OPTIMIZATION OF HOMOGENOUS FENTON PROCESS USING DEFINITIVE SCREENING DESIGN APPLIED FOR FLEXOGRAPHIC PRINTING WASTEWATER

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Abstract

The treatment of flexographic cyan dye synthetic solution and real printing effluent has been studied by using homogeneous Fenton process with the addition of $FeSO_4*7H_2O$ as a catalyst. The study demonstrate that applied treatment could significantly reduce dye concentration in the examined aqueous solutions. Operating parameters, such as initial dye concentration, iron dosage, hydrogen peroxide concentration and pH were varied to investigate their influence on decolorization efficiency, as well as their mutual interactions. The optimal conditions, found with definitive screening design (DSD) statistical method, were: dye concentration = 123 mgL^{-1}, Fe concentration = 60 mgL^{-1}, H_2O_2 concentration = 5.44 mM and a pH value = 2. Under these conditions decolorization efficiency resulted with 87% and 37% for cyan synthetic solution and real printing effluent, respectively.

Introduction

Wastewater generated from printing industry presents a prominent source of aquatic contamination as it is enreached with high content of organic matter, heavy metals and various forms of dyes, followed with high pH value and low BOD/COD ratio [1, 2]. The conventional treatments, such as coagulation/flocculation, adsorption or membrane filtration are difficult to apply, especially in regards to color removal, due to the complex polyaromatic structure of the dyes. It has been demonstrated that these methods can only transfer pollutants from one phase to another, leaving the final environmental problem unsolved, such as the mineralization of the contaminants and toxicity reduction [3, 4]. Therefore, the key result of the present work is the application of advanced oxidation process (AOP) – homogeneus Fenton process. Fenton reaction has been proved as efficient treatment processes in terms of many hazardous organic pollutants from water due to the *in situ* generation of highly reactive and non-selective hydroxyl radical ($HO^{\cdot}$), as a product of reaction between hydrogen peroxide and ferrous ions [4]. In order to determine the best optimum conditions such as catalyst dosage, hydrogen peroxide concentration, initial dye concentration and pH value, definitive screening design (DSD) as adequate statistical tool was applied.

The main objectives of this study were to investigate the possibility of homogeneous Fenton process application for the water-based Cyan flexographic printing dye removal, as well as to apply DSD in order to optimize the Fenton process.

Experimental

Materials. All chemicals used in this work were of analytical grade and all sample analyzes were carried out directly, without pre-treatment. Hydrogen peroxide (30%) was obtained from NRK engineering, Serbia, NaOH (>98.8%) and and $FeSO_4*7H_2O$ were obtained from POCH, while ccH_2SO_4 (>96%) was produced by J.T. Baker. Deionized water was used for the preparation of all working solutions within the desired concentrations. The Cyan wastewater and the sample of fresh Cyan dye used in the present study were obtained from flexographic printing facility located in Novi Sad, Serbia. Water-soluble Cyan flexographic dye (C.I.: PB15:3, chemical formula: $C_{32}H_{16}CuN_8$, molar mass: 576.07 g/mol) was produced from Flint Group.

Application of homogeneous Fenton process. All experiments were carried out in a glass beaker (250 ml) on JAR apparatus (FC6S Velp Scientific, Italy). The reaction suspension was prepared by adding a dye solution of various concentration (20-180 mgL^{-1}) and a catalyst in a form of $FeSO_4*7H_2O$ (0.75-60 mgL^{-1}). After adjusting the pH (2-10) with NaOH or ccH_2SO_4, a H_2O_2 in various concentration (1-11 mM) was added to the mixture. Decolorization efficiency was calculated as follows (1):

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

where A_0 is absorbance of Cyan dye aqueous solution pretreatment, whereas A represents absorbance of Cyan dye aqueous solution after Fenton treatment. Decolorization efficiency was determined by measuring the absorbance of the aqueous solutions at 636 nm by using UV/VIS spectrophotometer (UV 1800 Shimadzu, Japan).

Statistical analysis. A statistical methodology DSD was adopted to optimize the Fenton process. In this study, the influence of four main factors has been investigated: concentration of dye (X_1), iron concentrations (X_2), pH value (X_3) and hydrogen peroxide concentration (X_4), (Table 1), while the decolorization efficiency was considered as dependent factor. The results were analyzed with 95% confidence intervals using the JMP13 (SAS Institute, USA). All experiments were conducted in duplicate with two extra central points, resulting with 28 total runs.

Table 1. Process variables with experimental levels

Variables	**Unit**	**Symbol coded**	**Levels**		
			-1	**0**	**+1**
Dye concentration	mgL^{-1}	X_1	20	100	180
Iron concentration	mgL^{-1}	X_2	0.75	30	60
pH	-	X_3	2	6	10
H_2O_2 concentration	mM	X_4	1	6	11

Results and discussion

The results of 28 experimental runs contributed to decolorization efficiency from 1.09 to 78.09%, confirming the assumption that dye removal process is exceptionally dependable on the applied experimental conditions, i.e. the individual parameters contribute to the efficiency of the Fenton process to a certain extent. In order to derive the regression model that best fits the obtained results, JMP's regression analysis was applied. The regression model includes the main factors, their square values and dual factor interactions. The summarized presentation of the adopted regression model, as well as the coefficients of significant main parameters, their quadratic members and dual factor interactions for the obtained model are shown in Tables 2 and 3.

Table 2. The adopted model statistics

Descriptive factor	Value
R^2	0.917
R^2 Adjusted	0.861
RMSE	9.652
Number of experiments	28

Table 3. Estimated significant main parameters, their square members and dual factor interactions

Factor	Estimated parameters	Standard error	*t* value	Probability > |*t*|
Dye concentration	4.242	2.158	1.97	0.0670
Iron concentration	11.858	2.158	5.49	**<0.001**
H_2O_2 concentration	-1.261	2.158	-0.58	0.5672
pH	-22.182	2.158	-10.28	**<0.001**
Dye * H_2O_2	-3.565	4.531	-0.79	0.443
H_2O_2 * H_2O_2	-10.107	5.778	-1.75	0.099
Fe * pH	7.510	4.889	1.54	0.144

The results of statistical analysis indicate a high significance of iron concentration, but also the pH value in the homogeneous Fenton process. Significant interactions of individual factors have not been established. Optimal process conditions for the removal of cyan dye using a homogeneous Fenton process are shown in Figure 1. The statistical model proposed a process efficiency of 87.85% for the following optimum values of the investigated factors: dye concentration of 123 mgL^{-1}, iron concentration 60 mgL^{-1}, H_2O_2 concentration of 5.44 mM and a pH value of 2.

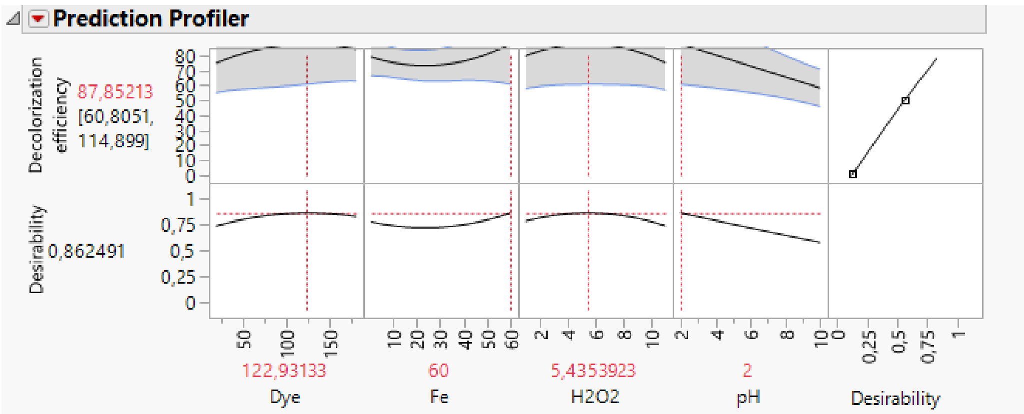

Figure 1. Optimal conditions for homogeneous Fenton process

Validation of the experiments was carried out with eight additional points under optimal conditions, yielding the following efficiency of the homogeneous Fenton process: 85.14; 86.43; 85.56; 86.03; 86.57; 87.29; 87.81; 87.20. The confidence interval [85.56 - 90.15%] confirms the adequacy of the selected model because the suggested efficiency of the homogeneous Fenton process of 87.85% enters the limits of the confidence interval.

In order to determine the possibility of using homogeneous Fenton process for real printing effluent treatment, wastewater generated after the printing process and colored with cyan dye was subjected to homogeneous Fenton process at optimal doses of the tested parameters. Dye removal efficiency was monitored for a period of 120 minutes and the results are shown in Figure 2.

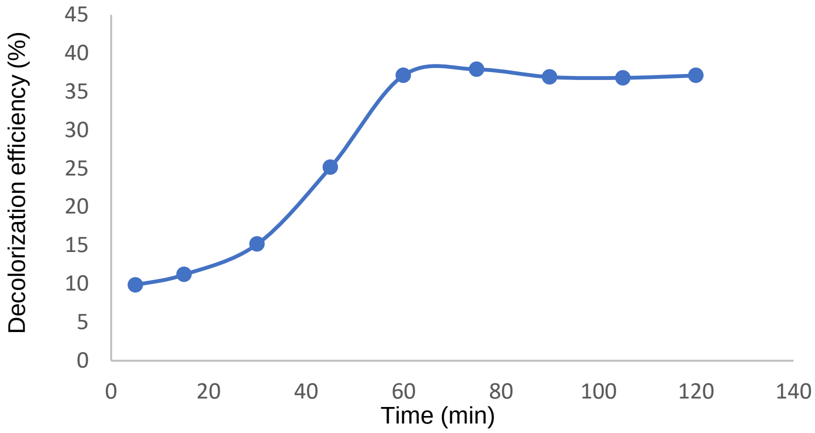

Figure 2. Dependence of the decolorization efficiency with the reaction time

Degradation efficiency after 60 minutes was 37.13% which is also the maximum efficiency. Compared to the treated synthetic dye solution, the proces efficiency in the case of a real printing effluent was lower, due to the presence of a compounds in the complex effluent matrix. Different organic and inorganic species can achieve an inhibitory effect on the dye degradation process, behaving as hydroxyl radical catchers, thereby achieving competition for active sites on the catalyst surface.

Conclusion

The paper examines the possibility of applying homogeneous Fenton process to the effective removal of the cyan dye from the synthetic dye solution and real effluent generated after the flexographic printing process. High decolorization efficiency, up to 78% is obtained in the case of synthetic dye solution, while a lower expected efficiency of 37% is achived within the wastewater treatment. Defintive screenig design, as a new three-level generation of experimental design, has enabled determination of the optimal conditions for the applied process in order to achieve maximum decolorization efficiency.

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.

References

[1] A. Mukamin, N. Zen, A. Purwanto, K.A. Wicaksono, H. Vistanty, A.S. Alfauzi, J.Environ. Chem. Eng. 5 (2017) 5222.
[2] V. Kecić, Đ. Kerkez, M. Prica, S. Rapajić, A. Leovac Maćerak, M. Bečelić–Tomin, D. Tomašević Pilipović, Journal of Graphic Engineering and Design 8 (2017) 35.
[3] V. Kecić, Đ. Kerkez, M. Prica, O. Lužanin, M. Bečelić-Tomin, D. Tomašević Pilipović, B. Dalmacija, J. Clean. Prod. 202 (2018) 65-80.
[4] R. Wang, X. Jin, Z. Wang, W. Gu, Z. Wei, Y. Huang, Z. Qiu, P. Jin, Bioresource Technol. 247 (2018) 1233.