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Optimization of the Fenton Oxidation of Synthetic Textile Wastewater Using Response Surface Methodology

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Abstract

This article presents the possibility of using the classical Fenton process (Fe(II)/H_2O_2) to purify synthetic textile wastewater (COD = 1872 mg O_2/dm^3, TOC = 660 mg/dm^3) containing azo dye Anilan Blue GRL 250% (200 mg/dm^3) and sodium lauryl sulphate (SLS) as anionic surfactant at a concentration of 95 mg/dm^3. Model studies were carried out using RSM, obtaining a good fit of approximated values to experimental values (R^2 = 0.9461 and R^2_{adj} = 0.7379). For optimal process parameters (pH 3, Fe(II) 0.85 g/dm^3, H_2O_2 14.5 g/dm^3), complete decolourisation (<10 mg Pt/dm^3) was achieved as well as a reduction in COD, TOC and SLS concentrations to 83%, 44% and 98%, respectively.

Key words: *textile wastewater, Fenton reagent, Response Surface Methodology, Anilan Blue, sodium lauryl sulphate.*

Introduction

Industrial wastewater generated in the manufacture of textiles, due to the presence of many inorganic and organic substances, including dyes often with complex chemical structure, are difficult to clean by biological methods. Many of the dyes currently used, exhibit toxicity to activated sludge microorganisms and are slightly biodegradable. Wastewater from textile production is characterised by varying pH, the high concentration of solutions, suspensions, dyes, and the high COD value. Because of the high water consumption in this branch of industry (21-377 m^3/Mg of finished product), the amount of wastewater produced at various stages of fabric preparation, dyeing and the finishing process is also relatively large [1]. It is estimated that around 10-15% of the annual world production of dyes of 7×10^5 Mg is introduced into the environment with wastewater from dyeing processes [2-5]. Some dyes and chemicals that result from their degradation are toxic to aquatic organisms, plants, fish and mammals [6-7]. In addition, they can undergo biological and chemical assimilation, reduce the concentration of dissolved oxygen in the water, and cause heavy metals to sequester and consequently increase the genotoxicity and microtoxicity of wastewater. In a broader sense, sporadic and excessive exposure to dye-containing wastewater is associated with a wide spectrum of immune, circulatory, respiratory and central nervous system disorders, neurological disorders, autoimmune diseases, and others [8-9]. The direct and indirect harmful effects of wastewater from the production of textiles impose the need to clean them in such a way that they do not adversely affect the environment. Literature describes a number of textile wastewater treatment methods, such as membrane filtration, ion exchange, adsorption, coagulation, electrocoagulation, and direct oxidation with ozone [4, 10-14]. Also used are advanced oxidation processes (AOPs), e.g.: Fenton reagent (Fe(II)/H_2O_2), UV-Fenton ((UV/Fe(II)/H_2O_2), UV/H_2O_2, O_3/OH$^-$, O_3/H_2O_2 and O_3/catalyst. in which hydroxyl radicals OH$^\bullet$ are generated [15-17]. These radicals are a very strong oxidizing agent that is capable of reacting with a wide variety of organic compounds under ambient conditions. For the treatment of textile wastewater, Fenton reagent is often used as a simple and efficient method for the degradation of organic pollutants and dyes in industrial effluents. For example, for washing wastewater containing acetic acid, an 87% reduction in COD after 24 h was achieved (initial COD 2190 mg O_2/dm^3, pH 3, $FeSO_4 \cdot 7H_2O$ 2 g/dm^3, H_2O_2 30 cm^3/dm^3) [15]. The optimum amounts of Fenton reagent (at pH 3) for decolorisation of aqueous solution containing Reactive Yellow 84 (azo dye) was 25 mg/dm^3 of Fe(II) and 250 mg/dm^3 of H_2O_2 for an initial dye concentration at 60 mg/dm^3. The decolorisation efficiency of Reactive Yellow 84 achieved 85% for a 20 min reaction time [18]. Furthermore no energy input is necessary to activate hydrogen peroxide. Therefore, taking into account the use of easy-to-handle reagents, this method offers a cost effective source of hydroxyl radicals [19]. The purpose of this study was to optimise the Fenton reagent parameters used to purify synthetic textile wastewater containing Anilan Blue GRL 250% (AB-GRL-250%) and sodium lauryl sulphate (SLS) as an anionic surfactant using Response Surface Methodology (RSM). RSM is an advanced method of optimisation which is relevant when testing multiple variables, which are likely to interact with each other. In this method, the tests follow a strictly specified design which depends on the type of impact the variables tested may have on the outcome (either linear or nonlinear) [19].

In the present research on optimal process parameters (pH, Fe(II), H_2O_2) obtained at the experiment planning and analysis stages, we carried out verification of the model of removal of COD from synthetic textile wastewater. For optimised parameters of the Fenton reagent, values of COD, TOC and SLS concentrations in purified effluents were determined.

Materials

Synthetic textile wastewater (***Table 1***) was prepared based on literature data relating to the composition of real textile wastewater with a total dye concentration of 200 mg/dm^3 [20]. To prepare synthetic

Table 1. *Chemical composition and physicochemical parameters of synthetic textile wastewater.*

Composition [21]			Physicochemical parameters of wastewater (value ± expanded uncertainty)			
Materials used	**Concentration, mg/dm^3**	**Function**	**Parameter**	**Unit**	**Raw**	**After treatment**
AB-GRL-250%	200	Coloring agent	pH	–	7.6 ± 0,1	10.0 ± 0,1
SLS	100	Scouring agent	Colour	g Pt/dm^3	0.313 ± 0.063	<0.01
$C_{12}H_{22}O_{11}$	600	Sizing agent	COD	g O_2/dm^3	1.872 ± 0.281	0.310 ± 0.047
$(C_6H_{10}O_5)_n$	1000	Sizing agent				
NaOH	175	Hydrolysis				
H_2SO_4	300	pH regulator	TOC	g/dm^3	0.660 ± 99	0.370 ± 0.056
Na_2CO_3	500	Fixing agent	Anionic surfactant (as SLS)	g/dm^3	0.095 ± 14	0.0019 ± 0.0003
NaCl	3000	Fixing agent				
CH_3COOH	200	Sizing agent				

Table 2. *Experimental conditions for synthetic textile wastewater.* ***Note:*** **center of the plan.*

Run	Variables		
	Factor 1	**Factor 2**	**Factor 3**
	pH	**Fe(II), g/dm^3**	**H_2O_2, g/dm^3**
1	2.00	0.250	6.000
2	2.00	0.250	12.000
3	2.00	0.800	6.000
4	2.00	0.800	12.000
5	4.00	0.250	6.000
6	4.00	0.250	12.000
7	4.00	0.800	6.000
8	4.00	0.800	12.000
9	1.32	0.525	9.000
10	4.68	0.525	9.000
11	3.00	0.063	9.000
12	3.00	0.987	9.000
13	3.00	0.525	3.955
14	3.00	0.525	14.045
15(C)*	3.00	0.525	9.000
16(C)*	3.00	0.525	9.000

textile wastewater we used Anilan Blue GRL 250% (2-[[4-ethyl(2-hydroxyethyl) amino]phenyl]azo]-6-methoxy-3-methylobenzotiazonium methylsulfate, CAS 12270-13-2, C.I. 11105, Boruta-Zachem S.A., Poland), sodium lauryl sulphate SLS (pellets, ≥99%, Sigma-Aldrich, Germany), $(C_6H_{10}O_5)_n$, CH_3COOH (99,5%), $C_{12}H_{22}O_{11}$, NaOH, H_2SO_4 (98%), Na_2CO_3 and NaCl (Chempur, Poland), which were dissolved in distilled water. The study also applied $FeSO_4 \cdot 7H_2O$ (POCH, Poland), 30% H_2O_2, (Chempur, Poland), and pH adjustment was carried out using H_2SO_4 (1+4) and 30% NaOH (Chempur, Poland). Prior to the experiments, the total amount of synthetic textile wastewater prepared for testing was filtered through a cotton filter fabric of weight 140-160 g/m^2. Analytical grade chemicals and distilled water were used in the studies.

Analytical methods

Values of pH were determined with the use of an inolab® pH/ION/Cond 750 and SenTix® 81 electrode [21]. The colour was determined using a PF-11 spectrophotometer after sample filtration through a syringe filter (0.45 µm) [22]. COD was determined by the dichromate method, applying sealed tubes using a PF-11 spectrophotometer, as well as the TOC content in relation to high temperature combustion at 680 °C with IR detection using TOC-L$_{CPH}$ by Shimadzu [23, 24]. The COD value determined was corrected for residual H_2O_2 because H_2O_2 increased the COD value, since it acts as a reductant, especially in the dichromate-based analysis of COD [25]. The residual amount of H_2O_2 was determined by the manganometric method [26], as well as anionic surfactants (as SLS) using the modified spectrophotometric method [27].

Conditions of experiments

Tests were carried out at a constant temperature of 21 ± 1 °C in beakers containing 500 cm^3 of the wastewater tested, which were stirred with a magnetic stirrer. After acidifying the effluent to the assumed pH, $FeSO_4 \cdot 7H_2O$ and H_2O_2 were added, then the pH was adjusted again and the Fenton reaction was performed for 60 min. The wastewater was then made alkaline to pH 10 to quench the reaction and precipitate iron(II) and iron(III) oxides and hydroxides. In the next step, the purified effluent was filtered through a medium filter paper (POCH, Poland) and subjected to chemical analysis. As the main criterion of the effectiveness of the Fenton process (including final neutralisation as a necessary part of the Fenton process in technical applications), also applied by other authors [28], we assumed the COD value, and as the auxiliary criterion we assumed the degree of colour removal from the wastewater. Optimization of the COD removal was carried out using RSM and Statistica 12 software (StatSoft, Poland), wherein the pH and Fe(II) and H_2O_2 concentrations were analysed. Based on the results of the Fenton study of other authors [28] on the actual effluents, the independent variables and range of values of these variables were selected for the development of the test plan (***Table 2***). As constants, the speed of mixing (250 rpm), the reaction time (60 min) and the temperature (21 ± 1 °C) were assumed. The following assumptions were used for the value of the dependent variable and independent variables: Z_1 – COD, g O_2/dm^3; x_1 – pH; x_2 – concentration Fe(II), g/dm^3; x_3 – concentration H_2O_2, g/dm^3. We also assumed the ranges of values for the following: pH (2 – 4), Fe(II) 0.25 – 0.8 g/dm^3 and H_2O_2 6 – 12 g/dm^3 [28, 29]. As a result of the planning of experiments (Central Composite Design), a research plan containing 16 experiments for 3 inde-

***Table 3.** Experimental results for synthetic textile wastewater.*

Run	Physicochemical parameters of wastewater (value ± expanded uncertainty)	
	COD, g O_2/dm^3	Colour, g Pt/dm^3
1	1.040 ± 0.156	0.085 ± 0.017
2	0.891 ± 0.134	0.054 ± 0.011
3	0.433 ± 0.065	0.054 ± 0.011
4	0.321 ± 0.048	0.033 ± 0.007
5	1.045 ± 0.157	0.044 ± 0.009
6	1.221 ± 0.183	0.035 ± 0.007
7	0.487 ± 0.073	0.044 ± 0.009
8	0.597 ± 0.090	0.027 ± 0.005
9	1.390 ± 0.209	0.031 ± 0.006
10	1.081 ± 0.162	0.037 ± 0.007
11	1.549 ± 0.232	0.062 ± 0.012
12	0.352 ± 0.053	0.037 ± 0.007
13	0.685 ± 0.103	>0.5 (yellow)
14	0.446 ± 0.067	0.011 ± 0.002
15(C)*	0.440 ± 0.066	<0.01
16(C)*	0.425 ± 0.064	<0.01

pendent factors was obtained (***Table 2***). Experimental results are shown in the response surface graphs, which allowed for detailed analysis of the influence of independent variables (pH, Fe(II), H_2O_2) on the dependent variable (COD).

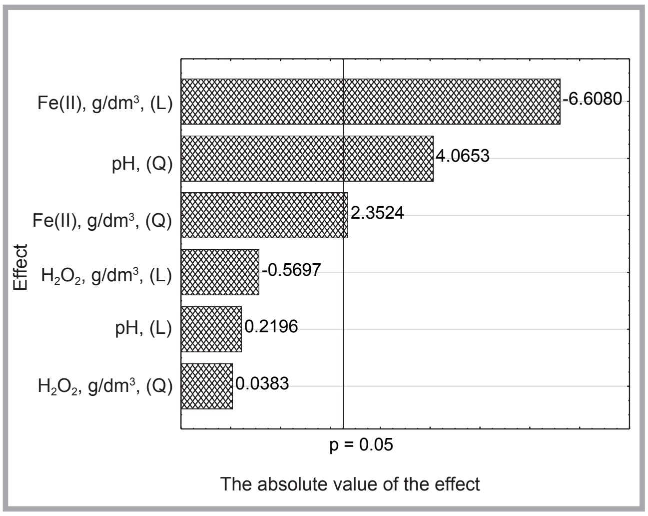
Results and discussion

As a result of 16 experiments, including 2 in the centre of the plan (for mean values pH, Fe (II) and H_2O_2 concentrations – 15C and 16C experiments), COD values and the colour for purified effluent were obtained (***Table 3***). The lowest values of COD (< 0.4 g O_2/dm^3) were obtained in experiments 4 and 12, while the highest COD value (1.549 g O_2/dm^3) was in experiment 11. In the case of colour removal, the lowest values (< 0.02 g Pt/dm^3) were obtained in experiments 14, 15 and 16, while the highest (> 0.5 g Pt/dm^3) was recorded in experiment 13. In this case there was no complete discoloration of the treated wastewater, but only a change of colour from intensely blue to yellow. Based on the results obtained, there was no direct relationship between the degree of removal of COD and the colour reduction of the effluent. ***Table 4*** presents the ANOVA effect coefficient sheet and model coefficients for normalised input values (pH, Fe(II), H_2O_2). The statistical analysis conducted indicated 3 statistically significant parameters ($p < 0.05$), i.e. pH, Fe(II) (L) and Fe(II) (Q). From a statistical standpoint, H_2O_2 concentration was defined as a non-significant parameter ($p > 0.05$), the reason for which may be the inverse proportional influence of the variable H_2O_2 concentration in subsequent experiments on the COD value obtained at different pH values. In experiments 1 and 2 (pH 2) the increase in H_2O_2 concentration from 6 to 12 g/dm³ resulted in a decrease in COD (1.040 and 0.891 g O_2/dm^3, respectively), and in experiments 5 and 6 (pH 4) this resulted in an increase in COD (up to 1.045 and 1.221 g O_2/dm^3, respectively). Similar observations of the lack of significance of H_2O_2 concentration using RSM for Fenton process optimisation were reported by other researchers [30]. The value of the determination coefficient and corrected coefficient of determination were $R^2 = 0.8795$ and $R^2_{adj} = 0.7992$, respectively, indicating a good fit of the model obtained to the experimental data. Other authors [31, 32] received similar values, but for model studies, it is suggested that the R^2 value be at least 0.8. ***Table 5*** shows results of verification of the model coefficients using ANOVA. The verification confirmed the significance of the three main input parameters (pH (Q), Fe (II) (L), Fe(II) (Q)), as shown in the Pareto graph (***Figure 1***), where the estimators of standardised effects were grouped according to their absolute value. Vertical lines were marked with minimal values of statistically significant effects, with the assumed significance level ($p = 0.05$). To determine and verify the adequacy of the model for the experimental data (COD) presented in ***Table 3***, a general linear model (GLM) using intergroup effects was applied, assuming that a grade II polynomial would be suitable for describing the removal of organic compounds from the researched wastewater. An approximation polynomial (1) describing the change in the dependent factor (COD) as a function of all independent factors (pH, Fe(II), H_2O_2) was obtained:

$$\begin{gathered}
\text{COD } (\text{g } O_2/L) = 4.381(\pm 1.378) \\
- 1.628(\pm 0.481)*[pH] \\
+ 0.239(\pm 0.067)*[pH]^2 \\
- 3.039(\pm 1.468)*[Fe(II), g/L] \\
+ 1.830(\pm 0.889)*[Fe(II), g/L]^2 \\
- 0.080(\pm 0.160)*[H_2O_2, g/L] \\
+ 0.0003(\pm 0.0075)*[H_2O_2, g/L]^2 \\
- 0.002(\pm 0.263)*[pH]*[Fe(II), g/L] + \\
0.023(\pm 0.024)*[pH]*[H_2O_2, g/L] - \\
0.004(\pm 0.088)*[Fe(II), g/L]*[H_2O_2, g/L]
\end{gathered} \quad (1)$$

***Table 4.** Analysis of the experiment with the central composite design using Statistica 12 – sheet of estimator effects ANOVA. **Note:** L-linear effect, Q-quadratic effect.*

Parameter	Evaluation of effects, COD, g O_2/dm^3, $R^2 = 0.8795$, $R^2_{adj} = 0.7992$ 3 parameter, 1 block, 16 experiments, MS=0.0321								
	Effect	Standard error	p-value	-95%, confidence intervals	+95%, confidence intervals	Factor	Standard error of factor	-95%, confidence intervals	+95%, confidence intervals
Constant value	0.451	0.126	0.0060	0.165	0.737	0.451	0.126	0.165	0.737
pH, L	0.021	0.097	0.8310	-0.198	0.240	0.011	0.048	-0.099	0.120
pH, Q	0.478	0.118	0.0028	0.212	0.744	0.239	0.059	0.106	0.372
Fe(II), g/dm³, L	-0.640	0.097	0.0001	-0.859	-0.421	-0.320	0.048	-0.430	-0.211
Fe(II), g/dm³, Q	0.277	0.118	0.0431	0.011	0.543	0.138	0.059	0.005	0.271
H_2O_2, g/dm³, L	-0.055	0.097	0.5828	-0.274	0.164	-0.028	0.048	-0.137	0.082
H_2O_2, g/dm³, Q	0.005	0.118	0.9703	-0.262	0.271	0.002	0.059	-0.131	0.135



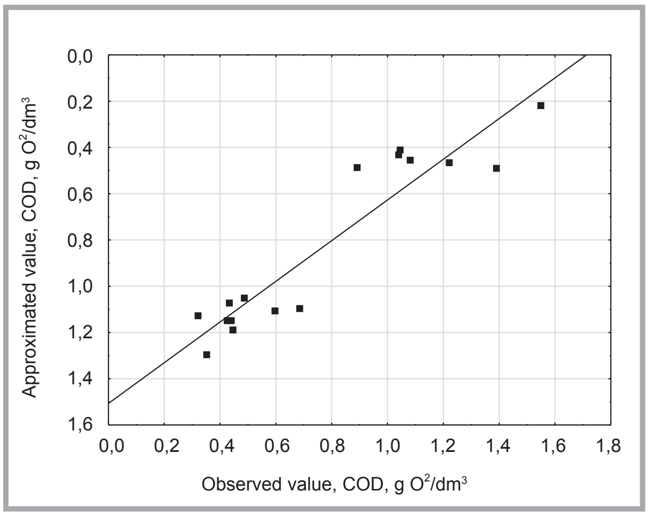


Figure 1. *Pareto chart – absolute value of standardised assessment of the effects (COD, g O_2/dm^3, 3 value, 1 block, 16 experiments, MS = 0.0321, L-linear effect, Q-quadratic effect).*

Figure 2. *Estimated vs. observed value plots (COD, g O_2/dm^3, 3 value, 1 block, 16 experiments, MS = 0.0321).*

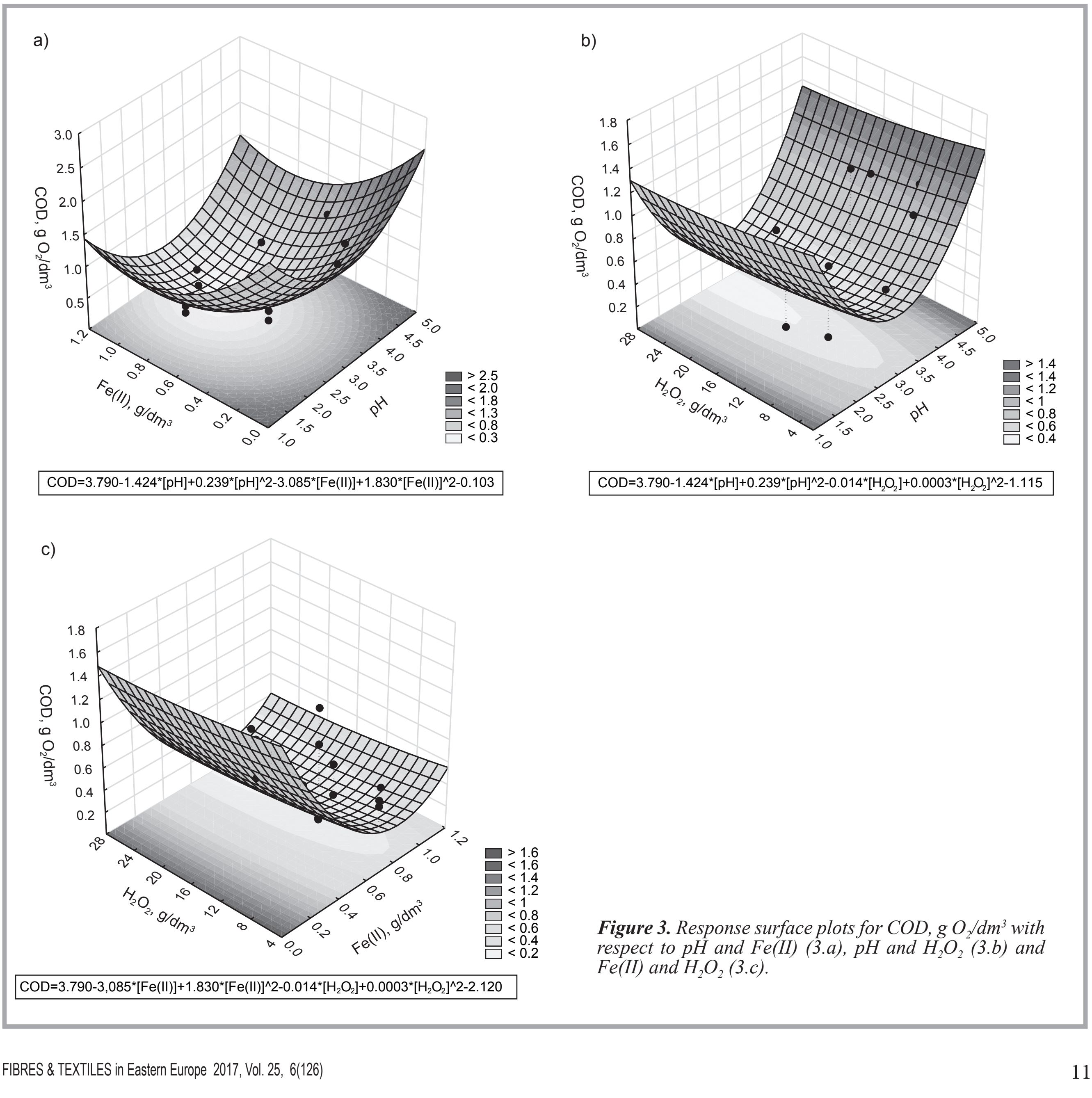


Figure 3. *Response surface plots for COD, g O_2/dm^3 with respect to pH and Fe(II) (3.a), pH and H_2O_2 (3.b) and Fe(II) and H_2O_2 (3.c).*

Table 5. *Analysis of the experiment with the central composite design using Statistica 12 – verification of the adequacy of the model using ANOVA.* ***Note:*** *L-linear effect, Q-quadratic effect, SS-predicted sum of squares, df-number of degrees of freedom, MS-mean square error, F-statistics, for df = 1, SS = MS.*

Parameter	Evaluation of effects, COD, g O_2/dm^3, $R^2 = 0.8795$, $R^2_{adj} = 0.7991$ 3 parameter, 1 block, 16 experiments, MS=0.0321				
	SS	df	MS	F	p-value
pH, (L)	0.001546	1	0.001546	0.048244	0.831048
pH (Q)	0.529769	1	0.529769	16.527074	0.002819
Fe(II), g/dm^3, L	1.399686	1	1.399686	43.665686	0.000098
Fe(II), g/dm^3, Q	0.177376	1	0.177376	5.533557	0.043139
H_2O_2, g/dm^3, L	0.010404	1	0.010404	0.324581	0.582806
H_2O_2, g/dm^3, Q	0.000047	1	0.000047	0.001467	0.970284

Table 6. *Value of the determination coefficient (R) for the full model – GLM method (General Linear Model).* ***Note:*** *SS-predicted residual error sum of squares, MS-mean square error, F-statistics.*

Parameter	Test SS for the full model relative to the SS for the rest							
	R^2	R^2_{adj}	SS model	MS model	SS rest	MS rest	F	p-value
COD, g O_2/dm^3	0.9461	0.7379	2.1432	0.2381	0.2510	0.0418	5.6927	0.0232

For some variables the error of value is greater than that of the variable, e.g. for [pH]*[Fe(II), g/l]. This means that the significance of the parameter is negligible, and its value is calculated with a large value. For the case indicated, p-value = 0.9934. Similar results were received by other authors [31]. Values of $R^2 = 0.9461$ and $R^2_{adj} = 0.7379$ indicate a good fit of the model obtained to the experimental data received (***Table 6***). The quality of the fit of experimental (COD) data obtained in 16 experiments for the model created has been checked by plotting the values approximated versus the values observed (***Figure 2***). The location of the experimental points along a straight line and at a short distance from it indicates the good fit of the values approximated to the experimental values, which, together with the determination coefficients calculated, indicates that the model created is suitable for the experimental data obtained. ***Figure 3.a*** shows the change in COD values depending on pH and Fe(II) concentration, assuming constant H_2O_2 concentration = 9 g/dm^3 (centre plan value, experiments 15C and 16C, ***Table 2***). The smallest COD values (< 0.3 g O_2/dm^3) were obtained at a pH of 2.6 to 3.4 at an Fe(II) concentration of 0.7-1.1 g/dm^3. Beyond these boundary values, there was a clear deterioration in the effects of COD removal. ***Figure 3.b*** shows the change in the COD value depending on pH and H_2O_2 concentration at a steady Fe(II) concentration = 0.525 g/dm^3 (centre value of the experiment plan, experiments 15C and 16C, ***Table 2***). Under these conditions, the lowest COD values (< 0.4 g O_2/dm^3) were obtained for the pH range of 2.9 to 3.6 at an H_2O_2 concentration greater than 21 g/dm^3. It should be noted, however, that with significantly lower H_2O_2 doses, the slight deterioration of COD removal occurred. The use of increased H_2O_2 concentrations (up to 30 g/dm^3) was also investigated by other researchers, but the largest removal of COD was observed at doses of H_2O_2 up to 13 g/dm^3 [29]. In turn, ***Figure 3.c*** shows the relationship between COD removal effects and Fe(II) and H_2O_2 concentrations at constant pH = 3 (value in the centre of the experiment plan, experiments 15C and 16C, ***Table 2***). The lowest COD values (< 0.2 g/dm^3) were obtained for Fe(II) concentrations in the range of 0.8-1.05 g/dm^3, with H_2O_2 doses greater than 22 g/dm^3, which from a practical point of view would be economically disadvantageous. Therefore for experimental verification of the COD value predicted in the model obtained, we assumed a dose of H_2O_2 = 14.5 g/dm^3, the value of which was in the middle of the range of doses of H_2O_2 (6-23 g/dm^3), making it possible to obtain values of COD < 0.4 g/dm^3 (***Figure 3.c***). Re-application of the Fenton reagent for the above-mentioned process parameters allowed the COD to be lowered to 310 mg O_2/dm^3 (***Table 1***), which reduced it by 83%, according to the assumptions based on the results of research obtained using the RSM. Under these conditions, TOC was also reduced by 44% (0.37 g/dm^3), SLS by 98% (0.0019 g/dm^3) and the total discoloration of wastewater was obtained (< 0.01 g Pt/dm^3). The COD/TOC ratio for treated wastewater was 0.84, while for raw water it was 2.84 (***Table 1***). For comparison, other authors [31] in real wastewater for the following parameters: pH 3, T 298 K, Fe(II) 1,79 mM & H_2O_2 73,5 mM obtained 62% COD removal. The COD/TOC ratio is characterised by changes in the chemical properties of pollutants in the wastewater after the oxidation process. In some cases, the value of this ratio also allows us to determine the amount of oxygen needed to oxidise organic matter relative to the carbon content in the structure of their molecules. In the case analysed, the COD/TOC value after the Fenton process was considerably reduced, which indicates the decay and change in chemical properties of the impurities (formation of intermediates) contained in the wastewater in the oxidation process.

Conslusions

- It was shown that RSM is a very useful tool for the mathematical description of the Fenton process. The application of this method enabled optimisation of the Fenton process for the purification of synthetic textile wastewater containing azo dye Anilan Blue GRL 250% and SLS as anionic surfactant. The values of determinants obtained ($R^2 = 0.9461$) and ($R^2_{adj} = 0.7379$) indicated a good fit of the model to the experimental data obtained.

- For optimum process conditions: pH 3, Fe(II) concentration 0.85 g/dm^3 and H_2O_2 14.5 g/dm^3, complete decolourisation was reached (< 0.01 g Pt/dm^3), and COD, TOC and SLS concentrations decreased by 83%, 44% and 98%, respectively. Significant reductions in the COD/TOC ratio from 2.84 (raw wastewater) to 0.84 in purified wastewater were observed, meaning that there was a decomposition and alteration of the chemical properties of pollution in the wastewater in the oxidation process with Fenton reagent.

- From a technological and economic point of view, in order to achieve an even better optimisation effect and greater elasticity of steering the process, depending on the requirements of removal of particular contaminants, one would need to extend the scope of the analysis by means of the reaction time and make an additional, separate optimization analysis by taking as the main criterion both the SLS concentration and colour removal.

- The easiest and most popular method of optimising technological processes is to identify repeatedly the impact of each variable tested on the constant values of other parameters. Despite its popularity, this technique has significant drawbacks, because it does not take into account possible interactions between variables tested. An advanced method of optimisation is the so-called response surface methodology (RSM), which is relevant when testing multiple variables, which are likely to interact with each other. In this method, the tests follow a strictly specified design, which depends on the type of impact the variables tested may have on the outcome (either linear or nonlinear). A disadvantage of the method presented may be the need to interpret statistical dates.

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