Cumhuriyet Sci. J., 45(1) (2024) 100-104
DOI: https://doi.org/10.17776/csj.1328817

Cumhuriyet Science Journal

| csj.cumhuriyet.edu.tr | Founded: 2002 ISSN: 2587-2680 e-ISSN: 2587-246X Publisher: Sivas Cumhuriyet University

Treatment of Sugar Industry Wastewater via Fenton Oxidation with Zero-Valent Iron

Ceren Orak [1,a,*]

[1] *Department of Chemical Engineering, Faculty of Engineering and Natural Sciences, Sivas University of Science and Technology, Sivas, Türkiye.*
**Corresponding author*

Research Article

History
Received: 17/07/2023
Accepted: 02/01/2024

ABSTRACT

The sugar industry is a significant contributor to wastewater production, primarily due to its substantial water usage. The treatment and reuse of this wastewater have become pressing concerns. In the present study, sugar industry wastewater was treated via Fenton oxidation using zero-valent iron (ZVI). The study focused on assessing the impact of key reaction parameters, namely pH, ZVI amount, $[H_2O_2]_0$ on the removal of TOC. Optimal reaction conditions for the Fenton oxidation process were identified, with a pH of 3.5, 2 g/L of ZVI, and 4 mM of H_2O_2, resulting in nearly 65% of TOC removal. The kinetic study revealed that the observed reaction adhered to a second-order kinetic reaction model. Furthermore, the activation energy for this observed reaction was determined as 49.14 kJ/mol. These findings suggest that Fenton oxidation, utilizing ZVI, holds promise as an effective method for treating wastewater originating from the sugar industry.

Keywords: Wastewater treatment, Fenton oxidation, Sugar industry, Zero-valent iron.

[a] *crn.orak@gmail.com* *https://orcid.org/0000-0001-8864-5943*

Introduction

Various industries (i.e., textile, paper, sugar, petrochemistry, etc.) generate a large amount of wastewater and industrial wastewater streams are one of the important contamination sources in the water environment. Therefore, it could lead to serious problems in the water environment and it might cause negative impacts on the ecosystem and human life. [1-4]. Before discharge, they must be treated and several wastewater treatment methods were applied to reduce TOC, COD, and BOD in various wastewater streams. In this context, the Fenton process is an effective, feasible control, and inexpensive wastewater treatment method in Advanced Oxidation Processes (AOPs) that have some advantages over biological treatment methods. Additionally, it could be used for the remediation of recalcitrant and biologically non-degradable compounds in industrial wastewater streams and it is applicable to various industrial wastewater streams [5, 6]. For instance, in the literature, it was used for the treatment of olive mills, textiles, antibiotics wastewater, etc. [7-10]. In addition to them, it could be used for sugar industry wastewater which produces large amounts of wastewater due to the high amount of water usage in sugar production steps. Turkey is the fifth country among the sugar beet producer countries in the world and a high amount of sugar is produced in our country [11]. Due to the production process of sugar, a high amount of wastewater is generated in the sugar factories in Turkey so they should be treated since they contain organic and inorganic compounds that are hazardous to the water and soil environment if they accumulate in these environments [12, 13]. Therefore, the remediation of sugar industry wastewater has become a significant concern for environmental health.

Zero-valent iron (ZVI) could be a good alternative to remediate the sugar industry wastewater via Fenton oxidation since it is non-toxic and inexpensive. In addition, it has high reactivity and fast kinetics and thus, it has some advantages in Fenton-like processes [5, 7-9]. In the presence of H_2O_2, iron ions easily release in acidic reaction media to initiate the Fenton reaction and these reactions are given in equation (1) and equation (2). Thereafter, the generated ferric ions react with ZVI as given in eqution (3) and hence, a continuous Fenton-like reaction could be achieved [5].

$$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O \quad (1)$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^- \quad (2)$$
$$2Fe^{+3} + Fe^0 \rightarrow 3Fe^{2+} \quad (3)$$

To our knowledge, various wastewater treatment methods based on biological and chemical treatment were used to treat sugar industry wastewater, however, it has not been treated via Fenton-like oxidation using ZVI. Therefore, in this study, ZVI was used to treat sugar industry wastewater, and the impact of reaction parameters (pH, initial H_2O_2 concentration, ZVI amount) over TOC removal % from sugar industry wastewater was investigated.

Material and Method

Sugar industry wastewater was supplied from Eskişehir Sugar Factory (Eskişehir, Turkey) and its characterization study was published elsewhere [14]. The other chemicals (ZVI (≥99.9), H_2O_2 (35%), HCl (37%), and NaOH(≥97, pellet)) were supplied from Sigma-Aldrich.

The experimental study was carried out using 100 mL of sugar industry wastewater at room temperature and the pH of wastewater was adjusted to the desired pH using 0.1 M of HCl and NaOH solutions. After pH adjustment, desired amounts of ZVI (1-4 g/L) and H_2O_2 (2-10 mM) were added into the wastewater. The experiments were carried out for 1 h and hence, the impacts of catalyst amount and initial H_2O_2 concentration over TOC removal % from sugar industry wastewater were investigated. The experimental set-up and conditions are given in Figure 1(a) and Figure 1(b), respectively. All experiments were performed three times and at the end of the experiments, liquid products were analyzed via TOC (Shimadzu TOC-Vcph TNM-1/SSM-5000A) to determine TOC removal % from sugar industry wastewater.

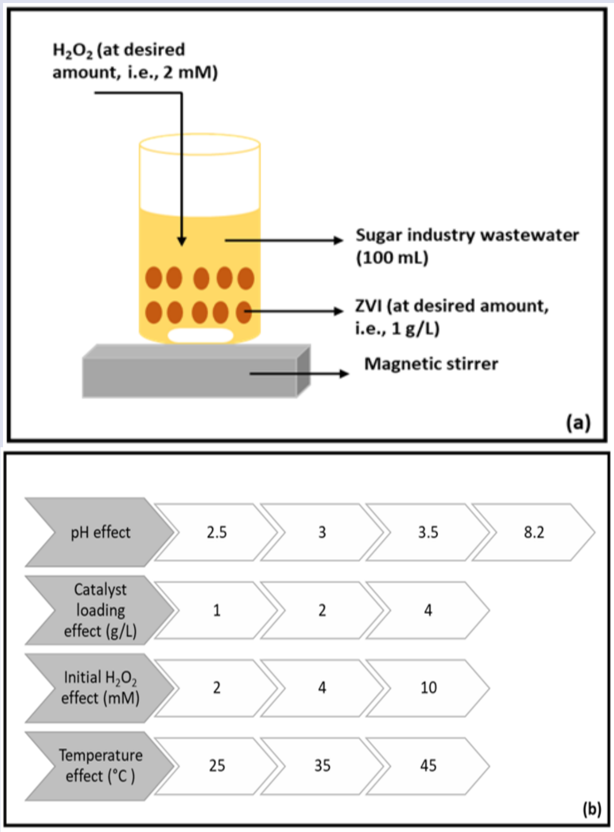

Figure 1. Experimental set-up (a) and reaction conditions (b)

Results and Discussion

The treatment of the sugar industry has significant importance because it consumes a high volume of water during sugar production. In the sugar production process, water is used to remove impurities by washing and flotation. Due to the high consumption of water, a high volume of wastewater is generated by the sugar industry [13,15]. In this study, sugar industry wastewater was treated via Fenton oxidation using ZVI, and impacts of reaction parameters (pH, ZVI loading, and, initial H_2O_2 concentration) and reaction temperature were investigated. The effect of pH of sugar industry wastewater was investigated within 2.5 and 8.2 (natural pH of sugar industry wastewater) of pH and the results are given in Figure 2. The highest TOC removal efficiency (~20%) was achieved at a pH of 3.5 whereas the lowest TOC removal was observed at the natural pH of sugar industry wastewater. Almost the same degradation efficiency was observed for pH 2.5 and 3. In acidic media, the formation of •OH radicals that are highly reactive to degrade organic compounds could enhance and it is expected that higher TOC removal efficiency might be observed with a decrease in pH [16, 17]. In this study, higher TOC removal efficiencies were observed in acidic reaction media and it is consistence with the literature. Therefore, the optimum pH value was selected as 3.5 for the sugar industry wastewater treatment using ZVI since usage of less amount of HCl acid to arrange the pH value of sugar industry wastewater offers an economical benefit. In addition, the set-up might prevent from its corrosive effects for a long term.

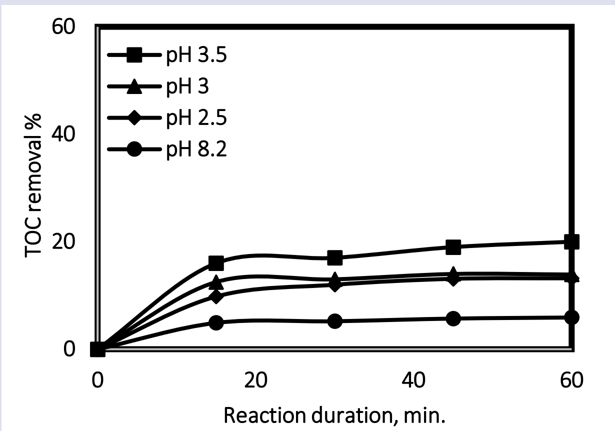

Figure 2. pH effect (Reaction conditions: 100 mL sugar industry wastewater, pH: 2.5-8.2, ZVI: 1 g/L, [H2O2]0: 2 mM, T: 25 °C t: 60 min)

After that, the effect of ZVI amount was investigated, and the results are given in Figure 3. The highest removal efficiency was observed using 4 g/L of ZVI. However, there is no significant difference between the TOC removal % when 2 g/L or 4 g/L of ZVI was used for the treatment of sugar industry wastewater. ZVI amount doubling did not result in a twofold increase in TOC removal efficiency. It only caused almost a %5 increase in TOC removal efficiency and thus, it is not considerable to use 4 g/L of ZVI. In addition, the usage of iron species might cause iron leaching in treated wastewater streams, and the allowable iron limit in drinking waters based on EU regulation is 0.2 ppm [18, 19]. To determine the optimum ZVI amount, the increase in TOC removal % should be considered alongside with the iron concentration that will leach into the treated wastewater. Therefore, to avoid the excess usage of ZVI and higher leaching amounts of ZVI in treated sugar industry wastewater, the optimum ZVI loading was selected as 2 g/L.

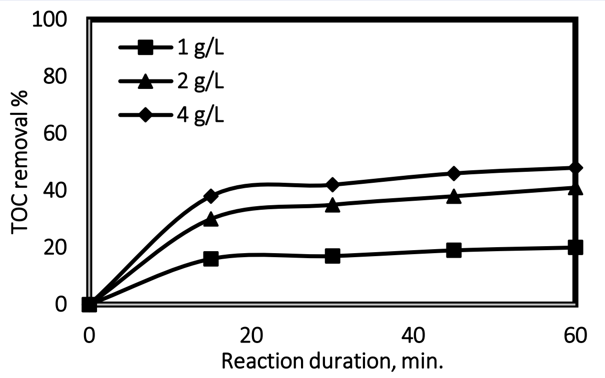

Figure 3. ZVI loading effect (Reaction conditions: 100 mL sugar industry wastewater, pH: 3.5, ZVI: 1-4 g/L, $[H_2O_2]_0$: 2 mM, T: 25 °C t: 60 min)

Another significant reaction parameter is the initial H_2O_2 concentration for Fenton processes because excessive usage of hydrogen peroxide might cause a scavenging effect so it should be optimized [20-22]. For this purpose, the experiments were carried out using 2, 4, and 10 mM of hydrogen peroxide, and the results are given in Figure 4. The utilization of 4 mM H_2O_2 demonstrated nearly double TOC removal efficiency compared to the usage of 2 mM. Therefore, it can be inferred that doubling the initial H_2O_2 concentration leads to a doubling of TOC removal.

The highest TOC removal % was observed using 10 mM of H_2O_2; however, it is not a considerable increase. In addition, H_2O_2 is generally considered to be a relatively environmentally friendly compound when used in appropriate concentrations and applications. However, like any chemical substance, hydrogen peroxide can have hazardous effects on environmental health under certain conditions. For instance, high concentrations of H_2O_2 may be toxic to aquatic organisms, including fish and other aquatic life. Discharge of untreated or high-strength H_2O_2 into water bodies may result in adverse effects on the local aquatic ecosystem [23-24]. Thus, considering the economic and environmental reasons, it could be decided that the usage of a lower concentration of H_2O_2 is more appropriate since in this study, a real wastewater stream was treated and hence, to avoid high H_2O_2 concentration in the treated wastewater, 4 mM of H_2O_2 was selected as the optimum initial H_2O_2 concentration. Consequently, optimum reaction conditions for the treatment of real sugar industry wastewater using ZVI were determined as pH of 3.5, 2 g/L of ZVI, and 4 mM of H_2O_2, and almost 65% of TOC removal was achieved at these reaction conditions.

In literature, Kallel et al. studied the treatment of olive-mill wastewater via Fenton oxidation using ZVI and H_2O_2. They found that higher COD removal was achieved at acidic reaction media (pH 2-4). Also, 20 g/L and 9.5 M were selected as the optimum ZVI amount and H_2O_2 concentration, respectively [8]. In addition to this study, Kallel et al. carried out another study to remove phenolic compounds from olive mill wastewater in the presence of ZVI and they found similar results [9]. In the present study, to treat sugar industry wastewater, relatively lower amounts of ZVI and H_2O_2 were used. Consequently, the results are in line with the literature.

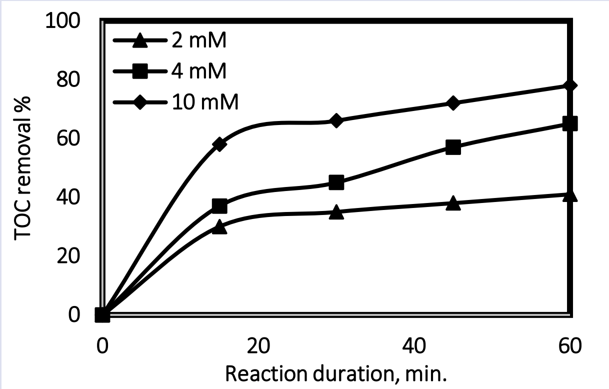

Figure 4. Initial H_2O_2 effect (Reaction conditions: 100 mL sugar industry wastewater, pH: 3.5, ZVI: 2 g/L, $[H_2O_2]_0$: 2-10 mM, T: 25 °C t: 60 min)

After that, a kinetic study was carried out to comprehend the characteristics of the reaction that occurred during the treatment of the sugar industry wastewater via Fenton using ZVI. In this context, the experiments were carried out at the optimum reaction conditions, and the effect of reaction temperature was investigated at 25, 35, and 45 °C. The results were given in Figure 5 and the obtained experimental data was analyzed to determine the reaction kinetic model and rate constants. The experimental data were fitted to the second-order reaction model and the linearized second-order kinetic model was given in Figure 6. The reaction rate constants were found as 0.00002, 0.00003, 0.00007 for 25, 35, and 45 °C and the activation energy for this reaction was determined from Figure 6 as 49.14 kJ/mol. In the literature, cork, and olive mill wastewater were treated using Fe^{+2}:H_2O_2, and the activation energies were found as 70.7 and 28.2 kJ/mol, respectively [25, 26]. Consequently, the determined activation energy in this study is in line with the previously reported values.

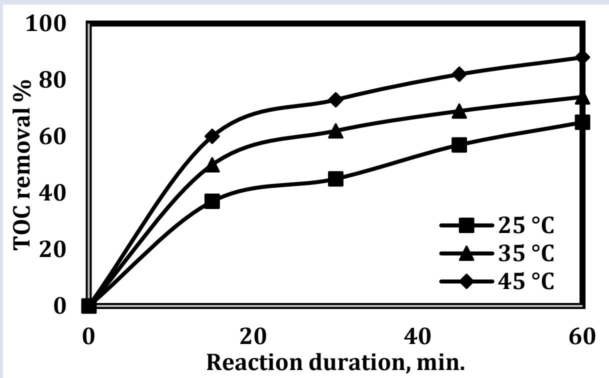

Figure 5. Temperature effect (Reaction conditions: 100 mL sugar industry wastewater, pH: 3.5, ZVI: 2 g/L, $[H_2O_2]_0$: 4 mM, T: 25-45 °C t: 60 min)

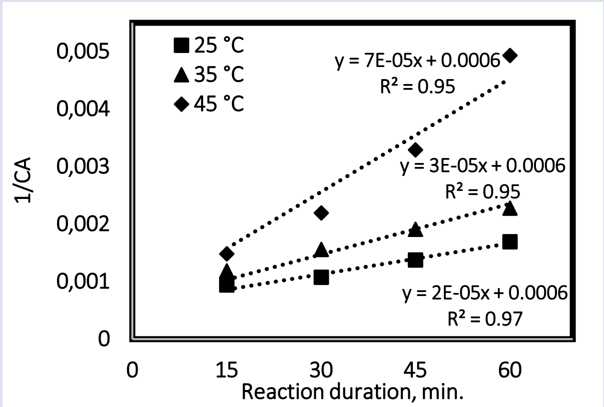

Figure 6. Linearized second-order kinetic plot (Reaction conditions: 100 mL sugar industry wastewater, pH: 3.5, ZVI: 2 g/L, $[H_2O_2]_0$: 4 mM, T: 25-45 °C t: 60 min)

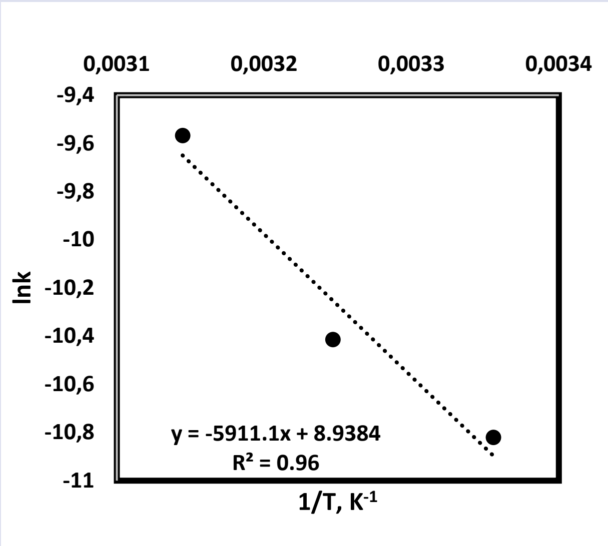

Figure 7. lnk vs 1/T

Conclusion

The sugar industry stands out as one of the major contributors to wastewater generation, underscoring the critical need for effective reuse and treatment methods within this sector. This study focused on employing Fenton oxidation in the presence of ZVI to treat wastewater from the sugar industry. Various wastewater treatment processes were explored previously, and the impact of different reaction parameters on the removal of total organic carbon (TOC) was assessed. Optimal conditions were identified as a pH of 3.5, 2 g/L of ZVI, and 4 mM of H_2O_2 in this study. Furthermore, the influence of reaction temperature was examined, and the results of kinetic study indicated that the observed reaction adhered to a second-order kinetic reaction model, with the activation energy calculated at 49.14 kJ/mol. These findings contribute to our understanding of effective wastewater treatment methods for the sugar industry, emphasizing the importance of specific reaction conditions in achieving optimal results.

Acknowledgment

I would like to thank Assoc. Prof. Dr. Aslı Yüksel Özşen and Assoc. Prof. Dr. Gülin Ersöz for their help and support to carry out this study.

Conflicts of interest

There are no conflicts of interest in this work.

References

[1] Ashrafi O., Yerushalmi L., Haghighat F. Wastewater treatment in the pulp-and-paper industry: A review of treatment processes and the associated greenhouse gas emission, *J. Environ. Manage*., 158 (2015) 146-157.

[2] Kishor R., Purchase D., Saratale G. D., Saratale R. G., Ferreira L. F. R., Bilal M., Chandra R., Bharagava R. N. Ecotoxicological and health concerns of persistent coloring pollutants of textile industry wastewater and treatment approaches for environmental safety, *J. Environ. Che. Eng.*, 9 (2021) 105012-105029.

[3] Verma S., Kumar P., Srivastava V. C., Štangar U. L., Application of Advanced Oxidation Processes (AOPs) for the Treatment of Petrochemical Industry Wastewater In: Roy, S., Garg, A., Garg, S., Tran, T.A. (eds) Advanced Industrial Wastewater Treatment and Reclamation of Water, *Environ. Sci. Eng.*, (2021) 103-128.

[4] Rakhmania; Kamyab H., Yuzir M. A., Abdullah N., Quan L. M., Riyadi F. A., Marzouki R., Recent Applications of the Electrocoagulation Process on Agro-Based Industrial Wastewater: A Review, *Sustainability*, 14 (2022) 1985-1204.

[5] Raji M., Mirbagheri S. A., Ye F., Dutta J., Nano zero-valent iron on activated carbon cloth support as Fenton-like catalyst for efficient color and COD removal from melanoidin wastewater, *Chemosphere*, 263 (2021) 127945-127954.

[6] Xie S., Su J., Zhao J., Yang H., Qian H., An amorphous zero-valent iron decorated by Fe_3O_4 significantly improves the Fenton-like reaction, *J. Alloys Compd.*, 929 (2022) 167306-167315.

[7] Kallel M., Belaid C., Mechichi T., Ksibi M., Elleuch B., Removal of organic load and phenolic compounds from olive mill wastewater by Fenton oxidation with zero-valent iron, *Che. Eng. J.*, 150 (2009) 391-395.

[8] Kallel M., Belaid C., Boussahel R., Ksibi M., Montiel A., Elleuch B., Olive mill wastewater degradation by Fenton oxidation with zero-valent iron and hydrogen peroxide. J. Hazard. Mater., 163 (2009) 550-554.

[9] Furia F., Minella M., Gosetti F., Turci F., Sabatino R., Di Cesare A., Corno G., Vione D., Elimination from wastewater of antibiotics reserved for hospital settings, with a Fenton process based on zero-valent iron, *Chemosphere*, 283 (2021) 131170-131169.

[10] Çalık Ç., Çiftçi D. İ., Comparison of kinetics and costs of Fenton and photo-Fenton processes used for the treatment of a textile industry wastewater, *J. Environ. Manage.*, 304 (2022) 114234-114239.

[11] www.sekerkurumu.gov.tr (access date: 12.12.2022)

[12] Kaya Ş., Asçı Y., Application of Combined Ultrasound and Fenton Reagent in Sugar Industry Wastewater Treatment, pp. 273-283. Atik, A. ed. 2019. *Research & Reviews in Engineering*. Gece Kitaplığı, Turkey, 361s.

[13] Kushwaha J. P., A review on sugar industry wastewater: sources, treatment technologies, and reuse, *Desalin. Water Treat.*, 53(2) (2013) 309-318.

[14] Orak C., Yüksel A., Photocatalytic hydrogen energy evolution from sugar beet wastewater, *ChemistrySelect*, 6(43) (2021) 12266-12275.

[15] Orak C., Öcal B., Yüksel A., Treatment of Sugar Industry Wastewater by Using Subcritical Water as a Reaction Media, *ChemistrySelect*, 8(1) (2023), e202203300.

[16] Rezaei F., Vione D., Effect of pH on Zero Valent Iron Performance in Heterogeneous Fenton and Fenton-Like Processes: A Review, *Molecules*, 23 (2018) 3127-3154.

[17] Donadelli J. A., Carlos L., Arques A., Einschlag F. S. G., Kinetic and mechanistic analysis of azo dyes decolorization by ZVI-assisted Fenton systems: pH-dependent shift in the contributions of reductive and oxidative transformation pathways, *App. Catal. B-Environ.,* 231 (2018) 51-61.

[18] Ramirez J. H., Maldonado-Hódar F. J., Pérez-Cadenas A. F., Moreno-Castilla C., Costa C. A., Maderina L. M., Azo-dye Orange II degradation by heterogeneous Fenton-like reaction using carbon-Fe catalysts, *App. Catal. B-Environ.*, 75 (2007) 312–323.

[19] Orak C., Atalay S., Ersöz G., Photocatalytic and photo-Fenton-like degradation of methylparaben on monolith-supported perovskite-type catalysts, *Sep. Sci. Technol.,* 52(7) (2017) 1310-1320.

[20] Li W., Wang Y., Irini A., Effect of pH and H_2O_2 dosage on catechol oxidation in nano-Fe_3O_4 catalyzing UV–Fenton and identification of reactive oxygen species, *Che. Eng. J.*, 244 (2014) 1-8.

[21] Hwang S., Huling S. G., Ko S., Fenton-like degradation of MTBE: Effects of iron counter anion and radical scavengers, *Chemosphere*, 78 (2010) 563-568.

[22] Jiang C., Pang S., Ouyang F., Ma J., Jiang J., A new insight into Fenton and Fenton-like processes for water treatment, *J. Hazard. Mater.*, 174 (2010) 813-817.

[23] Razas O., Vidal C., Baeza C., Jardim W. F., Rossner A., Mansilla H. D., Organic micropollutants (OMPs) in natural waters: Oxidation by UV/H2O2 treatment and toxicity assessment, *Water Res.,* 98 (2016) 109-118.

[24] de Oliveira T. D., Martini W. S., Santos M. D. R., Matos M. A. C., da Rocha L. L., Caffeine Oxidation in Water by Fenton and Fenton-Like Processes: Effects of Inorganic Anions and Ecotoxicological Evaluation on Aquatic Organisms, *J. Brazil Chem. Soc.*, 26(1) (2015) 178-184.

[25] Guedes A. M. F. M., Madeira L. M. P., Boaventura R. A. R., Costa C. A. V., Fenton oxidation of cork cooking wastewater—overall kinetic analysis, *Water Res.*, 37 (2003) 3061-3069.

[26] Lucas M. S., Peres J. A., Removal of COD from olive mill wastewater by Fenton's reagent: Kinetic study, *J. Hazard. Mater.*, 168 (2009) 1253-1259.