

DEGRADATION OF SULFAMETHAZINE BY SE-FENTON METHOD

DING, S. M.^{1,2*} – LI, M.¹

¹*College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China*

²*Chongqing Multiple-Source Technology Engineering Research Center for Ecological Environment Monitoring, Yangtze Normal University, Chongqing 408100, China*

**Corresponding author*

e-mail: ding717@126.com; phone: + 86-133-8329-3867

(Received 18th Mar 2019; accepted 17th May 2019)

Abstract. Photodegradation is one of the important methods of antibiotic treatment in water environment. This paper studies the treatment effect of sulfamethazine by solar electric-Fenton (SE-Fenton) technology, observes the contribution of OH concentration to degradation, and involves the effect of pH value, voltage and Fe²⁺ concentration on the treatment effect. The experiment shows that the degradation rate of sulfamethazine can be effectively improved by the solar-powered Fenton system. The optimum conditions for the degradation system are pH 3.0, 25 mg/L Fe²⁺ concentration, and the applied voltage of 3 V. This study provides a basis for the removal of sulfonamide antibiotic contamination in water environment.

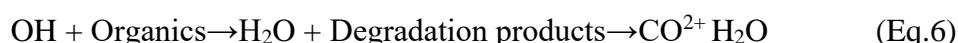
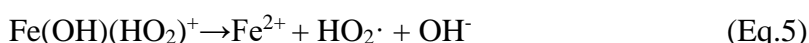
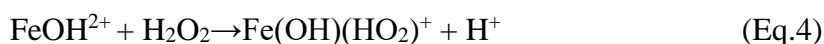
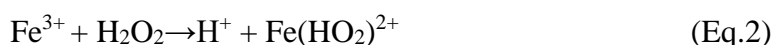
Keywords: *sulfanilamide, solar electric-Fenton, antibiotics, photolysis, advanced oxidation technology*

Introduction

The sulfonamide antibiotics are synthetic broad-spectrum antibiotics, with the structure of aminobenzene sulfonamide, and have been used in clinical medicine for 50 years. Because of its stable nature, convenient use and high safety, it is widely used in medicine. On the other hand, the absorption capacity of human beings or organisms is weak, and more than 80% of it is released into the environment in the original form, so it is often detected in the environment, with the detection rate ranking top among all kinds of drugs (Kolpin et al., 2002; Kemper, 2008). Because of its long-standing existence in the environment such as water and soil, it affects the original microbial population in the environment, gives birth to bacteria with extensive drug resistance, or induces gene mutations, thyroid hyperplasia or tumors in rodents (Martinez et al., 2008; Littlefieldna et al., 1989).

Due to the above reasons, the treatment technology of antibiotic pollution in the environment is getting more and more attention. Advanced oxidation technology is a water treatment technology developed in recent years, characterized by the generation of hydroxyl radicals (OH) with strong oxidizing ability, and is a method of oxidizing macromolecule refractory organics into low toxic or non-toxic small molecule substance under the reaction conditions of high temperature and high pressure, electricity, sound, light, catalyst and the like (Oller et al., 2011). Fenton technology is often used for the treatment of refractory organics. With good treatment efficiency of Fenton method and high mineralization rate of organic pollutants, it is simple and practical, and its application range is increasing continuously. In recent years, solar-Fenton (S-Fenton), electric-Fenton (E-Fenton), ultrasonic-Fenton and other advanced

oxidation technologies have been derived (Serna-Galvis et al., 2016). The Fenton technology forms hydroxyl radicals mainly by reaction, with the main reaction steps as follows (Christopher et al., 2007).



On the basis of Fenton method and the application of light, the content of Fe^{2+} in Fenton reagent can be reduced, the reaction rate of H_2O_2 and the production rate of OH can be increased, so that the mineralization of organics can be more thorough (Elmolla and Chaudhuri, 2009, 2011). The E-Fenton method produces Fe^{2+} and H_2O_2 by electrochemical process. The E-Fenton method mainly involves the cathode E-Fenton method, the basic principle of which is to spray oxygen on the cathode of the electrolytic cell and reduce it to H_2O_2 at the cathode as shown in *Equation 7*. Then, H_2O_2 reacts with the added Fe^{2+} to produce $\cdot\text{OH}$ and thus reacts with the organics (Brillas et al., 2009; Yahya et al., 2016).



Compared with the S-Fenton method, the E-Fenton method has the mechanism of generating H_2O_2 automatically, and higher utilization rate of H_2O_2 . The disadvantage is low current efficiency. If the amount of processing is very large, the amount of electricity input is increased and the cost will also be high, which limit its wide application. The photoelectric Fenton method, which combines the advantages of S-Fenton and E-Fenton, has attracted much attention in recent years. Compared with artificial light source, the low cost of sunlight makes it the research hotspot of S-Fenton method. The SE-Fenton technology simultaneously utilizes the characteristics of automatically generating H_2O_2 by the E-Fenton method and the advantage of circulating $\text{Fe}^{2+}/\text{Fe}^{3+}$ by S-Fenton to increase the concentration of $\cdot\text{OH}$, and save costs with sunlight. At present, the research is mainly applied to the treatment of refractory organics such as dyes and antibiotics (Valero et al., 2010; Mahmoodi et al., 2011; Almeida et al., 2015; Pérez et al., 2015, 2017). Casado and Fornaguera (2006) uses this method to treat organic acids such as p-benzoic acid, 2,4-dichlorophenoxyacetic acid and oxalic acid, and completely mineralize the organic acids for about 1 h. Flox et al. (2007) also studied the degradation of phenol-containing wastewater and 4-chloro-o-phenoxypropionic acid by SE-Fenton technology, with good results.

Sulfamethazine (SMT) is a kind of sulfonamides, which is mainly used to treat avian cholera, avian typhoid and chicken coccidiosis. More attempts have been made to treat sulfonamides with advanced oxidation technology (Alam et al., 2009; Batista and

Nogueira, 2012; Sopaj et al., 2016). Because of its stability in the environment, the degradation effect needs to be further improved. In this paper, the SE-Fenton technology is used to treat SMT, which provides basic data for the treatment of antibiotic wastewater.

Materials and methods

Drugs

Sulfamethazine (SMT, purity is equal to or more than 99%, SINOPHARM), methanol (chromatographic purity, Chengdu Kelong Chemical Reagent Factory), and acetonitrile (chromatographic purity, Tianjin Damao Chemical Reagent Factory). Ferrous sulfate (analytical purity), potassium dihydrogen phosphate (analytical purity), dipotassium hydrogen phosphate (analytical purity), sodium hydroxide and sulfuric acid are analytical purities. The experimental water is ultrapure water.

Main instruments

High Performance Liquid Chromatography (LC-2010A HT, Shimadzu, Japan); Circulating Water Vacuum Pump (Gongyi Yuhua Instrument Co., Ltd.), pH Meter (Shanghai LIDA Instrument Factory), TASI-8731 Digital Illuminometer (Suzhou TASI Electronics Co., Ltd.)

Experimental device

Experimental device of SE-Fenton is as *Figure 1*.

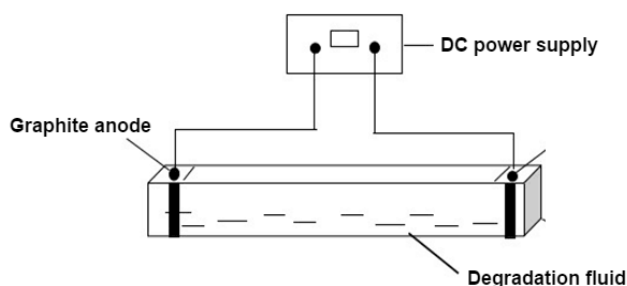


Figure 1. Experimental device

Experimental method

Determination of SMT

SMT in water is determined by HPLC with SHIMADZU VP-ODS-C18 column (25 cm × 4.6 mm, 5 μm). The detection wavelength is 270 nm. Mobile phase: 0.017 mol/L phosphate: Acetonitrile (80: 20) buffer solution; flow rate is 1 mL/min, sample volume is 20 μL, column temperature is 30 °C.

Control experiment

In the electrolyzing cell, 1 L of 10 mg/L SMT standard working fluid is added, and 1 mL of 25 mg/mL ammonium ferrous sulfate solution is added. The pH of NaOH

solution and H₂SO₄ solution is adjusted to be 3.0. Under different conditions, S-Fenton degradation, E-Fenton degradation (applied voltage 3 V) and SE-Fenton degradation reaction were carried out. Take 1 mL of the reaction solution in the sampling bottle at different time intervals to determine the SMT concentration.

Degradation of SMT under solar photovoltaic conditions

In the electrolyzing cell, 1 L 10 mg/L SMT standard working fluid is added, 25 mg/mL ammonium ferrous sulfate solution is added. The pH of the solution is adjusted with NaOH solution and H₂SO₄ solution. Graphite electrodes are inserted on both sides of the electrolyzing cell, DC power supply is connected and applied voltage is regulated. The oxygen for manufacturing H₂O₂ is supplied to the degradation system with an aerator at the cathode.

For sunshine conditions, select the sunny days from July to August in Chongqing, from 11: 00 a.m. noon to 14: 00 p.m. The light intensity (600 00~780 00 LUX) empowers the degradation system to the degradation reaction under sunlight, and samples are taken at different time periods. The SMT concentration of the system is measured by high performance liquid chromatograph at different sampling time.

Determination of ·OH in the process of degradation

Because benzene reacts with ·OH to form phenol with good selectivity and few by-products, benzene is often used as ·OH trapping agent to produce phenol, and its concentration represents the concentration of OH in solution. In preparing the degradation solution, add benzene, make the concentration of benzene in the degradation solution be 7000 μmol·L⁻¹, adjust to the desired pH value, carry out the degradation reaction, sample 1 mL at different time intervals as required, and determine phenol concentration in solution by high performance liquid chromatography. The determination conditions are as follows: SHIMADZU VP-ODS-C18 column (25 cm × 4.6 mm, 5 μm), column temperature of 30 °C, UV detector wavelength of 270 nm, the mobile phase of methanol (V): Water (V) = 60: 40, the flow rate of 1.0 mL·min⁻¹, the injection volume of 20 μL, and the retention time of phenol as 3.01 min.

Results and discussion

Degradation of SMT by different Fenton systems

Add 1 mL of 25 mg/mL ammonium ferrous sulfate solution to 1 L of 10 mg/L of SMT degradation solution, adjust the pH of the solution to be 3.0, and use E-Fenton, S-Fenton and SE-Fenton systems to degrade SMT, respectively. The degradation rate of SMT by different systems is shown in *Figure 2a*. From the figure, it can be seen that the degradation rate of three different Fenton systems increases with the increase of the reaction time. The OH produced during the degradation of three different systems is determined and the results are shown in *Figure 2b*. It is obvious that the degradation rate of SMT in different systems is positively related to the concentration of ·OH produced in the system. At the same time, the degradation rate of SMT is the highest by the SE-Fenton system, followed by the S-Fenton system and the lowest by the E-Fenton system. These results indicate that all three systems can promote the degradation of SMT, in which S-Fenton and E-Fenton technology can produce synergetic effect and enhance the degradation ability. However, the degradation effect of S-Fenton is better

than that of E-Fenton, mainly because of the synergistic effect of ultraviolet light and Fe^{2+} on the catalytic decomposition of H_2O_2 produced in the system.

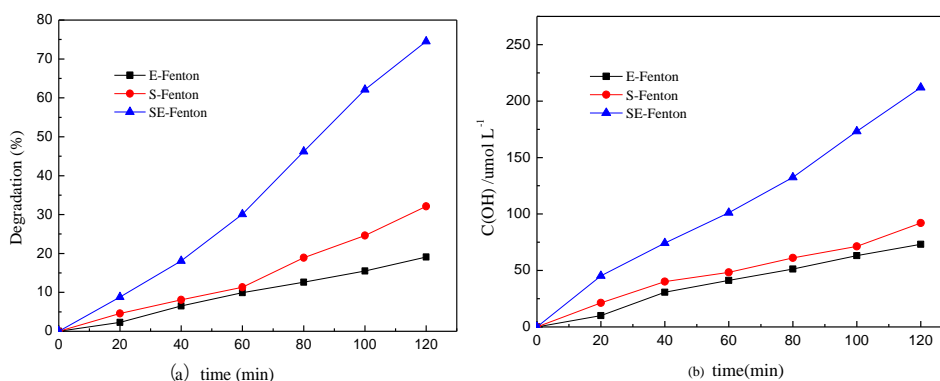


Figure 2. Degradation effect of SMT by different Fenton systems and the corresponding OH concentration of the system. SMT 10 mg/L, pH = 3.0, sunlight intensity (65000~78000 LUX)

Effect of pH on SE-Fenton degradation of SMT

Many studies have shown that Fenton systems usually have better ability to degrade organics under acidic conditions (Alam et al., 2009), so this experiment is carried out at pH 1.0, 3.0, 5.0, and 7.0. It can be seen from *Figure 3* that in the reaction time of the first 30 min, the degradation efficiency of SMT does not differ greatly under the conditions of pH 1.0, 3.0 and 5.0, and after 30 min, the system with pH 3.0 has the best effect on SMT degradation. When pH is higher than 3.0, ranging from 3.0 to 7.0, the degradation efficiency of SMT becomes smaller and smaller. In the system with pH 7, the degradation rate of SMT in 120 min is only about 10%. When the pH is lower than 3.0, the degradation rate of SMT is also greatly reduced. Some studies have shown that when pH is less than 3.0, the ferric ion concentration in the Fenton system decreases, thus inhibiting the formation of OH. When pH is higher than 4.0, $\text{Fe}(\text{OH})_3$ precipitates will occur in the solution. The higher the pH is, the more precipitates will be formed, which will prevent the circulation of Fe^{2+} and Fe^{3+} in Fenton system and is unfavorable to the formation of $\cdot\text{OH}$. Therefore, the optimum pH for SE-Fenton degradation of SMT is 3.0, and the pH of the system is 3.0 in the following experiments.

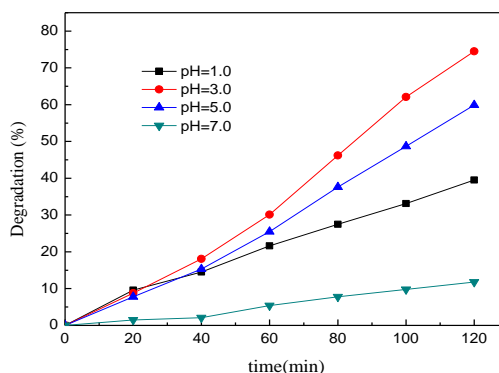


Figure 3. Effect of pH on SE-Fenton degradation of SMT. 1L 10 mg/L SMT degradation solution; E = 3V; Fe^{2+} concentration of 25 mg/L; light intensity: pH = 1.0(65500~72000 LUX); pH = 3.0(68000~72000 LUX); pH = 5.0(64000~735 00 LUX); pH = 7.0(61300~723 00 LUX)

Effect of applied voltage on SE-Fenton degradation of SMT

The degradation efficiency of the SMT increases as the applied voltage increases, as shown in *Figure 4*. This is due to an increase in the applied voltage of the electrolytic cell, which accelerates the generation of the cathode H_2O_2 , resulting in an increase in the concentration of $\cdot OH$. The difference among the voltages 3 V, 5 V and 7 V used in the experiments is not too large, so the degradation efficiency of SMT is not improved significantly. The influence of the applied voltage of 3 V and 7 V on SMT degradation is very small. In view of saving cost and energy, under this experimental condition, when the applied voltage is 3 V, the degradation effect of SMT is the best.

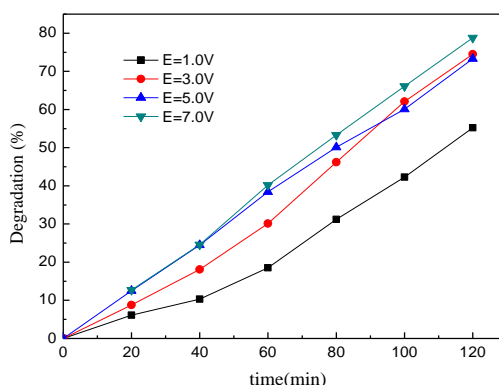


Figure 4. Effect of applied voltage on SE-Fenton degradation of SMT. 1L 10 mg/L SMT degradation solution; pH = 3; Fe^{2+} concentration of 25 mg/L; Light intensity: E = 1.0 V (65000~76000 LUX); E = 3.0 V (65000~78000 LUX); E = 5.0 V (55000~70000 LUX); E = 7.0 V (56700~69700 LUX)

Effect of Fe^{2+} dosage

The results of *Figure 5* show that in the range of concentration given in the experiment, when the concentration of Fe^{2+} is 25 mg/L, the degradation effect of SMT is the best.

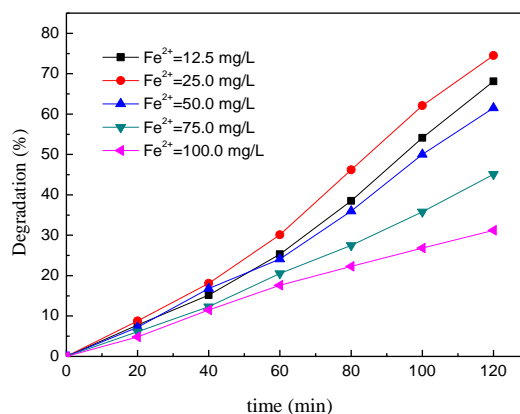


Figure 5. Effect of Fe^{2+} dosage. E = 3V; pH = 3; 10 mg/L SMT Degradation solution; Light intensity: Fe^{2+} = 12.5 mg/L (64000—70000 LUX); Fe^{2+} = 25 mg/L (65000—78000 LUX); Fe^{2+} = 50 mg/L (63000~75000 LUX); Fe^{2+} = 75 mg/L (63000~75700 LUX); Fe^{2+} = 100 mg/L (64200~76000 LUX)

When Fe^{2+} concentration is lower than this value, the degradation rate decreases. When the concentration of Fe^{2+} is higher than this value, the higher the concentration is, and the lower the degradation effect of SMT is. This is because a suitable concentration of Fe^{2+} will improve the utilization efficiency of H_2O_2 , too low Fe^{2+} is not sufficient to decompose H_2O_2 , and less $\cdot\text{OH}$ produced is not conducive to degradation. Some studies have shown that excessively high concentration of Fe^{2+} will decompose H_2O_2 , which is unfavorable to the formation of $\cdot\text{OH}$, resulting in the decrease of the degradation effect of SMT (Sire's et al., 2007).

Conclusions

(1) Under the same conditions, the degradation rate of sulfamethazine is 32.1%, 19.1% and 74.5% respectively by S-Fenton, E-Fenton and SE-Fenton systems separately. The degradation rate of sulfamethazine is greatly improved by SE-Fenton technology, and the advantages of the combined technologies are demonstrated by comparison with those of S-Fenton and E-Fenton.

(2) The results show that OH produced by SE-Fenton system is positively related to the degradation rate of SMT. Under the same conditions, the concentration of $\cdot\text{OH}$ produced in the degradation process of S-Fenton, E-Fenton and SE-Fenton in 120 min is $92 \mu\text{mol}\cdot\text{L}^{-1}$, $73.2 \mu\text{mol}\cdot\text{L}^{-1}$ and $212 \mu\text{mol}\cdot\text{L}^{-1}$ respectively, which indicates that the synergistic mechanism of photo-electric interaction in SE-Fenton system promotes the production of $\cdot\text{OH}$.

(3) In this experimental system, the optimum conditions for degradation of 1 L 10 mg/L SMT by SE-Fenton technology are as follows: pH is 3.0, concentration of Fe^{2+} is 25 mg/L, and the applied voltage is $E = 3 \text{ V}$, which has the best degradation effect.

(4) Solar photoelectric Fenton technology has good degradation efficiency for sulfonamide, but because of the unstable sunlight and $\text{pH}=3$ as the optimum degradation condition, the application of solar photoelectric Fenton technology is limited. Further research and development of sulfonamide degradation technology and methods in near-neutral water are needed.

Acknowledgements. This work was financially supported by Natural Science and Technology Project of Chongqing Municipal Education Commission (No. KJ111311).

REFERENCES

- [1] Alam Trovo, G., Raquel Nogueira, F. P., Ana, A., Amadeo, R. (2009): Degradation of sulfamethoxazole in water by solar S-Fenton. Chemical and toxicological evaluation. – *Water Research* 43: 3922-3931.
- [2] Almeida, L. C., Silva, B. F., Zamomi, M. V. (2015): Photoelectrocatalytic/photo E-Fenton coupling system using a nanostructured photoanode for the oxidation of a textile dye: kinetics study and oxidation pathway. – *Chemosphere* 136: 63-71.
- [3] Batista, A. P., Nogueira, R. P. (2012): Parameters affecting sulfonamide S-Fenton degradation - iron complexation and substituent group. – *Journal of Photochemistry and Photobiology A: Chemistry* 232: 8-13.
- [4] Brillas, E., Sirés, I., Oturan, M. A. (2009): E-Fenton technology and related electrochemical technologies based on Fenton's reaction chemistry. – *Chemical Reviews* 109(12): 6570-631.

- [5] Casado, J., Fornaguera, J. (2006): Pilot scale mineralization of organic acids by E-Fenton process plus sunlight exposure. – *Water Research* 40: 2511-2516.
- [6] Christopher, K., Duesterberg, T., David, W. (2007): Kinetic modeling of the oxidation of p-hydroxybenzoic acid by Fenton's reagent: implications of the role of quinones in the redox cycling of iron. – *Environ. Sci. Technol* 41: 4103-4110.
- [7] Elmolla, E. S., Chaudhuri, M. (2009): Degradation of the antibiotics amoxicillin, ampicillin and cloxacillin in aqueous solution by the S-Fenton technology. – *Journal of Hazardous Materials* 172(2-3): 1476-1481.
- [8] Elmolla, E. S., Chaudhuri, M. (2011): Combined S-Fenton-SBR process for antibiotic wastewater treatment. – *Journal of Hazardous Materials* 192(3): 1418-1426.
- [9] Flox, C., Pere-Llus, C., Centellas, F. et al. (2007): Solar photo E-Fenton degradation of cresols using a flow reactor with a boron-doped diamond anode. – *Applied Catalysis B: Environmental* 75: 17-28.
- [10] Kemper, N. (2008): Veterinary antibiotics in the aquatic and terrestrial environment. – *Ecol. Indic.* 8: 1-13.
- [11] Kolpin, D. W., Furlong, E. T., Meyer, M. T. E., Zaugg, S. D., Barber, L. B., Buxton, H. T. (2002): Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance. – *Environmental Science and Technology* 36(6): 1202-1211.
- [12] Littlefieldna, N. A., Gaylor, D. W., Blackwell, B. N., Allen, R. R. (1989): Chronic toxicity/carcinogenicity studies of sulphamethazine in B6C3F1 mice. – *Food Chem Toxicol* 27(7): 455-463.
- [13] Mahmoodi, N. M., Salchi, R., Arami, M. (2011): Binary system dye removal from colored textile wastewater using activated carbon: kinetic and isotherm studies. – *Desalination* 272(1/2/3): 187-195.
- [14] Martinez, J. L., Baquero, F., Canton, R. (2008): Antibiotics and antibiotic resistance in water environments. – *Current Opinion in Biotechnology* 19(3): 260-265.
- [15] Oller, I., Malato, S., Sanchez-Perez, J. A. (2011): Combination of advanced oxidation processes and biological treatments for wastewater decontamination—a review. – *Science of the Total Environment* 409(20): 4141-4166.
- [16] Pérez, T., Garcia-Segura, S., El-Ghenymy, A. (2015): Solar photoE-Fenton degradation of the antibiotic metronidazole using a flow plant with a Pt/air-diffusion cell and a CPC photoreactor. – *Electrochimica Acta* 165(9): 173-181.
- [17] Pérez, T., Sirés, I., Brillas, E., Nava, J. L. (2017): Solar photoE-Fenton flow plant modeling for the degradation of the antibiotic erythromycin in sulfate medium. – *Electrochimica Acta* 228: 45-56.
- [18] Serna-Galvis, E. A., Silva-Agredo, J., Giraldo, A. L., Florez, O. A., Torrespalma, R. A. (2016): Comparison of route, mechanism and extent of treatment for the degradation of a β -lactam antibiotic by TiO₂, photocatalysis, sonochemistry, electrochemistry and the S-Fenton system. – *Chemical Engineering Journal* 284: 953-962.
- [19] Sire's, I., Gamriddo, J. A., Mari'a, R. (2007): Catalytic behavior of the Fe³⁺/Fe²⁺ system in the E-Fenton degradation of the antimicrobial chlorophene. – *Applied Catalysis B: Environmental* 72: 382-394.
- [20] Sopaj, F., Oturan, N., Pinson, J., Oturan, M. A. (2016): Effect of the anode materials on the efficiency of the E-Fenton technology for the mineralization of the antibiotic sulfamethazine. – *Applied Catalysis B Environmental* 199: 331-341.
- [21] Valero, D., Ortiz, J. M., Expósito, E., Montiel, V., Aldaz, A. (2010): Electrochemical wastewater treatment directly powered by photovoltaic panels: electrooxidation of a dye-containing wastewater. – *Environmental Science & Technology* 44(13): 5182-5187.
- [22] Yahya, M. S., El, K. M., Oturan, N., Ei Kacemi, K., Oturan, M. A. (2016): Mineralization of the antibiotic levofloxacin in aqueous medium by E-Fenton technology: Kinetics and intermediates products analysis. – *Environmental Technology* 37(10): 1276-1287.