PURIFICATION OF MAGENTA DYE AQUEOUS SOLUTION WITH FENTON-LIKE OXIDATION PROCESS

Vesna Kecić[1], Đurđa Kerkez[2], Miljana Prica[1], Sanja Rapajić[3], Milena Bečelić-Tomin[2], Anita Leovac-Maćerak[2], Saša Petrović[1]

[1]Department of Graphic Engineering and Design, University of Novi Sad, Faculty of Technical Sciences,Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia.
[2]Department of Chemistry, Biochemistry and Environmental Protection, University of Novi Sad, Faculty of Sciences, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia.
[3]Department of Mathematics and Informatics, University of Novi Sad, Faculty of Sciences, Trg Dositeja Obradovića 4, 21000 Novi Sad, Serbia.
e-mail: kecic@uns.ac.rs

Abstract
In this study, heterogeneous Fenton oxidation processes is applied, with the usage of nZVI as a catalyst. Greener than the conventional Fenton process, it combines the advantages of nZVI reduction and Fenton oxidation. According to the central composite design and the analysis of variance, the model presents medium R^2 value of 73.02% for the Magenta removal. At the 60 min of contact time, dye removal efficiency raised more than 40% and 70% with the increase of hydrogen peroxide concentration and pH decrease, respectively. The experimental results indicate that the oxidation process leads to the reduction in dye concentration up to 97%, confirming the application possibility of Fenton-like oxidation process for the dye removal from the aqueous solution.

Introduction
High efficiency in the flexographic printing industry is achieved with the usage of CMYK dyes (Cyan, Magenta, Yellow and Key), whereby Magenta flexo dye is commonly used. Upon completion of the printing process and during the cleaning of dye delivery and storage systems, a great amount of colored effluent can be generated. A discharge of wastewater without proper treatment into recipient contributes to the ecosystem problems, inhibiting the penetration of sunlight into water, enabling the ingress of the dye contaminants, therefore disturbing aquatic and terrestrial life [1, 2]. Numerous physical and chemical methods can be applied in order to increase water quality by reducing dyes quantity, such as ozonation, coagulation, reverse osmosis, photodegradation, membrane separation, biosorption and adsorption [3 - 5]. Amongst these methods, advanced oxidation processes (AOPs) present a great alternative for the treatment of dye contaminated water, due to the generation of oxygen-based radicals, where these species take part in different reactions in order to degrade dye molecules completely. Within the AOPs processes, dyes can totally be decomposed to low-molecular-weight compounds, carbon dioxide, water and inorganic components, or they can be transformed into harmless products [6]. In the present study a central composite design has been employed to model the process condition for efficiently removal of Magenta dye from aqeous solution by using Fenton-like oxidation process, supported with "green" synthesized nano zero valent iron.

Experimental

Materials. The Magenta wastewater used in the present study was obtained from flexographic printing facility located in Novi Sad, Serbia. Magenta dye (C.I.: PR57:1, chemical formula: $C_{18}H_{12}N_2O_6$, MW: 352 g mol L^{-1}, l_{max}: 573 nm) as a pollutant was purchased from Flint group. All sample analyzes were carried out directly without special pre-treatment, and the chemicals used during the laboratory test were analytically pure (Merck, Germany).

Preparation of iron nanoparticles. The synthesis of iron nanoparticles combined with aqueous oak leaf extract was carried out as described by Machado et al., 2013. Briefly, 37 g of dried oak leaves (*Quercus Peatrea*) was mixed up with 1L of deionized water. The resulting mixture was heated to 80 °C for 20 min on a magnetic stirrer, allowed to cool and then vacuum filtered through a 0.2 mm filter paper. 0.1M $FeCl_3$ x $6H_2O$ solution was slowly introduced using a burette ensuring a 3:1 ratio v/v of oak leaves extract to $FeCl_3$, respectively [7]. The colour of the solution changed to black indicating the synthesis of nanoparticles. In that way, a Fe(0) concentration of 1.395 g L^{-1} in synthetized nanomaterial was obtained.

Dye decolorization. Decolorization activity was expressed in terms of decolourization efficiency (%) and was calculated as follows (1):

$$E(\%) = A_0 - A / A_0 * 100 \quad (1)$$

where A_0 is absorbance of Magenta dye aqueous solution without nanomaterial, whereas A represents absorbance of Magenta dye aqueous solution with nanomaterial. Decolorization efficiency was determined by measuring the absorbance of the aqueous solutions at 573 nm by using UV/VIS spectrophotometer (UV 1800 Shimadzu, Japan).

Statistical analysis. In order to investgate the effect of various operational parameters, including the catalyst dosage, H_2O_2 concentration, initial Magenta concentration and pH on the dye removal efficiency, response surface methodology (RSM) based on central composite design (CCD) was employed. Each variable was coded in five levels (Table 1). The experiments were done for different combinations of these parameters using statistically designed experiments in 60 min of the reaction time.

Table 1. Process variables with experimental levels

Variables	Unit	Symbol coded	Levels				
			-2	-1	0	1	2
nZVI concentration	mg L^{-1}	X_1	0.75	15.38	30	44.63	59.25
H_2O_2 concentration	mM	X_2	1	3.5	6	8.5	11
Dye concentration	mg L^{-1}	X_3	20	60	100	140	180
pH	-	X_4	2	4	6	8	10

Results and discussion

Obtained results for Magenta removal from aqueous solution indicated decolorization efficiency between 3.64 and 96.61%. The data were fitted with various models and subsequent ANOVA test showed that reaction of Magenta removal was most suitably described by quadratic polynomial model. The final model to predict the percentage of Magenta removal by enhanced Fenton process is shown in Eq. (1):

$$Y = 207.2321 + 1.7674 x_1 - 0.0245 x_1^2 - 8.4953 x_2 + 0.1053 x_1 x_2 + 0,7114 x_2^2 - \\ - 0.6120 x_3 - 0.0160 x_1 x_3 - 0.0223 x_2 x_3 + 0.00647 x_3^2 - \\ - 38.0163 x_4 + 0.1206 x_1 x_4 + 0.0971 x_2 x_4 + 0.01232 x_3 x_4 + \\ + 1.7260 x_4^2 \quad (1)$$

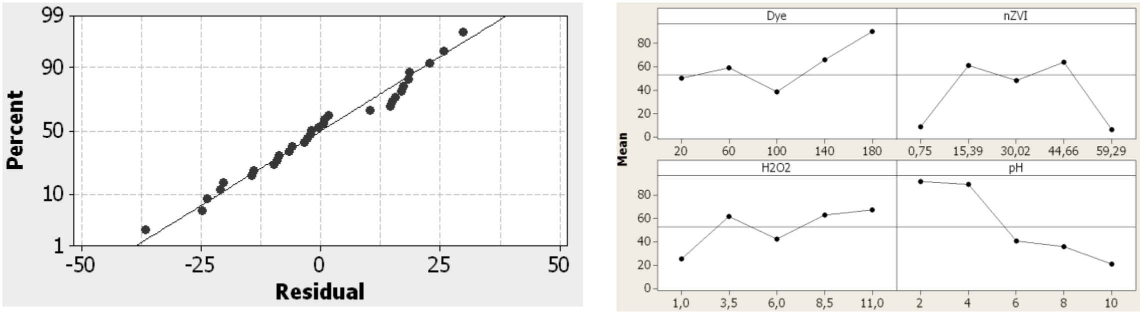
where Y is the percentage of Magenta removal efficiency and x_1, x_2, x_3 and x_4 are the values of the nZVI dosage, H_2O_2 concentration, initial Magenta concentration and pH, respectively. According to the ANOVA results, the model presents high R^2 value of 73.02% dye removal, indicated the medium accuracy of the polynomial model. Estimated regression coefficients, the *T* and *P* values for the Magenta removal efficiency (%)are presented in Table 2.

Table 2. Estimated regression coefficients of enhanced Fenton process

Variables	Regression Coefficient	Standard error	T_{stat}	P
1	207.232	105.684	1.961	0.068
X_1	1.767	2.164	0.817	0.426
X_2	-8.495	13.056	-0.651	0.524
X_3	-0.612	0.823	-0.743	0.468
X_4	-38.016	17.283	-2.199	0.043
X_1X_2	0.105	0.155	0678	0.507
X_1X_3	-0.016	0.010	-1.655	0.117
X_1X_4	0.121	0.194	0.621	0.543
X_2X_3	-0.022	0.056	-0.392	0.700
X_2X_4	0.097	1.136	0.085	0.933
X_3X_4	0.012	0.071	0.173	0.864
X_1^2	-0.024	0.019	-1.237	0.234
X_2^2	0.711	0.679	1.046	0.311
X_3^2	0.006	0.003	2.436	0.027
X_4^2	1.726	1.062	1.625	0.124

A P-value less than 0.05 indicates the statistical significance of each term at 95% confidence level. As shown in Table 2, the regression analysis of the experimental design demonstrated that the linear model term - pH, within its tested boundaries, is the only significant independent variable. In addition, the quadratic term x_3^2 were also found to be statistically significant. However, the nZVI dosage, H_20_2 concnetration and initial dye concentration proved irrelevant.

In order to investigate the normality assumption of the residuals in fitted model, the normal probability plot is created (Figure 1a). A normal distribution of the points, forming fairly straight line, explains good applicability of the model for the explanation of experimental data. In order to examine differences between level means for investigated factors, the main effects plot of a two-step fractional factorial design is presented in Figure 1b. All four examined variables are displayed within five levels.



a) b)

Figure 1. a) Normal probability plot; b) Main effects of dye concentration, nZVI dosage, H_2O_2 concentration and pH on dye removal efficiency

Lines with higher incline indicate a greater impact of the variable on the investigated process. Based on the main effects plot it can be concluded that pH value and the dye concentration actualize the greatest impact on the decolorization process. As it can be seen from Figure 1b, Magenta removal efficiency raised about 40% with the increasing of hydrogen peroxide concentration. This can be explained by the fact that oxidation power of Fenton reaction is improved with increasing hydroxyl radical amount attained from the decomposition of hydrogen peroxide. Results also indicated that dye removal efficiency increased for 70% with the decrease of pH value from 10 to 2. In the alkaline environment, Fenton oxidation reactions are slower, unlike the acid environment. In this paper, the maximum efficiency of the decolorization process is achieved at pH 2. Furthermore, the economic cost-effectiveness of the entire process can be explained within the fact that the acidity of the nano material suspension contributes to a significant reduction of the pH value of aqueous solution, so the pH corrections are minimal, while achieving very satisfactory decolorization efficiency. Considering the findings of this study, application of enhanced Fenton process can be suggested as an efficient system to enhance the efficiency of dye removal in printing aqueous solution.

Conclusion

The purpose of this study was to investigate the application of enhanced Fenton process using nano zero valent iron for treatment of aqueous solution containing Magenta dye, by using the response surface methodology. Based on experimental results, an empirical relationship between the response and independent variables is obtained and expressed by the quadratic polynomial model. Effect of experimental parameters on Magenta removal efficiency was established by the response surface and normal probability plot, as well as main effects plot of the model-predicted responses. High Magenta removal (97%) was obtained in the 60 min of the removal process. The greatest impact on the decolorization efficiency is achieved by the pH value. Analysis of variance showed a medium coefficient of determination value (R^2 = 0.730), ensuring a satisfactory adjustment of the second-order regression model with the experimental data. Thus, a Fenton-like oxidation is regarded as a very effective process for treating industrial wastewater that contains dyes and other waste products.

Acknowledgements

The authors acknowledge the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia within the Projects No. TR 34014 and III43005.

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