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Photodegradation of tetramic and tetronic acid insecticides in water by peroxydisulfate and sunlight. Comparative evaluation using ZnO and TiO_2 semiconductors

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Spirocyclic tetronic/tetramic acid (ketoenol) derivatives (spirodiclofen, spiromesifen and spirotetramat) are one of the most recently developed acaricide/insecticide classes for the control of a wide spectrum of sucking insects in numerous agricultural crops. This new insecticide family interferes with lipid biosynthesis and are thought to act as inhibitors of acetyl-coenzyme A carboxylase (ACCase) (1).

Peroxydisulphate ($S_2O_8^{2-}$ ion) is a strong oxidant (E° = 2.05 V) which has been used for treatment of polluted water by organic compounds through direct chemical oxidation (2, 3). However, the reactions of peroxydisulfate are generally slow at normal temperatures. Photochemical activated decomposition of $S_2O_8^{2-}$ ion to $SO_4^{\bullet-}$ radical usually enhances the photodegradation rate of organic pollutants. For this reason, in this study, the degradation of three spirocyclic tetronic/tetramic acid derivatives in water has been investigated using peroxydisulfate under solar irradiation.

The results show that the use of the $Na_2S_2O_8$ (250 mg L^{-1}) is a very effective and rapid method for the elimination of these insecticides (C_0=0.1 mg L^{-1}) in water under sunlight irradiation, except for spirotetramat. The residual levels of spirodiclofen, spiromesifen and spirotetramat at the end of the experiment (240 min) were 8, 3 and 40 µg L^{-1}, respectively. The primary degradation of spirodiclofen and spiromesifen followed a pseudo-first order kinetics. Similar kinetics was observed for the ZnO and TiO_2 semiconductors (200 mg L^{-1}).

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Photooxidation of Boscalid in Pure and Environmental Waters in Slurry Photoreactor containing Zinc Oxide

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Boscalid (BCL), a carboxamide fungicide is a relatively new active ingredient recommended for control of powdery mildew, *Alternaria* spp., *Botrytis* spp., *Sclerotinia* spp., and *Monilia* spp. on a range of fruit and vegetables (1). It is stable to hydrolysis at pH 4-9 S_W=4.6 mg L^{-1}, log K_{OW}= 2.96. Its chemical structure is shown in Figure 1.

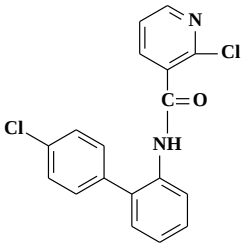

Figure 1: BCL

Results from some studies have indicated indicate that BCL is present in surface and groundwater (2, 3). BCL is a persistent compound and it has the potential to leach to groundwater (GUS= 2.5). Therefore, it is important to use methods to remove this pollutant from water. The TiO_2-mediated photocatalysis process has been successfully used to degrade pesticides during the past few years including BCL (4). However, no studies on the removal of BCL using ZnO have been reported. With this aim, in this study we have assessed the effectiveness of ZnO for the photooxidation of BCL in pure and environmental water in slurry photoreactor.

Photocatalytic experiments showed that the addition of ZnO (150 mg L^{-1}) in tandem with $Na_2S_2O_8$ (200 mg L^{-1}), used as electron acceptor, enhances the degradation rate of BCL (C_0=0.2 mg L^{-1}) in comparison with those carried out with catalyst alone and photolytic tests. The photodegradation of BCL followed first-order kinetics with an apparent rate constant K_{ap}=0.0963 min^{-1} ($t_{½}$=7 min) in pure water while in environmental water the decomposition of BCL slows down very significantly (K_{ap}=0.0052 min^{-1} and $t_{½}$=133 min) possibly due to the presence of some ions that can act as hydroxyl radical scavengers.

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