

Investigation of Direct Electrochemical Oxidation of Neonicotinoid Pesticide Thiamethoxam in Water

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In recent decades an increase usage of chemicals in many ways of modern life is evident. So, the possibility of its intake into organisms, human and animals poisoning and health damage, is nowadays on a high level, especially when it comes to disaster situations caused by using toxic chemicals in terrorist attacks or for military purposes. If we look ahead, the risk of pesticide contamination of the water and soil, as one of the most important resources for surviving, is always present. The wide spectra of pesticide negative effects on the environment initiate the increasing number of investigations of efficient pesticide removal methods, especially from water. The aim of this study was to investigate the efficiency of direct electrochemical oxidation as a method for in-situ degradation of pesticides in the aquatic environment, depending on the concentration of pesticides, present electrolytes, applied current and the pH value of the medium. As a model molecule, the neonicotinoid pesticide thiamethoxam was used. Kinetics of thiamethoxam degradation in aqueous solution was followed by UV/Vis spectrometry.

Key words: electrochemical oxidation, pesticides, kinetics parameters, IrOX anode, energy consumption, UV/Vis spectroscopy.

Introduction

THE modern way of life is in many ways connected with the increasing use of different chemical substances, which, depending on the circumstances, can be used in a positive context (for the needs of hygienic household maintenance, in agriculture with the aim of increasing the yield per unit area of arable land, *etc.*) or in a negative context: if applied for military purposes [1, 2] or for terrorist attacks [3, 4]. By applying the mentioned toxic chemical substances, a person is, literally, forced to live with poisons, aware of being faced with the current risk posed by acute poisonings with the possibility of chronic consequences. Some previous researches prove that organism exposure to pesticides and their natural residuals intake of pesticides into organism may have carcinogenic and mutagenic effects, also their toxicity includes increased oxidative stress, leading to cellular damage and the generation of toxic metabolites [5-8].

More attention has been aroused in recent years on the presence of pesticides, antibiotics and toxic metals in amounts higher than the ecosystem can receive without major consequences, especially in the wastewater originated from agriculture processes (e.g. involving crop farming, aquaculture, agricultural product processing industry) [9]. The presence of pesticides in water systems initiates the increasing of quality parameters values of water as total organic carbon (TOC) [10], chemical oxygen demands (COD) [11, 12], biological oxygen demand (BOD) [13], total dissolved solids [5]. High values of

these parameters have negative effects on conventional wastewater treatment, inhibiting the biological step of wastewater treatment [14]. The wide spectra of pesticide negative effects on the ecosystem initiate the increasing number of investigations of efficient pesticide removal methods from water and soil. A very important fact is that pesticides can be converted into the less toxic compounds by decomposition processes, although there is a possibility that the newly formed decomposition products will be extremely toxic [15]. According to previous researches, the promising processes for pesticide removal are adsorption [16, 17], electrochemical oxidation [18], and Advanced Oxidation Processes (AOPs) [19].

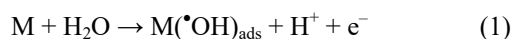
Depending on the mechanism of the oxidizing agent generation, electrochemical oxidation can be divided into direct and indirect electrochemical oxidation. In an indirect oxidation process, strong oxidants (mainly "active chlorine" species or hydroxyl radicals) are first produced in the bulk of solution via electrochemical reactions, and then these oxidants react with pollutants. The direct electrochemical oxidation using "active" anodes is based on direct electron exchange between organic compounds and an active surface of an anode. As a product of redox reactions onto the anode the intermediaries (e.g. "active oxygen" and hydroxyl radicals) are formed for further oxidation of organic compounds. In the first step of the direct electrochemical oxidation process (Eq.1), water molecules have been adsorbed onto the IrO_x surface (M) in hydroxyl radical form [20, 21]:

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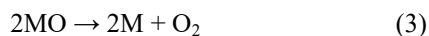
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Because of the "active" anode characteristic to highly interact with hydroxyl radicals, after desorption from IrO_x surface higher oxides (MO) can be generated. Generation of higher oxides is presented by Eq.2:



Further degradation of the higher oxides gives the molecular oxygen to the reactor (Eq.3):



The negative effects of organophosphates and carbamates presence in the environment initiate the development of neonicotinoid pesticides for plant protection [22]. Neonicotinoid pesticides are highly selective and efficiently activate the nicotinic receptors in the central nervous system of insects. The important characteristics of pesticides from the neonicotinoids group are low toxicity onto mammalian organisms during acute inhalation exposure, which makes these pesticides very acceptable for pest control [23]. The presence of neonicotinoids in food, aquatics, air, and indoor dust can be dangerous in multiple ways on mammals and humans, such as toxic effects on the nerve system, immune system and negative effects on kidneys and reproductive system [24]. The mentioned characteristics and easy availability of neonicotinoid pesticides posed a threat to the security of society due to their possible use for terrorist purposes. Besides the imidacloprid and acetamiprid, thiamethoxam (TMX) (Fig.1) is one of the three most important neonicotinoid pesticides for pest control.

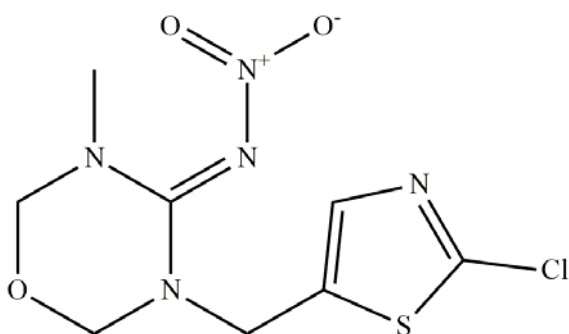


Figure 1. Molecular structure of neonicotinoid pesticide thiamethoxam

During the emergency situations caused by terrorist acts, or during the war, the water is one of the most important resources for surviving. The aim of this study was to investigate the efficiency of direct electrochemical oxidation as a method for in-situ degradation of pesticides in the aquatic environment, depending on the concentration of pesticides, electrolytes present, current strength and the pH value of the medium and the energy consumption during the process as an important parameter to obtain the viability of the process during war and terroristic actions. As a pesticide model molecule, the neonicotinoid pesticide thiamethoxam was used.

The electrochemical oxidation of thiamethoxam was only investigated by the Lebik-Elhadi et al. [11] using the "non-active" boron-doped-diamond anode. To our knowledge, direct electrochemical oxidation using IrO_x anode was not performed yet. The change of thiamethoxam concentration in aqueous solution was followed via UV/Vis spectrometry.

Experimental Part

Reagent & Materials

The neonicotinoid insecticide thiamethoxam was obtained from Shenzhen Yufull Industry Co. Ltd., Shenzhen, China. Na_2SO_4 was used as an electrolyte, purchased from Centrohem, Serbia. For pH value adjustment, H_2SO_4 and NaOH were used (Sigma-Aldrich, USA). The used chemicals were of analytical grade or higher. The deionized water used throughout the whole experiment was obtained using Millipore Waters Milli-Q (USA) purification system. The PAR M273 (Iskra, Slovenia) potentiostat/galvanostat in galvanostatic mode was used as a source of the current. 5 cm^2 plate of IrO_x (De Nora, Italy) was used as anode material, while 10 cm^2 plate made from austenite 18Cr/8Ni stainless steel series 304 was used as a cathode.

The pesticide degradation was followed by UV/Vis Shimadzu 1800 spectrophotometer (Japan). The pH value adjustment was controlled using Hanna pH Meter HI-2210 (Italy). The evenly mixing during electrochemical oxidation was obtained by the magnetic stirrer produced by Heidolph (Germany).

Electrochemical oxidation

The direct electrochemical oxidation was performed in undivided, open reactors at room temperature with 200 ml of electrolyte capacity with constant mixing speed of 750 rpm. The electrolytes used were consisted of dissolved Na_2SO_4 (0.15–0.30 M) and thiamethoxam water solution (0.125–0.5 $\times 10^{-4}$ M). The electrodes were immersed in an electrolyte solution with a 3 mm of the distance between anode and cathode. The continuous homogenization of the solution was obtained by mixing on a magnetic stirrer.

Kinetics of insecticide degradation was followed by UV-Vis spectroscopy. The pH value at the beginning of pesticide degradation was performed by the addition of 0.1 M H_2SO_4 for acidification or the same concentration of NaOH solution for an alkaline solution. During experiments, at least three measurements were done for each determination of all evaluated parameters.

Pesticide removal analysis and energy consumption

Pesticide degradation was monitored by absorbance measurement using UV-Vis spectrometry. The efficiency of thiamethoxam removal using IrO_x anode was calculated using Eq.4:

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_t)}{C_0} \cdot 100 \quad (4)$$

where C_0 and C_t represents the initial pesticide concentration and pesticide concentration at a specific time of the degradation process.

To design a wastewater treatment plant, the kinetics parameters obtained by modeling experimental data is a necessary parameter. The kinetics of thiamethoxam degradation by the direct electrochemical oxidation can be described using the pseudo-first-order kinetics model (Eq.5) [25]:

$$\ln \frac{C_t}{C_0} = -k \cdot t \quad (5)$$

where t presents time in minutes, while k (min^{-1}) is rate constant and C_t/C_0 are relative pesticide concentration.

From an economic point of view, the energy consumption of direct electrochemical oxidation is very important to calculate the cost of the process. Energy consumption per volume of pesticide solution was estimated in kWh m⁻³ and calculated by Eq.6 [25]:

$$\text{Energy consumption} = \frac{U \cdot I \cdot t}{V} \quad (6)$$

where U is average cell voltage (V), I is average applied current (A), t is electrolysis time expressed in hours and V is the volume of the reactor (m³).

Results and Discussion

Effect of initial pesticide concentration

The effect of initial concentration is important for reactor designing and calculation of the time required for treatment in a wastewater treatment plant. This effect was examined using the different initial concentration: 0.125, 0.250, 0.375 and 0.5 x 10⁻⁴ M of pesticide. Fig.2 shows the influence of different TMX concentrations on the degradation rate and rate constants during direct electrochemical oxidation on IrO_x anode.

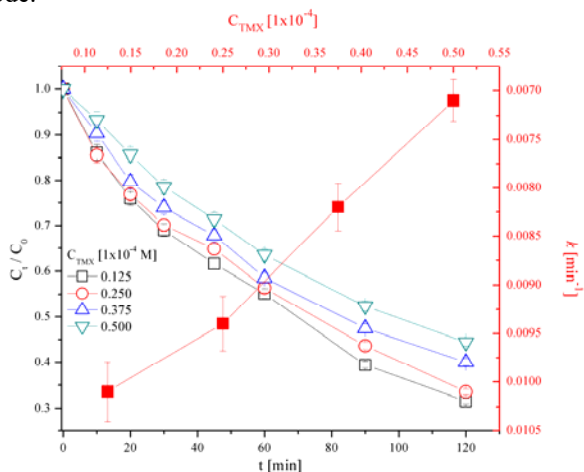


Figure 2. Dependence of direct electrochemical degradation of different relative thiamethoxam concentration (marked in the Figure) as a function of electrolysis time (black scale) and the dependence of reaction rate from thiamethoxam concentration (red scale). Conditions: [Na₂SO₄] = 0.25 M, $I=300$ mA, pH=5.8.

As it can be seen from Fig.2, the neonicotinoid insecticide degradation efficiency was decreased with increase of the initial pesticide concentration after 120 minutes of the reaction time of direct electrochemical oxidation. Increase of the initial pesticide concentration initiated decrease of the degradation rate of thiamethoxam, for 68.5, 66.5, 60.0, 55.6%, respectively. The reaction rate dependence of thiamethoxam concentration is depicted in Fig.2 (red scale) and the pseudo-first order kinetics plot and rate constants for degradation of thiamethoxam at different initial pesticide concentration is presented in Fig.3. The rate constants were decreased from 0.0101 min⁻¹ for [TMX] = 0.125x 10⁻⁴ M to 0.0071 min⁻¹ for [TMX] = 0.5x 10⁻⁴ M. The determined dependence is the result of insufficient adsorption site on the anode material at higher pesticide concentrations. The same phenomena were obtained by Yao Y. et al [26] using the Yb-doped PbO₂ anode for degradation neonicotinoid insecticide acetamiprid in presence of the Na₂SO₄ as an electrolyte, where degradation rate of acetamiprid after 120 minutes for a system with an initial concentration of 10 mg L⁻¹ was 98.53% and for a system with 80 mg L⁻¹ was 52.78%.

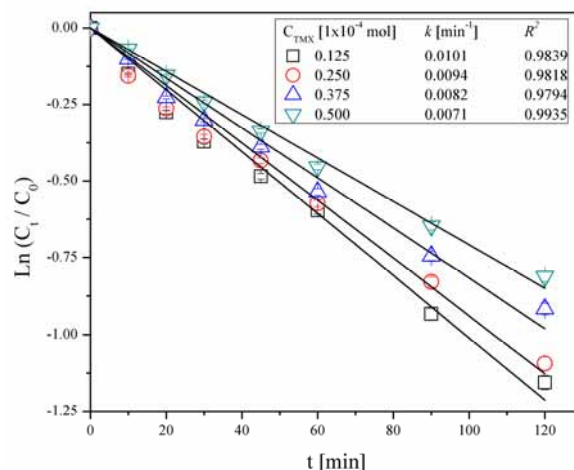


Figure 3. The pseudo-first order kinetics plot and rate constants for degradation of thiamethoxam at different initial pesticide concentration. Conditions: [Na₂SO₄] = 0.25 M, $I=300$ mA, pH=5.8.

Effect of electrolyte concentration

During direct electrochemical oxidation, the presence of Na₂SO₄ as an electrolyte in a solution initiates an increase of solution conductivity and improves electron-transfer during degradation especially during oxygen evolution [5, 25, 27, 28]. Effect of the electrolyte concentration was investigated at four different concentrations of Na₂SO₄ from 0.15 to 0.30 M. Results of the initial electrolyte concentrations and their pseudo-first order are presented in Fig.4. The pseudo-first order kinetics plot and rate constants for pesticide degradation at different initial electrolyte concentrations are depicted in Fig.5.

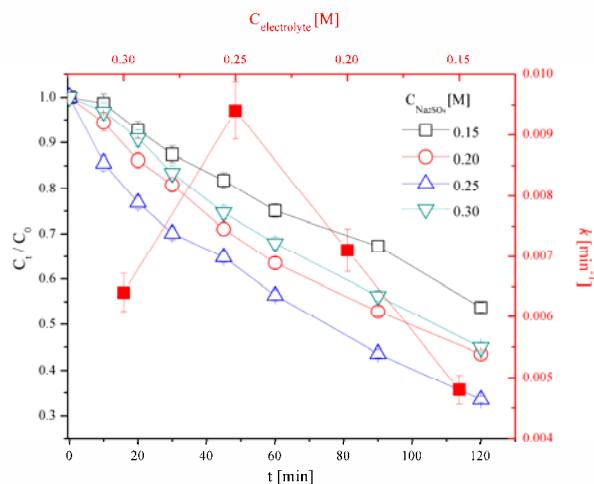


Figure 4. Dependence of direct electrochemical degradation of thiamethoxam of different electrolyte concentrations (marked in the Figure) as a function of electrolysis time (black scale) and the dependence of reaction rate from initial electrolyte (red scale) Conditions: [TMX] = 0.25x 10⁻⁴M, $I=300$ mA, pH=5.8.

Analyzing the results presented in Figures 4 and 5, it can be concluded that the increase of the electrolyte concentration to 0.25 M Na₂SO₄ initiate increase of process efficacy (66.5%) and reaction rate ($k=0.0094$ min⁻¹) as a result of forming higher concentrations of adsorbed radicals (Eq.1) and higher oxygen evolution (Eq.3). Further increase of electrolyte concentration decrease the efficacy of the process to 55% of degraded pesticide and reaction rate to $k=0.0065$ min⁻¹. Decreasing of the reaction rate can be caused by "scavenging" of formed hydroxyl radicals by SO₄²⁻ ions (Eq.7) [29]:

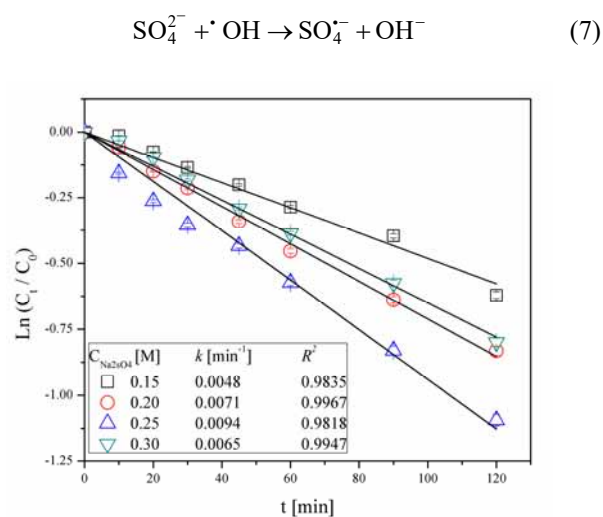


Figure 5. The pseudo-first order kinetics plot and rate constants for pesticide degradation at different initial electrolyte concentrations. Conditions: $[\text{TMX}] = 0.25 \times 10^{-4} \text{ M}$, $I = 300 \text{ mA}$, $\text{pH} = 5.8$.

The same phenomena were obtained during direct electrochemical oxidation of anthraquinone dye AB111, where the highest efficacy is obtained in the system with 0.17 M of Na_2SO_4 and further increasing of salt concentration initiates the decreasing the process efficacy [25]. Lebig-Elhadí et al. [11] studied the degradation of thiamethoxam by direct electrochemical oxidation using a boron doped diamond anode at different initial conditions and shows high pesticide mineralization efficiency. By cited study, under the applied conditions ($[\text{TMX}] = 2 \text{ mg L}^{-1}$, $[\text{Na}_2\text{SO}_4] = 0.1 \text{ M}$, $I = 16 \text{ mA cm}^{-2}$) thiamethoxam was completely degraded after 30 minutes.

Effect of applied current

In addition, direct electrochemical oxidation is highly dependent on the applied current [30]. The efficiency of thiamethoxam degradation by direct electrochemical oxidation using IrO_x anode was tested using five values of the applied current in the range 100-300 mA. Fig.6 presents the results of insecticide degradation (black scale) and the dependence of reaction rate from applied current during the reaction (red scale) at different values at the applied current during electrolysis time. The pseudo-first order kinetics plot and rate constants for pesticide degradation at different applied current are depicted in Fig.7.

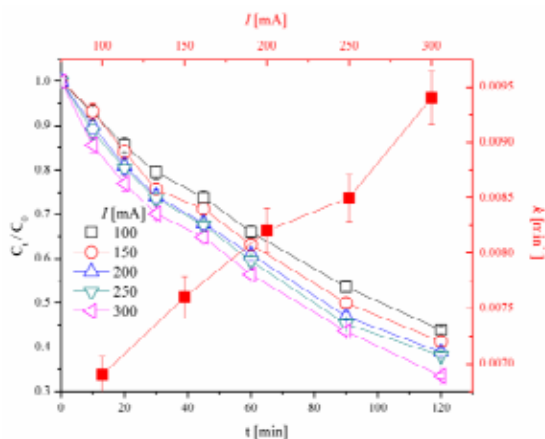


Figure 6. Dependence of direct electrochemical degradation of thiamethoxam of different applied current (marked in the figure) as a function of electrolysis time (black scale) and the dependence of reaction rate from applied current (red scale). Conditions: $[\text{TMX}] = 0.25 \times 10^{-4} \text{ M}$, $[\text{Na}_2\text{SO}_4] = 0.25 \text{ M}$, $\text{pH} = 5.8$.

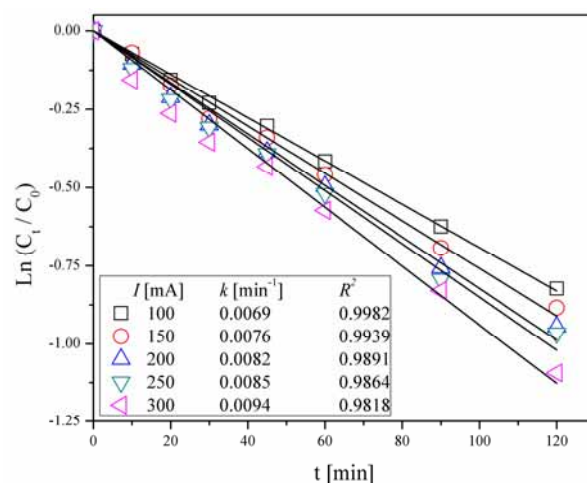


Figure 7. The pseudo-first order kinetics plot and rate constants for pesticide degradation at different applied current. Conditions: $[\text{TMX}] = 0.25 \times 10^{-4} \text{ M}$, $[\text{Na}_2\text{SO}_4] = 0.25 \text{ M}$, $\text{pH} = 5.8$.

Presented results show the influence of reaction rate: at the lowest applied current, the concentration of thiamethoxam decreased by 57.1% and the reaction rate was $k = 0.0069 \text{ min}^{-1}$ while increase of the applied current value increases the reaction rate. At the highest value of applied current ($I = 300 \text{ mA}$), 66.5 % of the initial pesticide amount was degraded and the reaction rate was $k = 0.0094 \text{ min}^{-1}$. The same correlation between increase of the applied current and increase of the reaction rate was obtained in our previous paper [25]. Increase of the applied current caused an increase of the formation of adsorbed radicals (Eq.1) and led to the forming of higher oxides (Eq.2), or oxygen evolution reaction (Eq.3).

Effect of initial pH value

The effect of the initial solution pH value was examined at acidic (pH 3.0), at pH value without adjustment (pH 5.8) and at alkali (pH 11.0) conditions. The results of the influence of the pH values at the beginning of insecticide degradation and the dependence of the reaction rate from initial pH value during the process are presented in Fig.8. The pseudo-first order kinetics plot and rate constants for pesticide degradation at different initial electrolyte concentrations are depicted in Fig.9.

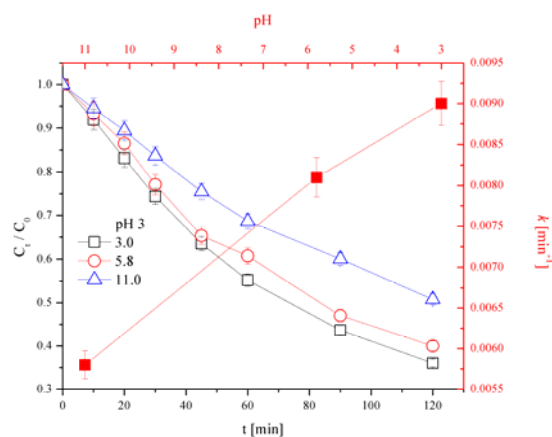


Figure 8. Dependence of direct electrochemical degradation of thiamethoxam of different initial pH value (marked in the figure) as a function of electrolysis time (black scale) and the dependence of reaction rate from initial pH value (red scale). Conditions: $[\text{TMX}] = 0.25 \times 10^{-4} \text{ M}$, $[\text{Na}_2\text{SO}_4] = 0.25 \text{ M}$.

Analyzing the presented results, the reaction rate depends on the initial pH value of the solution, at the acidic aqueous medium (pH 3.0) reaction rate was $k = 0.0090 \text{ min}^{-1}$, and increase of the pH value to 11.0 initiate decrease of the

reaction rate ($k = 0.0058 \text{ min}^{-1}$). The degradation rate has the same trend, the increase of process efficacy follows the decrease of pH value. In an acidic solution, 66.5% of thiamethoxam is degraded, and in alkali solution (pH 11) was degraded 49.3% of thiamethoxam. The same trend was obtained in thiamethoxam degrading by electrochemical oxidation using the BDD electrode [11]. Possible explanations for this trend are higher hydroxyl radicals production on the surface of the electrode at a lower pH value [31] while in alkaline solution the generation of OH^- is increased which causes a decrease of the reaction rate [25].

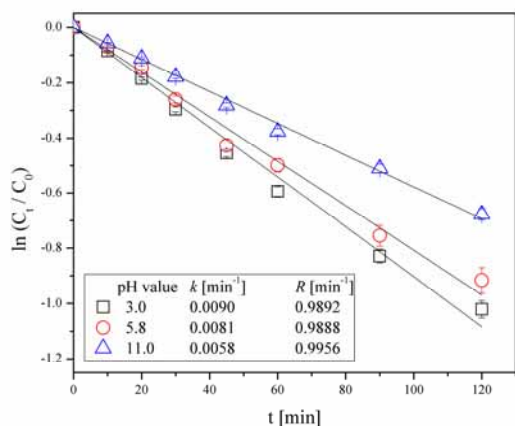


Figure 9. The pseudo-first order kinetics plot and rate constants for pesticide degradation at different initial pH value. Conditions: $[\text{TMX}] = 0.25 \times 10^{-4} \text{ M}$, $[\text{Na}_2\text{SO}_4] = 0.25 \text{ M}$.

Energy consumption

From the aspect of cost-effectiveness of the direct electrochemical oxidation of insecticide thiamethoxam, the most important factor is energy consumption. Energy consumption was calculated using Eq.6. Fig.10 presents the dependence of the relative voltage of the applied current.

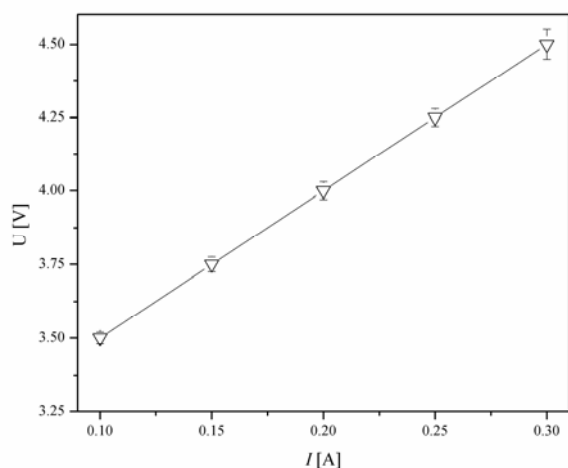


Figure 10. The relative voltage versus applied current in the direct electrochemical oxidation of thiamethoxam. Conditions: $[\text{TMX}] = 0.25 \times 10^{-4} \text{ M}$, $[\text{Na}_2\text{SO}_4] = 0.25 \text{ M}$, pH = 5.8.

Analyzing the result obtained by Eq.6 and from Fig.10, for the lowest applied current, the voltage was 3.5 V and the calculated energy consumption was 3.5 kWh m^{-3} . Increase of the used applied current causes increase of the voltage to 4.5 V and energy consumption to 13.5 kWh m^{-3} . Using the highest applied current increases the reaction rate from $k = 0.0069 \text{ min}^{-1}$ to $k = 0.0094 \text{ min}^{-1}$ which causes an increase of the energy consumption and has a negative effect on the cost-effectiveness of the process.

UV-Vis spectra

Parameters obtained by following the decrease of the thiamethoxam absorption peak at 251 nm of UV-Vis spectra during electrolysis time was used for kinetic parameters calculations. The UV-Vis spectra change during thiamethoxam degradation reaction under optimal conditions is presented in Fig.11.

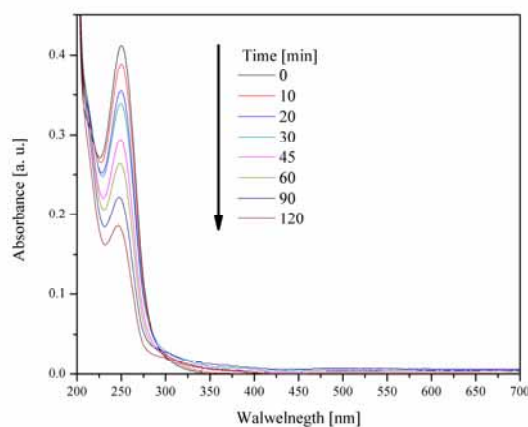


Figure 11. Typical UV/Vis spectra of thiamethoxam during direct electrochemical oxidation process. Conditions: $[\text{TMX}] = 0.25 \times 10^{-4} \text{ M}$, $[\text{Na}_2\text{SO}_4] = 0.25 \text{ M}$, $I = 300 \text{ mA}$, pH = 5.8.

The maximum absorption peak of thiamethoxam is at 251 nm (Fig.7). A change in the thiamethoxam absorption peak is observed during electrolysis time and decrease of absorbance value after 120 minutes shows the efficiency of the process over time. After 120 minutes, according to the measured absorbance value at 251 nm, the pesticide concentration was decreased to 60.0 %.

Conclusion

Direct electrochemical oxidation of thiamethoxam can be well described using the pseudo-first-order kinetic model. The increase of the initial pesticide concentration decreases the process efficacy and the reaction rate. The optimal Na_2SO_4 concentration is 0.25 M, while the higher concentrations initiates "scavenging" of hydroxyl radicals by sulphate ions. The direct electrochemical degradation in acidic solution is more efficient.

Increase of the applied current causes acceleration of redox reactions on the electrode surface, thus the process efficacy is higher at 300 mA than in the system with 100 mA. On the other side, use of higher applied current makes the process more expensive.

So, the optimal conditions for direct electrochemical oxidation of thiamethoxam are $[\text{TMX}] = 0.25 \times 10^{-4} \text{ M}$, $[\text{Na}_2\text{SO}_4] = 0.25 \text{ M}$, pH = 5.8.

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Istraživanje direktne elektrohemijske oksidacije neonikotinoidnog pesticida tiametoksam u vodi

Poslednjih decenija očigledna je sve veća upotreba hemikalija na mnogo načina u savremenom životu. Stoga je mogućnost njegovog unosa u organizme, trovanja ljudi i životinja i oštećenja zdravlja, danas na visokom nivou, posebno kada su u pitanju katastrofe izazvane upotrebom toksičnih hemikalija u terorističkim napadima ili u vojne svrhe. Ako gledamo unapred, rizik od zagađenja vode i tla pesticidima, kao jednim od najvažnijih resursa za preživljavanje, uvek je prisutan. Široki spektri negativnih efekata pesticida na životnu sredinu iniciraju sve veći broj ispitivanja efikasnih metoda uklanjanja pesticida, posebno iz vode. Cilj ovog rada bio je da se ispita efikasnost direktne elektrohemijske oksidacije kao metoda za in-situ razgradnju pesticida u vodenoj sredini, u zavisnosti od koncentracije pesticida, prisutnih elektrolita, primenjene struje i pH vrednosti medijuma. Kao model molekula korišćen je neonikotinoidni pesticid tiametoksam. Kinetika razgradnje tiametoksama u vodenom rastvoru praćena je UV/Vis spektrometrijom.

Cljučne reči: elektrohemijska oksidacija, pesticidi, kinetički parametri, IrOX anoda, potrošnja energije, UV/Vis spektroskopija.