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Photodegradation of selected pesticides: Photocatalytic activity of bare and PANI-modified TiO$_2$ under simulated solar irradiation

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Abstract: In this paper the efficiency of photocatalytic degradation of different pesticides was investigated using bare TiO$_2$ and modified TiO$_2$ nanoparticles with polyaniline under the simulated solar irradiation. Sulcotrione has shown the highest percentage of degradation and further experiments were related to this herbicide. Mineralization and cytotoxicity of starting compound and intermediate species formed during the decomposition in double distilled water (DDW), as well as efficiency of removal from various environmental waters were studied. Content of the most abundant ions present in river Danube was simulated in DDW and their influence was evaluated. It was found that cytotoxicity was in all cases below 11% and the efficiency of photocatalytic degradation in environmental waters decreased compared with DDW. Furthermore, addition of different scavengers revealed that the main path of degradation is through holes, while the presence of H$_2$O$_2$ decrease and KBrO$_3$ increase the efficiency of photocatalytic degradation compared with the system without mentioned electron acceptors.

Keywords: pesticides; bare TiO$_2$ nanoparticle; TiO$_2$/polyaniline nanocomposite; citotoxicity; environmental waters; radical, hole, and electron scavengers

INTRODUCTION

In order to protect crops from specified types of pests, today in agriculture, a usual practice is using different pesticides. Bearing in mind the importance and extensive use of pesticides in agriculture, mentioned chemicals can reach the environmental waters as a consequence of combination of run-off, accidental spillages, spray drift, drainage, or atmospheric deposition.

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Since the appearance of pyrethroids, neonicotinoid insecticides belong to the fastest growing insecticides on the market. In the past, the stability of neonicotinoids in the environment was extensively studied. For thiacloprid, it has been found that it is resistant to water hydrolysis at neutral and acidic pH. Also, thiacloprid showed significant photostability under the influence of simulated solar radiation.\(^2\)-\(^5\)

Herbicide clomazone is applied for suppression of various types of weeds in different cultivation fields.\(^6\) It has the potential for water pollution because of its high water solubility.\(^7\) Residues of clomazone were found in samples taken from river waters in rice cultivation areas.\(^6\)

Quinclorac belongs to quinoline group, which is a relatively new class of highly selective herbicides, with recently commercial use.\(^8\) This herbicide is relatively well soluble in water and hardly degradable.\(^9\) According to the Report from the Swedish Board of Agriculture and the Swedish Environmental Protection Agency\(^10\) quinclorac has been detected in ground, surface and drinking water. In addition, quinclorac can potentially cause pollution of the entire ecology through food chain leaving negative consequence also to human health.\(^11\)

Sulcotrione belongs to the class of triketone herbicides and is used to control dicotyledonous weeds and barnyard grass in maize production fields. Beside good properties in control of weeds, this herbicide is a potential pollutant, wherein sulcotrione and its degradation product (2-chloro-4-(methylosulfonyl) benzoic acid were detected in high concentrations in water from Klodnica River in Poland.\(^12\) Results of some studies have indicated that sulcotrione and/or its degradation products are toxic toward microorganism Vibrio fischeri,\(^13\) genotoxic toward Allium cepa root meristem\(^14\) and Vicia faba seedlings.\(^15\)

Considering that pesticides have negative influence on the living organisms, in the recent years more obvious was the need for their monitoring and control. Pollution of the aquatic environment due to the presence of pesticides has encouraged researchers to find ways to prevent such pollution.\(^16\) Clear and perceivable advantages were found using Advanced Oxidation Processes (AOPs) in the treatment of pesticides.\(^17\) Among different AOPs, heterogeneous photocatalysis represents low-cost, versatile, environmentally friendly, and one of the most promising green chemistry method for removal of different contaminants.\(^18\) In order to prevent the harmful effect which arises as a consequence of hazardous pollutants presence, photocatalytic degradation of water contaminants is used to detoxify or treat the wastewater.\(^19\)

The main disadvantage of photocatalytic degradation using TiO\(_2\) as photocatalyst is occurrence of electron–hole pair recombination, which as a consequence decreases the quantum efficiency. Besides, wide band gap, which is 3.0 eV for rutile, and 3.2 eV for anatase, narrows absorption of photons to
The ultraviolet region (wavelength < 390 nm). The last one reduces the practical use of mentioned processes in the presence of TiO$_2$ for solar light harvesting.$^{20}$

In the past decades, several studies were based on the combination of TiO$_2$ nanoparticles with polyaniline (PANI) due to the increased visible light absorption property as a result of the synergistic action between the conducting polymers and TiO$_2$.$^{21-24}$ The potential applicability of TiO$_2$/PANI (TP) nanocomposites synthesized with different molar TiO$_2$ : PANI ratios (TP-50, TP-100, and TP-150)$^{22}$ as a photocatalysts was checked following the photodegradation reaction of organic compounds: pharmaceuticals (propranolol, and amitriptyline) and pesticides (sulcotrione, and clomazone) using UV irradiation. It was found that the photocatalytic degradation of sulcotrione is the best of all investigated compounds and TP-150 was the most efficient catalyst in the mineralization of pesticides.$^{25}$ Further, results of the UV/Vis reflectance spectra$^{22}$ indicate that mentioned TP nanocomposites can be activated by UV and visible light simultaneously, which opens the possibility of their application as photocatalysts. Because of that the aim of this work was to investigate the photodegradation behaviour of selected pesticides (thiacloprid, clomazone, quinmera, and sulcotrione; Fig. S1, Supplementary material) in aquatic systems using simulated solar irradiation in the presence of bare TiO$_2$, as well as TP nanocomposites. In addition, due to the highest percentage of photodegradation and mineralization of sulcotrione using bare TiO$_2$, further investigations were related to sulcotrione. Namely, cytotoxicity of starting compound and intermediate species formed during the decomposition in double distilled water (DDW), as well as efficiency of sulcotrione removal from various environmental waters (Danube, Tisa, and Begej rivers, as well as Lake Moharač and Sot lake) were studied. Moreover, the most abundant ions which were identified in the water from river Danube were added to DDW in order to evaluate their influence. Finally, in order to investigate the influence of active radicals, holes and electrons on the efficiency of sulcotrione photodegradation using bare TiO$_2$ under simulated solar irradiation, different scavengers were added to the reaction mixture.

The kinetics of the photodegradation was monitored by ultrafast liquid chromatography with diode array detector (UFLC–DAD). The process of mineralization was accompanied by determination of total organic carbon (TOC). In order to evaluate the hazardousness to the environment of the photocatalytic treatment of waters containing sulcotrione and formed intermediates, for toxicity assessment mammalian cell lines were used (rat hepatoma (H-4-II-E), mouse neuroblastoma (Neuro-2a), human colon adenocarcinoma (HT-29), and human fetal lung (MRC-5).
EXPERIMENTAL

Chemicals, water samples and catalysts

All chemicals were given in the Supplementary Material. The environmental water samples collection and the physico-chemical characteristics of water samples were given in Table S1, Supplementary material.

$\text{TiO}_2$ catalysts, bare and modified with polyaniline in different $\text{TiO}_2$ : PANI molar ratios (TP-50, TP-100, and TP-150), were prepared as previously described. Details are given in Sojić Merkulov et al. The formation of nanocomposite was proved using Raman spectroscopy and TEM measurements.

Photodegradation procedure

The photocatalytic degradation was carried out in a cell described previously. For halogen lamp the visible light intensity was 63.85 mW cm$^{-2}$ and UV radiation intensity was 0.22 mW cm$^{-2}$. The radiation energy fluxes were measured using a Delta Ohm HD 2102.2 (Padova, Italy) radiometer which was fitted with the LP 471 UV (spectral range 315–400 nm) and LP 471 RAD (spectral range 400–1050 nm) sensor. Also, the lamp output was calculated to be ca. $1.7 \times 10^{-9} \text{Einstein cm}^{-3} \text{min}^{-1}$ using potassium ferrioxalate actinometry.

Experiments were performed using 20 cm$^3$ of 50 µmol dm$^{-3}$ pesticide (thiacloprid, clomazone, quinmerac, and sulcotrione) suspension containing 0.5 mg cm$^{-3}$ of catalyst (bare $\text{TiO}_2$ or TP). The aqueous suspension of catalyst was sonicated (50 Hz) in the dark for 15 min before irradiation, in order to uniformly disperse the photocatalyst particles and to attain adsorption equilibrium. Before irradiation, the suspension thus obtained was set at 25.0 °C in a stream of O$_2$ (3.0 cm$^3$ min$^{-1}$). During irradiation, the mixture was stirred at a constant rate under continuous gas flow. All experiments were performed at natural pH (for thiacloprid ~5.7, clomazone ~3.5, quinmerac ~4.6, and sulcotrione ~3), except when studying the effect of the quality of environmental waters on photocatalytic degradation of sulcotrione.

Analytical procedures

Experimental conditions for the UFLC–DAD, total organic carbon (TOC), and pH measurements can be found in the Supplementary Material.

Toxicity tests

Examination of the cytotoxic effect on the growth of cell lines was described in the Supplementary Material. The cell growth was evaluated by the colorimetric sulforhodamine B (SRB) assay of Skehan et al. modified by Četojević-Simin et al.

RESULTS AND DISCUSSION

Photocatalytic oxidation of selected pesticides using TiO$_2$/polyaniline nanocomposites

Recently, the novel modified TiO$_2$ nanostructures have gained great attention because of extended adsorption range to the visible light region. Several methods of TiO$_2$ modification have been proposed in order to achieve the utilization of visible light.

Conductive polymers such as polyaniline have been used as a sensitizer in polymer-sensitized TiO$_2$ nanocomposites due to its unique electrical, optical, and photoelectric properties and the advantages of easy synthesis and low cost. Owing to its good thermal conductivity and thermostability, nanoscale polyaniline can be used as substitute products of the solar materials in
photovoltaic devices.\textsuperscript{23} Under UV irradiation, conjugated polymers promote the separation efficiency of photoinduced electron–hole pairs due to high mobility of photoinduced holes in the conjugated polymers. Under visible light irradiation, conjugated polymers in hybrid materials are excited to produce photoinduced electron–hole pairs and then the photoinduced electrons are injected into the conduction band (CB) of TiO\textsubscript{2}. Namely, the electrons from TP nanocomposites coupled with the polymers can be excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital of the polymers under visible light irradiation. Then the excited electrons (e\textsuperscript{−}) can be injected to the conduction band of TiO\textsubscript{2} and react with the electron acceptors such as oxygen adsorbing on the TiO\textsubscript{2} surface to generate oxidative species, such as hydroxyl radicals and superoxide radical anions. The surface of TiO\textsubscript{2} is generally good adsorber of oxygen which act as an electron scavenger, due to position of CB of TiO\textsubscript{2} and potential of O\textsubscript{2}/O\textsubscript{2}\textsuperscript{•−} formation, while, in the case of TP nanocomposites polymer is hole scavenger. If bare TiO\textsubscript{2} nanoparticles were used as photocatalyst, hole scavengers were organic pollutants (thiacloprid, clomazone, quinmerac, and sulcotrione) and excited electrons were used for formation of super oxide radical ions, hydrogen peroxide, and hydroxyl radicals.\textsuperscript{30} The photoinduced holes (h\textsuperscript{+}) are left in HOMO of the polymers. Therefore, the photocatalytic activity of TiO\textsubscript{2} under visible light could be enhanced by using conductive polymers as stable photosensitizers to modify TiO\textsubscript{2} nanoparticles.\textsuperscript{25}

Radoi\v{c}i\v{c}\v{e}\v{c} \textit{et al.}\textsuperscript{22} reported that presence of the PANI-emeraldine salt in the case of TP-50; PANI-emeraldine salt and PANI-emeraldine base-like segments in the case of TP-100 and branched oligomers in the case of TP-150 were confirmed by Raman spectroscopy. Moreover, the surface of TiO\textsubscript{2} is most likely hindered in the case of TP-50 sample because of high content of PANI. Additionally, in the case of TP-150, TiO\textsubscript{2} surface is probably only partially covered due to the lowest content of PANI.\textsuperscript{22} The photocatalytic activities of TP nanocomposites, in the process of thiacloprid degradation, enhance as the content of PANI in the nanocomposite decreases, with a maximum value for TP-150 (13\%). In the case of TP-50, TiO\textsubscript{2} surface is hindered with positively charged PANI-emeraldine salt which probably causes repulsion of thiacloprid molecule (pK\textsubscript{a} value for thiacloprid is not applicable). As the content of PANI decreases and beside emeraldine salt, emeraldine base-like segments are also present, the interaction with thiacloprid is better. The highest efficiency of photocatalytic degradation of thiacloprid can be noticed in the presence of TP-150, where only branched oligomers are present. Moreover, examination of the photodegradation of selected pesticides under simulated solar irradiation suggests that TP nanocomposites showed higher photocatalytic activity for elimination of clomazone and quinmerac compared with bare TiO\textsubscript{2}. Namely, in the presence of bare TiO\textsubscript{2}, TP-50, TP-100, and TP-150 nanocomposites 10, 28, 25, and 26\% of
clomazone was removed and 0.5, 18, 27, and 8 % of quinmerac from the suspension after 240 min of irradiation, respectively (Fig. 1). TP nanocomposites showed very similar activity in the case of photocatalytic degradation of clomazone. Slight better activity showed TP-50 probably due to electrostatic or hydrogen bonding between positively charged PANI-emeraldine salt (−NH•−) and free electron pair on the nitrogen atom. The highest efficiency of photocatalytic degradation of quinmerac is noticed in the presence of TP-100. This may be also explained by electrostatic interaction of emeraldine salt with nitrogen atom and by protonation of emeraldine base-like segments. Furthermore, the surface of TiO₂ is less hindered with PANI groups which enable interaction of carboxyl group with the OH groups on the surface of TiO₂. While pKₐ value for clomazone also is not applicable, for quinmerac pKₐ value is 4.31. It means that at pH ~5 deprotonated form is mostly present in the suspension, wherein at this pH nanocomposites are protonated (pHₚzc is 5.2), therefore there is attraction between anion of quinmerac and nanocomposites. In contrast to mentioned pesticides, TiO₂ modified with polyaniline showed decrease of sulcotrione photocatalytic degradation efficiency compared with bare TiO₂.

Fig. 1. Efficiency of selected pesticides elimination using bare TiO₂ and TP nanocomposites after 240 min of simulated solar irradiation. Experimental conditions: c₀ = 50 µmol dm⁻³; catalyst loading 0.5 mg cm⁻³.

Namely, about 26 % of compound has been removed using TP-50 and TP-100, while 35 % has been removed using TP-150. The results can be viewed in different ways, concerning the optical properties of nanocomposites, bearing in mind the mechanism of light absorption, the molecular structure of selected pesticides and PANI layer in the nanocomposites.²² It can be assumed that molecules of sulcotrione have better interaction with OH groups on the surface of TiO₂ than with positively charged PANI-emeraldine salt. TP-150 showed slightly better activity than TP-50 and TP-100, due to smaller content of PANI, more available OH groups on the surface of TiO₂, and the presence of only branched
emeraldine oligomers. Besides, 52% of sulcotrione has been eliminated from the aquatic suspension using bare TiO$_2$. Namely, initial pH value of suspension in DDW was ~3 wherein the higher degradation rate may be probably attributed to interaction of sulcotrione anion ($pK_a = 3.13$) with the protonated sites of the catalyst ($pH_{pzc}$ for bare TiO$_2$ is 5.2).

Complete mineralization of the organic target compound to CO$_2$ and inorganic anions is the desirable result for every treatment process. The process of mineralization of selected pesticides was studied by TOC measurements (Table S2, Supplementary material). It was found that, in the case of thiacloprid, clomazone, and quinmerac photodegradation, mineralization practically did not occur, while 40% of sulcotrione was mineralized using bare TiO$_2$ after 240 min of irradiation. Furthermore, mineralization was slower than removal of sulcotrione, which can be explained by the forming of organic intermediates during the photocatalytic process. Since bare TiO$_2$ was the most efficient in the photocatalytic degradation of sulcotrione, citotoxicity experiments and efficiency of photocatalytic degradation of sulcotrione in environmental waters were carried out using mentioned catalyst under simulated solar irradiation.

Toxicity assessment

Degradation of pesticides in the environment can potentially generate many byproducts that are sometimes persistent and requires better knowledge on reactivity and toxicity. In order to evaluate the environmental hazardousness of the water containing sulcotrione and formed reaction intermediates using bare TiO$_2$ under simulated solar irradiation, in vitro growth of the H-4-II-E, Neuro-2a, HT-29, and MRC-5 cell lines was evaluated (Fig. S2, Supplementary material).

The blank test of aqueous solution of 5 μmol dm$^{-3}$ sulcotrione, as well as filtered aqueous suspension of 0.05 mg cm$^{-3}$ bare TiO$_2$ also have been tested (Fig. S3, Supplementary material). As can be seen, the effect of photodegraded mixtures on the growth of selected cell lines was dependent on the time of irradiation and type of cell line. Based on the results, it appears that both – growth inhibition and growth stimulation were observed within 240 min of irradiation using sulcotrione photodegraded mixtures in the case of all cell lines. The obtained results showed maximum inhibition of cell growth of 11% after 30 min of irradiation and the maximum stimulation of 5% obtained after 240 min of irradiation in HT-29 cell line. The inhibition of cell growth was influenced by the parent compound (blank test of sulcotrione with ~5% growth inhibition, Fig. S3, Supplementary material) and the mixture of sulcotrione and its photocatalytic degradation intermediates (Fig. S2, Supplementary material) after different irradiation times. In the case of cell line MRC-5, growth inhibition or stimulation is negligible for blank tests of sulcotrione and bare TiO$_2$ and also for photodegradation mixtures of obtained intermediates is below 2%. The highest inhibition of cell growth for blank test of sulcotrione (~6%) was noticed in the case of Neuro-2a cell line. However, during irradiation less toxic
intermediates were formed with stimulation or inhibition growth up to 2 %. Bare TiO$_2$ showed the highest toxicity, growth cell inhibition of ~9 %, at the cell line H-4-II-E (blank test, Fig. S3, Supplementary material). At the same cell line blank test of sulcotrione showed growth inhibition of ~4 %. Furthermore, photodegradated mixture in the presence of bare TiO$_2$ showed only growth inhibition with maximum value of ~7 % after 120 min of irradiation. At other irradiation times inhibition growth was less than 6 % with minimum inhibition of ~1 % after 60 min. In addition, toxicity was reduced, compared with blank tests, in the case of cell lines Neuro-2a and H-4-II-E, in the process of photocatalytic degradation of sulcotrione. However, citotoxicity in all cases was substantially lower compared to the cytotoxic drugs and the known toxicant, HgCl$_2$.\textsuperscript{31}

\textit{Photocatalytic activity of bare TiO$_2$ in environmental waters and evaluation of different ions influence}

It is well known that the composition of environmental waters can influence the efficiency of photocatalytic degradation of pesticides. In this context, it must also be considered that the real water might contain substances that could compete with the target pollutant for the oxidizing agent (•OH), such as other organic and inorganic compounds and natural organic matter. This usually causes a decrease of photodegradation efficiency.\textsuperscript{32} Because of that photocatalytic degradation of sulcotrione in environmental waters was investigated (Danube, Tisa, and Begej rivers, as well as Lake Moharač and Sot lake) using bare TiO$_2$. Examination of sulcotrione photodegradation under simulate solar irradiation suggest that herbicide removal of 15 % was only obtained in water from Sot lake after 240 min of irradiation (Fig. 2). On the other hand, it has been found that the degradation of herbicide was the most efficient in DDW.

![Fig. 2. Influence of water type on efficiency of sulcotrione photocatalytic degradation.](image)
Experimental conditions: $c_0$(sulcotrione) = 50 µmol dm$^{-3}$; bareTiO$_2$ loading 0.5 mg cm$^{-3}$.\textsuperscript{31}
This behaviour can be explained by the presence of inorganic and organic matter in examined environmental waters which affect the efficiency of photodegradation process. Other reason might be different pH values for DDW (~3) in comparison to environmental waters (~8). Namely, the higher degradation rate at a lower pH may be probably attributed to a more effective binding of sulcotrione molecule to the protonated sites of the catalyst.

Bearing in mind that photodegradation efficiency in the water from river Danube is among the least efficient, ions content in the concentrations for this water were added to DDW in order to simulate and evaluate their influence. First simulation of ions was investigated without adjusting pH value of suspension and the obtained results are presented in Fig. 3a. In the case of HCO$_3^-$, SO$_4^{2-}$, and Ca$^{2+}$ adding, photodegradation of sulcotrione was not observed. It is assumed that SO$_4^{2-}$, Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$ ions decrease the efficiency of photocatalytic degradation of sulcotrione by decreasing the adsorption of substrate on the surface of catalyst. Moreover, HCO$_3^-$ can react with *OH radicals (reaction 1) thus decreasing the efficiency of removal. Another reason for negligible photocatalytic degradation, in the case of adding HCO$_3^-$ and also Ca$^{2+}$ is pH value ~8 at which there is repulsion between deprotonated both bare TiO$_2$ and sulcotrione.

\[
\text{HCO}_3^- + \cdot\text{OH} \rightarrow \text{CO}_3^- + \text{H}_2\text{O} \quad \text{(1)}
\]

However, addition of humic acid in the system leads to improvement of sulcotrione photocatalytic degradation efficiency compared to DDW at natural pH ~3, wherein 63 % and 52 % of sulcotrione was removed, respectively. According to Wu et al., humic acid can promote the generation of *OH radicals which increases efficiency of sulcotrione removal.

In the same way all ions and humic acid were added separately to suspension and pH value was adjusted at 8, which corresponds to pH value of environmental waters (Fig. 3b).

Fig. 3. Influence of different ions addition on photocatalytic degradation efficiency of sulcotrione at: a) natural pH and b) pH 8. Experimental conditions: $c_0$(sulcotrione) = 50 µmol dm$^{-3}$; bareTiO$_2$ loading 0.5 mg cm$^{-3}$
Obtained results show that photocatalytic degradation of sulcotrione was not obtained in almost all cases. Slight degradation of 10% after 240 min of irradiation was observed in the case of HCO$_3^-$ addition. From the obtained results it may be concluded that pH value has strong influence on the efficiency of sulcotrione photocatalytic degradation.

Effect of *OH scavengers and holes

Information about the influence of active radicals and holes on the efficiency of photocatalytic degradation is very important in view of practical application. The results of our previous work clearly indicate that processes on the surface of catalyst play the main role in the sulcotrione photodegradation. Namely, the disappearance of sulcotrione under UV light using TiO$_2$ Degussa P25 takes place via *OH radicals and holes,$^{36}$ but in the case of TP-150 the main path of degradation is through holes and O$_2^*$, wherein surface *OH radicals are only partly involved in removal of sulcotrione in the presence of TP-150 under UV irradiation.$^{25}$ In the present work (Fig. 4) the effects of addition of NaF, tert-butanol, and EDTA as scavengers of surface *OH radicals, bulk *OH radicals, and holes, respectively, were investigated. It was found that EDTA has a remarkable influence on the photodegradation using bare TiO$_2$ under simulated solar irradiation. Furthermore, surface *OH radicals partly participate in the photocatalytic degradation of sulcotrione, wherein the main path of degradation is through holes. From Fig. 4 it can be seen that bulk *OH radicals have no influence on the efficiency of sulcotrione photocatalytic degradation.

Fig. 4. Effect of active radicals and hole scavengers (10 mmol dm$^{-3}$) on the efficiency of sulcotrione ($c_0 = 50$ µmol dm$^{-3}$) photocatalytic degradation using bare TiO$_2$ (0.5 mg cm$^{-2}$) under simulated solar irradiation.

Effect of the electron acceptors

Therefore, several approaches exist in order to improve the photocatalytic efficiency of TiO$_2$. One of the strategies for inhibiting electron–hole
recombination is to add other (irreversible) electron acceptors (H$_2$O$_2$, and KBrO$_3$), besides O$_2$, to the reaction.$^{20}$

The effect of H$_2$O$_2$ addition was investigated in the concentration range of 1.0–5.0 mmol dm$^{-3}$ (Fig. 5a), wherein it can be noticed that addition of H$_2$O$_2$ to the system has not improved efficiency of sulcotrione photocatalytic degradation. With increasing of H$_2$O$_2$ concentration, efficiency of sulcotrione photocatalytic degradation decrease. One of the reasons may be that H$_2$O$_2$ can also act as an $^\cdot$OH scavenger and thus generating less reactive hydroperoxyl radicals $^\cdot$HO$_2$. The second reason may be that H$_2$O$_2$ can react with TiO$_2$ and form peroxo compound which negatively influence on efficiency of photocatalytic degradation.$^{37}$ Also, excess of H$_2$O$_2$ might absorb and reduce UV light available for photocatalysis.$^{39}$

![Fig. 5. Effect of a) H$_2$O$_2$ and b) KBrO$_3$ on the efficiency of sulcotrione ($c_0$ = 50 µmol dm$^{-3}$) photocatalytic degradation using bare TiO$_2$ (0.5 mg cm$^{-3}$) under simulated solar irradiation.](image)

In the same way the influence of KBrO$_3$ on the efficiency of photocatalytic degradation of sulcotrione was investigated (Fig. 5b). It can be seen that at all concentrations of KBrO$_3$ efficiency of sulcotrione photodegradation was improved during 60 min of irradiation. This phenomenon may be probably due to reaction between BrO$_3^-$ ions and conduction band e$^-$, which results in reduced recombination between e$^-$ and h$^+$. Besides, electrons can reduce bromate ions, leading to formation of reactive oxidizing radicals such as BrO$_2^+$ and HOBr (reactions 2 and 3), thereby increasing the efficiency of sulcotrione degradation.$^{40}$

\[
\begin{align*}
\ce{BrO_3^- + 2H^+ + e^- &-> BrO_2^+ + H_2O} \\
\ce{BrO_3^- + 6H^+ + 6e^- &-> [BrO_2, HOBr] -> Br^- + 3H_2O}
\end{align*}
\]

CONCLUSION

The obtained results indicate that TP nanocomposites showed the highest photocatalytic activity for elimination of clomazone compared with bare TiO$_2$. However, sulcotrione using bare TiO$_2$ has shown the highest efficiency of photocatalytic degradation and mineralization from all investigated organic
compounds, wherein sulcotrione was chosen for further investigations. Moreover, cytotoxic experiments revealed that both growth inhibition and stimulation on different cell lines were observed and was below 11% in all cases. A comparison of sulcotrione removal in different water types has shown that efficiency of sulcotrione photocatalytic degradation in environmental waters was lower compared with DDW. Besides, content of ions present in water from river Danube showed that pH value mainly influence the efficiency of sulcotrione removal. In addition, results with scavengers indicate that \( ^\cdot \)OH radicals partly participate in the photocatalytic degradation of sulcotrione, wherein the main path of degradation is through holes. Also, addition of H\(_2\)O\(_2\) as electron acceptor decreased, while addition of KBrO\(_3\) increased efficiency of sulcotrione removal.

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SUPPLEMENTARY MATERIAL

Analytical and spectral data of the synthesized compounds are available electronically at the pages of journal website: http://www.shd-pub.org.rs/index.php/JSCS, or from the corresponding author on request.

ИЗВОД

ФОТОРАЗГРАДЊА ОДАБРАНИХ ПЕСТИЦИДА: ФОТОКАТАЛИТИЧКА АКТИВНОСТ ЧИСТОГ И ПОЛИАНИЛИНОМ МОДИФИКОВАНОГ TiO\(_2\) У ПРИСУСТВУ СИМУЛИРАНОГ СУНЧЕВОГ ЗРАЧЕЊА

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У овом раду је испитана ефикасност фотокаталитичке разградње различитих пестицида коришћењем TiO\(_2\) и модификованих TiO\(_2\) наночестица полианилином коришћењем симулираног сунчевог зрачења. Сулкотрион је показао највећи проценат разградње и даљи експерименти су се односили на овај хербицид. Прочуване су минерализација и цитотоксичност полазног једињења и интермедијера формираних током разградње у биодестилованој води (БДВ) као и ефикасност уклањања сулкотриона из различитих природних вода. Садржaj назаиступљених јона присутних у води из реке Дунав су додати у БДВ и процењен је њихов утицај. Утврђено је да је цитотоксичност у свим случајевима испод 11% и да је ефикасност фотокаталитичке разградње у природним водама мања у односу на БДВ. Надање, додатак различитих хватача је показало да се разградња у највећој мери одиграва преко шупљина, док је присуство H\(_2\)O\(_2\) смалило а KBrO\(_3\) пovećalo ефикасност фотокаталитичке разградње у односу на систем без поменутих електрон-акцептора.

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REFERENCES

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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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INTRODUCTION

Fig. S1. Structures of the pesticides.

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$_9$ClN$_4$S, $M_r = 252.8$, PESTANAL® analytical standard, 99.9 % purity) was purchased from Riedel-de Haën, herbicides clomazone (2-[(2-chlorophenyl)methyl]-3,5-diethyl-4-(2-hydroxyethoxymethyl)-6-methyl-2-pyrimidinone), CAS No. 72856-61-6, C$_{18}$H$_{16}$ClN$_2$O$_5$, $M_r = 329.7$, and quinmerac (4-[3-[(6-chloro-2-pyridinyl)methyl]thiophen-2-yl]aniline), CAS No. 73857-85-7, C$_{14}$H$_{13}$ClN, $M_r = 247.8$, and sulcotrine (2-chloro-4-[(6-chloro-3-sulfamoyl-2-pyridinyl)methyl]thiophene-3-carboxylic acid), CAS No. 48239-10-0, C$_{14}$H$_{12}$Cl$_2$N$_2$O$_2$S, $M_r = 320.7$, all from Aldrich.
thyl]-4,4-dimethyl-3-isoxazolidinone, CAS No. 81777-89-1, C12H14ClNO2, \( M_1 = 239.7 \), PESTANAL®, analytical standard, 98.8% purity), quinmerac ([7-chloro-3-methylquino line-8-carboxylic acid), CAS No. 90717-03-6, C11H16ClNO5, \( M_2 = 221.64 \), PESTANAL®, analytical standard, 98.2% purity) and sulcotrione (2-(2-chloro-4-(methylsulfonyl)benzoyl)-1,3-cyclohexanedione, CAS No. 99105-77-8, C22H21ClO9S, \( M_3 = 328.8 \), 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% H3PO4, Lachemi, Neratovice, Czech Republic; NaOH, ZorkaPharm, Sabac, Serbia; CaO, Carlo Erba, Milano, Italy; HPLC gradient grade methanol, J.T. Baker; KBrO3 and 60% HClO4, Merck, Darmstadt, Germany; Na2SO4, NaHCO3, Ba(OH)2, and NaF, Kemika, Zagreb, Croatia; SiSO4, BDH Laboratory, Safat, Kuwait; Dissodium ethylenediaminetetraacetic acid (EDTA), Dojindo, Rockville, MD USA; humic acid, 30% H2O2, and tert-butanol, 99.9% acetonitrile (ACN), sulforhodamine B (SRB) and antibiotic/antimycotic solution, Sigma–Aldrich, St. Louis; fetal calf serum (FCS) and Dulbecco’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.

The river water samples were collected from Danube (Petrovaradin, Serbia), Tisa (Titel, Serbia), and 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 S1). The samples of environmental waters were filtered through filter paper (Whatman, diameter of 125 mm pore size 0.1 µm).

Table S1. The physicochemical characteristics of the analyzed environmental waters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Water type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Danube</td>
</tr>
<tr>
<td>pH</td>
<td>7.92</td>
</tr>
<tr>
<td>El. conductivity at 25 °C, mS cm⁻¹</td>
<td>0.400</td>
</tr>
<tr>
<td>TOC, mg L⁻¹</td>
<td>5.17</td>
</tr>
<tr>
<td>Concentration of HCO₃⁻, mg L⁻¹</td>
<td>209</td>
</tr>
<tr>
<td>Concentration of fluoride, µg L⁻¹</td>
<td>69.0</td>
</tr>
<tr>
<td>Concentration of chloride, mg L⁻¹</td>
<td>4.91</td>
</tr>
<tr>
<td>Concentration of sulphate, mg L⁻¹</td>
<td>27.71</td>
</tr>
<tr>
<td>Concentration of nitrate, mg L⁻¹</td>
<td>1.74</td>
</tr>
<tr>
<td>Concentration of calcium, mg L⁻¹</td>
<td>47.9</td>
</tr>
<tr>
<td>Concentration of potassium, mg L⁻¹</td>
<td>2.79</td>
</tr>
<tr>
<td>Concentration of magnesium, mg L⁻¹</td>
<td>12.6</td>
</tr>
<tr>
<td>Concentration of sodium, mg L⁻¹</td>
<td>10.85</td>
</tr>
<tr>
<td>Concentration of arsenic, µg L⁻¹</td>
<td>2.7</td>
</tr>
<tr>
<td>Concentration of Barium, µg L⁻¹</td>
<td>21.2</td>
</tr>
<tr>
<td>Concentration of cadmium, µg L⁻¹</td>
<td>0.6</td>
</tr>
<tr>
<td>Concentration of chrome, µg L⁻¹</td>
<td>0.7</td>
</tr>
<tr>
<td>Concentration of copper, µg L⁻¹</td>
<td>3.8</td>
</tr>
<tr>
<td>Concentration of iron, µg L⁻¹</td>
<td>&lt; DL</td>
</tr>
<tr>
<td>Concentration of manganese, µg L⁻¹</td>
<td>&lt; DL</td>
</tr>
<tr>
<td>Concentration of nickel, µg L⁻¹</td>
<td>0.2</td>
</tr>
<tr>
<td>Concentration of strontium, µg L⁻¹</td>
<td>223.2</td>
</tr>
<tr>
<td>Concentration of zinc, µg L⁻¹</td>
<td>6.0</td>
</tr>
</tbody>
</table>
**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$_3$PO$_4$ (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$_3$PO$_4$ (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$_3$PO$_4$ (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$_3$PO$_4$ (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$^2$ flasks (Corning, New York, USA) at 37 °C in the atmosphere of 5% CO$_2$ and high humidity, and sub-cultured weekly. 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 ($c_i$) 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

**Fig. S2.** 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 ($n = 4$).

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. S2).

**Fig. S3.** 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 ($n = 4$).
Table S2. The mineralization degree of sulcotrione in the presence of bare TiO$_2$/TP nanocomposite suspension.

<table>
<thead>
<tr>
<th>Type of catalyst</th>
<th>Mineralization degree, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare TiO$_2$</td>
<td>40.45</td>
</tr>
<tr>
<td>TP-50</td>
<td>31.27</td>
</tr>
<tr>
<td>TP-100</td>
<td>10.62</td>
</tr>
<tr>
<td>TP-150</td>
<td>36.63</td>
</tr>
</tbody>
</table>