163	215	181	147
10^{-2}	175	131	118	171	122	52	183	132	114
10^{-3}	15.33	8.33	13.00	12.67	8.00	3.67	61.33	69.00	82.67
Dilution factor	No. of colonies/mL ($\times 10^3$)*								
10^{-1}	2.53	1.60	1.65	2.48	1.97	1.63	2.15	1.81	1.47
10^{-2}	17.53	13.07	11.83	17.10	12.17	5.23	18.27	13.23	11.37
10^{-3}	15.33	8.33	13.00	12.67	8.00	3.67	61.33	69.00	82.67
Total	35.39	23.00	26.48	32.25	22.14	10.53	81.75	84.04	95.50
Mean	11.80	7.67	8.83	10.75	7.38	3.51	27.25	28.01	31.83

*Mean of three replicates

Table 7 Bacterial count data of sterile initial samples

Dilution factor	Mean No. of microbial / bacterial pathogenic colonies*								
	1a	1b	1c	2a	2b	2c	3a	3b	3c
10^{-1}	0	0	0	0	0	0	0	0	0
10^{-2}	0	0	0	0	0	0	0	0	0
10^{-3}	0	0	0	0	0	0	0	0	0
Dilution factor	No. of colonies/mL ($\times 10^3$)*								
10^{-1}	0	0	0	0	0	0	0	0	0
10^{-2}	0	0	0	0	0	0	0	0	0
10^{-3}	0	0	0	0	0	0	0	0	0
Total	0	0	0	0	0	0	0	0	0
Mean	0	0	0	0	0	0	0	0	0

*Mean of three replicates

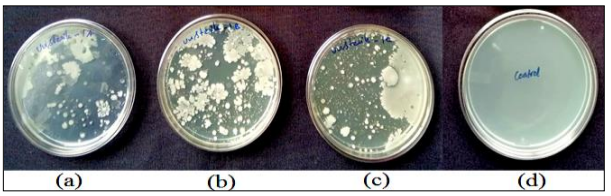
Table 7 Bacterial count data of sterile final samples

Dilution factor	Mean No. of microbial / bacterial pathogenic colonies*								
	1a	1b	1c	2a	2b	2c	3a	3b	3c
10^{-1}	0	0	0	0	0	0	0	0	0
10^{-2}	0	0	0	0	0	0	0	0	0
10^{-3}	0	0	0	0	0	0	0	0	0
Dilution factor	No. of colonies/mL ($\times 10^3$)*								
10^{-1}	0	0	0	0	0	0	0	0	0
10^{-2}	0	0	0	0	0	0	0	0	0
10^{-3}	0	0	0	0	0	0	0	0	0
Total	0	0	0	0	0	0	0	0	0
Mean	0	0	0	0	0	0	0	0	0

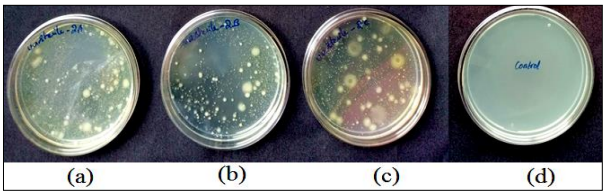
*Mean of three replicates

Impact of bacteria on pesticide degradation

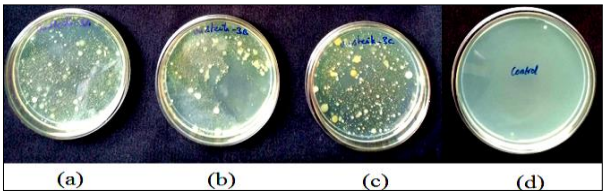
The results of bacterial Colony Forming Unit (CFU) count for unsterile samples were presented in (Table 5-6) and sterile samples were presented in (Table 7-8). Results revealed that photocatalytic degradation of selected pesticides in unsterile condition does not have any significant difference. in comparison with sterile condition, assistance of microbial degradation was absent in both cases for all the waters respectively. The images of microbial colonies formed in unsterile waters were mentioned in (Fig 7). Images of sterile samples which do not show any growth of microbial colonies were presented in (Fig 8).



Puzhal lake samples

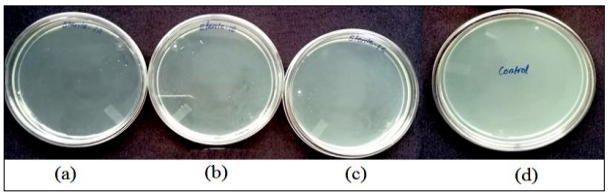


Kolavai lake Samples

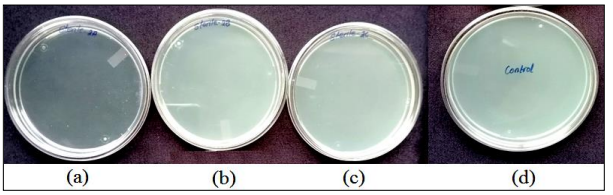


Madurantakam lake samples

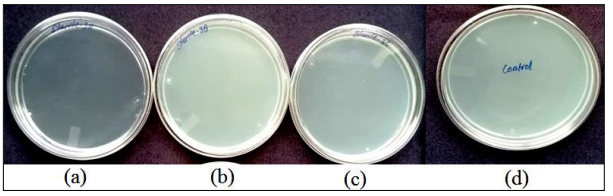
Fig 7 The experimental images of unsterile water samples a) Diuron; (b) Flufenacet; (c) Cyflufenamid; (d) Control medium



Puzhal lake samples



Kolavai lake Samples



Madurantakam lake samples

Fig 8 The experimental images of sterile Water samples a) Diuron; (b) Flufenacet; (c) Cyflufenamid; (d) Control medium

CONCLUSION

In the current investigation the photocatalytic degradation of pesticides (diuron, flufenacet and cyflufenamid) in different natural waters and the assistance of microbial degradation were determined. Fruitful results have been obtained for the conducted experiment and that we conclude the photocatalytic degradation was more efficient than the photolytic degradation of these pesticides in natural water. The impact of microbial degradation is less pronounced rather than the photocatalytic activity for the degradation of pesticides dominants.

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