Chemosphere 92 (2013) 1361–1366

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Technical Note

Degradation of pesticide mixture on modified matrix of a biopurification system with alternatives lignocellulosic wastes

C. Urrutia [a], O. Rubilar [b], G.R. Tortella [b], M.C. Diez [b,*]

[a] Universidad de La Frontera, Avenida Francisco Salazar, 01145 Temuco, Chile
[b] Scientific and Technological Bioresource Nucleus, Universidad de La Frontera, Casilla 54-D, Temuco, Chile

HIGHLIGHTS

- We evaluated the composition of biomixture for degradation pesticides.
- The type of lignocellulosic material effected the pesticides degradation.
- The biomixture composed with oat husks showed higher pesticides degradation.
- The biomixture composed with barley husks showed lowest pesticides degradation.

ARTICLE INFO

Article history:
Received 10 December 2012
Received in revised form 24 April 2013
Accepted 28 April 2013
Available online 6 June 2013

Keywords:
Biobed
Pesticide mixture
Lignocellulosic waste
Biological activities

ABSTRACT

The biobed systems were designed to retain and to degrade pesticides through the properties of a biomixture composed of straw (ST), topsoil and peat (PT) 2:1:1 v/v. The ST is the main substrate in the biomixture, as it allows the proliferation of fungi that promotes pesticide degradation. The use of readily available components in the biomixture is an important aspect to build a biobed. Therefore, potential use of readily available wastes as barley husk (BH), sawdust (SW) and oat husk (OH), as total or partial substitutes of ST were tested in pesticide degradation studies. Metabolite formation and the biological activities were also evaluated. Biomixture composed of OH was highly efficient in pesticide degradation, with $t_{½}$ values of 28.6, 58.9 and 26.8 d for atrazine (ATZ), chlorpyrifos (CHL) and isoproturon (ISP). On the other hand, comparable for degrading capacities with the ST based biomixture were obtained with SW and BH, but only as partial replacement. Contrarily, high $t_{½}$ values (more than 100 d) were obtained in biomixtures with total substitution of ST by SW or BH. Metabolite formation was observed in all biomixtures tested, but without clear formation patterns. Moreover, high and stable biological activity was observed in the biomixtures composed of OH. Therefore, our results demonstrated that ST can be partial or totally replaced by OH in the biomixture allowing an efficient degradation of pesticide mixture. However, it is recommended that ST can be only partially replaced by BH and SW in the biomixture to allow efficient pesticide degradation.

1. Introduction

The inadequate pesticide handling in agriculture may increase the risk of environmental contamination due to the dispersion into non-target sites. Some studies have demonstrated the presence of pesticide residues such as ATZ (Bhagobaty et al., 2007), CHL (Kolpin et al., 2000) and ISP (Stangroom et al., 1998) in water resources. Pesticide contamination can occur through non-point source or point source contamination. However, studies have been demonstrated that point source contamination, during filling and cleaning of sprayers can contribute to accumulation of these compounds in surface and groundwater (Carter, 2000; Neumann et al., 2002; Castillo et al., 2008).

Biobed is a low-cost biopurification system composed of a biomixture of ST, topsoil and PT 2:1:1 v/v, which has the ability to retain and degrade pesticide (Torstensson and Castillo, 1997; Castillo and Torstensson, 2007). The soil provides sorption capacity and is an important source of pesticide-degrading bacteria and PT contributes to sorption capacity, moisture control and pH decrease promoting fungi development (Torstensson, 2000). The ST is the main substrate in the biomixture as it allows the development of ligninolytic fungi that promote pesticide degradation in the biomixture (Castillo and Torstensson, 2007). This biomixture composition has been efficient in the degradation of several pesticides (Vischetti et al., 2004; Castillo and Torstensson, 2007). However, the biomixture has had to be adapted due to the greater

* Corresponding author. Tel.: +56 45 325476; fax: +56 45 325053.
E-mail address: cristina.diez@ufrontera.cl (M.C. Diez).

0045-6535/$ - see front matter © 2013 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.chemosphere.2013.04.088

availability of others lignocellulosic wastes in some countries. In this sense, Karanasios et al. (2010) reported that local Mediterranean lignocellulosic materials as sun flower crop residues, olive leaves, grape stalks among others, can be used replacing the ST in the biomixture to enhanced adsorption and degradation of several pesticides. In other work, Coppola et al. (2007) reported that the use of urban compost and citrus peel in the biomixture caused a high chlorpyrifos degradation, but an accumulation of their metabolite 3,5,6-trichloro-2-pyrinidol (TCP) was observed. In this same way, Kravvariti et al. (2010) demonstrated that cotton crop residues enhanced the degradation of hydrophilic pesticides and the adsorption of hydrophobic pesticides.

Although, several lignocellulosic residues have been evaluated as a biomixture component for pesticide degradation, the use of other readily available residues at no cost as SW, BH and OH has been less studied. Almost, most studies of pesticide degradation in modified biomixture have been performed with application of one pesticide and not with a mixture of pesticides. However, some studies (Fogg et al., 2003; Leistra and Matser, 2004; Karanasios et al., 2010) have shown evidence that the persistence of a number of pesticides may be changed when used in combination with other pesticides.

Therefore, the aim of this research was to evaluate the potential utilization of BH, SW and OH as a replacement for partial or total ST in biomixture for the degradation of a mixture of pesticides (ATZ, CHL and ISP). These lignocellulosic residues can be found in sufficient amounts at low or no cost and hence can be potentially used in biobed biomixture for pesticide degradation.

2. Materials and methods

2.1. Chemicals

Formulated pesticides ATZ (atranex 500SC), ISP (Fuego 50SC) and CHL (chlorpyrifos S480) were purchased from Agan Chemicals Manufacturers Ltd. Deethylatrazine (DEA), deisopropylatrazine (DIA), monodesmethyl-isoproturon (MDPIPU), TCP, 3-methyl-2-benzothiazolinone hydrazone (MBTH) and 3-(dimethylamino) benzoic acid (DMAB) were purchased from Aldrich. All other chemicals and solvents were of analytical reagent grade and were purchased from Equilab and Merck Chile.

2.2. Preparation of the biomixtures

For the preparation of the biomixtures, an Andisol topsoil (0–20 cm depth) belonging to Temuco series (38°42′S, 73°35′W), BH, SW, OH and ST as lignocellulosic material and commercial peat were used. Lignocellulosic wastes like BH, OH and ST were collected from crop residues; and SW was collected from sawmill waste. All lignocellulosic wastes were cut in small pieces (2–3 mm) using a food processor and soil was sieved (to 3 mm). The constituents were mixing vigorously to obtain a homogeneous biomixtures and in volumetric proportions as been described in Table 1. The biomixture moisture content was adjusted to 60% of the water holding capacity (WHC) by adding distilled water. All biomixtures were placed in polypropylene bags for maturation processes and stored in dark at 20 ± 2 °C for 40 d before being used in the experiments. The composition and characteristics of the biomixtures and their components were measured as shown in Table 1.

2.3. Degradation studies

A bulk sample (630 g dry weight) from each biomixture was separated into 21 sub-samples (30 g dw) in triplicate. These sub-samples were placed in glass flasks (500 mL) and were sprayed individually with a mixture of formulated pesticides ATZ, CHL and ISP corresponding to a dose of approximately 100 mg a.i. kg^{-1}. In addition, 21 sub-samples per each biomixture without pesticides were used as control. The biomixture moisture content was adjusted to 60% of the WHC by regular adding of distilled water. Afterwards, all biomixtures were incubated in dark at 20 ± 2 °C for 90 d. Immediately after mixing, samples of treated biomixtures and control were periodically up to 90 d for residual pesticide and their main metabolite analysis.

ATZ, CHL and ISP degradation in different biomixtures was described with the first-order kinetic equation as $C = C_0\, e^{-kt}$, and from the equation, we obtained (Eq. (1)):

$$t_{1/2} = \mathrm{Ln}(2)/k \quad (1)$$

Biological activities in different biomixtures during the degradation study were determined by measuring microbial respiration, phenoloxidase activity and fluorescein diacetate (FDA) hydrolysis. All biological activities were performed in the samples with and without pesticide mixture dose (100 mg a.i. kg^{-1} approximately of each pesticide) on 0, 10, 30, 60 and 90 d of incubation.

2.4. Analytical procedures

2.4.1. Characterisation of the biomixture

The pH was measured using a mixture of air-dried substrate and deionised water (1:5 w/v). The organic carbon was measured using the Walkley and Black (1934) method, the total nitrogen level was measured using digestion with H_2SO_4 according to the AOAC official method 976.06; the lignin and acid detergent fibre (ADF) content was measured using the AOAC standard method 973.18 (AOAC, 1990a), and neutral detergent fibre (NDF) content was measured using the AOAC standard method 992.16 (AOAC, 1990b). The cellulose content was calculated indirectly from the percentage of ADF and lignin (% ADF minus % lignin) (Mani et al., 2006). The WHC was determined gravimetrically by saturating the substrate (50 g) with distilled water and allowing it to drain for 1 h.

2.4.2. Extraction and pesticide analysis

Residual pesticides were extracted from the biomixtures (5 g dw) by shaking (1 h, 250 rpm) with 20 mL of acetone and ultrasonication (30 min). After centrifugation (10000 rpm), 5 mL of the supernatant was collected, filtered through a PTFE membrane (0.2 μm pore size, Millipore), evaporated with fluxed N_2 to dryness, and dissolved with 1 mL of acetonitrile. They were subsequently analysed as described below. Recovery of ATZ, CHL and ISP was >85%.

The concentrations of ATZ, CHL, ISP and their metabolites were determined by HPLC using a Merck Hitachi L-2130 pump, a Rheodyne 7725 injector with a 20 μL loop and a Merck Hitachi L-2455 diode array detector. Separation was achieved using a C18 column (Chromolit RP-8e, 5 μm 4.6 × 100 mm). Eluent A was 1 mM ammonium acetate, and eluent B was acetonitrile. The gradient conditions used for the separation of pesticides was as follows: 0–2 min of 95% A, 2–4 min of 95–70% A, 4–7 min of 70% A, 7–12 min of 70–30% A, 12–16 min of 30% A, 16–17 min of 30–95% A and 17–20 min of 95% A. The flow rate was set as follows: 0–12 min at 1.0 mL min^{-1}, 12–16 min of a 1.0–2.0 mL min^{-1} increase and 16–20 min at a constant 2.0 mL min^{-1}. The column temperature was maintained at 30 ± 1 °C. The detector was set at three wavelengths for data acquisition 220, 245 and 290 nm. Instrument calibrations and quantifications were performed against pure reference standards (0.1–10 mg L^{-1}) for each compound.