CHARACTERIZATION AND KINETIC STUDY OF MAGENTA PRINTING EFFLUENT AFTER HOMOGENEOUS FENTON TREATMENT

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Abstract
The objectives of this study were to determine the physico-chemical characterization of Magenta printing effluent treated with homogeneous Fenton process, as well as kinetic model that best describes degradation process of organic pollutant. Physico-chemical characterization of printing effluent before and after homogeneous Fenton treatment included measurements of pH, electrical conductivity, temperature, turbidity, chemical oxygen demand, biochemical oxygen demand, total organic carbon and toxicity test. Three kinetic models (first-order, second-order, and Behnajady-Modirshahla-Ghanbary) were evaluated in order to best describe Magenta degradation process. Results indicated that dye degradation process is followed with the increase of conductivity and biological oxygen demand due to the formation of various by-products and release of inorganic ions. The obtained results are in accordance with the established dye mineralization degree on the basis of chemical oxygen demand and total organic carbon content. However, treated printing effluent is characterized as nontoxic due to the *Vibrio fischeri* inhibition of 18.16%.

Introduction
In last two decades, researchers have emphasized the use of advanced oxidation processes (AOPs) as techniques that take prominence among various treatments, in order to reduce the concentration of inorganic and organic pollutants in industrial effluents. The advantages of these processes are reflected in the generation of hydroxyl radicals ($HO^{\bullet}$), powerful oxidizing agents, with a pronounced tendency for degradation of difficult biodegradable compounds, or transformation of pollutants into less toxic products of small molecular weight through rapid and non-selective radical reactions. The most commonly AOPs used in wastewater treatment are ozonization, photocatalysis, electrochemical oxidation, Fenton and Fenton-like processes [1]. In our previous work [2], the homogeneous Fenton process ($FeSO_4/H_2O_2$ treatment) was applied in order to examine the possibility of Magenta dye removal from flexo printing wastewater. The process was optimized and maximum decolorization efficiency of 95.91% was achived. The aim of this study was to determine physico-chemical characterization of Magenta printing effluent treated with homogeneous Fenton process. Further more, three kinetic models were used to describe degradation process of Magenta dye in printing effluent.

Experimental
Materials. Experiments were performed on Magenta printing effluent obtained from flexographic printing facility located in Novi Sad, Serbia. Magenta dye (C.I.: PR57:1, CAS number: 5281-4-9, chemical formula: $C_{18}H_{12}N_2O_6$, molar mass: 352 g/mol; $\lambda_{max} = 573$ nm) was produced from Flint Group and belongs to the group of azo dyes.

Physico-chemical analysis of printing effluent before and after Fenton treatment. Physico-chemical characterization of printing effluent before and after homogeneous Fenton treatment included determination of pH, electrical conductivity, temperature (AD110 Adwa instrument), turbidity (Turb 430 IR WTW), chemical oxygen demand (COD), biochemical oxygen demand (BOD), total organic carbon (TOC) (LiquiTOC II - Elemental, Germany), as well as toxicity evaluation. COD measurement was conducted using the potassium dichromate volumetric method - SRPS ISO 6060: 1994 [3]. Determination of BOD after 5 days at 20 °C was carried out by the manometer method - H1.002 (Velp Scientifica Italia, Lowibond and WTW), while the method SRPS ISO 8245:2007 [4] was used to determine the TOC value, which was used to estimate the mineralization degree of treated effluent according to the equation (1):

$$TOC\ (\%) = \frac{TOC_0 - TOC}{TOC_0} * 100 \qquad (1)$$

where: TOC_0 represent total organic carbon content in the printing effluent before the homogeneous Fenton treatment, and TOC is the total organic carbon content in the printing effluent after the homogeneous Fenton treatment.
Determination of anionic surface active substances (dodecylbenzene sulfonate - DBS) was measured by the index of methylene blue spectrophotometric method based on SRPS EN 903:2009 [5]. Chloride content was determined according to ISO 9297/1: 2007 [6], while the phosphorus content was determined with spectrophotometric method with ammonium-molybdate according to the SRPS EN ISO 6878:2008 [7].
Standard ISO 11348-3:2009 method was applied to test the toxicity of printing effluent before and after treatment, in order to evaluate negative impact of printing wastewater on living organisms [8].

Kinetics of homogeneous Fenton process. Numerous mathematical models have been used to describe the degradation kinetics of organic pollutants, based on the equilibrium state approximation. The main assumptions are based on the facts that the concentration of $HO^{\bullet}$ radicals is correlated with the concentration of hydrogen peroxide, or that the $HO^{\bullet}$ radicals formation rate is equal to their consumption rate [9, 10]. Since the whole dye degradation process cannot be described by simple kinetic model, the first-order, second-order and Behnajady-Modirshahla-Ghanbary (BMG) models were used to study Magenta degradation kinetics by the homogeneous Fenton oxidation process [11, 12]. The mathematical models of the first and second order reaction kinetics, as well as the BMG model are present in equations 2 - 4 [13]:

$$\frac{dA_t}{dt} = -k_1 A_t \qquad (2)$$

$$\frac{dA_t}{dt} = -k_2 (A_t)^2 \qquad (3)$$

$$\frac{A_t}{A_0} = 1 - \left(\frac{t}{m+bt}\right) \qquad (4)$$

where A_0 and A_t represent the initial dye absorbance over a period of time from zero to t, k_1 and k_2 are the first and second order constants, while b and m are the BMG model constants, related to the reaction kinetics and oxidation capacity, respectively.
The parameters of kinetic models were calculated using linear forms of first- and second-order mathematical models, as well as BMG models (equations 5 - 7):

$$A_t = A_0 * e^{-k_1 t} \qquad (5)$$

$$\frac{1}{A_t} = \frac{1}{A_0} + k_2 t \quad (6)$$

$$\frac{t}{1-\frac{A_t}{A_0}} = m + bt \quad (7)$$

By plotting the dependence graphs $ln(A_0/A_t)$ in function t for the first-order model, $(1/A_t)$ in function t for second-order model and $t/1-(A_t/A_0)$ in function t for BMG model, the kinetic model parameters were calculated and used to interpret the kinetics of the observed reactions.

Results and discussion

The obtained values of physico-chemical parameters (Table 1) indicate that homogeneous Fenton treatment is characterized with the conductivity and BOD increase, pointing to the formation of numerous degradation by-products. The experimental results indicate that the mineralization percentage of Magenta dye of 49.82% is followed with 71.44% of COD reduction (Figure 1). On this basis, Magenta dye degradation resulted within the formation of low molecular weight fragments during the homogeneous Fenton process.

Table 1. Physico-chemical characterization of printing effluent before and after treatment

Parameter	Printing effluent	Treated printing effluent
pH	7.60	7
Conductivity [μScm^{-1}]	403	560
Temperature [°C]	22.1	22.6
Turbidity [NTU]	18.81	10.3
COD [mgO_2L^{-1}]	377.7	107.87
BOD [mgO_2L^{-1}]	5	27
TOC [$mgCL^{-1}$]	166.4	83.49
DBS [mgL^{-1}]	0.77	<0.1
Phosphate [$mgPL^{-1}$]	<0.011	<0.011
Chlorides [$mgClL^{-1}$]	21.60	22.30

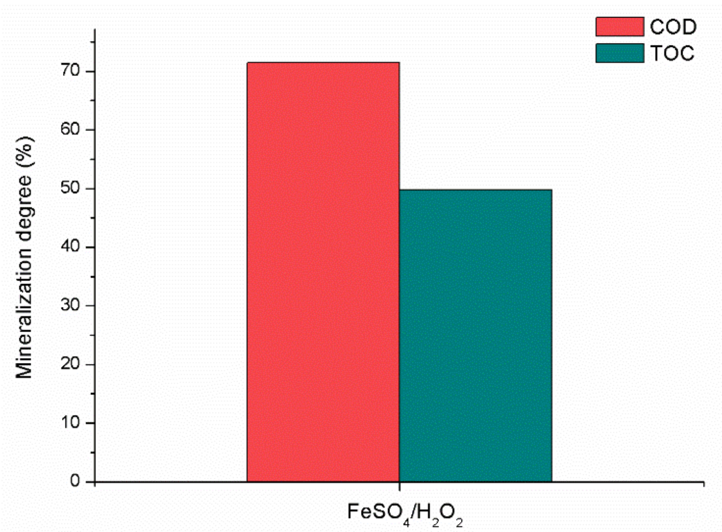

Figure 1. Mineralization degree of printing effluent after homogeneous Fenton treatment

The results of acute toxicity test on *Vibrio fischeri* bacteria (Table 2) indicated slightly increased toxicity of treated printing effluent after homogeneous Fenton process. This percentage of inhibition falls within the range below 50%, confirming that the treated printing effluent is nontoxic.

Table 2. Results of toxicity test by *Vibrio Fischeri* inhibition

Sample	**GL**	**Inhibition (%)**
Wastewater before Fenton treatment	4	15.11
$FeSO_4/H_2O_2$ treatment	2	18.16

The results of the kinetic studies used to analyze the Magenta dye degradation in printing effluent are presented in Table 3 and Figure 2. The highest values of correlation coefficient were established using the BMG model, which best describes the dye degradation process.

Table 3. Kinetic parameters of selected models for Magenta dye degradation

Model	**First-order**		**Second-order**		**[a]BMG model**			
Process	K_1 (min^{-1})	R^2	K_2 ($l\ mg^{-1}min^{-1}$)	R^2	b	m	1/m	R^2
$FeSO_4/H_2O_2$	0,031	0,649	0,062	0,602	0,905	18,439	0,054	0,986

[a]Behnajady-Modirshahla-Ghanbary model

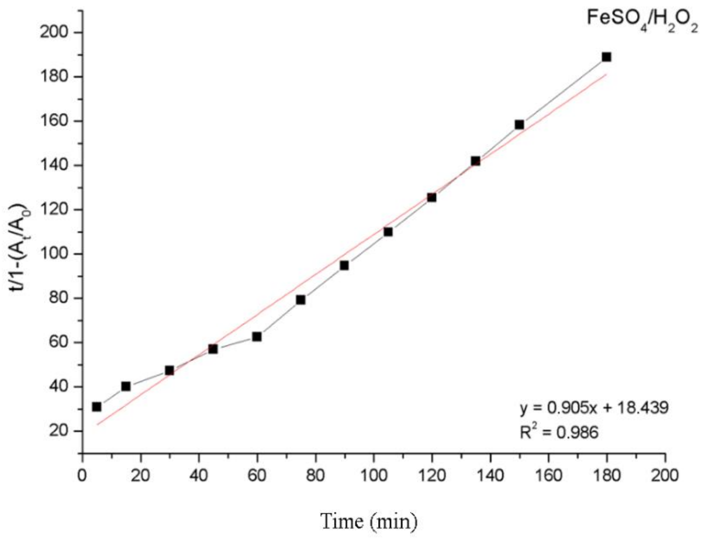

Figure 2. Decolorization kinetics of printing effluent under optimal process conditions - BMG model

Linear plot of $t/(1-A_t/A_0)$ versus t was used to determine the parameters b and m, which describes the oxidizing capacity and the initial rate of decolorization reaction, respectively. Based on R^2 value, chosen model offers satisfactory interpretation of the kinetic process, while the obtained high value of *1/m* indicates high initial rate of Magenta dye degradation.

Conclusion

Due to the high homogeneous Fenton efficiency in our previous work a physico-chemical characterization of treated printing effluent was investigated. Conductivity and biological oxygen demand increasment was established, which together with the obtained mineralization degree indicated the formation of numerous low molecular weight fragments during the homogeneous Fenton process. However, the isolated by-products did not contribute to the toxicity increase, confirming that the treated printing effluent is nontoxic. Behnajady-Modirshahla-Ghanbary, as most appropriate kinetic model, indicated high initial rate and oxidation capacity of Magenta dye degradation during the homogeneous Fenton treatment.

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References

[1] S. Karimifard, M. Moghaddam, Sci. Total. Environ. 640-641 (2018) 772.
[2] V. Kecić, M. Prica, Đ. Kerkez, M. Bečelić-Tomin, A. Kulić, A. Leovac Maćerak, B. Dalmacija (2018) 13th International Scientific Conference "Flexible Technologies" - MMA, 331.
[3] Water quality - Determination of the chemical oxygen demand SRPS ISO 6060: 1994.
[4] Water quality - Guidelines for the determination of total organic carbon (TOC) SRPS ISO 8245:2007.
[5] Water quality - Determination of anionic surfactants by measurement of the methylene blue index MBAS (ISO 7875-1:1984 modified) SRPS EN 903:2009.
[6] Water quality - Determination of chloride - Silver nitrate titration with chromate indicator (Mors method) - Amendment 1 SRPS ISO 9297/1:2007
[7] Water quality - Determination of phosphorus - Ammonium molybdate spectrometric method (ISO 6878:2004) SRPS EN ISO 6878:2008.
[8] Water quality - Determination of the inhibitory effect of water samples on the light emission of vibrio fischeri (luminescent bacteria test) - part 3, ISO 11348-3:2009
[9] T. Liu, H. You, React. Kinet. Mech. Cat. 109 (2013) 233.
[10] M. El-Haddad, A. Regti, R. Laamari, R. Mamouni, N. Saffaj, Journal of Materials and Environmental Science 5 (2014) 667.
[11] A. Hassan, M. Rahman, G. Chattopadhay, R. Naidu Environmental Technology and Innovation 15 (2019) 100380.
[12] M. Behnajady, N. Modirshahla, F. Ghanbary, J. Hazard. Mater. 148 (2007) 98
[13] N. Ertugay, F. Acar, Arab. J. Chem. 10 (2017) S1158.