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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 TiO_2 nanoparticles modified with polyaniline under simulated solar irradiation. Sulcotrione showed the highest percentage degradation and further experiments were related to this herbicide. Mineralization and cytotoxicity of the starting compound and intermediate species formed during the decomposition in double distilled water (DDW), as well as the efficiency of removal from various environmental waters were studied. The contents of the most abundant ions present in the River Danube were 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 was decreased compared with DDW. Furthermore, addition of different scavengers revealed that the main path of degradation is through holes, while the presence of H_2O_2 decreased and $KBrO_3$ increased the efficiency of photocatalytic degradation compared with the system without the mentioned electron acceptors.

Keywords: pesticides; bare TiO_2 nanoparticle; TiO_2/polyaniline nanocomposite; cytotoxicity; environmental waters; radical, hole and electron scavengers.

INTRODUCTION

In order to protect crops from specific types of pests, today in agriculture, the usual practice is to use different pesticides. Bearing in mind the importance and extensive use of pesticides in agriculture, such chemicals could reach the

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environmental waters as the consequence of a combination of run-off, accidental spillages, spray drift, drainage, or atmospheric deposition.[1]

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 was found that it is resistant to water hydrolysis at neutral and acidic pH values. Furthermore, thiacloprid showed significant photostability under the influence of simulated solar radiation.[2–5]

The herbicide clomazone is applied for the suppression of various types of weeds in different cultivation fields.[6] It has the potential to pollute water because of its high water solubility.[7] Residues of clomazone were found in samples taken from river waters in rice cultivation areas.[6]

Quinmerac belongs to the quinoline group, which is a relatively new class of highly selective herbicides, with recent commercial use.[8] This herbicide is relatively well soluble in water and hardly degradable.[9] According to a report from the Swedish Board of Agriculture and the Swedish Environmental Protection Agency,[10] quinmerac has been detected in ground, surface and drinking water. In addition, quinmerac can potentially cause pollution of the entire ecology through the food chain thereby having negative consequences 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 the 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 the 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 towards *Allium cepa* root meristem[14] and *Vicia faba* seedlings.[15]

Considering that pesticides have a negative influence on living organisms, the need for their monitoring and control has become more obvious in recent years. 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 a low-cost, versatile, environmentally friendly, and one of the most promising green chemistry method for the removal of different contaminants.[18] In order to prevent the harmful effect which arises as a consequence of the presence of hazardous pollutants, photocatalytic degradation of water contaminants is used to detoxify or treat wastewater.[19]

The main disadvantage of photocatalytic degradation using TiO_2 as a photocatalyst is the occurrence of electron−hole pair recombination, which as a consequence decreases the quantum efficiency. In addition, the wide band gap, of

TiO_2, which is 3.0 eV for rutile, and 3.2 eV for anatase, narrows the absorption of photons to the ultraviolet region (wavelength < 390 nm). This reduces the practical use of the 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 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 was the best of all the investigated compounds and TP-150 was the most efficient catalyst in the mineralization of pesticides.[25] Furthermore, the results of the UV/Vis reflectance spectra[22] indicate that mentioned TP nanocomposites could be activated by UV and visible light simultaneously, which opens the possibility of their application as photocatalysts. As a consequence, the aim of this work was to investigate the photodegradation behaviour of selected pesticides (thiacloprid, clomazone, quinmerac, and sulcotrione; Fig. S-1 of the Supplementary material to this paper) 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, the cytotoxicity of the 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 that were identified in the water from the 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 a 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 the formed intermediates, mammalian cell lines (rat hepatoma (H-4-II-E), mouse neuroblastoma (Neuro-2a), human colon adenocarcinoma (HT-29) and human foetal lung (MRC-5) were used for toxicity assessment.

EXPERIMENTAL

Chemicals, water samples and catalysts

All the used chemicals are listed in the Supplementary Material. The collection of the environmental water samples and their physicochemical characteristics are given in Table S-I of the Supplementary material.

The TiO_2 catalysts, bare and modified with polyaniline in different TiO_2:PANI mole ratios (TP-50, TP-100 and TP-150) were prepared as previously described.[22] Details are given in Šojić Merkulov *et al.*[25] The formation of nanocomposites was proved using Raman spectroscopy and TEM measurements.[22]

Photodegradation procedure

The photocatalytic degradation was realised in a previously described cell.[26] For the 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 a LP 471 UV (spectral range 315–400 nm) and a LP 471 RAD (spectral range 400–1050 nm) sensor. Additionally, the lamp output was calculated to be *ca.* 1.7×10^{-9} Einstein cm^{-3} min^{-1} using potassium ferrioxalate actinometry.[27]

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 TiO_2 or TP). The aqueous suspension of the catalyst was sonicated (50 Hz) in the dark for 15 min before irradiation, in order to uniformly disperse the particles of photocatalyst and to attain adsorption equilibrium. Before irradiation, the thus obtained suspension 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 the photocatalytic degradation of sulcotrione.

Analytical procedures

Experimental conditions regarding 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 is described in the Supplementary material. The cell growth was evaluated by the colorimetric sulforhodamine B (SRB) assay of Skehan *et al.*,[28] modified by Četojević-Simin *et al.*[29]

RESULTS AND DISCUSSION

Photocatalytic oxidation of selected pesticides using TiO_2/polyaniline nanocomposites

Recently, novel modified TiO_2 nanostructures have gained great attention because of their 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 the sensitizer in polymer-sensitized TiO_2 nanocomposites due to their 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 a substitute product of the solar materials in photovoltaic devices.[23] Under UV irradiation, conjugated polymers promote the separation efficiency of photoinduced electron–hole pairs due to the 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_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^-) can be injected into the conduction band of TiO_2 and react with electron acceptors such as oxygen adsorbed on the TiO_2 surface to generate oxidative species, such as hydroxyl radicals and superoxide radical anions. The surface of TiO_2 is generally a good adsorber of oxygen, which acts as an electron scavenger, due to the position of the CB of TiO_2 and the potential of $O_2/O_2^{\bullet-}$ formation, while, in the case of TP nanocomposites, the polymer is a hole scavenger. If bare TiO_2 nanoparticles were used as a photocatalyst, the hole scavengers would be organic pollutants (thiacloprid, clomazone, quinmerac and sulcotrione) and the excited electrons are used for the formation of superoxide radical ions, hydrogen peroxide, and hydroxyl radicals.[30] The photoinduced holes (h^+) are left in the HOMO of the polymers. Therefore, the photocatalytic activity of TiO_2 under visible light could be enhanced by using conductive polymers as stable photosensitizers to modify TiO_2 nanoparticles.[23]

Radoičić *et al.*[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 as confirmed by Raman spectroscopy. Moreover, the surface of TiO_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_2 surface is probably only partially covered due to the lowest content of PANI.[22] The photocatalytic activities of TP nanocomposites in the process of thiacloprid degradation are enhanced as the content of PANI in the nanocomposite decreases, with a maximum value for TP-150 (13 %). In the case of TP-50, the TiO_2 surface is hindered with positively charged with PANI-emeraldine salt, which probably leads to repulsion of the thiacloprid molecule (the pK_a value for thiacloprid is not applicable). As the content of PANI decreases beside emeraldine salt, emeraldine base-like segments are also present, and 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_2. Namely, in the presence of bare TiO_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 ($-NH^{\bullet +}-$) and free electron pair on the nitrogen atom. The highest efficiency of photocatalytic degradation of quinmerac was noticed in the presence of TP-100. This may be also explained by electrostatic interaction of emeraldine salt with the nitrogen atom and by protonation of emeraldine base-like segments. Furthermore, the surface of TiO_2 is less hindered with PANI groups, which enable interaction of carboxyl group with the OH groups on the surface of TiO_2. While pK_a value for clomazone is also not applicable, for quinmerac, the pK_a value is 4.31. This means that at pH ~5, the deprotonated form is mostly present in the suspension whereby at this pH the nanocomposites are protonated (pH_{pzc} is 5.2) and therefore there is attraction between the anion of quinmerac and the nanocomposites. In contrast to mentioned pesticides, TiO_2 modified with polyaniline showed a decrease in the efficiency of sulcotrione photocatalytic degradation compared with bare TiO_2. Namely, about 26 % of the compound was removed using TP-50 and TP-100, while 35 % was removed using TP-150.

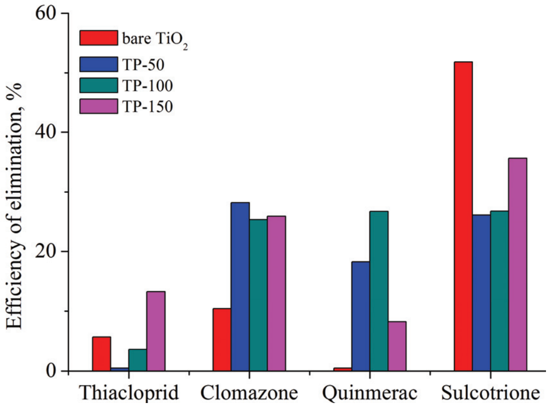

Fig. 1. Efficiency of selected pesticides elimination using bare TiO_2 and TP nanocomposites after 240 min of simulated solar irradiation. Experimental conditions: c_0 = 50 μmol dm^{-3}; catalyst loading 0.5 mg cm^{-3}.

The results can be viewed in different ways, concerning the optical properties of the nanocomposites, bearing in mind the mechanism of light absorption, the molecular structure of the selected pesticides and the PANI layer in the nanocomposites.[22] It could be assumed that the sulcotrione molecules have a better interaction with OH groups on the surface of TiO_2 than with positively charged PANI-emeraldine salt. TP-150 showed a slightly better activity than TP-

-50 and TP-100, due to the smaller content of PANI, more available OH groups on the surface of TiO_2, and the presence of only branched emeraldine oligomers. Besides, 52 % of sulcotrione was eliminated from the aquatic suspension using bare TiO_2. Namely, the initial pH value of the suspension in DDW was ~3 whereby the higher degradation rate may probably be attributed to interaction of sulcotrione anion ($pK_a = 3.13$) with the protonated sites of the catalyst (the 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 S-II, Supplementary material). It was found that in the cases 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 could be explained by the formation of organic intermediates during the photocatalytic process. Since bare TiO_2 was the most efficient in the photocatalytic degradation of sulcotrione, cytotoxicity experiments and efficiency of photocatalytic degradation of sulcotrione in environmental waters were performed using the mentioned catalyst under simulated solar irradiation.

Toxicity assessment

Degradation of pesticides in the environment could potentially generate many by-products that are sometimes persistent and requires better knowledge on their reactivity and toxicity. In order to evaluate the environmental hazard of water containing sulcotrione and the formed reaction intermediates using bare TiO_2 under simulated solar irradiation, *in vitro* growth of H-4-II-E, Neuro-2a, HT-29 and MRC-5 cell lines was evaluated (Fig. S-2, Supplementary material).

Blank tests of an aqueous solution of 5 μmol dm^{-3} sulcotrione and of a filtered aqueous suspension of 0.05 mg cm^{-3} bare TiO_2 were also performed (Fig. S-3, 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, for the HT-29 cell line. The inhibition of cell growth was influenced by the parent compound (blank test of sulcotrione with ~5 % growth inhibition, Fig. S-3, Supplementary material) and the mixture of sulcotrione and its photocatalytic degradation intermediates (Fig. S-2, Supplementary material) after different irradiation times. In the case of the cell line MRC-5, growth inhibition or stimulation was negligible for the blank tests of sulcotrione and bare TiO_2 and also for the photodegradation mixtures of the obtained intermediates was below 2 %. The highest inhibition of cell growth for the blank test of sulcotrione (≈6 %) was noticed in the case of the Neuro-2a cell line. However, during irradiation, less toxic intermediates were formed with stimulation or inhibition of growth of up to 2 %. Bare TiO_2 showed the highest toxicity, *i.e.*, cell growth inhibition of ≈9 % for the cell line H-4-II-E (blank test, Fig. S-3, Supplementary material). For the same cell line, the blank test of sulcotrione showed a growth inhibition of ≈4 %. Furthermore, the photodegraded mixture in the presence of bare TiO_2 showed only growth inhibition with a 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, the toxicity was reduced, compared with blank tests, for the cell lines Neuro-2a and H-4-II-E, in the process of photocatalytic degradation of sulcotrione. However, cytotoxicity in all cases was substantially lower compared to cytotoxic drugs and the known toxicant, $HgCl_2$.[31]

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 real water might contain substances that could compete with the target pollutant for the oxidizing agent ($^{\bullet}OH$), such as other organic and inorganic compounds and natural organic matter. This usually causes a decrease in the photodegradation efficiency.[32] Due to this, photocatalytic degradation of sulcotrione in environmental waters was investigated (the 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 suggested that a herbicide removal of 15 % was only achieved in water from Sot Lake after 240 min of irradiation (Fig. 2). On the other hand, it was found that degradation of the herbicide was the most efficient in DDW.

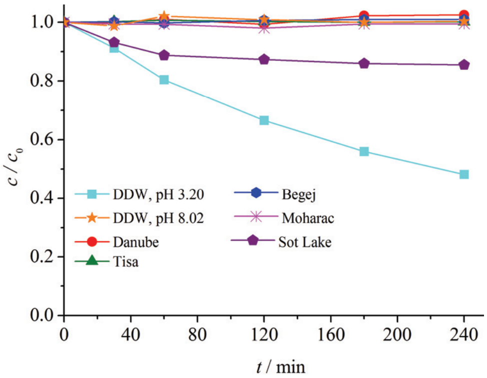

Fig. 2. Influence of water type on the efficiency of sulcotrione photocatalytic degradation. Experimental conditions: c_0(sulcotrione) = 50 μmol dm^{-3}; bare TiO_2 loading 0.5 mg cm^{-3}.

This behaviour could be explained by the presence of inorganic and organic matter in the examined environmental waters that affect the efficiency of the photodegradation process. Another reason might be the different pH values for DDW (≈3) in comparison to environmental waters (≈8). Namely, the higher degradation rate at the lower pH may probably be attributed to the more effective binding of the sulcotrione molecule to the protonated sites of the catalyst.

Bearing in mind that the photodegradation efficiency in the water from the River Danube was among the least efficient, ions 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 the pH value of the suspension and the obtained results are presented in Fig. 3a. In the case of the addition of HCO_3^-, SO_4^{2-} and Ca^{2+}, no photodegradation of sulcotrione was observed. It is assumed that SO_4^{2-}, Ca^{2+}, Sr^{2+} and Ba^{2+} decrease the efficiency of the photocatalytic degradation of sulcotrione by decreasing the adsorption of the substrate on the surface of the catalyst.[33,34] Moreover, HCO_3^- can react with $^\bullet OH$ (reaction (1)):

$$HCO_3^- + {}^\bullet OH \rightarrow CO_3^\bullet + H_2O \qquad (1)$$

thereby decreasing the efficiency of removal. Another reason for the negligible photocatalytic degradation, in the case of addition of HCO_3^- and also Ca^{2+} is the pH value ~8, at which there is repulsion between deprotonated bare TiO_2 and sulcotrione.

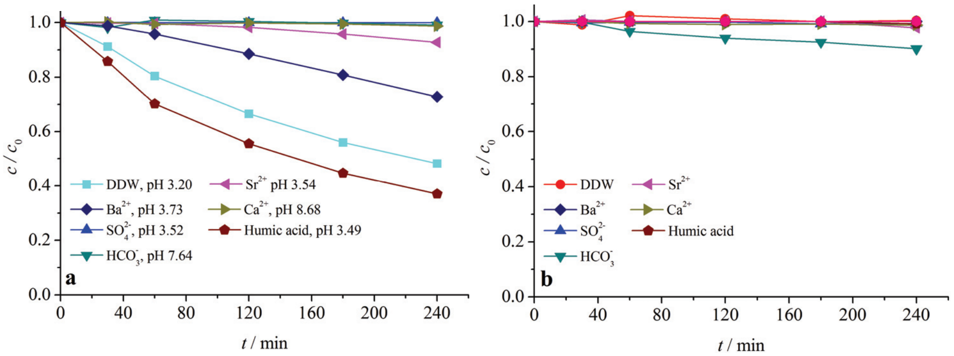

Fig. 3. Influence of the addition of different ions on photocatalytic degradation efficiency of sulcotrione at: a) natural pH and b) pH 8. Experimental conditions: c_0(sulcotrione) = 50 μmol dm^{-3}; bare TiO_2 loading: 0.5 mg cm^{-3}.

However, addition of humic acid to the system leads to improvement of the efficiency of sulcotrione photocatalytic degradation compared to DDW at natural pH ~3, when 63 and 52 % of sulcotrione was removed, respectively. According to Wu *et al.*,[35] humic acid can promote the generation of $^\bullet OH$, which increases the 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).

The obtained results show that in almost all cases photocatalytic degradation of sulcotrione did not occur. 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 the pH value has a 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 a previous work clearly indicated that processes on the surface of catalyst play the main role in the photodegradation of sulcotrione. Namely, the disappearance of sulcotrione under UV light using TiO_2 Degussa P25 occurs *via* $^•$OH and holes,[36] but in the case of TP-150, the main path of degradation is through holes and $O_2^{•–}$, whereby surface $^•$OH is only partly involved in the removal of sulcotrione.[25] In the present work (Fig. 4), the effects of addition of NaF, *tert*-butanol and EDTA as scavengers of surface $^•$OH, bulk $^•$OH 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 partly participate in the photocatalytic degradation of sulcotrione, whereby the main path of degradation is through holes. From Fig. 4, it could be seen that bulk $^•$OH have no influence on the efficiency of sulcotrione photocatalytic degradation.

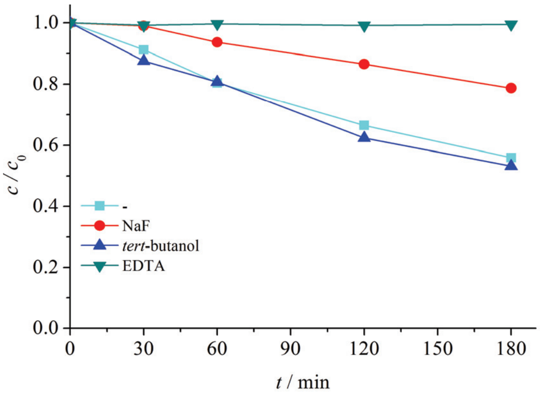

Fig. 4. Effect of active radicals and hole scavengers (10 mmol dm^{-3}) on the efficiency of sulcotrione (c_0 = 50 μmol dm^{-3}) photocatalytic degradation using bare TiO_2 (0.5 mg cm^{-3}) under simulated solar irradiation.

Effect of 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_2O_2 and $KBrO_3$), besides O_2, to the reaction.[20]

The effect of H_2O_2 addition was investigated in the concentration range 1.0–5.0 mmol dm^{-3} (Fig. 5a), whereby it could be noticed that the addition of H_2O_2 to the system did not improve efficiency of sulcotrione photocatalytic degradation. With increasing of H_2O_2 concentration, the efficiency of sulcotrione photocatalytic degradation decreased. One of the reasons may be that H_2O_2 could also act as an $^{\bullet}OH$ scavenger, thereby generating less reactive hydroperoxyl radicals $HO_2^{\bullet}$.[37] The second reason may be that H_2O_2 can react with TiO_2 and form a peroxo compound that negatively influences the efficiency of photocatalytic degradation.[38] Furthermore, excess H_2O_2 might absorb UV light leaving less available for photocatalysis.[39]

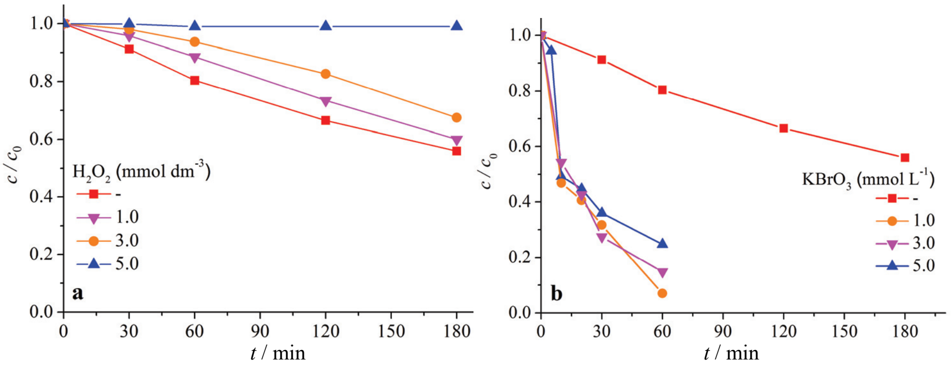

Fig. 5. Effect of: a) H_2O_2 and b) $KBrO_3$ on the efficiency of sulcotrione (c_0 = 50 µmol dm^{-3}) photocatalytic degradation using bare TiO_2 (0.5 mg cm^{-3}) under simulated solar irradiation.

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 $KBrO_3$ concentrations the efficiency of sulcotrione photodegradation was improved during 60 min of irradiation. This phenomenon may probably be due to reaction between BrO_3^- and conduction band e^-, which results in reduced recombination between e^- and h^+.[37] Besides, electrons can reduce bromates, leading to formation of reactive oxidizing radicals such as $BrO_2^{\bullet}$ and HOBr (reactions (2) and (3)), thereby increasing the efficiency of sulcotrione degradation:[40]

$$BrO_3^- + 2H^+ + e^- \rightarrow BrO_2^{\bullet} + H_2O \tag{2}$$

$$BrO_3^- + 6H^+ + 6e^- \rightarrow [BrO_2^-, HOBr] \rightarrow Br^- + 3H_2O \tag{3}$$

CONCLUSIONS

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 showed the highest efficiency of photocatalytic degradation and mineralization of all investigated organic compounds and therefore, sulcotrione was chosen for further investigations. Moreover, cytotoxic experiments revealed that both growth inhibition and stimulation of different cell lines were observed, which were below 11 % in all cases. A comparison of sulcotrione removal in different types of water showed that the efficiency of sulcotrione photocatalytic degradation in environmental waters was lower compared with that in DDW. Moreover, the content of ions present in water from the River Danube showed that the pH value mainly influences the efficiency of sulcotrione removal. In addition, results with scavengers indicated that $^{\bullet}$OH partly participate in the photocatalytic degradation of sulcotrione, although the main path of degradation was through holes. Furthermore, the addition of H_2O_2 as an electron acceptor decreased, while addition of $KBrO_3$ increased the efficiency of sulcotrione removal.

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SUPPLEMENTARY MATERIAL

Additional data 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. Проучаване су минерализација и цитотоксичност полазног једињења и интермедијера формираних током разградње у бидестилованој води (BDV) као и ефикасност уклањања сулкотриона из различитих природних вода. Садржај најзаступљенијих јона присутних у води из реке Дунав су додати у BDV 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 BDV. Надаље, додатак различитих хватача је показало да се разградња у највећој мери одигрrécава преко шупљина, док је присуство H_2O_2 смањило а $KBrO_3$ повећало ефикасност фотокаталитичке разградње у односу на систем без поменутих електрон-акцептора.

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