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SUPPLEMENTARY MATERIAL TO

Photodegradation of selected pesticides: Photocatalytic activity of bare and PANI-modified TiO_2 under simulated solar irradiation

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STRUCTURES OF THE PESTICIDES

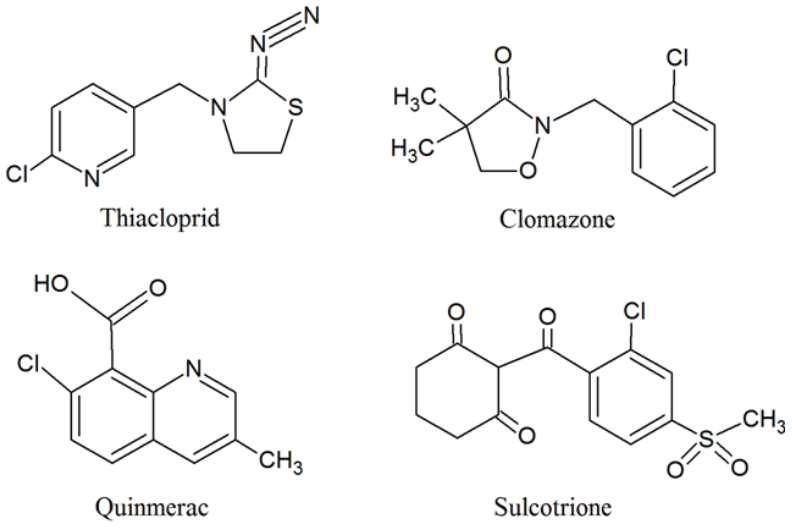

Fig. S-1. Structures of the pesticides.

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EXPERIMENTAL

Chemicals

All chemicals were of reagent grade and used without further purification. Insecticide thiacloprid, {(*Z*)-3-(6-chloro-3-pyridylmethyl)-1,3-thiazolidin-2-ylidenecyanamide}, CAS No. 111988-4998, $C_{10}H_9ClN_4S$, M_r = 252.8, PESTANAL®, analytical standard, 99.9 % purity) was purchased from Riedel-de Haën, herbicides clomazone {2-[(2-chlorophenyl)methyl]-4,4--dimethyl-3-isoxazolidinone}, CAS No. 81777-89-1, $C_{12}H_{14}ClNO_2$, M_r = 239.7, Pestanal®, analytical standard, 98.8% purity), quinmerac (7-chloro-3-methylquinoline-8-carboxylic acid), CAS No. 90717-03-6, $C_{11}H_8ClNO_2$, M_r = 221.64, PESTANAL®, analytical standard, 98.2 % purity) and {sulcotrione [2-(2-chloro-4-(methylsulfonyl)benzoyl]-1,3-cyclohexanedione}, CAS No. 99105-77-8, $C_{14}H_{13}ClO_5S$, M_r = 328.8, PESTANAL®, analytical standard, 99.9 % purity) were purchased from Fluka. Other chemicals, used without further purification, were *p.a.* purity. Namely, 35 % HCl and 85 % H_3PO_4, Lachema, Neratovice, Czech Republic; NaOH, ZorkaPharm, Šabac, Serbia; CaO, Carlo Erba, Milano, Italy; HPLC gradient grade methanol, J.T. Baker; $KBrO_3$ and 60 % $HClO_4$, Merck, Darmstadt, Germany; Na_2SO_4, $NaHCO_3$, $Ba(OH)_2$, and NaF, Kemika, Zagreb, Croatia; $SrSO_4$, BDH Laboratory, Safat, Kuwait; Disodium ethylenediaminetetraacetic acid (EDTA), Dojindo, Rockville, MD USA; humic acid, 30 % H_2O_2 and *tert*-butanol, 99.9 % acetonitrile (ACN), sulforhodamine B (SRB) and antibiotic/antimycotic solution, Sigma−Aldrich, St. Louis; foetal calf serum (FCS) and Dulbeco's modified essential medium (DMEM), PAA Laboratories GmbH., Pasching, Austria; penicillin and streptomycin, Galenika, Belgrade, Serbia; trypsin, Serva, Heidelberg, Germany; EDTA, Laphoma, Skopje, North Macedonia, were used in the experiments.

The river water samples were collected from the Danube (Petrovaradin, Serbia), the Tisa (Titel, Serbia), and the Begej (Zrenjanin, Serbia) in November 2014. The lake water samples from Lake Moharač (Erdevik, Serbia) and Sot Lake (Sot, Serbia) were also taken in November 2014 (Table S-I). The samples of environmental waters were filtered through filter paper (Whatman, diameter of 125 mm pore size 0.1 μm).

TABLE S-I. The physicochemical characteristics of the analyzed environmental waters

Parameter	Water type				
	Danube	Tisa	Begej	Lake Moharač	Sot lake
pH	7.92	7.60	7.61	8.20	7.91
El. conductivity at 25 °C, mS cm^{-1}	0.400	0.385	0.575	0.570	0.503
TOC / mg L^{-1}	5.17	6.43	9.75	9.47	7.73
Concentration of HCO_3^-, mg L^{-1}	209	155	240	329	293
Concentration of fluoride, μg L^{-1}	69.0	69.0	37.0	67.0	68.0
Concentration of chloride, mg L^{-1}	4.91	4.92	3.23	4.71	4.87
Concentration of sulphate, mg L^{-1}	27.71	27.08	14.44	26.76	27.13
Concentration of nitrate, mg L^{-1}	1.74	1.85	2.13	1.59	1.42
Concentration of calcium, mg L^{-1}	47.9	35.4	39.6	31.6	33.0
Concentration of potassium, mg L^{-1}	2.79	4.08	6.98	5.134	1.76
Concentration of magnesium, mg L^{-1}	12.6	7.62	13.48	32.6	28.6
Concentration of sodium, mg L^{-1}	10.85	20.87	45.98	20.20	12.64
Concentration of arsenic, μg L^{-1}	2.7	2.5	3.6	5.9	3.3
Concentration of barium, μg L^{-1}	21.2	21.1	24.2	14.0	14.4
Concentration of cadmium, μg L^{-1}	0.6	0.4	0.6	0.75	0.65

TABLE S-I. Continued

Parameter	Water type				
	Danube	Tisa	Begej	Lake Moharač	Sot lake
Concentration of chrome, μg L^{-1}	0.7	0.5	0.9	0.5	0.7
Concentration of copper, μg L^{-1}	3.8	3.0	5.3	1.1	7
Concentration of iron, μg L^{-1}	< DL	14.5	2.5	2.5	1.4
Concentration of manganese, μg L^{-1}	< DL	0.32	< DL	2.4	0.7
Concentration of nickel, μg L^{-1}	0.2	2.4	0.8	0.3	0.8
Concentration of strontium, μg L^{-1}	223.2	153.6	189.2	184.5	170.0
Concentration of zinc, μg L^{-1}	6.0	1.7	6.8	1.1	2.2

Analytical procedures

For the kinetic studies of the removal of pesticides from water, samples of about 0.5 cm^3 of the reaction suspension were taken at the beginning of the experiment, as well as at regular time intervals of irradiation (volume variation *ca*. 10 %), and after that filtered through Millipore (Millex-GV, 0.22 μm) membrane filters. The absence of adsorption of pesticide on the filter was confirmed by a preliminary test.

For the UFLC–DAD monitoring of thiacloprid 20-μl sample was injected and analysed using a Shimadzu UFLC–DAD, equipped with an Eclipse XDB-C18 column (150 mm × 4.6 mm i.d., particle size 5 μm, 25 °C). The UV/Vis DAD detector was set at 242 nm (wavelength of the maximum absorption of thiacloprid). The mobile phase (flow rate 1.0 cm^3 min^{-1}) was a mixture of ACN and 0.1 % aqueous H_3PO_4 (30:70, v/v, pH 2.25). The retention time for thiacloprid was 5.9 min. In the case of photocatalytic degradation of clomazone a 10-μl sample was injected. The UV/Vis DAD detector was set at 210 nm (wavelength of the maximum absorption of clomazone). The mobile phase (flow rate 1.0 cm^3 min^{-1}) was a mixture of ACN and 0.1 % aqueous H_3PO_4 (60:40, v/v, pH 2.65). The retention time for clomazone was 3.6 min. In the case of photocatalytic degradation of quinmerac, a 20-μl sample was injected. The UV/Vis DAD detector was set at 224 nm (wavelength of the maximum absorption of quinmerac). The mobile phase (flow rate 1.0 cm^3 min^{-1}) was a mixture of ACN and 0.1 % aqueous H_3PO_4 (50:50, v/v, pH 2.54). The retention time for quinmerac was 2.2 min. In the case of photocatalytic degradation of sulcotrione a 10-μl sample was injected. The UV/Vis DAD detector was set at 231 nm (wavelength of the maximum absorption of sulcotrione). The mobile phase (flow rate 1.0 cm^3 min^{-1}) was a mixture of ACN and 0.1 % aqueous H_3PO_4 (40:60, v/v, pH 2.50). The retention time for sulcotrione was 5.8 min.

For TOC analysis, aliquots of 10 cm^3 of the reaction suspension were taken before the beginning of the experiments (0 min of irradiation) and after 60 min of irradiation (each separate probe was performed). Subsequently, aliquots diluted to 25 cm^3 were analyzed on an Elementar Liqui TOC II analyzer according to the Standard US 120 EPA Method 9060A. In repeated runs, the results agreed within 3−10 %.

The pH of the suspension was measured using a combined glass electrode (pH-Electrode SenTix 20, WTW) connected to a pH-meter (pH/Cond 340i, WTW).

Toxicity tests

For the estimation of cytotoxic effect on the growth of mammalian cell lines, aliquots of 2 cm^3 of a suspension of sulcotrione (c_0 = 50 μmol dm^{-3}) was taken at the beginning of the experiment and at different time during the irradiation, filtered through 0.22 μm membrane

filters (Sartorius, Goettingen, Germany). The cell lines H-4-II-E (ATCC CRL-1548), HT-29 (ECACC 91072201), MRC-5 (ECACC 05090501), and Neuro-2a (ATCC CCL-131) were grown in DMEM medium, supplemented with 10 % heat inactivated FCS, 100 IU cm^{-3} of penicillin, 100 µg cm^{-3} of streptomycin, and 0.25 µg cm^{-3} of amphotericin B. Cells were cultured in 25 cm^3 flasks (Corning, New York, USA) at 37 °C in an atmosphere of 5 % CO_2 and high humidity, and sub-cultured twice a week. A single cell suspension was obtained using 0.1 % trypsin with 0.04 % EDTA.

Reaction mixtures after filtration of sulcotrione and catalyst (20 µl) were added to 180 µL of the culture medium with cells. The same volume (20 µL) of DDW was added to the control wells. Thus, the final concentration of all substrates (c_f) was 5 µmol dm^{-3}. Blank tests were performed using an aqueous suspension of bare TiO_2 (0.05 mg cm^{-3} without substrate), that were sonicated in the dark for 15 min and filtered through 0.22 µm membrane filters.

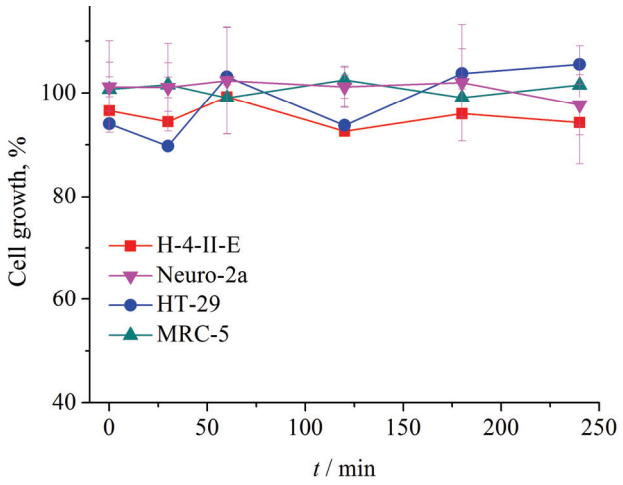

Fig. S-2. Effect of reaction mixtures of sulcotrione and formed intermediates on the growth of selected mammalian cell lines using bare TiO_2 after different irradiation times. Values represent mean ± *SD* of at least four measurements (n = 4).

Results and discussion. The cytotoxic effects of 5 µmol dm^{-3} sulcotrione, as well as aqueous suspension of 0.05 mg cm^{-3} bare TiO_2, depended on the histologic type of cell line. The obtained results showed that the highest inhibition of cell growth in the case of sulcotrione and bare TiO_2 was obtained in Neuro-2a (5.8 %) and H-4-II-E (8.8%) cell lines, respectively (Fig. S-2).

TABLE S-II. The mineralization degree of sulcotrione in the presence of bare TiO_2/TP nanocomposite suspensions

Type of catalyst	Mineralization degree, %
Bare TiO_2	40.45
TP-50	31.27
TP-100	10.62
TP-150	36.63

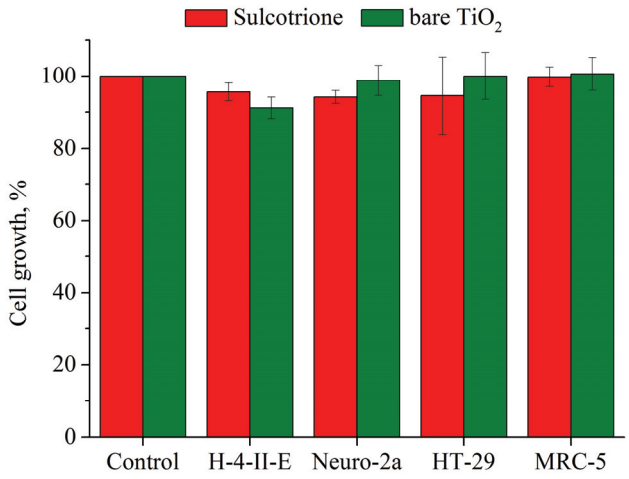

Fig. S-3. Effects of sulcotrione solution and filtered aqueous suspension of bare TiO_2 nanocomposite on the growth of selected mammalian cell lines.
Values represent mean ± *SD* of at least four measurements (n = 4).