Biobed system to reduce four pesticide organophosphorus point contamination at farm level

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ABSTRACT

A potential method for cleaning water from point-source pollution by organic compounds using biological reactors. In this study, five reactors were tested for their ability to retain and degrade pesticides. The pesticides tested were the insecticide chlorpyriphos ethyl (CE), malathion (MAL), dimethoate (DIM) and methamidophos (MET). The reactors were filled with differing mixtures of soil, bleaching earth and straw. The reactor volume was 10 L. Forced circulation of the contaminated solution was programmed to decontaminate the solution. Both retention and degradation of the compounds by the reactors was studied. The degradation rate of the pesticides in the reactors was fast. The reactors retained CE, MAL and DIM very strongly, and retained MET less strongly. The half-life of all pesticides in the reactors was less than 21 days, compared to literature values of 60–70 days in soil. The combined retention and fast degradation make the biofilter a feasible technique to reduce spill-related and point environmental contamination by pesticides. The technique is most effective against persistent pesticides, while for mobile pesticides, the efficiency can be improved with several passages of the contaminated solution through biofilters.

Key words: Biobeds, pesticides, soil, bleaching earth and straw.

INTRODUCTION

Contamination of water bodies with agricultural pesticides poses a significant threat to aquatic ecosystems and drinking water resources (Dabrowski and Schulz, 2003). A major point source of this contamination is spills during filling and cleaning of spraying equipment. These activities often are performed at particular on-farm sites due to the convenience of a water supply and high concentrations of pesticide residues have been found at such sites (Helweg, A, 1994). If spillages take place in a farmyard where the topsoil layer has been replaced by a layer of gravel and sand, there is an obvious risk of groundwater contamination from leaching. Several techniques have been developed for the removal of pesticides from water. Sorption on activated carbon is the most widespread

technology used to deal with purification of water contaminated by pesticides and other hazardous chemicals (Baup *et al.,* 2000; Heijman and Hopman, 1999). However, due to high cost of activated carbon, its use in the field is sometimes restricted due to economical considerations. Moreover, the high cost associated with its regeneration led to explore new inexpensive materials (Gupta *et al.,* 2006). For the last decades, sorption of contaminants by sorbents of natural origin has gained important credibility due to the good performance and low cost of these complex materials (Bras *et al.,* 1999; Chubar *et al.,* 2003; Sheng *et al.,* 2005; Yang and Sheng, 2003a,b). A technique which uses natural materials (agricultural waste products or products available on-farm) to create a pesticide retaining and degrading environment to clean contaminated water on-farm, has been developed in the first time in Sweden (Torstensson and Castillo, 1997; Torstensson, 2000) and was called a biobed. it consist to intercept and treat contaminated runoff from the farmyard and/ or drips and spillages arising during the filling process. Biobeds rely on a mixture of organic matter and soil as biofilters for retaining and biodegrading pesticides employed in agricultural crop protection (Torstensson and Castillo, 1997, Fogg *et al.,* 2003a, Henriksen *et al.,* 2003) and are effective in reducing point source contamination (Torstensson, 2000). The typical Swedish biomix consists of straw, topsoil, and peat (50-25-25% v/v). The straw stimulates the growth of lignin-degrading fungi and the activity of ligninolytic enzymes (such as manganese and lignin peroxidases), which can degrade many different pesticides (Castillo *et al.,* 1997, 2000 2001a,b). The soil provides sorption capacity and other degrading microorganisms, and the peat contributes to high sorption capacity and also regulates the humidity of the system. A grass layer covering the biobed helps to keep the correct humidity and can be used as an indicator to reveal pesticide spills. To adapt this biological system to Mediterranean operating conditions, there is a need to identify organic materials that can act in the same effective way as those in the original Swedish composition. The type of organic material present in the biobed is crucial for the amount, activity, and genotypic and phenotypic versatility of microorganisms responsible for degradation of pesticides and their metabolites. Studies have demonstrated that biobeds can effectively retain and degrade pesticides (Rose *et al.,* 2003, Torstensson, 2000, Fogg *et al.,* 2003a,b, Henriksen *et al.,* 2003), such that the concentrations of pesticides being released from the farmyard are significantly reduced.

The aim of this work is to evaluate the degradation capacity of an organic mixture constituted of bleaching earth, straw and soil against four pesticides such as chlorpyriphos ethyl, malathion, methamidophos and dimethoate. These pesticides were considered as test substances because they are widely used citrus crop system in Morocco and characterized by different physico-chemical characteristics and different microbial metabolism. In particular, the influence of several factors such as initial concentration, co-application and repeated applications on these pesticides degradation was investigated in order to ascertain the suitability of the organic mixture tested to be used as a biofilter in biobed systems.

MATERIAL AND METHODS

Chemicals

Chlorpyriphos Ethyl (O,O–diethyl O-3,5,6 trichloro-2-pyridylphosphorothioate), Malathion (Diethyl (dimethoxy-thio-phosphoryl-thio) succinate), Methamidophos (O,S-Dimethyl-phosphor-amido-thioate) and dimethoate (O,O-dimethyl S-methylcarbamoyl methyl phosphoro-dithioate) were supplied by Dr. Ehrenstorfer GmbH (Augsburg, Germany). The active substance, chemical name, molecular weight, hemical formula and commercial name of each formulation are shown in Table 1. The organic solvents were obtained from Panreac (Barcelona, Spain). Each standard was dissolved in acetone to obtain stock solutions of approximately 200 mg/L, which were stored light protected at 4 ºC until further use. The freshly working standard solutions were obtained by dilutions with n-hexane. Florisil adsorbent (16–30 mesh) was obtained from Sigma–Aldrich (St. LOUIS, MO, USA).

Biofilters and reactors

Five biofilters were prepared with farm-available materials: Soil, bleaching earth and straw in different percent. The composition of this biofilters is reported in the Table 2.

The five different mixtures (1,05 kg) were placed in confined tin reactors of 10 l volume after a conditioning period of 15 days, useful to give a mixing of different materials. An additional reactor with no biofilter was used as a reference. The reference and measurement reactors are shown in Fig. 1. Daily, 5 l of water (based on volumes of waster likely to be generated on a farm) was washed through the reactor using a peristaltic pump with 0.3 L min^{-1} flow rate (taking 16.67 min). The water was previously contaminated with 0.3 g L^{-1} of each of the four pesticides used in this study. The four pesticides were used in actual citrus crop system in Morocco and the doses are related to normal agricultural applications. The main experiment continued for six weeks. Weekly, five 50 ml of water samples were collected from each reactor and analyzed for the four pesticides. Every two weeks 20 g samples of solid organic materials were collected from biofilters and analyzed for the four pesticides.

Instruments apparatus and chromatographic conditions

Analysis of the all pesticides were carried out with a Hewlett–Packard 6890 gas chromatograph equipped with an NPD Detector, on column injection port, and fused silica capillary column HP-5 column (5% diphenyl and 95% dimethylpolysiloxane, 25 m ´ 0.32 mm ID, 0.52 µm film thickness); and temperature programming from 80ºC to 160ºC (25°C/min), 160-220 °C at 10°C/min. 220 – 240 °C at 10°C/min, 80 °C (3.00 min), 160 °C (2.00 min), 220 °C (10.00 min), 240 °C (8.80 min) ; injector temperature 73ºC to 250ºC (180ºC/min); and detector temperature 300ºC. Carrier gas (helium) flow rate, 2.6 mL/min; makeup gas (nitrogen) flow rate, 10 mL/min; Air 60 ml/min; H$_2$ 3 ml/min. injection volume, 1 µl; Data were acquired and the equipment controlled by using HP Chem-Station software, which was run under Microsoft Windows NT on an hp compatible personal computer. The identification of the a.i. peaks and the absence of interfering substances were assessed by comparing the sample chromatograms with those of a pesticide standard mixture and of an untreated sample. The internal standard method was used to quantify the residues by measuring peak areas vs. concentrations.

Pesticide extraction and analysis

The method used for the extraction of pesticide on water and soil was adapted from Charles and Raymond (Charles *et al.,* 1991). For each 5 g of soil or 1 ml of water, 150 ml of acetone was added and the mixture was homogenised for 2 minutes and after mixed during 2 hours. The mixture was filtered with glass wool. After filtration, the acetone residues were partitioned with saturated aqueous sodium chloride (30 ml) and dichloromethane (70 ml) in a separating funnel. The
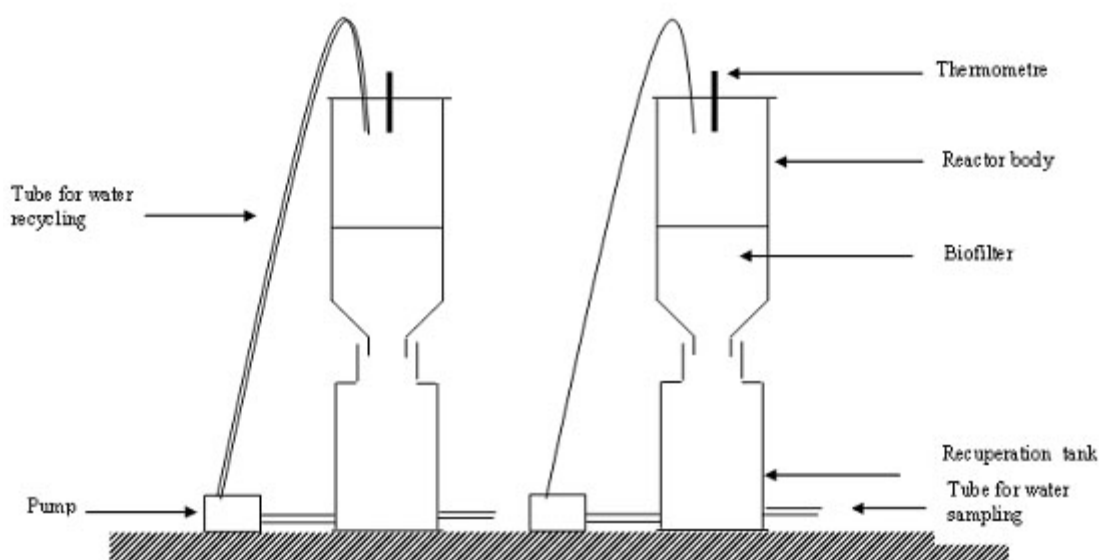

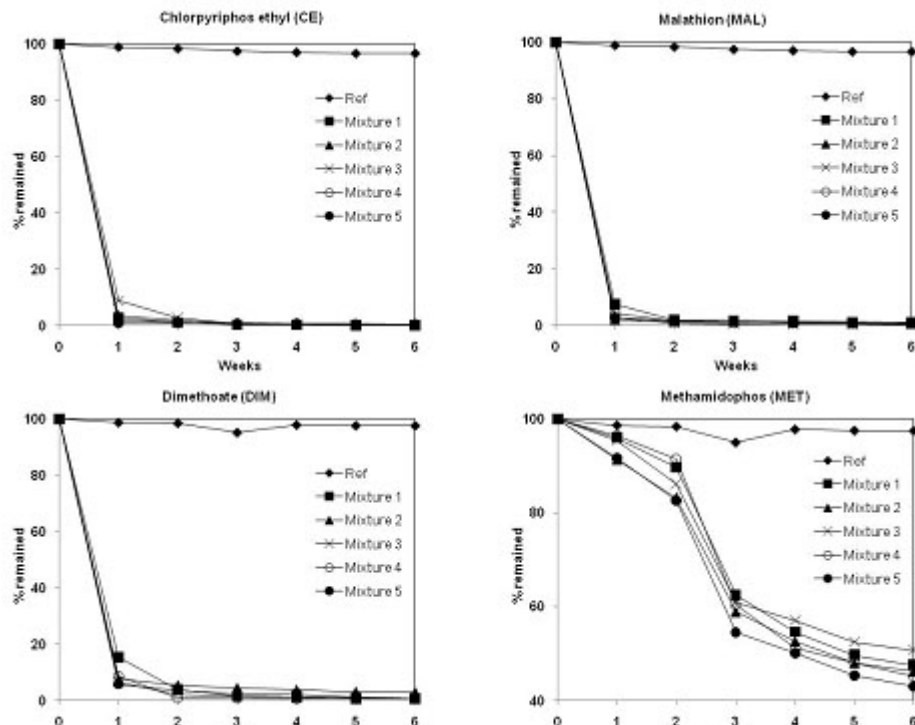**Fig. 1: Schematic representation of the measurement**

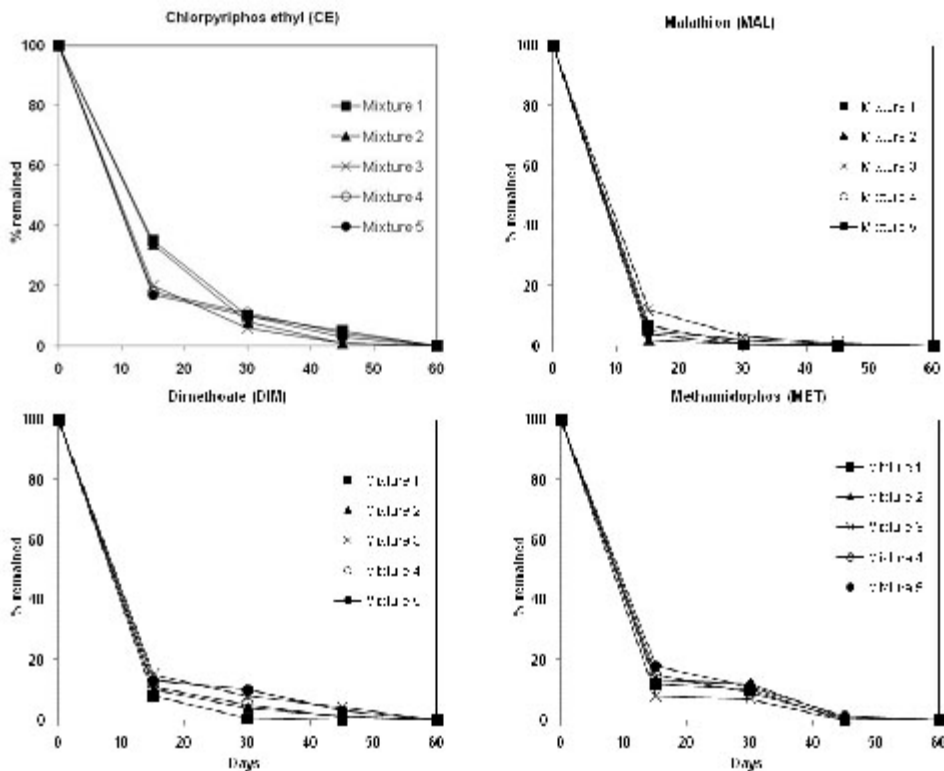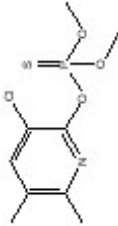**Fig. 2: Concentration of the four pesticides in water of the reference and measurement**
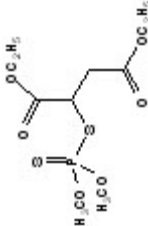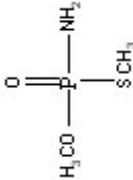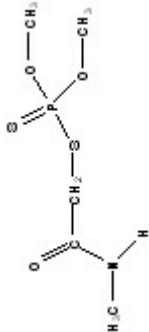

Fig. 3: Degradation curves of the four pesticides in the five substrates (mixture 1, 2 , 3, 4 and 5)

Table 1: Pesticides used in the study

Active substance	Chemical name	Molecular weight	Chemical formula	Commercial name	Soil t1/2 (days)
Chlorpyriphos	O,O-diethyl O-3,5,6trichloro-2-pyridylphosphorothioate	350.6		Deviban 1.5 DP	60
Malathion	Diethyl(dimethoxythiophos 60 phorylthio)succinate	330.3			Devimalt
Methamidophos	O,S-Dimethyl phosphoramidothioate	141.14		Tamaron	60
Dimethoate	O,O-dimethyl S-methylcarbamoylmethyl phosphorodithioate	299.2		Devigon	70

extraction was repeated with other 70 ml of dichloromethane and dried over anhydrous sodium sulphate. The dichloromethane fraction was collected and evaporated on a rotatory vacuum evaporator at 40°C and the residues were dissolved in hexane (5 ml). The eluate was evaporated to dryness under a stream of nitrogen and reconstituted in 1 ml of hexane, and this solution was injected into the GC system.

RESULTS AND DISCUSSION

Fig. 2 shows the change in concentration of the four pesticides in the water of the reference and measurement reactors. The quote of pesticide decay due to temperature effect and photodecomposition and volatilization is very slight or completely absent, looking at curves of reference reactors. Decay curves in measurement reactors show a very rapid disappearance of CE, MAL and DIM from water of all reactors, mainly due to the

immediate and very strong adsorption on biofilters, and a moderate disappearance of METI from all mixtures, indicating a low depuration efficiency of these biofilters for this pesticide. The effect of the three composts is clear for MET in organic material used in biofilters studied. At week 6 more than 40 % of MET remained in water, while water was clean for three others pesticides studied in all mixtures used in biofilters studied.

It is important to know what happened in the biofilter, once the pesticides were retained in order to evaluate not only their retention capacity, but also their degradation ability. Degradation curves in biofilters are reported in Figure 3. The start of the curves (100%) represents the amount of pesticides in biofilters after the first washing cycle which is different depending on substrate and pesticide. In spite of long half-life of the four pesticides in standard soils (Table 1), the half-life values in biofilters varied from 9 to 12 days for CE, while MAL, DIM and MET

Table 2: Composition of organic materials used in biofilters.

Mixture	Weight of soil (g)	Weight of bleaching earth (g)	Weight of straw (g)
1	300	700	50
2	400	600	50
3	500	500	50
4	600	400	50
5	700	300	50

disappeared after 21 days. These results indicate that degradation in the biofilter appears to be fast enough to allow a decontamination of the substrates occurring a few weeks after the beginning of the experiment, with the possibility of re-utilizing the materials more than once or for agricultural uses, such as amendments, and to avoid the presence of pesticides in the environment.

CONCLUSIONS

The reactor technique presented here has proved to be very efficient for the cleaning of water contaminated with pesticides. The degradation rate of the pesticides in the reactors was fast. The reactors retained CE, MAL and DIM very strongly, and retained MET less strongly. When applied at

the field scale, polluted water would pass several times through the filter, allowing even poorly retained pesticides time to degrade. Therefore the biomassbed proposed could help in reducing the pesticide point contamination at farm level.

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