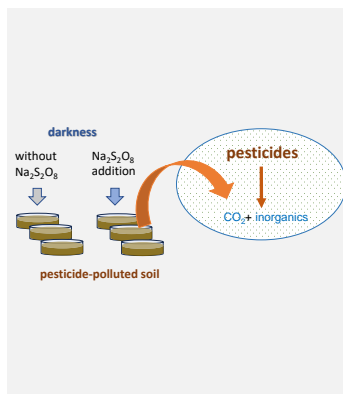


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In this work, we have evaluated the degradation of two anthranilic diamides (cyantraniliprole and chlorantraniliprole) insecticides, two triazole (triadimenol and tebuconazole) fungicides and two strobilurin (azoxystrobin and kresoxim-methyl) fungicides in soil using persulfate. The results showed that persulfate enhanced pesticide degradation rates in comparison with the control. The studied pesticides showed a high degradation rate. Thus, the remaining mean percentage of anthranilic diamide insecticides, triazole fungicides and strobilurin fungicides in soils varied from 1.1 to 3.1%, from 7.3 to 8.7% and from 0 to 0.2%, respectively. Finally, the results suggest that the use of persulfate without active activation has favourable prospects to be considered a credible alternative technology for remediation of pesticide polluted soils.

### Introduction

The pesticides can be discharged into the soil environment. Therefore, the remediation of pesticides-contaminated soil is necessary to protect human health and the environment. In recent years, Advanced Oxidation Processes (AOPs) have attracted great attention due to their efficiency in removing a wide range of soil pollutants, including pesticides. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), permanganate (MnO<sub>4</sub><sup>-</sup>), ozone (O<sub>3</sub>) and persulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) are some oxidants used in soil remediation to degrade pesticides. Persulfate (PS) is a strong oxidant (2.01 V) that can degrade most organic contaminants in soil. It has the advantages of relative stability, wider pH range, high reaction rate, high efficiency, simplicity and low cost. Usually, PS can be activated by heat, alkali, electricity, light radiation, and catalysts to generate more strongly oxidizing sulfate radicals (2.6 V). However, without activation, PS can also achieve considerable degradation of organic chemicals in soil [1]. The physicochemical properties of soil and dosage of PS are the main factors affecting the application of PS in soil. The aim of this work was to evaluate at laboratory scale the efficacy of persulfate without activation for the degradation of two anthranilic diamide (cyantraniliprole and chlorantraniliprole) insecticides, two triazole (triadimenol and tebuconazole) fungicides and two strobilurin (azoxystrobin and kresoxim-methyl) fungicides from soil.

### Material and Methods

Analytical standards of cyantraniliprole (≥98%), chlorantraniliprole (≥99%), triadimenol (≥98%), tebuconazole (≥98%), azoxystrobin (≥99%) and kresoxim-methyl (≥99%) were purchased from Chem Service, Inc (PA, USA) and Dr. Ehrenstorfer GmbH (Augsburg, Germany). Sodium persulfate (98%) was supplied by Panreac Química (Barcelona, Spain). Pure water was obtained from a Milli-RX purification system

from Millipore. Physicochemical properties of the selected soil were: silty clay loam texture (19.9% sand, 51.6% silt, 28.5% clay); pH 7.9; OM 0.03% (w/w); EC 2.14 dS m<sup>-1</sup>. Soil was spiked with active ingredients of cyantraniliprole, chlorantraniliprole, triadimenol, tebuconazole, azoxystrobin and kresoxim-methyl to reach a level of 1000 µg kg<sup>-1</sup> for each one. Then, 30 g of polluted soil were weighed in the corresponding Petri plates (90 × 15 mm) and 30 mL of Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 10% (w/v) solution was added. Soil samples were exposed to darkness. Two treatments were assayed: i) PS addition and darkness, and ii) no PS addition and darkness. In all cases, soil moisture content was kept constant. The extraction of insecticide residues from soil samples were conducted according to the procedure developed by Fenoll et al. [2]. Quantification of pesticides was carried out using a 1260 Infinity UHPLC combined with an Agilent 6465BA QqQ Mass Spectrometer (LC-MS/MS). The analytical column was a Zorbax Eclipse XDB-C8.

### Results and Discussion

PS loading and moisture content were previously optimized. Table 1 shows the degradation of pesticides residues during the experiment. PS showed a high disappearance rates for anthranilic diamide insecticides and triazole and strobilurin fungicides. Thus, the residual levels of cyantraniliprole, chlorantraniliprole, triadimenol, tebuconazole and azoxystrobin were 0.31, 0.11, 0.73, 0.87 and 0.02 µg kg<sup>-1</sup>, respectively. However, kresoxim-methyl was totally degraded. In the absence of PS, the decomposition of these compounds ranged from 85.3-86.7 % for anthranilic diamide insecticides, 94.6-96.9 % for triazole fungicides and 89.9-99.6 % for strobilurin fungicides, respectively.

This behaviour can be due to the oxidation potential of PS [3] and the minerals present in the soil. The presence of minerals in the soil can promote the decomposition of PS

to produce active substances that further remove pollutants [4,5].

**Table 1.** Remaining of pesticides in soil with PS treatment.

Pesticide	Remaining (%)	
	Control treatment	PS treatment
cyantraniliprole	85.3	3.1
chlorantraniliprole	86.7	1.1
triadimenol	96.6	7.3
tebuconazole	89.9	8.7
azoxystrobin	89.9	0.2
kresoxim-methyl	99.6	-

### Conclusions

The results suggest that persulfate without active activation can be considered as a suitable technology to remove pesticides from agricultural soil. Once shown its effectiveness, this technology achieves the remediation of soil polluted with pesticides and could also be applied on a field scale.

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