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A Remediation Technique for Removal of Fenvalerate from Contaminated Soil

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Abstract: Fenvalerate is a synthetic pyrethroid used for controlling pests in agriculture. Fenvalerate has the property to adsorb soil particles and when it comes in contact with aqueous environment causes pollution leading to the toxicity in soil-water environment. The technique for removal of fenvalerate from soil has been developed in the present study. Fenvalerate is amended in the soil at varying concentration viz. 25 ppm, 50 ppm and 100 ppm and taken in the surface soil treatment unit. The activated cow-dung slurry is used as a source of microbial consortium for bioremediation of fenvalerate amended soil. The physico-chemical parameters have been maintained for bioremediation of fenvalerate in contaminated surface soil. The research finding shows that the fenvalerate was degrading over a period of seven days with the formation of prominent intermediates such as 4-chloro-alpha (1-methylethyl) benzene acetic acid and 3-phenoxy-benzoic acid. These intermediates are less toxic than the parent compound and further on longer acclimatization in the environment would be mineralized into inorganic, biomass and CO_2. This technique has been proved successful for bioremediation of pesticides in particular fenvalerate from contaminated agricultural surface soil.

Key words: Fenvalerate, bioremediation, activated biomass, surface soil, treatment unit.

Introduction

Modern agricultural technology comprising introduction of high yielding varieties, use of pesticides and chemical fertilizers, irrigation and improved agronomic techniques during last few decades has enabled the farmers in increasing the crop production. However, intensive cropping systems have given way to emergence of diseases, pest and weed problems necessitating the use of pesticides. Indiscriminate and uncontrolled use of pesticides has resulted into several ill effects such as health hazards, ecological imbalance and environmental pollution. Besides, increased level of pesticide residues have also been noticed in soil, water and food.

Synthetic pyrethroids are a diverse class, having more than 1000 powerful, broad-spectrum insecticides used to control insect pests in agriculture, households, and stored products. The important pyrethriods used at present for insect control are fenvalerate, cypermethrin, deltamethrin and bethrin. Fenvalerate {alpha-cyano-3-phenoxybenzyl-2-(4-chlorophenyl)-3-methylbutyrate} is a potent insecticide that is being used from 1976. It is a racemic mixture of four optical isomers and belongs to synthetic pyrethroid class of pesticides (WHO, 1990). Approximately 1000 tonnes of fenvalerate per year are used worldwide. It is employed in agriculture, insect control at homes, garden, on cattle and for commercial purposes. Fenvalerate is a yellow/brown viscous liquid having a molecular weight of 419.9. Fenvalerate is highly soluble in organic solvents whereas solubility in water is upto 2 µg/litre only. Boiling point of fenvalerate is 300°C at 37 mmHg; relative density at 25°C is 1.175 and vapour

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pressure at 25°C is 0.037 mPa. Fenvalerate has the property to strongly adsorb onto soil and organic particle.

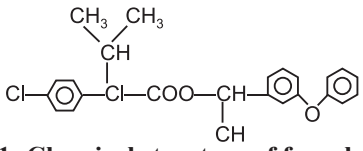


Figure 1: Chemical structure of fenvalerate.

Microorganisms are the principal agents known to cleave and modify the complex structure of pesticide molecules. The biodegradation of fenvalerate in the environment is rapid. The major route of biodegradation is via ester cleavage, diphenyl ether cleavage, ring hydroxylation of phenoxy phenyl group, and hydration of cyano group to amide and further oxidation of the fragments would form carbon dioxide and inorganic nutrients (WHO, 1990).

In the present experimental technique, a surface soil treatment unit has been designed for bioremediation of soil contaminated with fenvalerate using activated cow dung biomass containing bacteria, fungi and actinomycetes. The aim of the study is to investigate the degradation potential of activated cow dung biomass towards fenvalerate and its intermediates. The aerobic bioremediation by activated cow dung biomass under controlled environmental conditions will prove to be an effective technique for biodegradation of fenvalerate in soil.

Materials and Methods

The technical grade fenvalerate has been procured from pesticide manufacturing industry for developing a simulated technique for bioremediation of fenvalerate-contaminated surface soil. The soil (alluvial) was collected from Palghar, 200 km away from Mumbai city. A surface soil treatment unit has been designed (22 cm × 10 cm × 6 cm) for bioremediation. Cow dung mixed with water in the ratio of 1 : 1 was filtered to remove suspended particles and was aerated and activated for a period of one week. The soil and cow-dung slurry was characterized for physico-chemical (Jackson, 1973; APHA, 1995) and microbial parameters. In the experimental set-up, fenvalerate was spiked to alluvial soil (1 kg) at different concentrations viz. 25 ppm, 50 ppm and 100 ppm in the respective surface soil treatment unit (Brinch et al., 2002). A control treatment unit was also set up which contained zero concentration of pesticides. The cow-dung slurry was added to fenvalerate contamined soil as a source of biomass for bioremediation. A surfactant Tween 80 (0.05%) was added to the soil as a surfactant to prevent adsorption of fenvalerate to soil particles. The bioremediation conditions were monitored and maintained in the surface soil treatment unit. Soil samples (10 gm) were collected after every 24 hrs over a period of seven days. The soil samples were dried at room temperature and the biodegraded compounds were extracted from soil into acetone by using Soxhlet Extraction assembly (EPA, 2003). The soil extracts were analyzed for degradation of fenvalerate and its intermediates using GC-MS at Indian Institute of Technology, Mumbai.

Results and Discussion

The agricultural application of pesticides causes contamination of surface soil. Parts of the toxicants find their ways into soil, surface water, sediment, ground water, biota and finally enters into the food chain thus deteriorating the quality of environment and damaging the ecological balance. Bioremediation using microbial technology would be an effective treatment technique for pesticides like fenvalerate. In the present laboratory experiment, a treatment unit for bioremediation of pesticide-contaminated surface soil has been designed, wherein technical grade fenvalerate was amended in alluvial soil at three different concentrations viz. 25 ppm, 50 ppm and 100 ppm and bioremediation of fenvalerate is carried out using activated cow-dung biomass.

Table 1 illustrates the physico-chemical and microbial characterization of activated cow-dung biomass and soil. The data shows the presence of inorganic nutrients in cow-dung slurry and soil, which served as a source of nutrient for the growth and maintenance of microbial community. The microbial characterization of cow-dung biomass and soil shows presence of diverse microbial community. The presence of nutrients as well as microorganisms in cow-dung and soil has been found responsible for the bioremediation of surface soil contaminated with fenvalerate. The bioremediation conditions like pH, moisture, temperature, dissolved oxygen and nutrient level (C : N : P) were monitored and maintained in surface soil treatment unit (Table 2).

Correlation of fenvalerate degradation with variation in COD and BOD has been observed. Changes in COD of fenvalerate-amended soil during the bioremediation in a surface soil treatment unit is shown in Figure 2. The decrease in COD with increasing duration of bioremediation was observed. The percentage decrease in Chemical Oxygen Demand (COD) measured during

Table 1: Physico-chemical and microbial characterization of activated cow-dung slurry and soil

Physico-chemical characterization			*Microbial characterization*		
Parameter	*Soil*	*Slurry activated*	*Parameter*	*Soil*	*Slurry activated*
pH	7.6	7.4	Total viable count/g	1920	65×10^9
Moisture	4.5 %	–	Total coliform count /g	760	189×10^7
Alkalinity/100 gms	0.6 meq	1.2 meq	Total yeast and mould count/g	320	72×10^3
Dissolved oxygen	6 ppm	9 ppm	Pseudomonas count/g	<30	59×10^3
Temperature	26°C	28°C	Actinomycetes count/g	1340	83×10^4
Cation exchange capacity/100 gms	108 meq	–	E.coli count/g	Absent	23,600
% organic carbon	1.08	0.34	Anaerobic bacterial count	<30	<30
Phosphorus	0.25 ppm	0.78 ppm	Thermophilic bacterial count	560	790
Kjeldahl nitrogen	2100 ppm	8.6 ppm	S. aureus	Present	Absent
Sulphate	2.5 ppm	26 ppm	Flavobacterium	Present	Absent
Calcium	8727 ppm	8.6 ppm	Alcaligen	Present	Absent
Chloride	1930 ppm	6 ppm	Bacillus	Present	Absent
Potassium	344 ppm	161 ppm	Streptococcus	Absent	Present
Sodium	423 ppm	92.8 ppm	Sarcina	Absent	Present
Magnesium	15440 ppm	147 ppm	Serratia	Present	Absent
COD	220 ppm	200 ppm	Nocardia	Absent	Present
BOD	4 ppm	8 ppm	Mucor	Present	Present

Table 2: Bioremediation conditions maintained and monitored during fenvalerate bioremediation

Parameter	*Range*
C:N:P	100 : 10 : 1
pH	6.5-8.0
Temperature	25-28°C
Moisture	60-80%
Dissolved oxygen	10-12 ppm

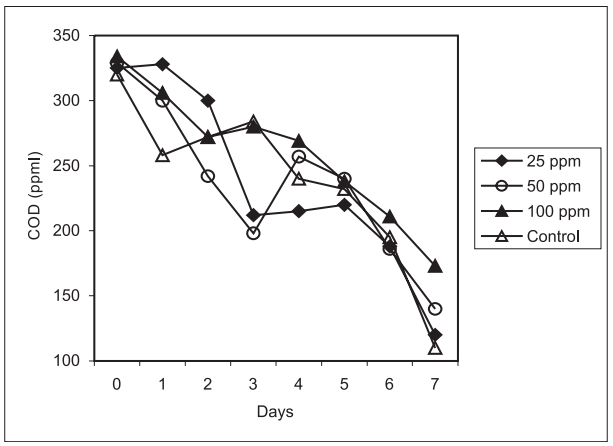


Figure 2: Variation in COD during bioremediation of fenvalerate-amended soil.

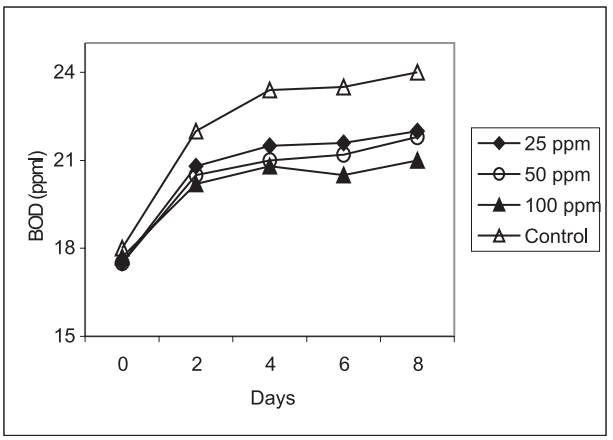


Figure 3: Variation in BOD during bioremediation of fenvalerate-amended soil.

the bioremediation shows 63% COD reduction in the case of 25 ppm fenvalerate amended soil, 57.4% COD reduction for 50 ppm fenvalerate amended soil and 48.2% reduction in the COD for 100 ppm fenvalerate amended soil while in control soil the percentage COD decrease was around 65.6% (Figure 2). Figure 3 shows the variation in BOD of the experimental soil. Variation in the biological oxygen demand of the soil amended with fenvalerate indicates the activity of microorganisms during bioremediation. Similarly, percentage variation

in Biological Oxygen Demand (BOD) measured during bioremediation shows 25.7% increase in BOD in the case of 25 ppm fenvalerate amended soil, 24.5% increase in BOD in the case of 50 ppm fenvalerate amended soil and 18.6% increase in BOD in the case of 100 ppm fenvalerate amended soil, while in control soil the percentage increase in BOD was 33.3% (Figure 3).

During bioremediation in the designed treatment unit, degradation pattern, pathway and persistence of fenvalerate and its intermediates in contaminated surface soil at 25 ppm, 50 ppm and 100 ppm were studied. The concentration of fenvalerate and its intermediates during the bioremediation at varying concentration in soil was estimated and presented in Table 3. It was found from

Table 3: Concentration of fenvalerate and intermediates analyzed every day during the bioremediation in surface soil treatment unit

Compound	*0th day*	*1st day*	*2nd day*	*3rd day*	*4th day*	*5th day*	*6th day*	*7th day*
				25 ppm fenvalerate amended surface soil				
A	18	15	11	9	-	-	-	-
B	-	5	11	12	12	10	8	7
C	-	7	12	14	14	8	6	6
D	-	4	4	-	-	-	-	-
E	-	6	4	3	3	3	-	
F	-	Trace	Trace	2	2	5	4	4
G	-	Trace	Trace	-	3	3	5	7
				50 ppm fenvalerate amended surface soil				
A	36	29	29	26	22	16	12	-
B	-	12	16	14	14	12	12	12
C	-	10	18	15	13	13	11	10
D	-	14	10	5	5	4	-	-
E	-	8	10	6	6	-	-	-
F	-	4	4	7	9	9	7	8
G	-	4	5	7	10	12	11	11
				100 ppm fenvalerate amended surface soil				
A	72	72	71	68	65	65	61	60
B	-	-	4	10	14	16	18	22
C	-	2	6	11	16	19	21	20
D	-	-	4	7	7	9	11	10
E	-	10	10	10	8	-	-	-
F	-	-	2	5	10	9	9	12
G	-	-	Trace	7	5	12	11	11

Note: All values are expressed in ppm.

A fenvalerate

B 4-chloro-alpha (1-methylethyl) benzene acetic acid

C alpha cyano-3-phenoxybenzyl alcohol

D alpha-cyano-3-hydroxybenzyl-1-2- (4-chlorophenyl)-3-methylbutyrate

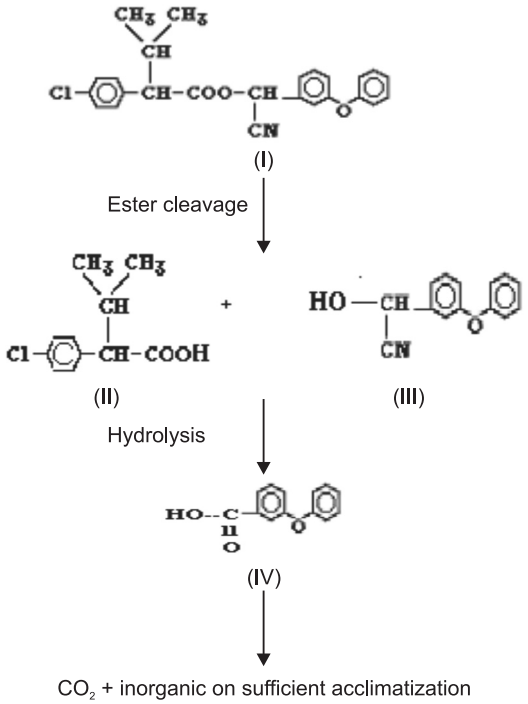
E alpha-cyano-3- (4'-hydroxyphenoxy) benzyl-2-(4-chlorophenyl)-3-methylbutyrate

F 3-phenoxy-benzyl alcohol

G 3-phenoxy-benzoic acid

the GC-MS analytical data that the fenvalerate was rapidly broken down via cleavage at the ester functional moiety (Figure 4). Hydroxylation of fenvalerate has also been found to take place, which is followed by ester and ether cleavage and subsequently with oxidation and hydrolysis of conjugates.

The compounds such as 4-chloro-alpha (1-methylethyl) benzene acetic acid and alpha-cyano-3-phenoxybenzyl alcohol were found to be the principal intermediates of fenvalerate degradation. Compounds like 3-phenoxy benzyl alcohol and 3-phenoxy benzoic acid have started appearing predominantly during the later stages of biodegradation. After a duration of one week, at 100 ppm concentration, fenvalerate was found persisting in the soil while at 50 ppm and 25 ppm, fenvalerate was found completely disintegrated into its intermediates by the action of microorganisms. The degradation of fenvalerate in 100 ppm concentration is found to be 16.6% after one week duration. This is in agreement to a novel investigation done by Maloney et al. showing that *Bacillus cereus, Pseudomonas fluorescens* and *Achromobacter* sp were able to transform fenvalerate in presence of Tween 80 within a duration of five days.



I Fenvalerate
II 4-chloro-alpha (1-methylethyl) benzene acetic acid
III alpha-cyano-3-phenoxybenzyl alcohol
VI 3-phenoxy-benzoic acid

Figure 4: Degradation pathway of Fenvalerate in surface soil treatment unit using activated biomass.

The bioremediation study shows that the parent compound fenvalerate has been degraded rapidly into principal intermediates 4-chloro-alpha (1-methylethyl) benzene acetic acid and alpha-cyano-3-phenoxybenzyl alcohol due to the microbial action at ester functional moiety. Figure 4 demonstrates the pathway identified for fenvalerate degradation in surface soil treatment unit using activated biomass. Unlike the specially designed treatment unit for bioremediation of fenvalerate contaminated surface soil, the degradation of fenvalerate in the natural environment is rather sluggish depending upon the microbial activity. In plants, ester cleavage and certain photo-initiated reactions are the major routes of decomposition whereas in soil-water ecosystem, the formation of organic matter bound pesticide conjugate and the evolution of carbon dioxide are the major processes observed under both aerobic and anaerobic conditions.

Thus, the present bioremediation study in specially designed surface soil treatment unit shows that the fenvalerate at a concentration of 25 ppm to 50 ppm can be degraded rapidly by activated microbial consortium. The laboratory technique developed using designed Surface Soil Treatment Unit for bioremediation of fenvalerate contaminated surface soil by the action of microbial consortium would be a successful technique which can be adopted for the removal of fenvalerate from the contaminated agricultural soil to prevent its toxicity to the biotic and abiotic environment.

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