Comparative study as pH effect on photocatalytic degradation of Diuron, Flufenacet and Cyflufenamid

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ABSTRACT: : *Theinfluence of pH on the photocatalytic degradation of three pesticides: Diuron, Flufenacet and Cyflufenamid has been analyzed. The photocatalytic degradation of 20 mg L^{-1} concentration of pesticides in different buffers (pH 4, pH 7 and pH 9) was performed by using catalytic amount of 0.1g/L of ZLT and dropwise addition of 0.01M H2O2 under stirred condition. The degradation percent of diuron was 40%, 56%, 75% after 2 hours flufenacet was 27%, 35%, 49% and cyflufenamid was 31%, 35%, 50% after 4 hours in pH 4, pH 7 and pH 9 buffers respectively. Results reveal that alkaline buffer (pH 9) has more effect on degradation of all the three pesticides than in neutral (pH 7) and acidic buffers (pH 4).*

Key Words: *pH; Photocatalytic degradation; Diuron; Flufenacet; Cyflufenamid.*

Introduction

At present, pesticides used in agriculture have posed environmental problems such as soil and underground water contaminations these are also a harmfulchemicals that affects human health and equilibrium of ecosystems. Apart from lixiviates coming from agricultural fields, the washing of pesticide containers and the lack of treatment for the solutions also contribute to this problem, producing highly polluted effluents that should be treated before their disposal in the environment [1-2]. Most herbicides, insecticides and fungicides perform best in slightly acidic water. The pH also can change the chemical charge of a pesticide molecule, limiting its ability to penetrate the leaf cuticle and reach the site action, hence reducing its efficacy. Diuron (N-(3,4-dichlorophenyl)-N,N-dimethyl-urea) is an herbicide which belongs to the phenylamide family and to the subclass phenylurea. It represents an important class of contact herbicides that have been used worldwide for more than 40 years [3]. Regardless of its low solubility, diuron can slowly penetrate through soil and become a serious contamination in underground and surface water because of its potent toxicity and great chemical stability [4-6]. Diuron contamination has become a very serious environmental problem in many countries [7-9]. Flufenacet is an herbicide applied as pre-emergence to control annual grasses and some broadleaf weeds in a variety of crops. Due to its chemical stability along with mobility it causes contamination of the ground water via leaching through soil as well as surface water supplies via dissolved run-off and/or erosion [10]. Cyflufenamid acts as both a protective and curative fungicide used to control powdery mildew on vegetables, fruits and outdoor landscaped and nursery ornamentals. Its environmental fate and mobility leads to ground water contamination and it has potential to bioaccumulate in aquatic organisms. It is "not readily biodegradable" according to a standard test (OECD 301/B)[11] of ready biodegradability following incubation with an activated sludge inoculum. In the present work we have investigated the photocatalytic degradation of three pesticides: diuron, flufenacet, cyflufenamid and effect of pH on the degradation rate of the pesticides. Similar experiments were conducted for these pesticides in the presence of catalyst (ZLT) in aquatic ecosystem and proved ZLT is non-toxic and as well as toxicity reducing species of pesticides: diuron, flufenacet, cyflufenamid, respectively [12-13]. This paper presents the results of a study regarding the photocatalytic degradation of selected pesticides in buffers.

Materials and methods

Materials

Acetonitrile, Potassium biphthalate, Sodium phosphate dibasic, Potassium phosphate monobasic, Sodium tetraborate and Hydrogen peroxide were purchased from Merck specialties, Mumbai. All chemicals were used as received with no further purification.

Physical measurements

The quantification of residues of pesticides 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 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; detector was at 235 nm with an injection volume of 20 µL. The peak of diuron, flufenacet and cyflufenamid was eluted at a retention time of 4.6, 4.9, 6.0 minutes.

Methods

Preparation of different pH buffers

pH 4 - Dissolved 50.60 g of Potassium biphthalate (0.05 M) in 5000 ml of water.

pH 7 - Dissolved 17.65 g of Sodium phosphate dibasic (0.05M) and 16.95 g of Potassium phosphate monobasic (0.05M) in 5000 ml of water.

pH 9 - Dissolved 19.0 g of Sodium tetraborate (0.01 M) in 5000 ml of water.

Design of Degradation experimental procedure

The design of degradation experiment (Fig. 1) consisted of aquarium tank sized 60 x 30 x 45cm (lbh) each filled with 5 L of buffer of pH4, pH7, pH9 for all the three pesticides (diuron, flufenacet, cyflufenamid), 20 ppm of pesticide solution, ZLT 0.5g and 20 mM of H_2O_2 added dropwise. All the aquariums were kept under direct sunlight with stirring. The course of the degradation was monitored at the regular intervals and the pattern of degradation was analyzed using HPLC method.

Results and discussion

The image of synthesized catalyst (ZLT) (Fig. 2) which was prepared by a combination of Lanthanumions doped TiO_2 nanoparticles encapsulated in NaY Zeolite and impregnated in polystyrene film (ZLT), respectively [12]. The pH selective efficient on the photocatalytic degradation of three pesticides was conducted in buffers of pH 4, pH 7 and pH 9. The pesticide concentration in all the three buffers of pH 4, pH 7, pH 9 during every interval of the sample collection shows constant degradation of pesticide. The degradation percent of diuron was 40%, 56%, 75% after 2 hours, flufenacet was 27%, 35%, 49% after 4 hours and cyflufenamid was 31%, 35%, 50% after 4 hours in pH 4, pH 7 and pH 9 buffers respectively. Fig. 3-5 represents the degradation curve of all the pesticides (diuron, flufenacet, cyflufenamid) in pH 4, pH 7 and pH 9 buffers. Table 1-3 represents the DT_{50} values of the pesticides (diuron, flufenacet, cyflufenamid) in pH 4, pH 7 and pH 9 buffers. Experimentally the results showed highest degree of degradation for all the three pesticides in pH 9 (alkaline buffer) when compared with pH 7(neutral buffer) and pH 4(acidic buffer) with a DT_{50} values of 2.03, 1.52 hours, 44.57 minutes for diuron, 4.84, 3.46, 1.84 hours for flufenacet and 3.92, 2.78, 1.57 hours for cyflufenamid in pH 4, pH 7 and pH 9. The influence of hydrogen peroxide showed no significant decrease of DT_{50} value but in presence of catalyst with a dropwise addition of the hydrogen peroxide yielded very rapid degradation of pesticides.

Conclusions

In this study we compared the pH effect on photocatalytic degradation of three pesticides: diuron, flufenacet, cyflufenamid. From the results it was observed that highest degradation percent for all the three pesticides seen in pH 9 (alkaline buffer) when compared with pH 7(neutral buffer) and pH 4(acidic buffer). Based on the DT_{50} results 2.03, 1.52 hours, 44.57 minutes for diuron, 4.84, 3.46, 1.84 hours for flufenacet, 3.92, 2.78, 1.57 hours for cyflufenamid in pH 4, pH 7 and pH 9, it could be concluded that ZLT is an efficient and selective catalyst at pH 9 buffer when compared to pH 4 and pH 7 buffers. The degradation pattern was in the manner of pH 9 > pH7 > pH4.

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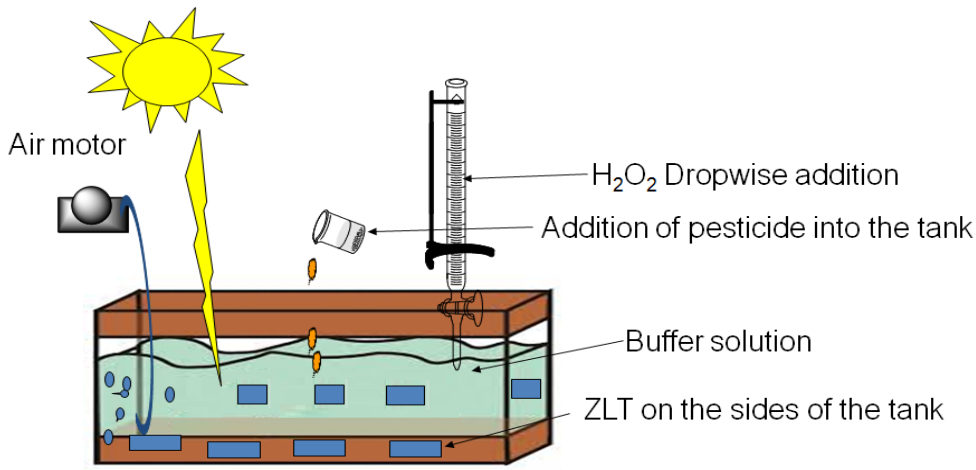

Fig. 1 Design of the experiment

Fig. 2 Image of the synthesized catalyst (Lanthanum ions doped nano TiO_2 encapsulated in NaY Zeolite and impregnated in a polystyrene film)

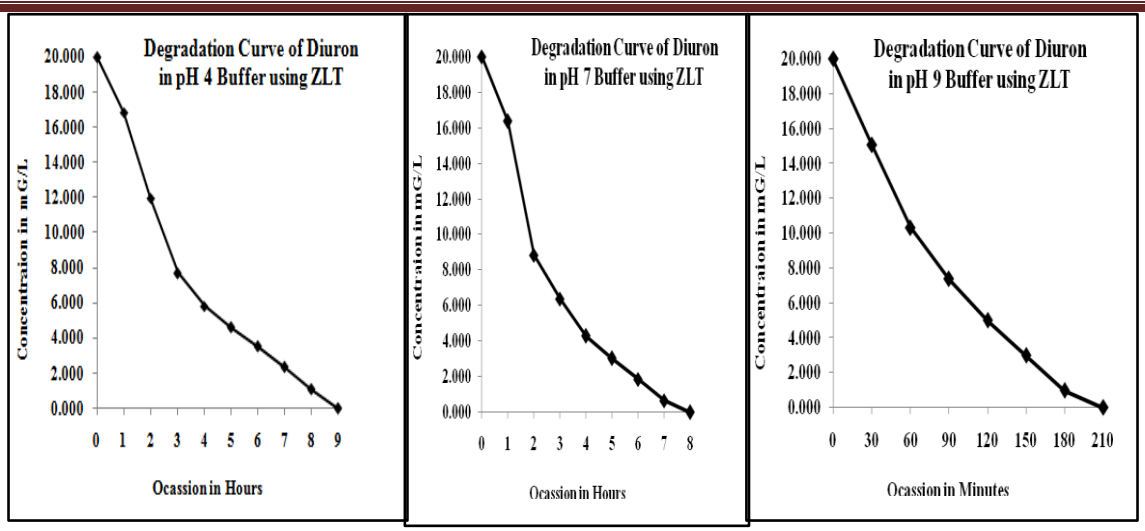

Fig. 3 Degradation curve of Diuron in pH 4, 7 and 9 buffers using ZLT

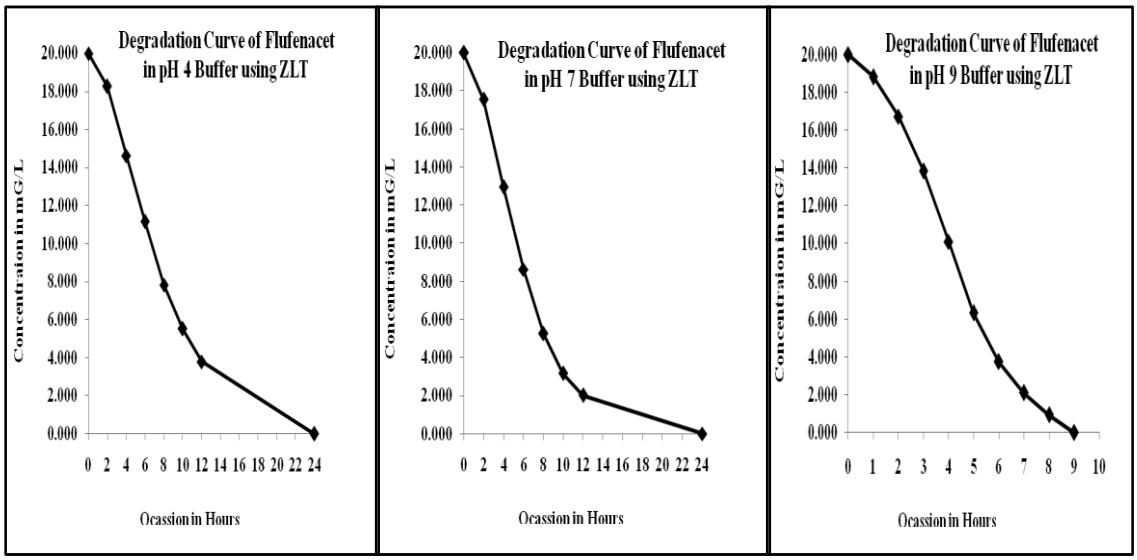

Fig. 4 Degradation curve of Flufenacet in pH 4, 7 and 9 buffers using ZLT

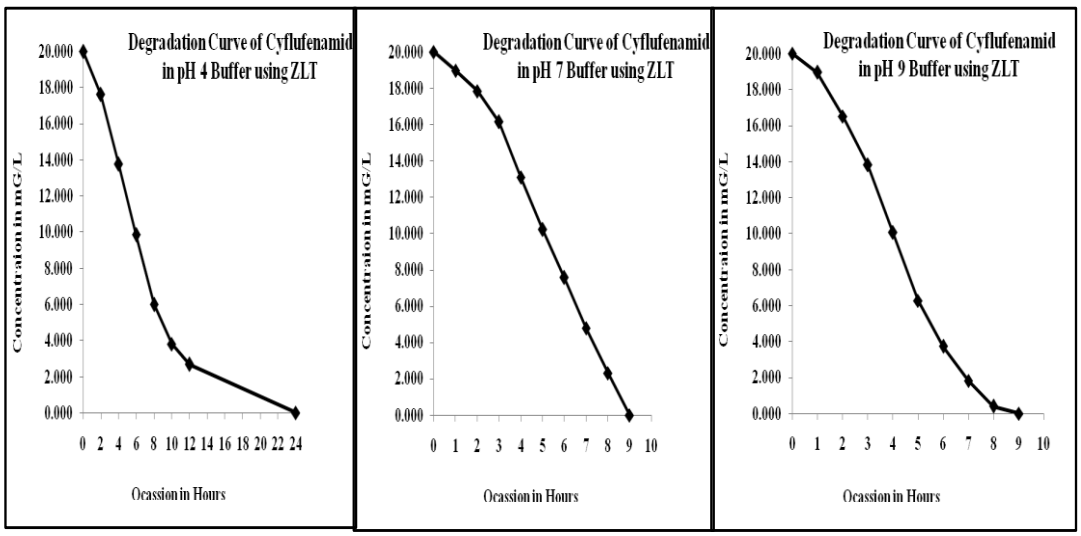

Fig. 5 Degradation curve of Cyflufenamid in pH 4, 7 and 9 buffers using ZLT

4			7			9		
Hours	Concentration (mg/L)	Log of concentration	Hours	Concentration (mg/L)	Log of concentration	Minutes	Concentration (mg/L)	Log of concentration
0	20.000	1.3010	0	20.000	1.3010	0	20.000	1.3010
1	16.854	1.2267	1	16.357	1.2137	30	15.054	1.1777
2	11.979	1.0784	2	8.836	0.9463	60	10.321	1.0137
3	7.713	0.8872	3	6.373	0.8043	90	7.373	0.8676
4	5.825	0.7653	4	4.285	0.6320	120	4.985	0.6977
5	4.612	0.6639	5	3.021	0.4802	150	2.976	0.4736
6	3.526	0.5473	6	1.876	0.2732	180	0.965	-0.0155
7	2.331	0.3675	7	0.654	-0.1844	210	0.000	0.0000
8	1.097	0.0402	8	0.000	0.0000	Slope		-0.0068
9	0.000	0.0000	Slope		-0.1985			
Slope		-0.1484						
DT_{50}		2.03	DT_{50}		1.52	DT_{50}		44.57

Table 1 DT_{50} values of Diuron in pH 4, 7 and 9 buffers using ZLT

4			7			9		
Hours	Concentration (mg/L)	Log of concentration	Hours	Concentration (mg/L)	Log of concentration	Hours	Concentration (mg/L)	Log of concentration
0	20.000	1.3010	0	20.000	1.3010	0	20.000	1.3010
2	18.254	1.2614	2	17.532	1.2438	1	18.824	1.2747
4	14.621	1.1650	4	12.945	1.1121	2	16.736	1.2237
6	11.162	1.0477	6	8.631	0.9361	3	13.845	1.1413
8	7.825	0.8935	8	5.245	0.7197	4	10.112	1.0048
10	5.512	0.7413	10	3.174	0.5016	5	6.321	0.8008
12	3.786	0.5782	12	2.017	0.3047	6	3.736	0.5724
24	0.000	0.0000	24	0.000	0.0000	7	2.114	0.3251
Slope		-0.0621	Slope		-0.0869	8	0.936	-0.0287
						9	0.000	0.0000
						Slope		-0.1635
DT_{50}		4.84	DT_{50}		3.46	DT_{50}		1.84

Table 2 DT_{50} values of Flufenacet in pH 4, 7 and 9 buffers using ZLT

4			7			9		
Hours	Concentration (mg/L)	Log of concentration	Hours	Concentration (mg/L)	Log of concentration	Hours	Concentration (mg/L)	Log of concentration
0	20.000	1.3010	0	20.000	1.3010	0	20.000	1.3010
2	17.614	1.2459	1	18.973	1.2781	1	18.954	1.2777
4	13.768	1.1389	2	17.856	1.2518	2	16.521	1.2180
6	9.836	0.9928	3	16.151	1.2082	3	13.815	1.1404
8	6.003	0.7784	4	13.094	1.1171	4	10.058	1.0025
10	3.821	0.5822	5	10.225	1.0097	5	6.284	0.7982
12	2.693	0.4302	6	7.565	0.8788	6	3.726	0.5712
24	0.000	0.0000	7	4.794	0.6807	7	1.836	0.2639
Slope		-0.0768	8	2.305	0.3627	8	0.401	-0.3969
			9	0.000	0.0000	9	0.000	0.0000
			Slope		-0.1082	Slope		-0.1911
DT_{50}		3.92	DT_{50}		2.78	DT_{50}		1.57

Table 3 DT_{50} values of Cyflufenamid in pH 4, 7 and 9 buffers using ZLT