Kinetics of neonicotinoids destruction by UV irradiation

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1.- Introduction –Among other priority pollutants, the Directive 2008/105/EC of the European Parliament includes a group of neonicotinoid pesticides, which are a new class of neuro-active insecticides chemically similar to nicotine. Only around 5% of the neonicotinoid active ingredient is taken up by crop plants and most instead disperses into the environment [1]. In recent years, several studies have raised concerns about the negative impact of neonicotinoids on non-target organisms, in particular on honeybees and bumblebees, vertebrates and even humans [2]. According to this, the present work was designed to investigate the photodegradation of the five neonicotinoid insecticides included in the list of substances of the Decision (EU) 2015/495: thiamethoxam (TMX), imidacloprid (ICP), clothianidin (CTD), thiacloprid (TCP) and acetamiprid (AMP). The aim of this research was, in a first step, to evaluate the individual reactivity of these compounds towards UV irradiation, and to determine the quantum yields. Secondly, the simultaneous photodegradation of the five nicotinoid insecticides dissolved in both, UV water and real waters, by using UV irradiation alone and the combinations UV/H_2O_2 and UV/PS was investigated in order to assess the increase in the degradation efficiency as a result of the additional presence of HO· and SO_4·$^-$.

2. Results and Discussion - A first kinetic approach was made by assuming that the reaction follows pseudo-first order kinetics. Following this procedure, these rate constants k_{app} were deduced for each compound, at 20 ºC: 1.40±0.04, 0.65±0.02, 0.56±0.02, 0.28±0.02, and 0.10±0.01 min^{-1} for TMX, CTD, ICP, TCP and AMP, respectively. Later, the quantum yields ϕ for the photodegradation of neonicotinoids at 254 nm were evaluated, being the average values at 20 ºC: (77±3)x10^{-3}, (43±2)x10^{-3}, (48±1)x10^{-3}, and (17±2)x10^{-3} mol E^{-1} for TMX, CTD, ICP and TCP, respectively. Meanwhile, a lower value was obtained for AMP, ranging from 4.8x10^{-3} to 6.8x10^{-3} mol E^{-1}.

In a next stage, the photolysis of mixtures of the five selected nicotinoids simultaneously dissolved in waters was investigated. Thus, TMX presents the highest photodegradation rate, followed by ICP and CTD with almost similar rates, TCP, and finally, AMP with the lowest photodegradation rates. The additional presence of inorganic ions (i.e. bicarbonate, nitrate, nitrite and chloride) exerted a negative influence only on the photolysis TCP, the least photoreactive pollutant. However, the presence of humic acids inhibited the photolysis of the selected insecticides, probably due to the attenuation of UV irradiation (light screening). On the contrary, the additional presence of H_2O_2 and PS had different effects on the photodegradation of selected neonicotinoids, being their presence especially positive for the removal of AMP. Therefore, the contribution of indirect photolysis (radical pathway) is only important in the case of pollutants with low value of quantum yield such as AMP.

The presence of natural organic matter in real water matrices decreased the photodegradation rates. As occurred in UP water, the positive effect of the application of the AOPs UV/H_2O_2 and UV/PS was more pronounced on the degradation of AMP than on the remaining pollutants. However, this enhancement in the removal of neonicotinoids due to the additional presence of HO· and SO_4·$^-$ was lower in the real waters tested than in UP water. The UV/PS process led to greater degradation levels than the UV/H_2O_2 system due to the lower reactivity of SO_4·$^-$ than HO· with NOM and inorganic anions such as bicarbonate. All these results reveal that single UV irradiation and the AOPs UV/H_2O_2 and UV/PS could be effective processes to remove neonicotinoids from contaminated waters.

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3. References

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