

N°880 / PC

TOPIC(s) : Alternative technologies / Waste valorization

Remediation of soils contaminated with neonicotinoids insecticides by intermittent ozonation

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PURPOSE OF THE ABSTRACT

Neonicotinoid insecticides are substances used to control a variety of pests. They have a structural similarity to nicotine and act on certain kinds of receptors, affecting the synapses in the insect central nervous system (1). The use of these substances protects and increases the crop yield. However, they may produce several environmental risks such soil contamination. In order to solve this problem, several techniques could be utilized for elimination of pesticides in soil including thermal, biological and chemical treatments (2). Advanced oxidation processes (AOPs) are considered among the most promising approaches for degradation of pesticides residues. These processes are characterized by the formation of various radical species such as the hydroxyl radicals (OH·) (3). Among these processes, the utilization of ozone (O₃) for the removal of pesticides in soil can be a good alternative, since ozone is a strong oxidant and can rapidly oxidize a number of these pollutants. Furthermore, as a result of ozone decomposition, hydroxyl radicals can also be generated. However, the effectiveness of this oxidant may be limited by factors such as competing reactions with soil organic matter and soil conditions, porosity and pH (4). The aim of the study was to determine the usefulness of gaseous ozone for degradation of residues of four neonicotinoid insecticides (thiamethoxam, imidacloprid, acetamiprid and thiacloprid) in soil.

Soil samples were extracted with acetonitrile and analyzed according to the procedure described by Fenoll et al. (5). The separation, identification and quantification of the selected insecticides were carried out using a Agilent Series 1200 liquid chromatograph interfaced to a G6410A triple quadrupole mass spectrometer from Agilent. Two single reaction monitoring (SRM) transitions for quantitation and confirmation were monitored for every pesticide. Figure 1 lists the analytical conditions for each compound.

The laboratory scale ozone tests were carried out in a glass container (volume 150 L). Ozone was generated with an OSMAQUA OZONO generator from dry air at maximal efficacy 1.06 g (O₃) h⁻¹. The influent ozone concentration (milligrams of gaseous ozone per cubic meter of ambient air) was about 14 g m⁻³ and the flow rate was 7 L min⁻¹. The ozone concentration in the gas phase was measured from the gas streams of influent and effluent by using a BMT 964 analyser. All assays were carried out using a pyrex glass vessels (110 mm long, 80 mm diameter) containing 100 g of clay-loam soil spiked at 1 mg Kg⁻¹ of each active ingredient. The vessels were placed in the glass container. Intermittent ozonation treatment the soils were treated every day for a period of 6 days (the generator was stopped each day when the effluent ozone concentration was equal to 10 g m⁻³). An

ozone destructor was installed at the outlet of the container. To monitor the degradation process three replicates of contaminated soil were taken at scheduled time intervals and analyzed under the same conditions described above. A control experiment was also conducted using soil not exposed to ozonation.

As shown in Figure 2, 75.1% thiamethoxam, 60.6% imidacloprid, 71.9% acetamiprid and 60.8% thiacloprid were removed in 6 days in intermittent ozonation treatment, while in the absence of ozone the decomposition of these compounds occurs at a very slow rate and only a 3% reduction of its concentration is achieved after 6 days. Therefore, ozonation is a promising and efficient technology for the remediation of soils contaminated with pesticides. However, the reaction between ozone and soils contaminated with pesticides is very complex due to different kinetics joining in this reaction, such as ozone decomposition rate in soil water, reaction rate between ozone and soil matrix and degradation rate of pesticides. Moreover, soil characteristics would affect the remediation efficiency of ozonation.

FIGURES

Insecticide	t_R (min)	SRM ₁	Fragmentor ₁ (V)	Collision Energy ₁ (V)	SRM ₂	Fragmentor ₂ (V)	Collision Energy ₂ (V)
thiamethoxam	13.71	292→211	90	5	292→181	90	20
imidacloprid	15.60	256→209	120	10	256→175	120	10
acetamiprid	16.52	223→126	120	30	223→90	140	30
thiacloprid	18.63	253→126	110	20	253→186	110	10

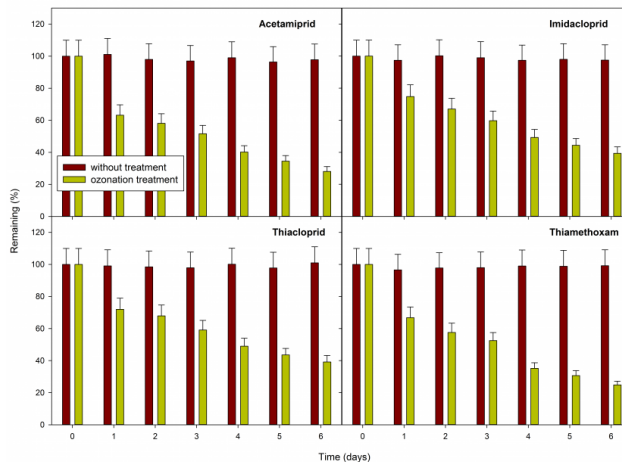


FIGURE 1

Figure 1

Analytical conditions of insecticides studied.

FIGURE 2

Figure 2

Removal of neonicotinoid insecticides from soil by ozonation. Error bars represent one standard deviation (n = 3).

KEYWORDS

soil | ozone | descontamination | pesticides

BIBLIOGRAPHY