



Degradation of neonicotinoids by UV irradiation: Kinetics and effect of real water constituents

Juan L. Acero*, Francisco J. Real, F. Javier Benitez, Esther Matamoros

Departamento de Ingeniería Química, Instituto Universitario de Investigación del Agua, Cambio Climático y Sostenibilidad (IACYS), Universidad de Extremadura, Avda. de Elvas s/n, Badajoz, Spain

ARTICLE INFO

Keywords:

Neonicotinoids
UV irradiation
Quantum yield
Sulfate and hydroxyl radicals
Water treatment

ABSTRACT

Neonicotinoids are a new class of insecticides whose potential side-effects on the human health and the environment have not yet been well investigated. Recently, the EU approved the Decision 2015/495 establishing a watch list of substances for Union-wide monitoring in the field of water policy, which includes five neonicotinoids: thiamethoxam (TMX), imidacloprid (ICP), clothianidin (CTD), thiacloprid (TCP) and acetamiprid (AMP). The photodegradation of neonicotinoids by monochromatic UV irradiation (254 nm) has been investigated. The photolysis rate followed pseudo-first order kinetics, with rate constant values depending on the nature of the specific compound, pH, and the presence or absence of radical scavengers. A method based on atrazine actinometry provided the following quantum yields at pH = 7: $(77 \pm 3) \times 10^{-3}$, $(43 \pm 2) \times 10^{-3}$, $(48 \pm 1) \times 10^{-3}$, $(17 \pm 2) \times 10^{-3}$ and $(5 \pm 2) \times 10^{-3}$ mol E⁻¹ for TMX, CTD, ICP, TCP and AMP, respectively. The effects of the presence of bicarbonate, nitrate, nitrite and chloride ions on the simultaneous photodegradation of neonicotinoids were not very significant, and only the removal of AMP, the least photosensitive neonicotinoid, was negatively affected. However, the photodegradation of neonicotinoids was clearly inhibited by the addition of humic acids. The results obtained in experiments performed in the presence of hydrogen peroxide or persulfate indicated that while direct UV photolysis was the main degradation pathway for TMX and even for CTD, ICP and TCP, the contribution of indirect photolysis (radical pathway) was important in the case of pollutants with low values of quantum yield such as AMP. Although the presence of natural organic and inorganic matter in real water matrices decreased the degradation rate of the selected neonicotinoids, UV photolysis and the AOPs UV/H₂O₂ and UV/PS processes constitute efficient technologies for the removal of these pollutants from contaminated waters.

1. Introduction

The European Commission, in its Decision (EU) 2015/495, provides an additional list of substances to be monitored in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament [1]. Besides other contaminants, this list includes a group of neonicotinoid pesticides, 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 [2]. In recent years, several studies have raised concerns about the negative impact of neonicotinoids on non-target organisms, in particular on honeybees and bumblebees [3], vertebrates [4] and even humans [5]. Since the 1990s, neonicotinoid pesticides have become the most widely used class of insecticide in the world [6]. As a consequence of the increase use, they have been detected in

environmental media such as plants, soil and water [7]. Because of their persistence through treatment systems such as wastewater treatment plants (WWTPs) [8], several neonicotinoids have been found with concentration in the order of ng L⁻¹ in surface water [9] and tap water [10]. Even at this low concentration, neonicotinoids may have a negative effect on non-target organisms [3].

The removal of pollutants in waters can be achieved by appropriate physical or chemical methods [11]. Among these techniques, the photodegradation processes based on the use of UV irradiation have shown to be very effective in advanced water treatment technologies for groundwater and drinking water remediation [11–13]. Low- and medium- pressure mercury lamps are the most common sources used for photolysis processes. Treatment with UV light (specifically its UV-C component at 254 nm) uses the ability of compounds to absorb light and suffer direct photodegradation. In addition, UV light at 254 nm is

* Corresponding author.

E-mail address: jlacero@unex.es (J.L. Acero).

<https://doi.org/10.1016/j.seppur.2018.09.076>

Received 25 July 2018; Received in revised form 13 September 2018; Accepted 25 September 2018

Available online 26 September 2018

1383-5866/ © 2018 Elsevier B.V. All rights reserved.

widely used for disinfection purposes. The quantum yield (ϕ) the parameter that indicates how efficiently a compound is degraded after absorption of a photon [14].

UV light can also be combined with a second chemical in the so-called advanced oxidation processes (AOPs). Common UV-based AOPs, such as the combinations UV/H₂O₂ and UV/S₂O₈²⁻, are known to be effective barriers to degrade and mineralize recalcitrant pollutants due to the generation of reactive species, such as hydroxyl and sulfate radicals [15,16]. Specifically, the combination of UV/H₂O₂ is characterized by the generation of hydroxyl radical (HO[•]), which reacts with most organic compounds with high rate constants in the range 10⁷–10¹⁰ L mol⁻¹ s⁻¹ [17]. On the other hand, persulfate ion (PS, S₂O₈²⁻) is the most common oxidant used for the generation of sulfate radical (SO₄^{•-}). The standard reduction potential of SO₄^{•-} (E° = 2.5–3.1 V) is almost similar to that of HO[•] (E° = 1.9–2.7 V), so that SO₄^{•-} can also act as a powerful and selective oxidant to degrade organic compounds through electron transfer mechanism [18]. Another advantage of the AOPs based on SO₄^{•-} is that the final product of the oxidation is sulfate ion (SO₄²⁻), which is practically inert and is not considered to be a pollutant [19].

Photolytic degradation of some neonicotinoids by various light sources and also some UV-based AOPs has been described in the literature [14,20–22]. Thus, the photolysis of some neonicotinoids has been investigated under natural sunlight conditions and the values of ϕ have been determined in the range 290–360 nm [14,20]. UV irradiation at 254 nm has also been applied to investigate the removal of certain neonicotinoid insecticides by either single photolysis [21], or by the combined process UV/chlorine [22]. Although values of ϕ determined at 254 nm for some neonicotinoids have been proposed in different investigations [21,22], the experimental conditions are not comparable, and independent verification is required. While most of these publications are focused on the identification of degradation products, the influences of the main operating variables and the presence of water matrix constituents (i.e. inorganic ions and organic matter) on the photodegradation of neonicotinoids have not been investigated in detail so far.

Therefore, 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 neonicotinoid insecticides by using UV irradiation alone and the combinations UV/H₂O₂ 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 SO₄^{•-}. And finally, the photodegradation of these compounds in several synthetic and real waters was evaluated in order to establish the influence of the natural substances present in these water matrices on their elimination.

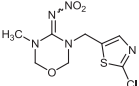
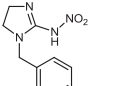
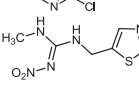
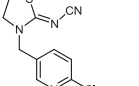
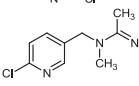
2. Materials and methods

2.1. Reagents and water systems

The selected neonicotinoids of the highest purity available (99%) were purchased from Sigma-Aldrich (Germany). Table 1 summarizes their chemical structures and physico-chemical properties. Sodium persulfate (Na₂S₂O₈), hydrogen peroxide (H₂O₂) and humic acids (HA) were also purchased from Sigma-Aldrich and used as received without further purification. Organic solvents (HPLC grade) and other chemicals for analysis (analytical grade) were supplied by Panreac (Spain). Ultra-pure water (UP) was obtained from a Milli-Q Water System (Millipore Iberica, Spain) with a specific resistance of 18 M Ω cm.

In addition to UP water, three water matrices were also used in different experiments: the first one was surface water (SW) collected

Table 1
Physico-chemical properties of selected neonicotinoids.

Neonicotinoid	Chemical Structure	MW, g mol ⁻¹	$\epsilon_{254\text{nm}}$, M ⁻¹ cm ⁻¹	pK _a
Thiamethoxam (TMX)		291.71	17,867	–
Imidacloprid (ICP)		255.67	11,433	11.1
Clothianidin (CTD)		249.68	15,033	11.1
Thiacloprid (TCP)		252.73	16,400	–
Acetamiprid (AMP)		222.68	19,133	–

from the public reservoir “Peña del Aguila”, in the Extremadura Community. The other water systems were two secondary effluents (SE1 and SE2) collected from municipal wastewater treatment plants located also in the Extremadura Community. The main quality parameters of these real waters are summarized in Table 2. The values of these parameters indicate that the sequence of the pollutant organic matter content was: SE2 > SW > SE1 > UP. These real water matrices were shipped in 20 L bottles, filtered through a 0.45 μ m cellulose nitrate filters within 24 h after sampling, and stored in a refrigerator at 4 °C until the experiments were performed.

2.2. Experimental procedures

The experiments were carried out in a 500 cm³ jacketed cylindrical glass reactor, thermostated at the consigned temperature and stirred by a magnetic stirrer. This reactor was equipped with an irradiation lamp located in axial position and a quartz sleeve housing the lamp. The irradiation source consisted in a low pressure mercury vapour lamp (TNN 15/32 nominal electrical power 15 W; Heraeus, Spain) which emitted a monochromatic irradiation at 254 nm. Previous chemical actinometry experiments, with the use of actinane (ATZ) as actinometer [23], were conducted to determine the photon fluence rate emitted by the irradiation source into the reactor. In the next group of experiments, the individual photolysis of the selected pollutants in UP water was investigated. The reactor was filled with 350 cm³ of an aqueous buffered solution of one neonicotinoid contaminant (1 μ M) and the temperature was kept constant at 20 °C. The concentration of each EC (1 μ M) was higher than typically found in environmental samples in

Table 2
Quality parameters of the selected real water matrices.

	SW	SE1	SE2
pH	7.4	8.2	7.8
Conductivity (μ S cm ⁻¹)	101.4	850	615
A _{254nm} (cm ⁻¹)	0.213	0.101	0.169
DOC (mg L ⁻¹)	6.5	4.3	9.4
COD (mg O ₂ L ⁻¹)	17	10	25
Alkalinity (mg CaCO ₃ L ⁻¹)	15.3	244	183
Nitrate (mg NO ₃ ⁻ L ⁻¹)	1.0	8.0	21.8
Nitrite (μ g NO ₂ ⁻ L ⁻¹)	40	237	842
Ammonium (mg NH ₄ ⁺ L ⁻¹)	0.02	0.07	0.42
Total nitrogen (mg N L ⁻¹)	1.60	2.72	5.6
Total phosphorus (mg P L ⁻¹)	0.07	1.60	0.31

Download English Version:

<https://daneshyari.com/en/article/11023725>

Download Persian Version:

<https://daneshyari.com/article/11023725>

[Daneshyari.com](https://daneshyari.com)