Supplementary Material

Photodegradation of selected pesticides: TiO_2/polyaniline nanocomposites catalytic activity under simulated solar irradiation

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EXPERIMENTAL

Chemicals

All chemicals were of reagent grade and were 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 are also used without further purification and 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

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antibiotic/antimycotic solution, Sigma−Aldrich, St. Louis; fetal 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, FYROM were used in experiments.

Analytical procedures

For the kinetic studies of pesticides removal 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 thiacloprid maximum absorption). 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 clomazone maximum absorption). 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 quinmerac maximum absorption). 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 sulcotrione maximum absorption). 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 is performed). After that aliquots diluted to 25 cm^3 and analyzed on an Elementar Liqui TOC II analyzer according to Standard US 120 EPA Method 9060A.

In repeated runs, the results agreed within 3−10%.

pH of suspension was measured using a combined glass electrode (pH-Electrode SenTix 20, WTW) connected to the 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 suspension of sulcotrione (c_0 = 50 μmol dm^{-3}) was taken at the beginning of the experiment, as well as at different time during the irradiation and after that 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 the 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}. The blank tests were performed using the 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.

RESULTS AND DISCUSSION

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 show 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. S1).

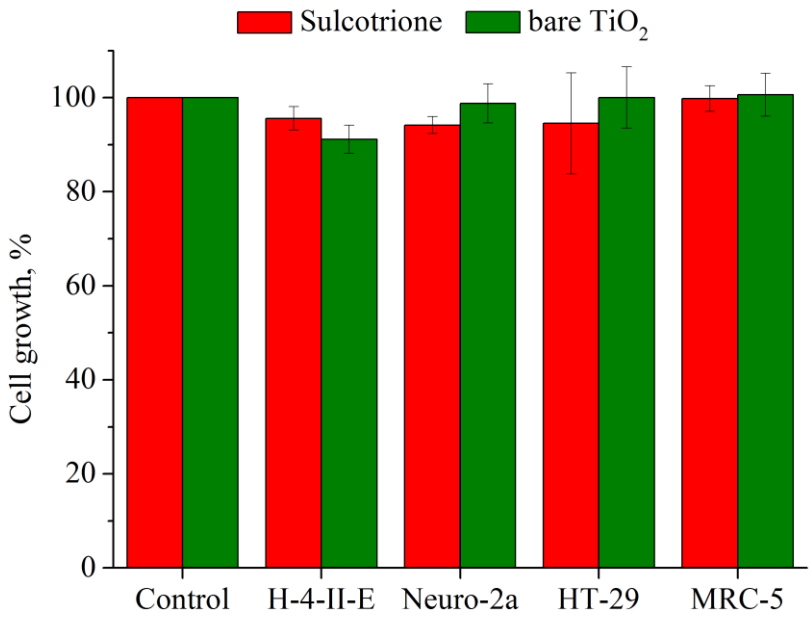

Fig. S1. Effects of sulcotrione solution and filtered aqueous suspension of bare TiO_2 nanocomposite on the growth of selected mammalian cell lines. Values represent mean ± SD of at least four measurements (n = 4).