Supplementary Information

S1. Photocatalytic Experiments

For the photocatalytic removal of pesticides from the water matrix, the commercial titania Evonikc Aeroxide P25 was selected as model photocatalyst. The experiments were carried out in open vessel glass vials in batch-mode, using 10 mL of aqueous solutions of thiamethoxam (TMX), or flonicamid (FND). Depending on the experiment, the contaminants' concentration was varied from 1 to 20 ppm, while 1 mg of P25 (0.1 g/L) was suspended in the aforementioned solutions. In brief, the photodegradation process of the pesticides with P25 held inside a lab-made photoreactor, equipped with four UV-A lamps (350-390 nm, 0.5 mW cm^{-2}). The pesticides concentration and total organic carbon (TOC) were calculated with analytical methods, and then the photocatalytic efficiencies were determined.

The vials were placed into a photoreactor equipped with four UV-A lamps (Sylvania 15W/BLB, emitting at 350-390 nm, with power density 0.5 mW·cm^{-2}), at a distance of 15 cm and were illuminated for a period of 90 minutes for TMX and 60 for FND, which followed the adsorption experiment in dark [25]. During the photocatalytic experiments, at precise time intervals, the catalyst was separated from the aqueous suspension through filtration with PTFE filters and the supernatant solution was analyzed by HPLC-MS, in order to determine the pollutants' decomposition rate. Each experimental point in the respective graphs corresponds to consecutive photocatalytic runs, by using a new vial of 10 mL, under the same conditions. The photodegradation efficiency (%) was calculated by the following equation:

$$\Delta C/C_0\,(\%) = (C_0 - C)/C_0 \times 100\% \quad (1)$$

where C_0 is the pesticide concentration after adsorption equilibrium (mg/L) and C is the pesticide concentration at any time during the experiment (mg/L).

In order to evaluate to effect of acidic or alkaline medium on photocatalysis, the pH was first adjusted appropriately using HCl (0.1 M) and NaOH (0.1 M) solutions. In the case of scavengers' trap experiments, isopropyl alcohol (IPA), potassium iodide (KI), p-benzoquinone (BZQ) or potassium bromate ($KBrO_3$) were also added in the batch solutions as quenchers of hydroxyl radicals ($^{\bullet}OH$), holes (h^+), superoxide anions ($O_2^{\bullet-}$) or electrons (e^-), respectively. The added concentration of the scavengers was proportional to concentration, as proposed in other studies [41].

S2. Analytical Methods

Chromatographic analysis was achieved by using a ProStar 420 AutoSampler, an online degassing system and two Varian ProStar 210 pumps (Varian, Palo Alto, CA, USA). Detection was achieved using a triple quadrupole mass spectrometer (Varian model 1200 L) equipped with an electrospray ionization interface operating in positive mode. Typical source parameters were as follows: capillary voltage and collision energy varied depending on the precursor or product ion, source temperature was set at 250°C and drying gas temperature at 250°C.

For TMX, its metabolite Clothianidin and FND, a reverse-phase Zorbax SB C_{18} 3.5 μm particle size, 150 mm × 2 mm analytical column (Agilent) was used. Chromatography was achieved at a flow rate of 250 μL/min with a mobile phase consisting of H_2O/ACN (90:10 v/v)—1 mM ammonium formate, 0.1% HCOOH (solvent A) and ACN/H_2O (90:10 v/v)—1 mM ammonium formate, 0.1% HCOOH (solvent B) using the gradient program in Table S1 [48].

Table S1. Chromatography parameters with time for the pesticides' detection.

Time (min)	Solvent A%	Flow rate (μL/min)
0:00	80	250

0:40	80	250
06:30	100	250
10:00	80	250
15:00	80	250

A gradient program was used consisting of 80% of solvent A and 20% of solvent B, hold for 0.4 min and ramped linearly over the course of 6.3 min to 100% of solvent B. This composition was held for a further 4.7 min before returning to the initial condition. The column was re-equilibrated for 5 min at the initial mobile phase composition. The total run-time was 15 minutes. The injection volume was 5 μL. In order to avoid carryover, the autosampler syringe was purged with a mixture of methanol/water (50:50 v/v) before sample injection.

For FND metabolites 5-trifluoromethylnicotinic acid (TFNA) and 4-(trifluoromethyl)nicotinol glycine (TFNG), a Hypercarb 5 μm particle size, 100 mm × 2.1 mm analytical column (Thermo) was used [49]. Chromatography was achieved with a mobile phase consisting of 1% acetic acid in water + 5% methanol (solvent A) and 1% acetic acid in methanol (solvent B) using the gradient program in Table S2.

Table S2. Chromatography parameters with time for the detection of FND metabolites.

Time (min)	Solvent A%	Flow rate (μL/min)
0:00	100	200
10:00	70	200
11:00	70	400
18:00	70	400
19:00	10	400
22:00	10	400
22:06	100	200
30:00	100	200

Typical source parameters were as follows: capillary voltage and collision energy varied depending on the precursor or product ion as shown in Table S3.

Table S3. Overview of the LCMS-MS parameters for the analytes investigated.

	MRM	Capillary voltage	Collision energy
Thiamethoxam	292>211	40	6
	292>181	40	11
Clothianidin	250>132	57	20
	250>169	57	10
Flomicamid	230>203	64	7.5
	230>148	64	21.5
TFNA	192>148	64	16
	192>79	64	36
TFNG	249>148	28	14.5
	249>176	28	14

Moreover, in order to elucidate the degree of mineralization during the short irradiation period of 90 minutes, measurements of the Total Organic Carbon (TOC) were also accomplished by an online TOC analyzer (BioTector B3500, Hach, USA). The carbon removal efficiency (%) was calculated by the following equation:

$$\Delta(TOC)/TOC_0\,(\%) = (TOC_0 - TOC)/TOC_0 \times 100\% \quad (2)$$

where TOC_0 is the initial carbon concentration after adsorption equilibrium (mg/L) and TOC is the final carbon concentration after the photocatalytic run (mg/L).

S3. Photocatalytic Degradation and reaction kinetics of Pesticides

For a millimolar solution concentration, was assumed to calculate the corresponding degradation rate constant k_{app} (min^{-1}) for pseudo first-order kinetics, from the following equation:

$$\ln(C_0/C) = k_r \cdot K_{LH} \cdot t = k_{app} \cdot t \quad (3)$$

where C_0 is the initial concentration in mg/L, C is the concentration (mg/L) at a given time t (min), k_r is the reaction rate constant (mg/L·min) and K_{LH} is the adsorption constant of the reactant (L/mg). In addition, the initial degradation rate $r_{r,0}$ can be derived from the following equation:

$$r_{r,0} = k_{app} \cdot C_0 \quad (4)$$

Moreover, the linear form of the L-H model, expressed by the following equation, determines the dependence of $1/r_{r,0}$ values on the respective $1/C_0$ values:

$$1/r_{r,0} = 1/k_r + 1/k_r K_{LH} \cdot 1/C_0 \quad (5)$$

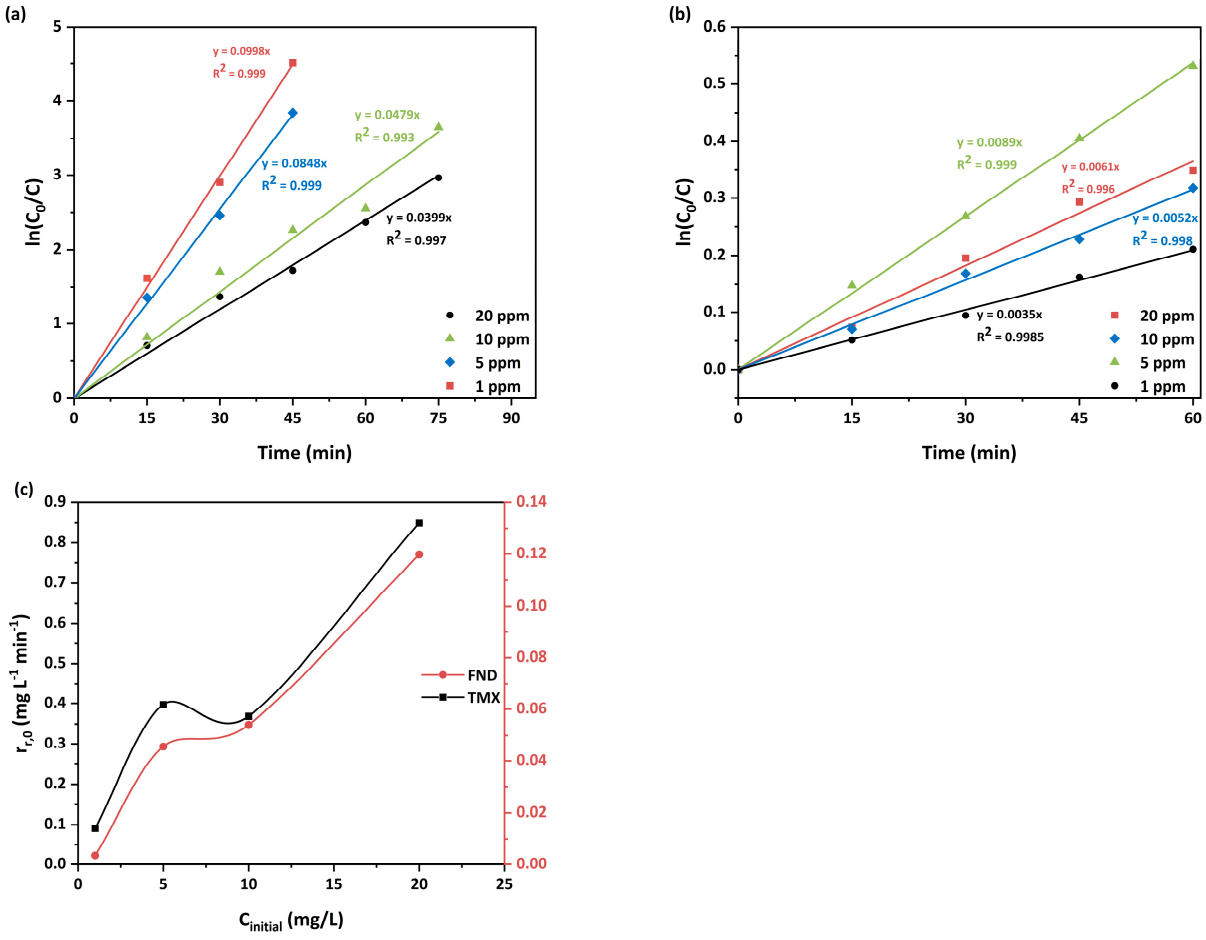

Figure S1. Degradation kinetics of photocatalytic degradation of (a) Linear transform $\ln(C_0/C) = f(t)$ of thiamethoxam (TMX) and (b) flonicamid (FND) using titania P25 at the studied concentrations (UV-A irradiation, 0.1 g/L TiO_2, natural pH, 25°C); Effect of the concentration on the initial degradation rate of both pesticides (c).

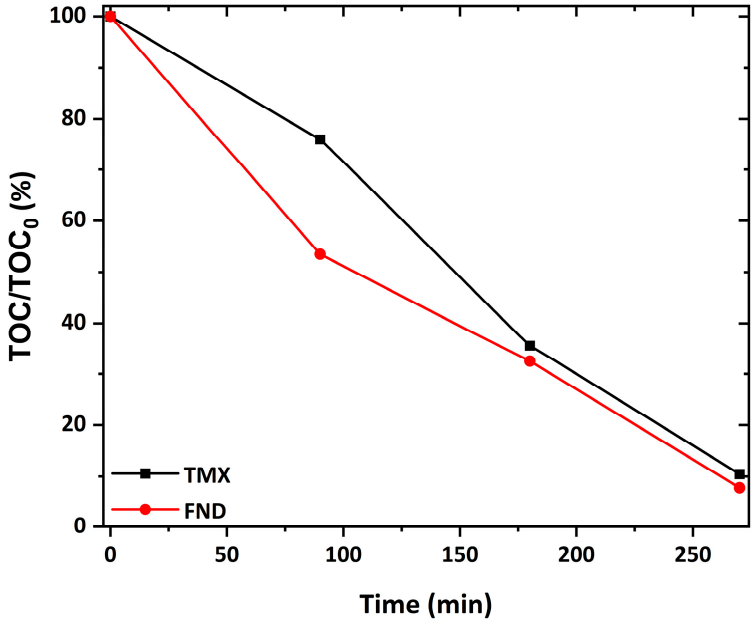

Figure S2. Total mineralization efficiency of thiamethoxam (TMX) and flonicamid (FND) during the photocatalytic process (UV-A irradiation, 0.1 g/L P25 TiO_2, 10 ppm concentration, natural pH, 25°C).