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DEGRADATION OF NICOSULFURON USING FENTON AND FENTON-LIKE REACTIONS

Article Highlights

- Nicosulfuron was subjected to different Fenton reactions at the pH of a nicosulfuron aqueous solution
- The Fenton reaction was much faster and more efficient than the Fenton-like reaction
- The photo-Fenton reaction proceeded much faster and more efficient than the Fenton reaction
- The MW-Fenton reaction proceeded with increased efficiency in comparison to the Fenton reaction
- The toxicity tests showed the decrease in toxicity after the treatment

Abstract

Nicosulfuron, a sulfonylurea herbicide, was subjected to different Fenton reactions at pH of a nicosulfuron aqueous solution (pH 5). Usually, the optimal pH for the Fenton reaction is between 3 and 4, but the addition of acids is not environmentally acceptable. This is the reason why the reactions were performed at a higher pH value than usual. So, classical Fenton and Fenton-like reactions were applied as well as photo-Fenton and photo-Fenton-like reactions. In addition, microwave Fenton and Fenton-like reactions were used in nicosulfuron degradation. Influences of Fe^{2+} and Fe^{3+} concentrations, as well as hydrogen peroxide concentrations, were studied. The Fenton reaction was much faster and more efficient than the Fenton-like reaction, while the photo-Fenton reaction proceeded much faster and more efficiently than the Fenton reaction. The microwave-Fenton and microwave-Fenton-like reactions proceeded with increased efficiency in comparison to the Fenton and Fenton-like reactions. The phytotoxicity and acute toxicity of the reaction products of nicosulfuron oxidation by the photo-Fenton reaction were analyzed. The toxicity testing of nicosulfuron treatment by photo-Fenton process showed a decrease in phytotoxicity, while the acute toxicity tests showed that the samples after treatment had lower toxicity.

Keywords: iron salt, hydrogen peroxide, microwaves, phytotoxicity, acute toxicity.

Nicosulfuron (Figure 1, $C_{15}H_{18}N_6O_6S$, 2-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulfamoyl)-*N,N*-dimethylnicotinamide) is a sulfonylurea herbicide which was initially patented in the USA [1]. It is mainly used in corn fields in order to control the annual grass [2].

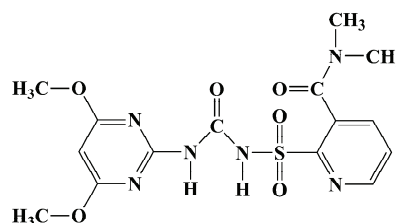


Figure 1. Nicosulfuron structure.

According to the European Food Safety Authority, nicosulfuron has 1st order DT50 of 7-46.3 days and is classified as low to moderately persistent in soil [3]. Although nicosulfuron has a low to moderate

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persistence in soil, it was reported that its residues could be found in soil, and surface waters [4].

Nicosulfuron can be removed from water using different methods. Vukčević *et al.* have studied the removal of nicosulfuron from aqueous solutions *via* adsorption using a carbon monolith [5]. A study of nicosulfuron hydrolysis showed that this reaction is much faster in acidic solutions [4,6]. Different bacteria were also used to remove nicosulfuron from water *via* biodegradation [2,7]. Photodegradation of nicosulfuron was also studied. Benzi *et al.* [8] reported photoinduced aqueous degradation of nicosulfuron, while ter Halle *et al.* described photolysis of nicosulfuron on a simulated cuticular wax film [9]. In addition, the photocatalytic degradation of nicosulfuron was studied using different catalysts. ZnO, WO₃, SnO₂ and ZnS were used as photocatalysts for the degradation of nicosulfuron under natural sunlight [10]. Fenoll *et al.* reported the photocatalytic degradation of nicosulfuron with TiO₂ and ZnO in tandem with Na₂S₂O₈ among 30 different sulfonylurea herbicides [11]. Recently, we have reported the photocatalytic degradation of nicosulfuron using TiO₂ [12]. It was shown that, after 30 min of irradiation, nicosulfuron was completely degraded, while the phytotoxicity was reduced from 56.8 to 14.8% after 90 min of photocatalysis. The overview of recent works on nicosulfuron treatment is available from the author upon request.

Advanced oxidation processes (AOPs) were used for the degradation of organic as well as inorganic pollutants in water based primarily on the generation of hydroxyl radicals [13]. Since hydroxyl radicals have a very short lifetime, they are produced during application, *e.g.*, by combination of ultraviolet light or sunlight irradiation with a photocatalyst or hydrogen peroxide and catalysts (such as Fe²⁺). The second AOP is known as the Fenton reaction [14]. Fenton, Fenton-like and photo-Fenton reactions have been widely used for the removal of various organic contaminants including pesticides [15–18]. Sulfonylureas were also subjected to the Fenton reaction. Chlorimuron-ethyl, sulfonylurea herbicide, was degraded *via* Fenton and photo-Fenton processes [19]. Another sulfonylurea herbicide, metsulfuron-methyl, was oxidized by Fenton's reagent and the phytotoxicity of the reaction products was determined by Lemna (duckweed) bioassay [20]. To our knowledge, no studies of nicosulfuron degradation by Fenton's reagent were reported so far.

The aim of this work was the study of nicosulfuron degradation by Fenton and Fenton-like reactions at the pH of a nicosulfuron aqueous solution.

Usually, the optimal pH value for the Fenton reaction is between 3 and 4, but the addition of acids is not environmentally acceptable. This is the reason why the reactions were performed at a higher pH than usual. In addition, photo-Fenton and photo-Fenton-like reactions were applied as well as microwave Fenton and Fenton-like reactions. The toxicity of the reaction products of nicosulfuron oxidation by the Fenton reaction was analyzed.

EXPERIMENTAL

Materials

Nicosulfuron (technical grade, 98.1%) was obtained from Galenika-Fitofarmacija, Serbia. Iron(II) sulfate heptahydrate (98%), iron(III) sulfate pentahydrate (97%), potassium dichromate (99%), hydrogen peroxide (30%, hydrochloric acid (p.a.), sodium chloride (p.a.), acetonitrile (HPLC) and acetic acid (≥ 99.8) were obtained commercially (Sigma-Aldrich, J.T.Baker). Deionized water was obtained from a Millipore Waters Milli Q purification unit.

Fenton degradation experiments

Prior to the degradation experiments, solutions of nicosulfuron, iron sulfate and hydrogen peroxide were prepared. 25 mL of nicosulfuron and iron sulfate solutions were added to a glass batch reactor and stirred on a magnetic stirrer (500 rpm). Afterwards, a hydrogen peroxide solution was added. The Fenton and Fenton-like reactions were performed in the dark. Aliquots were taken at time intervals and the nicosulfuron concentration was analyzed *via* HPLC.

The procedure for photo-Fenton and photo-Fenton-like reactions was the same except that the reactions were performed under irradiation of Osram Ultra Vitalux[®] 300 W lamp (mixture of lights UV-A:UV-B = 13.6:3) placed 400 mm above the surface of the reaction mixture.

Microwave (MW) experiments were performed in a Anton Paar Monowave 300 reactor using a 30 mL reactor vial. The solutions of nicosulfuron, iron sulfate and hydrogen peroxide were mixed (the volume of reaction mixture was 10 mL) and irradiated. After the reaction, the concentration of nicosulfuron was analyzed *via* HPLC.

HPLC analysis

All samples were filtered through 0.45 μ m syringe filters and analyzed at 240 nm and at ambient temperature (25 °C) on a SpectraSystem P4000 liquid chromatograph with a SpectraSystem UV1000 detector, equipped with a reversed-phase column type Zorbax SB C8 (150 mm \times 4.6 mm i.d., 5 μ m particle

size). The mobile phase (flow rate 1.0 mL min^{-1}) was a mixture of acetonitrile:water (45:55 volume ratio), and a 0.1% acetic acid solution. The sample injection volume was $20 \text{ }\mu\text{L}$ ($t_{\text{R}}(\text{nicosulfuron}) = 2.9 \text{ min}$).

Phytotoxicity testing

The phytotoxicity was studied using the method described previously [12]. Briefly, samples before and after 30 and 90 min of the reaction were collected and submitted to toxicity testing using *Vigna mungo* seeds. In each petri dish, 10 seeds were placed and watered daily in the dark with appropriate nicosulfuron solutions. After 5 days, the seeds were analyzed in terms of radicle length and the phytotoxicity was calculated as follows:

Phytotoxicity = $100(\text{Radicle length of control} - \text{Radicle length of sample})/\text{Radicle length of control}$

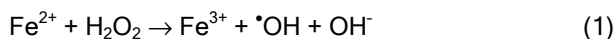
Acute toxicity testing

Brine shrimp were used as a bioindicator in this acute toxicity testing. The testing was performed as it was previously described [21]. In brief, brine shrimp nauplii were hatched in synthetic marine water for 24 h at $24\text{--}28 \text{ }^\circ\text{C}$. The obtained larvae were transferred into the test tubes containing nicosulfuron solutions (10 ml) before and after the degradation with appropriate dilutions (10, 40, 60, 80 and 100%). Apart from these samples, positive ($\text{K}_2\text{Cr}_2\text{O}_7$, 100 mg L^{-1}) and negative (artificial sea water, NaCl concentration 32 g L^{-1}) control samples were analyzed. The EC_{50} value was calculated *via* the Probit analysis method.

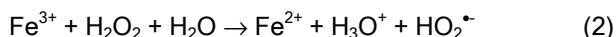
RESULTS AND DISCUSSION

The Fenton reaction

In the classical Fenton system [22], the mixture of H_2O_2 and Fe^{2+} represents a source of hydroxyl radicals. This mixture is known as "Fenton's reagent". The mechanism includes the oxidation of Fe^{2+} to Fe^{3+} while H_2O_2 is reduced to a hydroxide ion and hydroxyl radical [23]:



This reaction is usually run at ambient temperature and pressure. The conventional Fenton reaction is usually carried out in the dark. Fe^{3+} formed during the reaction can be reduced back to Fe^{2+} [24]:



This reaction of hydrogen peroxide with Fe^{3+} is known as a Fenton-like reaction. Reaction (2) is much slower than reaction (1), and the Fenton reaction requires higher amounts of Fe^{2+} for pollutant degradation.

In the first part of this work, the influence of H_2O_2 solely on the degradation of nicosulfuron was investigated (Figure 2b). The concentration of H_2O_2 varied from 88 to $529 \text{ }\mu\text{M}$ and it was recorded that, at the highest concentration, after a reaction time of 30 min, 15% of the pesticide had degraded. When Fe^{2+} was introduced into the system (Figure 2a), using the same H_2O_2 concentrations, a much higher degradation of nicosulfuron was recorded. Namely, with the lowest concentration ($88 \text{ }\mu\text{M}$, $[\text{H}_2\text{O}_2]/[\text{nicosulfuron}]$ ratio = 1.80) after 30 min of the reaction time, 80% of the pesticide had degraded. On the other hand, when the highest H_2O_2 concentration was used ($529 \text{ }\mu\text{M}$, $[\text{H}_2\text{O}_2]/[\text{nicosulfuron}]$ ratio = 10.84), a degradation of 90% of the pesticide was observed after 10 min.

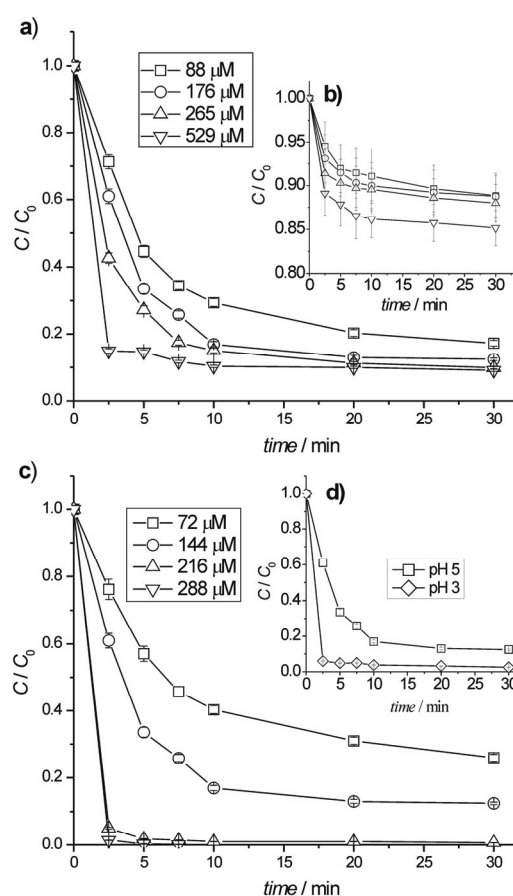


Figure 2. a) The influence of the hydrogen peroxide concentration on the nicosulfuron degradation in the Fenton reaction (nicosulfuron concentration = $48.8 \text{ }\mu\text{M}$, Fe^{2+} concentration = $144 \text{ }\mu\text{M}$, room temperature); b) the influence of the hydrogen peroxide concentration on the nicosulfuron degradation without catalyst; c) the influence of the Fe^{2+} concentration on the nicosulfuron degradation in the Fenton reaction (nicosulfuron concentration = $48.8 \text{ }\mu\text{M}$, hydrogen peroxide concentration = $176 \text{ }\mu\text{M}$, room temperature); d) the influence of pH on the Fenton reaction (nicosulfuron concentration = $48.8 \text{ }\mu\text{M}$, Fe^{2+} concentration = $144 \text{ }\mu\text{M}$, hydrogen peroxide concentration = $176 \text{ }\mu\text{M}$, room temperature).

The faster and more efficient degradation was recorded with the increase of the catalyst concentration (Figure 2c). The complete degradation of nicosulfuron was obtained with a Fe^{2+} concentration of 216 μM ($[\text{Fe}^{2+}]/[\text{nicosulfuron}]$ ratio = 4.42). The $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ ratio for this run was 1.23 at the initial pH of nicosulfuron solution (pH 5). Usually, the optimal pH for the Fenton reaction is between 3 and 4 [18], but the addition of acids is not environmentally acceptable. This is the reason why the reactions were performed at a higher pH value than usual. However, the Fenton reaction was also performed at a pH value of 3 and the obtained results are presented in Figure 2d. The obtained result is in agreement with the literature [18,25] since the reaction at pH 3 was much faster and more efficient than the one at pH 5. The slower reaction at pH 5 is due to the precipitation of a catalyst as a hydroxide, as well as to the lower oxidation potential of hydroxyl radicals [16]. The efficiency of the Fenton reaction at pH 5 can be increased by using a higher concentration of H_2O_2 or Fe^{2+} (Figure 2). This can lead to an increase in operation costs, as well as to the scavenging effect of excess H_2O_2 and the present catalyst [16, 18].

The Fenton-like reaction

The use of Fe^{3+} as catalysts in the Fenton reaction is known as the Fenton-like reaction and is already described by reaction (2). The use of Fe^{3+} salt can reduce the cost of the Fenton reaction, since Fe^{3+} salts are cheaper than Fe^{2+} salts [26]. Just as in the first part of the study, the influence of H_2O_2 and the catalyst on the reaction was studied. The concentration of H_2O_2 varied from 44 to 265 μM (Figure 3a). As in the Fenton reaction, the increase in the H_2O_2 concentration increased the reaction rate and its efficiency. When the highest concentration of H_2O_2 was used, 85% of nicosulfuron had degraded after 30 min of the reaction. The $[\text{H}_2\text{O}_2]/[\text{nicosulfuron}]$ ratio varied from 0.90 to 5.43, while the $[\text{Fe}^{3+}]/[\text{H}_2\text{O}_2]$ ratio varied from 4.91 to 0.81. The influence of the Fe^{3+} concentration on the reaction is given in Figure 3b. The Fe^{3+} concentration varied between 72 and 288 μM , while the $([\text{Fe}^{2+}]/[\text{nicosulfuron}]$ ratio was between 1.48 and 5.9. On the other hand, the $[\text{Fe}^{3+}]/[\text{H}_2\text{O}_2]$ ratio was between 0.51 and 1.64. The highest recorded degradation of nicosulfuron was 85%.

It was pointed out that the reaction given by reaction (2) is much slower than reaction (1), *i.e.*, that the Fenton reaction is much faster than the Fenton-like reaction [24]. In order to illustrate this, Figure 3c shows the Fenton and Fenton-like reactions of nicosulfuron under the same reaction conditions. It is

obvious that the Fenton reaction is much faster and more efficient than the Fenton-like reaction. The same was observed in the degradation of C.I. Acid black 1 [27], nitrobenzene [28] and phenol [29].

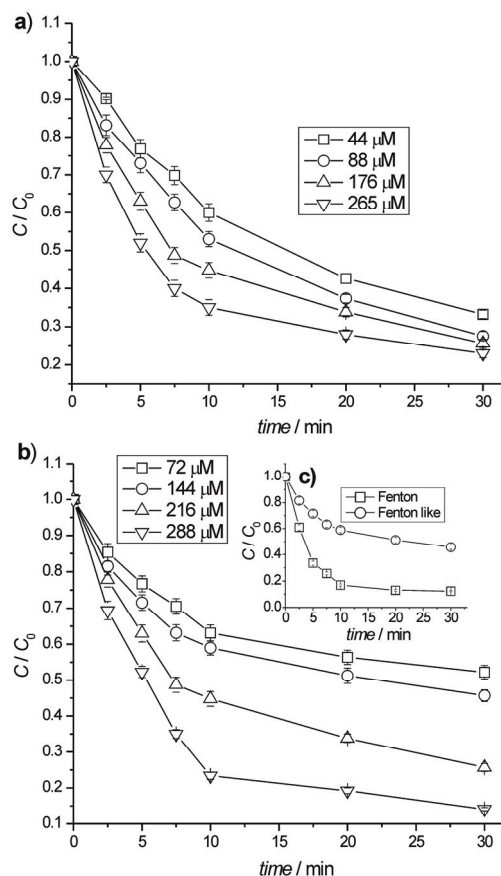
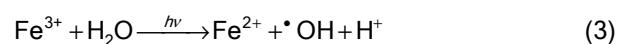


Figure 3. a) The influence of the hydrogen peroxide concentration on the nicosulfuron degradation in the Fenton-like reaction (nicosulfuron concentration = 48.8 μM , Fe^{3+} concentration = 216 μM , room temperature); b) the influence of the Fe^{3+} concentration on the nicosulfuron degradation in the Fenton reaction (nicosulfuron concentration = 48.8 μM , hydrogen peroxide concentration = 176 μM , room temperature); c) Fenton vs. Fenton-like reaction ($[\text{Fe}^{2+}] = [\text{Fe}^{3+}] = 144 \mu\text{M}$).

The photo-Fenton and the photo-Fenton-like reactions

It was found out that Fenton reaction can be accelerated using UV/Vis light [30]. This acceleration is due to the photochemical reduction of Fe^{3+} to Fe^{2+} :



During this reaction, not only is Fe^{2+} regenerated but additional hydroxyl radical is also produced. As a result, the photo-Fenton reaction should be faster than the conventional Fenton reaction. Since the regeneration of Fe^{2+} occurs by light, involving water, H_2O_2 is consumed less [24]. So, the photo-Fenton

reaction was applied in the degradation of nicosulfuron. The lower initial concentrations of H_2O_2 (88 and 176 μM) were used (Figure 4a). The $[\text{H}_2\text{O}_2]/[\text{nicosulfuron}]$ ratio was 1.80 and 3.60, while the $[\text{Fe}^{3+}]/[\text{H}_2\text{O}_2]$ ratio was 1.64 and 0.81 for the experiments with $[\text{H}_2\text{O}_2]$ of 88 and 176 μM , respectively. After a reaction time of 30 min, about 99% of nicosulfuron had been degraded. The photo-Fenton and Fenton reactions were compared (Figure 4b) and it is obvious that the photo-Fenton reaction proceeds much faster and more efficiently than the Fenton reaction.

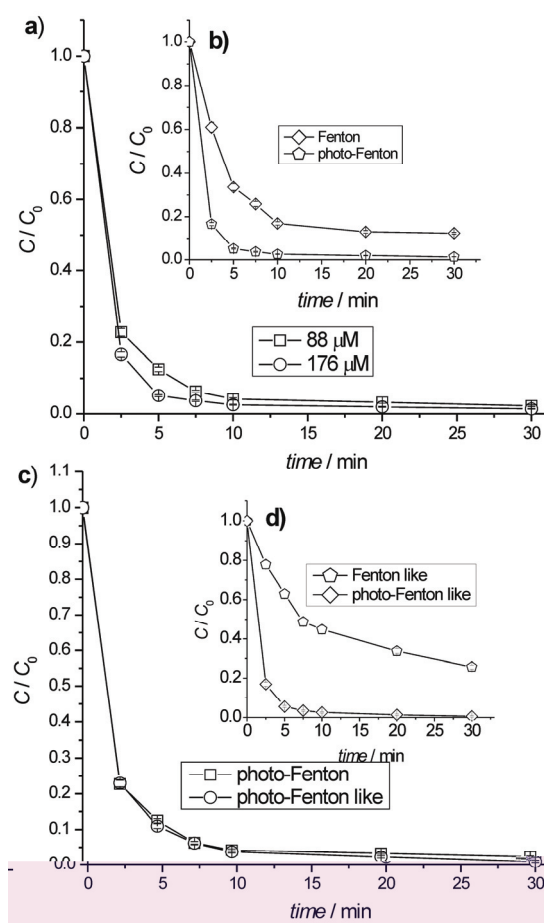


Figure 4. a) The influence of the hydrogen peroxide concentration on the nicosulfuron degradation in photo-Fenton reaction (nicosulfuron concentration = 48.8 μM , Fe^{2+} concentration = 144 μM , room temperature); b) Fenton vs. photo-Fenton reaction (nicosulfuron concentration = 48.8 μM , Fe^{2+} concentration = 144 μM , hydrogen peroxide concentration = 176 μM , room temperature); c) photo-Fenton vs. photo-Fenton-like reaction ($[\text{Fe}^{2+}] = [\text{Fe}^{3+}] = 144 \mu\text{M}$), nicosulfuron concentration = 48.8 μM , hydrogen peroxide concentration = 88 μM , room temperature); d) Fenton-like vs. photo-Fenton-like reaction (nicosulfuron concentration = 48.8 μM , Fe^{3+} concentration = 144 μM , hydrogen peroxide concentration = 176 μM , room temperature).

In addition, the photo-Fenton-like and the Fenton-like reactions in the degradation of nicosulfuron

were compared (Figure 4d). As in the case of the photo-Fenton and the Fenton reactions, the photo-Fenton-like reaction proceeded much faster than the Fenton-like reaction. It should be pointed out that when the photo-Fenton and the photo-Fenton-like reactions were compared, a similar behavior of the system was observed: the photo-Fenton-like reaction being slightly faster (Figure 4c). This could be expected, since it was reported that the Fe^{3+} oxalate complexes have an extended absorption range and give a higher quantum yield of Fe^{2+} in comparison to the Fe^{2+} hydroxyl complexes [23,31].

The microwave Fenton and Fenton-like reactions

Microwave (MW) irradiation can be used in chemistry as an energy source [32]. Also, MW can enhance and accelerate the heating process. In comparison to conventional heating, it provides uniform and rapid heating. MW can be combined with other techniques to enhance the removal of pollutants from wastewaters [33]. Among the combinations, the MW-Fenton reaction was also studied [34–36].

Microwave experiments were performed in a dedicated MW reactor (see Experimental part). First, the influence of the reaction temperature was studied. Since the reactor could not operate properly at temperatures lower than 50 $^{\circ}\text{C}$, the influence of the reaction temperature on the Fenton reaction was investigated in the range 50–70 $^{\circ}\text{C}$. As can be seen from Figure 5b, there is certain influence of the reaction temperature in the investigated temperature range on the Fenton reaction after 1 min of irradiation. The increase in reaction temperature increased the efficiency of the Fenton reaction, since at higher temperatures, the generation of OH radicals should be increased [35]. Although, the short reaction time (1 min) yielded a nicosulfuron degradation of almost 85%. The longer reaction times (longer than 2.5 min) increased the nicosulfuron degradation up to 96%, even at 50 $^{\circ}\text{C}$. The H_2O_2 concentration also has an influence on the Fenton as well as the Fenton-like reaction (Figure 5c). The concentration of H_2O_2 varied from 12 to 118 μM . The increase in the H_2O_2 concentration increased the efficiency of the nicosulfuron degradation in the MW-Fenton, as well as in the MW-Fenton-like reaction. The $[\text{H}_2\text{O}_2]/[\text{nicosulfuron}]$ ratio varied from 0.25 to 2.42, while the $[\text{Fe}^{2+}=\text{Fe}^{3+}]/[\text{H}_2\text{O}_2]$ ratio varied from 12 to 1.22. The highest recorded degradation of nicosulfuron in the MW-Fenton reaction was 96%, while in the MW-Fenton-like reaction was 89%. The MW-Fenton and MW-Fenton-like reactions request less hydrogen peroxide at shorter reaction times for the same efficiency. The increased efficiency of MW reactions

in comparison to the Fenton and Fenton-like reactions is due to the rapid as well as selective heating of H_2O_2 and water molecules [37]. It was shown that the Fenton reaction in comparison to the MW-Fenton reaction at the same reaction temperature is less efficient, so the combination of MW and Fenton reaction is needed in order to increase the treatment efficiency [38]. As well as in the classical Fenton and Fenton-like reactions, the MW-Fenton reaction proceeds faster and more efficiently than the MW-Fenton-like reaction.

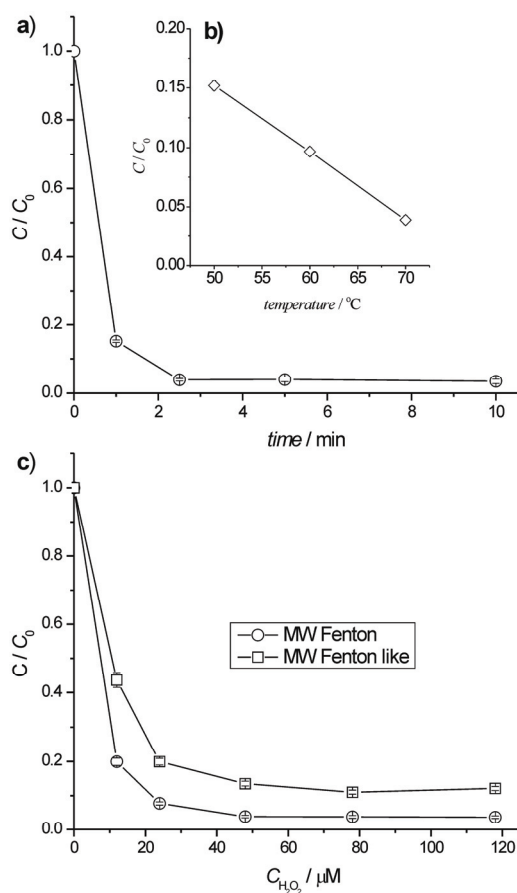


Figure 5. a) The influence of the reaction time on the nicosulfuron degradation in the microwave Fenton reaction (nicosulfuron concentration = $48.8 \mu\text{M}$, $[\text{Fe}^{2+}] = 144 \mu\text{M}$, hydrogen peroxide concentration = $48 \mu\text{M}$, reaction temperature = $50 \text{ }^{\circ}\text{C}$, mixing speed = 600 rpm); b) the influence of the reaction temperature on the Fenton reaction (reaction time = 1.0 min); c) the influence of the hydrogen peroxide concentration on the nicosulfuron degradation in the microwave Fenton and Fenton-like reactions (nicosulfuron concentration = $48.8 \mu\text{M}$, $[\text{Fe}^{2+}] = [\text{Fe}^{3+}] = 144 \mu\text{M}$, reaction time = 2.5 min , reaction temperature = $50 \text{ }^{\circ}\text{C}$, mixing speed = 600 rpm).

In addition, nicosulfuron degradation by the Fenton and Fenton-like reactions can be described by a pseudo-first-order reaction model [18]. The reaction

rate constants were calculated from the slope of $\ln(dC_0)$ vs. time plots and the obtained results are available from the author upon request. The values of the reaction rate constants were found to be between 0.048 and 1.380 min^{-1} , depending on the reaction conditions. The highest reaction rate was found for the MW-Fenton reaction.

Toxicity testing

Phytotoxicity testing

The phytotoxicity testing was performed in order to evaluate the effect of degradation products after photo-Fenton treatment on plants, since it was reported that pesticide degradation products can accumulate in soil and plants, and exert phytotoxic effect on plants [39]. The phytotoxicity study results are graphically presented in Figure 6a. It is evident from Figure 6a that nicosulfuron treatment using photo-Fenton process contributed in phytotoxicity decrease.

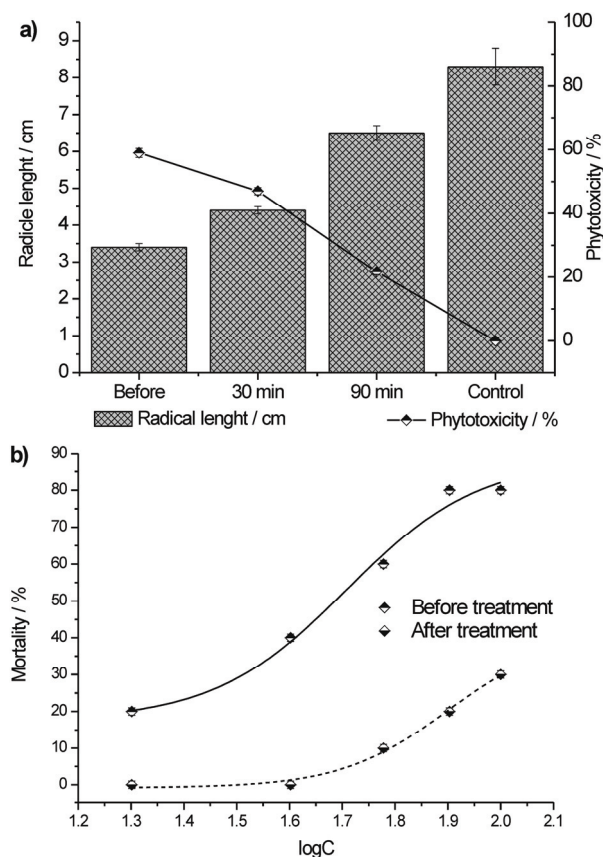


Figure 6. a) Phytotoxicity evaluation in the samples of nicosulfuron obtained after photo-Fenton process degradation (nicosulfuron concentration = $48.8 \mu\text{M}$, Fe^{2+} concentration = $144 \mu\text{M}$, hydrogen peroxide concentration = $176 \mu\text{M}$, room temperature); b) EC_{50} determination using *A. salina nauplii* after photo-Fenton process degradation (nicosulfuron concentration = $48.8 \mu\text{M}$, Fe^{2+} concentration = $144 \mu\text{M}$, hydrogen peroxide concentration = $176 \mu\text{M}$, room temperature).

Radicle lengths of mung bean seeds were 8.3 ± 0.5 and 6.5 ± 0.2 cm for control and the sample after the photo-Fenton treatment. Viewed from the aspect of phytotoxicity, in the sample after the treatment $21.69 \pm 0.9\%$ of toxicity was observed. It is also clear that as the reaction progresses, the toxicity decreases. Namely, the observed phytotoxicity in the sample before treatment was $59.0 \pm 1.4\%$, while, after 30 min of treatment, the phytotoxicity decreased to $47.0 \pm 1.1\%$. The results obtained in this experimental setup are similar to the results obtained after nicosulfuron degradation using TiO_2 as a catalyst [12].

Acute toxicity testing

In order to predict the influence of nicosulfuron and its degradation products on living organisms, acute toxicity testing was performed after photo-Fenton treatment and the results are given in Figure 6b.

Acute toxicity tests are of great importance because they predict the impact of certain pollutants on living organisms. Using *Artemia salina* cysts, the nicosulfuron solution before and after the treatment on living organisms was examined. The obtained results are presented in Figure 6b. EC_{50} values served as the indicator for toxicity of the examined solutions. Thus, in the solution before the treatment, the EC_{50} value was 51.0. Meanwhile in the photo-Fenton process, the treated nicosulfuron solution EC_{50} reached a value of 78.9. The obtained values confirm an acute toxicity decrease after the treatment.

The EC_{50} value after the treatment is in the range of $100\% > EC_{50} > 75\%$ and it is classified as a low toxicity sample. Meanwhile, the sample before treatment is classified as toxic, based on the range to which it belongs ($25\% < EC_{50} < 75\%$) [40].

CONCLUSION

The faster and more efficient degradation was recorded with the increase of the catalyst as well as hydrogen peroxide concentrations in the Fenton reaction. The complete degradation of nicosulfuron was obtained with the Fe^{2+} concentration of $216 \mu\text{M}$ at the initial pH value of the nicosulfuron solution (pH 5). The Fenton reaction at pH 3 was much faster and more efficient than the one at pH 5. The Fenton reaction is much faster and more efficient than the Fenton-like reaction.

The photo-Fenton reaction proceeds much faster and more efficiently than the Fenton reaction. Also, the photo-Fenton-like reaction proceeds much faster than Fenton-like reaction. When the photo-Fenton and the photo-Fenton-like reactions were compared, a similar behavior of the system was observed,

the photo-Fenton-like reaction being slightly faster.

The MW Fenton and Fenton-like reactions request less hydrogen peroxide at shorter reaction time for the same efficiency. The MW-Fenton reaction proceeds faster and more efficiently than the MW-Fenton-like reaction.

The toxicity testing of nicosulfuron treatment by the photo-Fenton process using *Vigna mungo* seeds showed decrease in phytotoxicity. In addition, the acute toxicity tests using *A. salina* nauplii showed that the EC_{50} value after the treatment is classified as a low toxicity sample.

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NAUČNI RAD

DEGRADACIJA NICOSULFURONA POMOĆU FENTON I FENTON-SLIČNE REAKCIJE

Fenton i Fenton-slična reakcija su primenjene u degradaciji nikosulfurona, sulfonilurea herbicida, pri pH vodenog rastvora nikosulfurona (pH 5). Obično, optimalna pH vrednost u Fenton reakciji je između 3 i 4, ali dodavanje kiseline nije ekološki prihvatljivo. To je razlog zašto su reakcije izvodene na višem pH nego obično. U toku istraživanja, primenjene su klasična Fenton i Fenton-slična reakcija kao i foto-Fenton i foto-Fenton-slična reakcija. Osim toga, korišćene su mikrotalasna Fenton i mikrotalasna Fenton-slična reakcija. Ispitivan je uticaj početnih koncentracija Fe^{2+} i Fe^{3+} kao i početne koncentracije vodonik-peroksida na efikasnost reakcija. Utvrđeno je da je Fenton reakcija mnogo brža i efikasnija od Fenton-slične reakcije, dok se foto-Fenton reakcija odvija mnogo brže i efikasnije nego Fenton reakcija. Mikrotalasna Fenton i mikrotalasna Fenton-slična reakcija su efikasnije od klasičnih reakcija. Takođe je ispitivana fitotoksičnost i akutna toksičnost reakcionih proizvoda oksidacije nikosulfurona tokom foto-Fenton reakcije. Dobljeni rezultati pokazuju da primenom foto-Fenton reakcije dolazi do smanjenja fitotoksičnosti kao i akutne toksičnosti.

Ključne reči: soli gvožđa; vodonik-peroksid; mikrotalasi; fitotoksičnost; akutna toksičnost.