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Transformation of Z-thiacloprid by three advanced oxidation processes: Kinetics, intermediates and the role of reactive species

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ABSTRACT

Three advanced oxidation processes (AOPs), heterogeneous photocatalysis, vacuum ultraviolet (VUV) photolysis and γ radiolysis were used for the generation of reactive primary free radicals to induce the transformation of Z-thiacloprid in aqueous solution. The effects of dissolved oxygen and the initial concentration (from 10^{-6} to 10^{-4} mol L^{-1}) were investigated. The initial reaction rates increased with the initial concentration of thiacloprid, both in oxygen saturated and oxygen free solutions. Dissolved oxygen had significant effect on the transformation rate only in case of heterogeneous photocatalysis. Three main intermediates and the E-thiachloprid were detected using all three methods. One of these intermediates could be related to the reaction with e_{aq}^-, while the other two could be related to the $^\bullet$OH-initiated reactions. Heterogeneous photocatalysis showed the highest efficiency regarding the transformation of intermediates in presence of dissolved oxygen, while thiacloprid transformed with the highest initial reaction rate during VUV photolysis. However, according to the Electric energy per order (E_{EO}) data γ radiolysis was found to be the economically most feasible method, requiring several orders of magnitude less energy than VUV photolysis and heterogeneous photocatalysis for reduction of the target compound concentration by one order of magnitude in a unit volume.

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1. Introduction

Large number of methods have been suggested in the literature for the degradation of harmful organic molecules, for instance pesticide residues, in water and wastewater [1]. In these studies more and more attention is focused on the neonicotinoid family (imidacloprid, thiamethoxam, acetamiprid, clothianidin, dinotefuran, nitenpyram and thiacloprid), the fastest growing group among the insecticides. These compounds have long term impact on the ecosystem, especially they have harmful effects on bees, weakening their immune system, and increasing their sensitivity to pathogenic viruses [2]. The name neonicotinoids suggests similarity in the chemical structure with nicotine and acetylcholine, for exerting their effects on the acetylcholine receptors [3].

One of the representative members of neonicotinoides is Z-thiacloprid ({3-[(6-Chloropyridin-3-yl) methyl]-1,3-thiazolidin-2-ylidene} cyanamide) (Fig. 1). It has very high stability and good solubility in water (184 mg L^{-1} at 20 °C) [4]. This compound can be accumulated in the environment through the trophic network [5], and therefore, it is detected in an increasing amount in surface waters.

Due to the three biologically active groups in its structure, chloropyridine and thiazolidine rings, and the cyanoimino group, thiacloprid is strongly toxic with lethal dose of $LD_{50} = 444$ mg kg^{-1} for rats. In agriculture it is used against sucking and chewing pests [6] in crops, such as rapeseed, sunflower, potatoes, apple, as well as for corn seed dressing. Stability tests showed that thiacloprid was less persistent in acidic solution, but in alkaline media, it was stable for about 30 days [7].

The decomposition of neonicotinoids has been examined by several advanced oxidation processes (AOP) [8]. Zbiljić et al. showed, that the removal of acetamiprid using photo-Fenton process is

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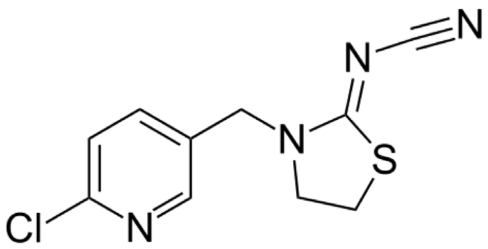

Fig. 1. Chemical structure of thiacloprid.

twice as effective (~10 min) as using Fenton processes only [9]. Imidacloprid transformation needed ~60 min using both Fenton and photo-Fenton processes combined with hydrodynamic cavitation [10]. Malato et al. reported that the degradation of imidacloprid using titanium dioxide (TiO_2) photocatalyst under UV-A irradiation is a relatively slow process (~0.61 mg L^{-1} min^{-1}) [11]. The photocatalytic degradation of imidacloprid, thiamethoxam and clothianidin on immobilised TiO_2 has also been studied. Within 2 h of photocatalysis, all three neonicotinoids were degraded following first order kinetics [12]. Thiamethoxams' transformations were investigated also using UV photolysis, ozonation and their combinations [13]. The effect of dissolved ozone and ferric ions on the intermediates of thiacloprid formed during TiO_2-based heterogeneous photocatalysis was investigated in suspensions [14–16] and using immobilized catalyst [17].

To our best knowledge no results have been published yet on the vacuum ultraviolet (VUV) photolysis and γ radiolysis of thiacloprid.

To understand the mechanism of transformation of organic compounds, one of the most important steps is gathering information about the nature of reactions of the target compound with the reactive species generated by AOPs.

Among the AOP methods VUV photolysis and γ radiolysis are good candidates to investigate the role of hydroxyl radical ($^{\bullet}OH$) and hydrated electron (e_{aq}^{-}) in the degradation of organic molecules. In contrast to the VUV photolysis, during γ radiolysis in dissolved oxygen (DO) free solutions beside the $^{\bullet}OH$, the role of the e_{aq}^{-} is also relevant. Although the basic mechanism of the TiO_2-based heterogeneous photocatalysis had been investigated by a great number of research groups [18,19] the identities of reactive species are still under intensive discussion. During the illumination of photocatalysts by UV light (λ_{max} = 365 nm for TiO_2) valence band holes (h^+, a localized oxidizing state) and conduction band electrons (e^-) form (Eq. (1)). The oxidation of organic solutes (OS) is assumed to take place directly by the surface hole, or through a $^{\bullet}OH$ on the surface (Eq. (4)) formed in the reaction of the hole with a hydroxyl anion or water molecule (Eq. (2)). It is an open question if the OS can react directly with the e^- at the surface of the catalyst. In the presence of DO its reaction with e^- (Eq. (3)) produces superoxide radical anion ($O_2^{\bullet-}$). In further reactions $O_2^{\bullet-}$ yields H_2O_2, which finally transforms into $^{\bullet}OH$ (Eq. (3), [19,20]).

$$TiO_2 + \text{UVphoton}_{\lambda = 365\,\text{nm}} \rightarrow e^- + h^+ \quad (1)$$

$$h^+ + {}^{-}OH(H_2O) \rightarrow {}^{\bullet}OH_{surf}({}^{\bullet}OH_{surf} + H^+) \quad (2)$$

$$e^- + O_2 \rightarrow O_2^{\bullet-} \rightarrow HO_2^{\bullet} \rightarrow HO_2^{-} \rightarrow H_2O_2 \rightarrow 2^{\bullet}OH \quad (3)$$

$$h^+(\text{or}\,{}^{\bullet}OH_{surf}) + OS \rightarrow \text{oxidizedproducts} \quad (4)$$

During the **VUV photolysis** of aqueous solutions, using a commercial Xe_2^* excimer lamp (λ = 172 nm), homolytic dissociation of water molecules results in $^{\bullet}OH$ and hydrogen radical ($H^{\bullet}$) with quantum yield of 0.42 (Eq. (5)) [21,22]. With low yield ionization also takes place. The so-called dry electron released in ionization may stabilize in the form of e_{aq}^{-} (Eq. (6)) [22,23]:

$$H_2O + \text{VUVphoton}_{\lambda = 172\,\text{nm}} \rightarrow H^{\bullet} + {}^{\bullet}OH$$
$$\Phi_{172\,\text{nm}}({}^{\bullet}OH, H^{\bullet}) = 0.42 \quad (5)$$

$$H_2O + \text{VUVphoton}_{\lambda = 172\,\text{nm}} \rightarrow H^+ + e_{aq}^{-} + {}^{\bullet}OH$$
$$\Phi_{172\,\text{nm}}(e_{aq}^{-}) < 0.05 \quad (6)$$

In VUV photolysis at 172 nm the photons are absorbed in a very thin layer of a few μm. In this reaction zone there is a strong competition between the reactions of reactive species ($^{\bullet}OH$ and $H^{\bullet}$) with each other and with thiacloprid and its intermediates.

During **γ radiolysis** of aqueous solutions the decomposition of water molecules results in $^{\bullet}OH$, e_{aq}^{-} and (in lower yield) $H^{\bullet}$, as primary radicals (Eq. (7)) with yields (so-called *G*-values) of 0.280, 0.280 and 0.062 μmol J^{-1}, respectively [24,25].

$$H_2O + \gamma\text{photon} \rightarrow {}^{\bullet}OH + e_{aq}^{-}(+{}^{\bullet}H) \quad (7)$$

In the presence of DO the reductive primary species ($H^{\bullet}/e_{aq}^{-}$) transform to less reactive hydroperoxyl radical/superoxide radical anion ($HO_2^{\bullet}/O_2^{\bullet-}$) (Eqs. (8) and (9)) [26].

$$^{\bullet}H + O_2 \rightarrow HO_2^{\bullet} \qquad k_8 = 1.2 \times 10^{10}\,\text{L mol}^{-1}\,\text{s}^{-1} \quad (8)$$

$$e_{aq}^{-} + O_2 \rightarrow O_2^{\bullet-} \qquad k_9 = 1.9 \times 10^{10}\,\text{L mol}^{-1}\,\text{s}^{-1} \quad (9)$$

In heterogeneous photocatalysis, VUV photolysis and γ radiolysis $^{\bullet}OH$ are assumed to play a key role in the pollutants' degradations, mainly in the presence of DO. However, their distributions in space are significantly different: i) in TiO_2 photocatalysis the reactive species are on the catalyst surface, ii) in VUV photolysis they are produced close to the window, with inhomogenous distribution, and iii) in γ radiolysis the reactive species, with the yields mentioned above, are more-or-less homogeneously distributed in the solution bulk.

Thiacloprid has three sensitive parts for the $^{\bullet}OH$-induced oxidation: 2-cloropyridine, thiazolidine and the cyanoimino part. Pyridine reacts with $^{\bullet}OH$, e_{aq}^{-} and $^{\bullet}H$ with the rate constants of 3.0×10^9 L mol^{-1} s^{-1}, 7.7×10^9 L mol^{-1} s^{-1} [27] and 6.0×10^8 L mol^{-1} s^{-1} [28], respectively. $^{\bullet}OH$ reacts with nicotinic acid with rate constant of 5.6×10^9 L mol^{-1} s^{-1} [29]. Due to the electron withdrawing Cl substituent the rate constant of 2-cloropyridine with $^{\bullet}OH$ (1.8×10^9 L mol^{-1} s^{-1} [29]) is smaller than that of pyridine. $^{\bullet}OH$ generally attacks the thioether groups also with rate constants of about 10^9 L mol^{-1} s^{-1}. The double bond in the cyanoimino part of the molecule may also be involved in reaction with this radical. In case of thiazolidine no data are available about its reactions with these primary radicals. Only one value of the $^{\bullet}OH$ rate constant with thiacloprid was determined using flash photolysis (7.5×10^{10} L mol^{-1} s^{-1} [30], however this rate constant is unrealistic since it is half of an order of magnitude higher than the diffusion limited value). There is no information available about the reactions of neonicotonoid insecticides with e_{aq}^{-} and $H^{\bullet}$.

The aim of this work was the comparison of thiacloprid transformation using heterogeneous photocatalysis, VUV photolysis and γ radiolysis in the presence and absence of DO, the study of the kinetic properties of thiacloprid reactions with the primary reactive species formed in these processes, and the identification of the intermediates formed during the applied treatments. The economic feasibility of the three methods was compared based on the Electrical energy per order (E_{EO}).

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