

Removal of Oxamyl in Soil by Different Treatments

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ABSTRACT

The remediation of the oxamyl pesticide, applied, at a rate of 50 µg/gm soil and amended with different materials namely, Tergitol NP9 (nonionic surfactant), charcoal, lorandeat and iron fillings at rate of 300, 250, 250 and 300 Kg/Fadden, respectively, was investigated. The oxamyl residue levels in loamy sand was extracted at different time intervals after treatment based on the solid phase extraction (SPE) with methanol and then analyzed by HPLC. Only the peak corresponding to oxamyl was observed in the chromatogram and no intermediate metabolites could be detected. At the end of the experiment (21 days), the dissipation percentage of oxamyl reached about 88, 78, 73 and 72% in soil amended with NP-9, Fe, lorandeat and charcoal, respectively. The rate of disappearance was 2 times higher than in unamended-soil, while Fe, lorandeat and charcoal enhanced the dissipation rate by 1.77, 1.65 and 1.61 times, respectively. The disappearance rate constants and half-life values of the compound were obtained from the exponential decay equations. The decomposition of oxamyl in the control, charcoal and lorandeat followed the first order kinetics with $t_{1/2}$ of about 22.08, 13.8 and 13.2 days. On the other hand, a biphasic model was assumed to explore the disappearance of oxamyl in soil amended with NP-9 and Fe where the rate of disappearance in the first phase was faster than the second phase. This is clearly reflected in the half-life ($t_{0.5}$) values for the first and second phases, where the $t_{0.5}$ values of oxamyl ranged from 3.3 to 12.7 and 6.5 to 15.6 days, respectively. The results demonstrated that using NP-9, Fe, charcoal and lorandeat may offer an efficient remediation treatment for oxamyl-polluted soil.

Key words: (soil – removal – charcoal – lorandeat – Tergitol NP-9 – iron fillings – oxamyl)

INTRODUCTION

Pesticides are widely used in agriculture to control a variety of pernicious organisms that spoil the crops. More than kinds of agrochemical are used around the world (Miyake *et al.*, 1999). The use of large quantities of pesticides in agriculture practices is one of the main causes of soil pollution. Soil acts like an active filter, where chemical compounds are degraded by physical-chemical, and biological processes (Cornejo *et al.*, 2000). Both the accumulation of pesticides in the soil and their dispersion in the environment depend chiefly on the characteristics and overall functioning of the ecosystem. Among the most important factors to

consider are the physicochemical and biological properties of the soil (texture, structure, pH, organic matter content, and microbiological activity), the environmental conditions (mainly temperature and humidity), and the characteristics of the pesticide itself. The transport of pesticides beyond the area of application results in the presence and accumulation of these compounds in many parts of the hydrosphere. Several pesticides were detected in groundwater (García de Llasea and Bernal-González, 2001; Johnson *et al.*, 2001; Kadian *et al.*, 2008). The amount and type of pesticides in the water of a particular area depend largely on the intensity of production and type of crops being cultivated (Belmonte Vega *et al.*, 2005). Groundwater contamination not only affects the health of human beings, as it is directly used for drinking purposes, but also can act as a source of contamination in the food chain, when used for irrigation.

Carbamate pesticides are intensively used as pesticides in agriculture because of their broad spectrum of activity. These compounds are rarely detected in freshwater systems as their stability decreases quite markedly in aquatic environments, where they can only persist for between 4 and 12 weeks, depending on temperature, pH, and other constraints (Albanis *et al.*, 1998). On the contrary, carbamates were detected in streams and rivers of the Caribbean island of Martinique (Bocquené and Franco, 2005) and affected cold and warm fish, freshwater invertebrates, and birds (García de Llasea and Bernal-González, 2001). They have toxicological effects on the environment, as well as in human beings, since they are inhibitors of acetylcholine esterase (Ecobicon, 2001) by carbamylation of its active site (USEPA, 2004). Oxamyl is a carbamate compound used in a wide range of agricultural situations. It is systemic and active as an insecticide (Mowry, 2005) or a nematicide (Tomlin, 2002; Minnis *et al.*, 2004). Also, oxamyl can be integrated with horse manure, sesame-oil-cake, or *Bacillus thuringiensis* to improve eggplant growth response and reduce development of the nematode *Meloidogyne incognita* (El-Sherif *et al.*, 2007). Oxamyl has high solubility in water (280 g/L) with a very low soil sorption coefficient ($K_{oc}=25$), and is defined as a highly toxic compound having an acute oral LD_{50} for the male rat of 3.1 mg kg⁻¹ (Tomlin, 2002) it is moderately toxic to fish and induces a

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Received May 13, 2015, Accepted May 25, 2015

concentration dependent increase in genomic DNA damage (Sorensen *et al.*, 2005). Moreover, the non-target effects of oxamyl in soil include reduction of a predator that plays a role in management of pest population (Tillman and Mullinix, 2004), the bacteria-feeding nematode, *Bursilla* sp. (Bell *et al.*, 2006). The environmental behavior of oxamyl in soil (Bansal, 1983; Smelt *et al.*, 1987) and in water (Leistra and Boesten, 1989). Therefore, rapid elimination of oxamyl from soil could help to protect the environment. Such concerns have heightened the need for innovative and advanced technologies for effective removal of oxamyl from a variety of contaminated environmental sources including water, sediments, and soils. Therefore, the present study was undertaken to amend soil with different treatments to remedy oxamyl-polluted soil.

MATERIALS AND METHODS

Chemicals

Analytical grade standard of oxamyl, [2-(dimethylamino)- N-[[[(methylamino) carbonyl] oxy]- 2-oxoethanimidothioate], with a purity of 95%, was provided by the Shenzhen King Quenson Industry Co., Ltd., China, while formulated oxamyl (24% a.i., SL) was purchased from the local market of the Alexandria, Egypt. Certified HPLC-grade acetonitrile and methanol were purchased from the CHROMASOLV[®] chemicals Ltd.(USA), while solid phase extraction columns (C18 Supelco, 500 mg per column) Taiwan. All other chemicals used in this study were of the highest grade available.

Soil

Soil samples were collected from an organic farm, dried at room temperature, sieved and mixed with sand at ratio of 1:1 sand: soil. The soils were sterilized at 121°C in autoclave for 2 hrs. for 3 days. The physicochemical parameters of the tested soil were determined according to Vomocil (1957) and Jackson (1962). The properties of soil were listed in Table (1).

Soil treatments

The experiments were conducted in pots; each had 200 g of soil, which amended with iron fillings, charcoal, lorandeat, and Tergitol (NP-9) at rate of 0.19gm, 0.159gm, 0.159 gm and 0.19 gm/ pot, respectively. Soil treated only with oxamyl served as control. The selected pesticide, oxamyl was added at concentration of 50 ppm (a.i) to the amended soils. Soil samples were collected in triplicate after 0, 1, 3, 5, 7, 14 and 21 days after treatment and kept at -18 °C until extraction and chromatographic analysis.

Chromatographic analysis Extraction of oxamyl from soil

Oxamyl in soil was extracted as described by Osman *et al.* (2009). Soil sample (3 x5 g) were taken at different time intervals, and shacked with 20 ml of methanol for 24 h at room temperature. The mixture was filtered under vacuum through a porcelain funnel, evaporated to dryness by a gentle stream of nitrogen, dissolved in 1 ml of methanol, and then subjected to solid phase extraction (SPE). Each cartridge was conditioned with 2 x3 ml of methanol and slowly aspirated. Extracts were loaded onto the cartridges and eluted with methanol (2 x 3 ml) under vacuum using a manifold at rate of 1 ml/min into glass vials (10 ml). The solvent had passed through the extraction column and the residual was forcibly removed from the column by vacuum aspiration under increased vacuum. The elute was evaporated to dryness under a gentle stream of nitrogen and then re-dissolved in 2 ml of acetonitrile, vortex-agitated and then analyzed by HPLC.

HPLC system

The quantitative analysis was performed using a high performance liquid chromatography (HPLC) (Agilent, 1200 Series HPLC) system consisting of a quaternary pump, 50µl sample loop, a UV/Vis detector (1200 Series) and chromatograph integrator. The analytical column was ODS (C₁₈, 5µm, 250 mm x 4.6 mm ID). A guard column (C₁₈) 40 mm x 2 mm i.d, was filled in the front of the analytical column. A mixture of acetonitrile and MilliQ water (80: 20 v/v) was used as mobile phase at a flow rate of 1 ml/min. The UV detector wavelength was 220 nm and the sample injection volume was 20 µl. The limits of detection (LOD) and quantification (LOQ) were calculated according to Keith *et al.* (1983). The HPLC response was linear ($R^2=0.999$) for oxamyl in the range of 1–25 µg/ml with correlation coefficient (R)= 0.9994. The LOD and LOQ of oxamyl were 0.03 and 0.10 mg/g, respectively. The HPLC chromatogram of oxamyl is shown in figure 1.

Recovery analysis

For the study of extraction efficiency of the established methods, a recovery experiment was conducted. Untreated soil samples (3 x 5gm) were spiked with 1 and 25 mg of oxamyl/ g soil for determination of percentage recovery. Extraction and analysis were performed in triplicates with the procedures described above.

Statistical analysis

Data were calculated as mean ± SD and analyzed using ANOVA. A probability of 0.05 or less was considered significant.

Table 1. Physicochemical characteristics of the tested soil.

Parameter	Value
EC	1.40 dSm ⁻¹
pH	8.01
Field capacity	30.5%
Bulk density	1.34 g cm ⁻³
Texture	Loamy-sand
Sand %	62.2%
Silt%	22.5%
Clay	15.3%

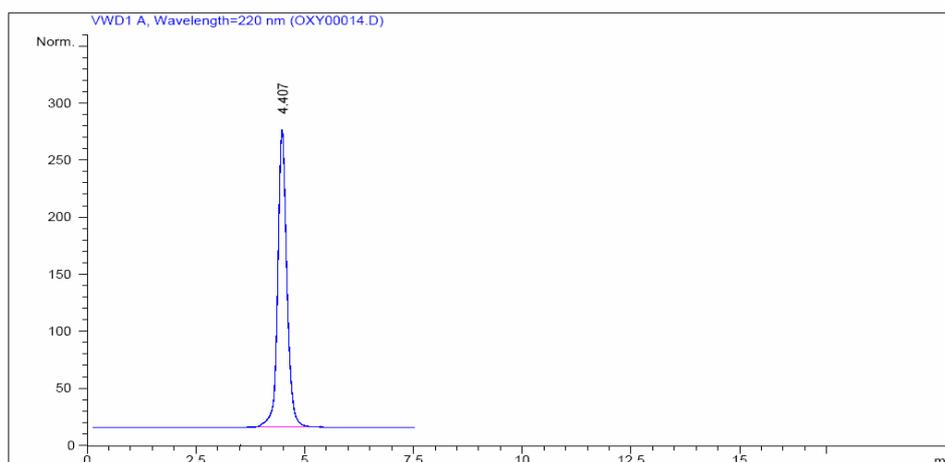


Figure 1. The chromatogram of oxamyl (1µg/ml)

The statistical package of the SAS program (V 9.13) was used for all chemometric calculations.

RESULTS AND DISCUSSION

Fortification study

The data indicated that the recovery percentages ranged from 88 to 91.5%, with an average of 89.75%.

Remediation of oxamyl in soil by different treatments

Table (2) illustrate the residue levels (µg/g) of oxamyl in soil after different treatments; it was found that the amount of oxamyl was significantly decreased exponentially as the time increased in the soil amended with the tested treatments, compared with the unamended soil. There were significant variations regarding to the percentage of oxamyl removal between the treatment of soil with NP9, charcoal, lorandeat and Fe compared to control values. In case of soil amended with NP9 and Fe roughly 55 and 40% of oxamyl was removed during the first five days. After this period, removal percentage increased to 70 and 69% within the first 10 days and then increased to 88% and 78% by the end of the experiment (21 days). In case of soil amended with lorandeat and Charcoal, 55.86and 46% of

the available oxamyl was removed within the first ten days; and then increased to about 73% and 71.6% by the end of the experiment illustrate. The dissipation patterns of oxamyl in soil in the absence of any of the tested treatments or in the presences of lorandeat or charcoal were found to be monophasic (Equation 1) , while in presence of NP9 or Fe it was found to be biphasic (Equation 2)

$$C_t = A_0 e^{-\alpha t} \dots \dots \dots (1)$$

$$C_t = A_0 e^{-\alpha t} + B_0 e^{-\beta t} \dots \dots \dots (2)$$

where C_t is the recovered amount of oxamyl at t (day), A_0 and B_0 are functions of the initial concentration of oxamyl, α , and β are the disappearance rate constants for the first and second phases, respectively. The calculated K_α , K_β , $t_{0.5\alpha}$ and $t_{0.5\beta}$ are illustrated in Table (3). The $t_{0.5\alpha}$ values for oxamyl were 22.08, 3.29, 6.55, 13.2, 13.8 days for unamended soil and soil amended with NP9, Fe, lorandeat and charcoal, respectively. However, $t_{0.5\beta}$ values for oxamyl in the second phase model were 12.7 and 15.57 day for soil amended with control, NP9 and Fe, respectively.

Table 3. Kinetic parameters for the oxamyl dissipation in soil by different treatments

Treatment	A_0 ($\mu\text{g gm}^{-1}$)	K_a (day^{-1})	$t_{0.5a}$ (day)	B_0 ($\mu\text{g gm}^{-1}$)	K_b (day^{-1})	$t_{0.5b}$ (day)	R^2
NP9	48.18	0.210	3.29	25.26	0.0546	12.70	0.951
Charcoals	44.81	0.0502	13.8	-	-	-	0.958
Lorandeat	43.05	0.0525	13.20	-	-	-	0.932
Iron fillings	48.14	0.1058	6.55	24.05	0.0445	15.57	0.964
Control	47.97	0.0313	22.08	-	-	-	0.983

DISCUSSION AND CONCLUSION

The present data are in parallel with that found by Bromilow *et al.* (1980) and Gerstl (1984), who found that the decomposition of oxamyl in soils followed the first order Kinetics. However, when soils amended with NP-9 or Fe the dissipation pattern of oxamyl was biphasic. The biphasic model is characterized by rapid phase, and a much slower phase (Osaman *et al.*, 2009). The remaining residues are often quite resistant to degradation (Alexander, 1994). The relative importance of these phases depends on the availability of the pollutants, hydrophobicity, and affinity of organic matter. Also, the present results are close to those found by Smelt *et al.* (1983), where $t_{0.5}$ for oxamyl in the aerobic soils was 26 days in loamy fine sand (pH 8). The rate of oxamyl degradation with the tested treatment was almost 1.6-2 times faster than the control treatment. The rapid degradation of oxamyl in soil make it unlikely that oxamyl will leach to groundwater. The present findings demonstrate that lorandeat, NP-9, Iron fillings, and charcoal can reduce the persistence of oxamyl in soil and can play a vital role in the management of pesticide leaching in soil. Also, these types of treatments will be useful practice in loamy sand soil.

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