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Experimental design of photo-Fenton process decolorization of Reactive Red 120 by using mathematical statistics models

ABSTRACT

A statistical design of experiments was used to evaluate the potential use of clay catalyst (CuOFeB) during photo-Fenton process in which the concentration of hydrogen peroxide (H_2O_2), catalyst loading and pH values were selected as effective experimental factors in the process of dye decolorization. The photo-Fenton oxidation of Reactive Red 120 (RR120) has been investigated using a concentrating solar parabolic reactor with constant solar radiation of 950 W/m^2 during summer period of the year. Under the optimal reaction conditions catalyst showed good catalytic activity in the processes with dye removal over 90%. Also, experiment confirmed that decolorization efficiency depends on the pH and concentration of H_2O_2, wherein better results were achieved under lower pH values and higher concentration of H_2O_2.

KEY WORDS
light fastness, blue wool scale, printing ink, colour change, printability

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Introduction

In the textile industry wastewater is treated with various physical-chemical (coagulation, flocculation, ozonisation, gravity separation, filtration methods, adsorption, etc.) and biological treatments (removal of nitrogen, phosphorus, organic matter etc.) (Chandran, 2016; Urbas et al., 2016; Boczkaj and Fernandes, 2017). Disadvantages of physical and chemical processes are the formation and disposal of sludge, while the presence of traces of heavy metals and substances such as aromatic hydrocarbons in the biological process inhibits the growth of microorganisms, which requires additional treatment that can be expensive and dangerous (Chandran, 2016; Boczkaj and Fernandes, 2017). Therefore, the development of simple, safe, economical, efficient processes that are not harmful to the environment is of great importance. In recent years, advanced oxidation processes (AOPs) have been

studied in order to apply new methods for the treatment of organic wastewater (Glaze, Kang and Chapin, 1987; Wanget al., 2016) defined AOPs as water treatment processes characterized by generating reactive hydroxyl radicals at room temperature and atmospheric pressure (Pouran, Aziz and Ashri Wan Daud, 2015). Hydroxyl radicals have a high standard redox potential (2.8 V), higher than sulphates, chlorine, permanganate, persulphate anion, hydrogen peroxide and ozone, lower only than fluorine (3.03) (Herney-Ramírezand Madeira 2010; Pouran, Aziz and Ashri Wan Daud, 2015; Boczkaj and Fernandes, 2017), as well as a high reaction rate constant ranges from 10^6 to 10^{10} $M^{-1}s^{-1}$ (Moreira et al., 2017). The benefits of the AOPs process relative to conventional processes are the transformation of organic compounds to CO_2 and H_2O without the production of sludge, which discards the need for additional treatment. AOPs are useful in the treatment of persistent pollutants resistant to other treatments such as biological (Giannakis et al., 2016; Boczkaj and Fernandes, 2017). In addition, wastewater with very low organic load (in ppb) containing dissolved organic compounds that are difficult to remove can be treated with advanced oxidation processes (Pouran, Aziz and Ashri Wan Daud, 2015; Boczkaj and Fernandes, 2017). Photo-Fenton (or photo-assisted Fenton) process as a part of AOPs involves the use of solar radiation or artificial source of radiation, which increases the rate of degradation of contaminants stimulating the reduction of ferric ion (Fe^{3+}) to ferro ion (Fe^{2+}). This process shows high efficiency of oxidation of organic pollutants and inactivation of microorganisms in wastewater (Villegas-Guzman et al., 2017). Photo-Fenton process is a combination of iron ions, hydrogen peroxide and solar and UV/vis radiation (λ < 600 nm), which leads to higher production of hydroxyl radicals through the following reactions: i) reduction of Fe^{3+} to Fe^{2+} (Equation (1)) and ii) photolysis of hydrogen peroxide at smaller wavelengths (Equation (2)) (Pouran, Aziz and Ashri Wan Daud, 2015; Villegas-Guzman et al., 2017).

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + HO^{\cdot} \qquad (\lambda < 580\ \text{nm}) \qquad (1)$$

$$H_2O_2 + hv \rightarrow 2HO^{\cdot} \qquad (\lambda < 310\ \text{nm}) \qquad (2)$$

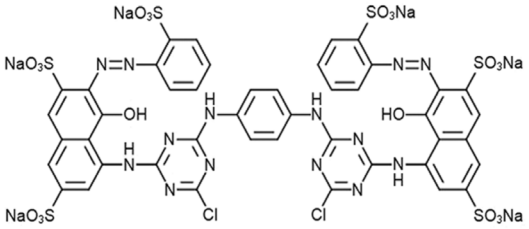
Also, as a source of iron and ability to extend the range of the solar spectrum to 450 nm, thus allowing further benefit from solar radiation, photosensitive ferrioxalate complexes have been applied in the solar photo-Fenton (Chandran, 2016; Boczkaj and Fernandes, 2017). Moreover, in an acid medium, ferrioxalate photolysis produces Fe^{2+} ions and more hydrogen peroxide.

Knowing that average solar radiation in Serbia is approximately 40% higher than the European average, better utilization of solar energy and implementation of solar reactor in this kind of processes is very important and represents challenge for researchers (Pucar Milidrag et al., 2018). For that reason, the aim of this study was to provide optimal process conditions (H_2O_2, concentration of the catalyst, pH and concentration of Reactive Red (RR120)) using mathematical models, in order to achieve the best performance of the process as well as high efficiency of decolorization.

Material and methods

Reagents

Commercial RR120 (CAS No. 61951-82-4, EC No. 263-351-0), $H_2C_2O_4$, $Fe(NO_3)_3{\cdot}9H_2O$, H_2SO_4, NaOH, $CuCl_2{\cdot}2H_2O$ and H_2O_2 (30%) were obtained from Sigma-Aldrich. All used chemicals were analytical grade and used without further purification. All solutions were prepared with deionised water. Bentonite (Claris-p70), which was used in experiments, is a product of Bentoproduct Ltd. from Šipovo. Molecular structure of the dye is shown in Figure 1.



» **Figure 1:** *Molecular structure of RR120*

Catalyst preparation

For preparation of CuOFeB catalyst, modified methods according to the procedure of Ayodele and Hameed (2013) has been used. CuOFeB was prepared by dissolving $CuCl_2{\cdot}2H_2O$ (Cu^{2+} = 0.0352 mol/dm^3) and NaOH, maintaining a ratio of OH/Cu = 2.25 and adjusting pH = 4.1. Then, the prepared solution was easily added to the prepared suspension of clay (1:25 g/w) and stirred continuously for 12 h. After washing the suspension, a solution of $Fe(NO_3)_3{\cdot}9H_2O$ and $H_2C_2O_4$ (1:0.832 Fe/oxalate) was added in a suspension of pillared copper bentonite and stirred for 6 h under heating at 50 °C in the dark. Then, it was washed and dried at 110 °C and calcined at 350 °C for 2 h.

Photoreactor

Solar photocatalytic experiments were performed in a static parabolic trough collector (Figure 2). The collector consists of a Pyrex glass absorber tube (length 129.70 cm, outer diameter: 1.86 cm, inside diameter: 1.26 cm), tracking mechanism and concentrator reflective surface (length 129.70 cm, width of the parabola 113 cm, rim angle 90 °), with a capacity of 175 mL. The reflector was made of stainless steel sheet. Solar radiation is reflected by the concentrator reflective surface and focused on the absorber tube. The ends of the pipe have valves, one for

filling a sample of water and another for the sampling. The tracking mechanism enables sunlight to focus on the absorber tube all the time, which is located along the focal line of the concentrator reflective surface.

Photo-Fenton experiments

The experiments of photo-Fenton process were conducted in the Campus of the University of Novi Sad on an open rooftop (Latitude: 45°14′44.19″ N; Longitude: 19°51′11.29″ E) during the summer period (June/July) of the year under clear-sky conditions, with constant solar radiation of 950 W/m^2. The intensity of the solar radiation was kept constant by rotating the collector along its axis and oriented East–South. The maximum time of exposure to solar radiation was 390 min from 8:30 am to 3 pm, followed by centrifuging at 3000 rpm for 5 min. The aliquots were immediately analysed.

» **Figure 2:** *Solar Parabolic reactor used for photocatalytic experiments*

The experiments were performed in the following manner: after adding prepared catalyst (0.01–0.2 g) into the solution of the RR120 (100 mg/L), pH value was adjusted (3–7) and hydrogen peroxide was added (0.625–10 mM). To ensure contact of the catalyst with the model pollutant RR120, the whole mixture was stirred in the dark on a magnetic stirrer for 5 min before setting in the solar reactor.

The efficiency of dye decolorization was obtained by application of the following formula:

$$E(\%) = \frac{A_0 - A}{A_0} x100 \quad (3)$$

where the A value was received after a certain reaction time and A_0 is the initial absorbance.

Analytical methods

Decolorization of the synthetic dye solution was monitored by measuring the absorbance (A) at the wavelength 511.9 nm using a UV–vis spectrophotometer PG Instruments Ltd. T80 + UV–vis, Model: UV 1800 (Shimadzu, Japan). Measurement of pH was performed using a pH meter inoLab pH/ION 735 (WTW GmbH, Germany). The intensity of solar radiation was measured by a PL-110SM Solar Radiation Measuring Instrument (Voltsraft, Germany).

Design of experiment

The operating variables in this experiment were pH value, H_2O_2 concentration and catalysts loading, so experimental runs were conducted based on the combinations of those variables. The response surface analysis provided by Design-Expert 11.0.3. software (Stat-Ease Inc., Mineapolis, USA), is used in order to determine the influence of selected variables on the decolorization efficiency of synthetic dye solution. The range for pH values was 3-7, while the range for H_2O_2 concentration and catalysts loading were 0.625-10 mM and 0.01-0.2 g, respectively. Table 1 shows the fifteen sets of experimental conditions for which the response is obtained.

Table 1

Experimental design matrix for CuOFeB

Run	pH	H_2O_2 (mM)	Catalyst (g)
1	3	5	0.2
2	4	5	0.2
3	5	5	0.2
4	6	5	0.2
5	7	5	0.2
6	7	0.625	0.2
7	7	1.25	0.2
8	7	2.5	0.2
9	7	5	0.2
10	7	10	0.2
11	7	5	0.01
12	7	5	0.025
13	7	5	0.05
14	7	5	0.1
15	7	5	0.2

Results and discussion

Study of the activity and stability of the CuOFeB catalyst

The advantage of using copper in pillared clays enables to conduct the reaction at higher pH values, due to its characteristic that it is less sensitive to changes of pH. Also, some authors indicate the occurrence of increased catalytic activity due to presence of copper in pillared clays (Timofeeva et al., 2009). In addition, copper-containing catalysts are considered to accelerate a catalytic reaction due to the generation of a large number of hydroxyl radicals (Ramirez et al., 2010). Therefore, researches were conducted in order to find the optimal concentration of copper and Fe/oxalate ratio, in which high decolorization efficiency is achieved with minimal metal leaching (Cu and Fe). All samples were exposed to the natural light source, under clear-sky conditions. The conditions of the reaction were as follows: [CuOFeB] = 0.2 g, pH = 3.5 mM H_2O_2, 5 min of stirring, [RR120] = 100 mg/L, Fe/oxalate ratio 1:0.4. Three different copper concentrations were tested: 0.0352 mol/dm^3, 0.0704 mol/dm^3 and 0.1408 mol/dm^3. Table 2 shows that at all used concentrations of copper high decolorization efficiency was achieved (about 100%), however, at the lowest concentration of 0.0352 mol/dm^3 lowest metal leaching occurred.

Table 2

Application of different copper concentrations

Sample Cu (mol/dm^3)	Cu (mg/L)	Fe (mg/L)	Efficiency (%)	Reaction time (h)
0.0352	0.189	1.031	99.67	24
0.0704	0.554	3.359	99.77	
0.1408	1.414	5.682	99.66	

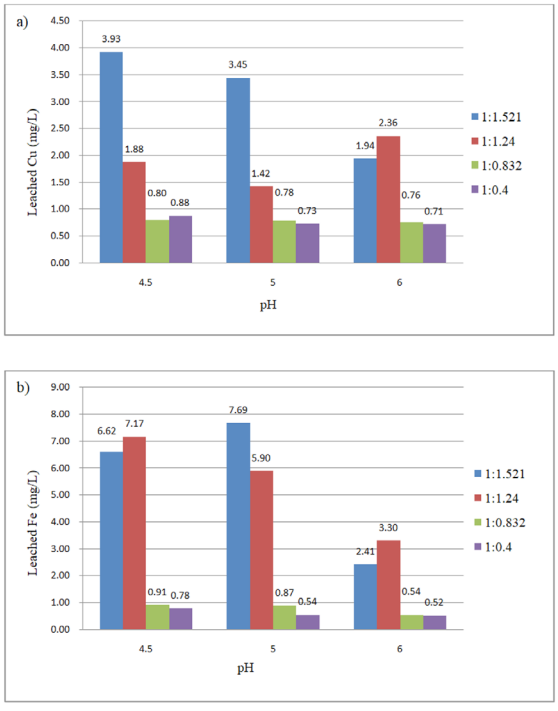
The most stable Fe/oxalate ratio corresponds to a stoichiometric molar ratio of 1:3, in which three bidentate oxalate ions are bound to the center of iron. Lower ratio leads to insufficient oxalate that can lead to a decrease in the yield of the ferro ion regeneration, due to which the lack of oxalate can not form complexes with Fe^{3+} ions. On the other hand the excess of oxalate can lead to an increase in organic carbon, reduce the penetration of solar radiation, or can be found in competition for hydroxyl radicals, thereby reducing the rate of mineralization of the organic compound (Nogueira et al., 2017; Monteagudo et al., 2010). In order to achieve good process performance using the low Fe/oxalate ratio following researches were performed. The conditions of the reaction were as follows: [CuOFeB] = 0.2 g, pH = 3.5 mM H_2O_2, 5 min of mixing, [RR120] = 100 mg/L, [Cu] = 0.0352 mol/dm^3. Three different Fe/oxalate relations (1:1.521; 1:1.24; 1:0.832) were tested in the pH range of 4.5-6.

Based on the obtained results at lower Fe/oxalate ratios the decolorization efficiency decreases and duration of the reaction increases (Table 3). Figure 3a,b shows that with decreasing ratio metal leaching reduces. Therefore, the optimum ratio of Fe/oxalate from the aspect of the metal leaching, and achieving high decolorization efficiency, at high pH values is 1:0.832.

Table 3

Testing Fe/oxalate ratio at different pH values

Fe/oxalate	pH	Time (days)	Efficiency (%)
1: 1.521	4.5	4	98.29
1: 1.521	5	5	98.53
1: 1.521	6	11	98.31
1:1.24	4.5	3	99.41
1: 1.24	5	7	99.43
1: 1.24	6	10	99.01
1: 0.832	4.5	5	98.02
1: 0.832	5	6	98.08
1: 0.832	6	13	97.80
1: 0.4	4.5	6	94.81
1: 0.4	5	7	91.77
1: 0.4	6	15	88.31



» **Figure 3:** *Concentrations of metal leaching: a) Cu and b) Fe*

Optimization of the oprocess using the Design Expert software

Based on the response obtained for the designed set of operating variables given in Table 4, linear model was analyzed by the Design Expert software as suggested model.

Table 4

Fit summary based on Sequential Model Sum of Squares

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	1.005E+05	1	1.005E+05			
Linear vs Mean	**5409.75**	**3**	**1803.25**	**7.12**	**0.0063**	**Suggested**
2FI vs Linear	0.0000	0				Aliased
Residual	2786.78	11	253.34			
Total	1.087E+05	15	7245.42			

The Model F-value of 7.12 and p-value of 0.0063 imply that linear model is significant (Table 5), so this model is used to show the relationship between three independent variables and decolorization efficiency. The statistical significance of model was analysed by ANOVA-analysis of variance. There is only a 0.63% chance that an F-value this large could occur due to noise. P-values less than 0.05 indicate that model terms are significant. Based on this, Table 5. shows that H_2O_2 concentration is the only significant model term.

Table 5

Obtained ANOVA results for linear model significance

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	5409.75	3	1803.25	7.12	0.0063	significant
A-pH	509.49	1	509.49	2.01	0.1839	
B-H_2O_2	4302.32	1	4302.32	16.98	0.0017	significant
C-Catalyst	66.33	1	66.33	0.2618	0.6190	
Residual	2786.78	11	253.34			
Lack of Fit	2786.58	9	309.62	2961.92	0.0003	significant
Pure Error	0.2091	2	0.1045			
Cor Total	8196.54	14				

As we mentioned, the linear model is chosen to describe the effects of pH value, H_2O_2 concentration and catalysts loading on decolorization efficiency, so experimental data are fitted with linear function, where Y is a percentage of decolorization efficiency, while A, B and C are values of pH, H_2O_2 concentration and catalysts loading, respectively. The obtained regression equation is Equation (4):

$$Y = 92.55 - 9.93A + 39.55B + 3.0 \quad (4)$$

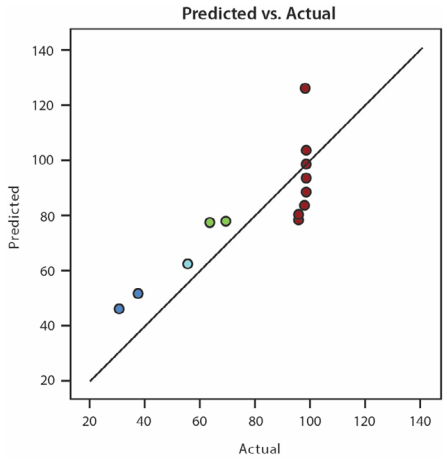
The signal to noise ratio is measured by adequacy precision, which comprised the predicted value at the design points and the average prediction error. As the adequacy precision ratio in this study is 9.6244 (greater than 4), it can be said that it is desirable. So, the developed model can be used in a further study.

The order of runs, the real experimental and predicted values for the efficiency of dye decolorization during the treatment are given in Table 6. It can be concluded that the actual values for the efficiency of decolorization vary between 30 and 97%. Figure 4 presents constructing diagnostic plots such as predicted versus actual values of the final responses and confirms good agreement between experimental data and model, which points out that linear model is adequate.

Table 6

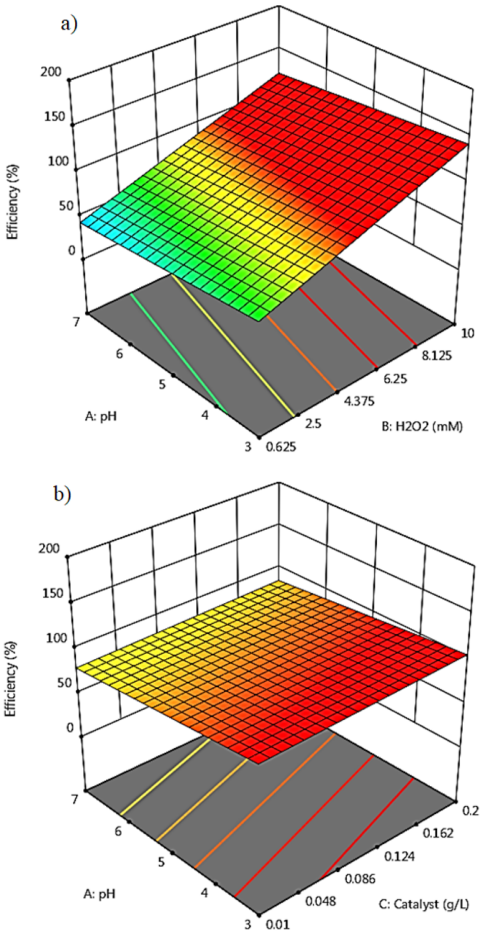
Report of predicted and actual values of decolourization efficiency

Run Order	Actual Value	Predicted Value
1	97.85	102.9
2	97.94	97.91
3	97.95	92.94
4	97.95	87.97
5	97.29	83.01
6	30.60	46.09
7	37.30	51.36
8	55.32	61.91
9	97.85	83.01
10	97.80	125.2
11	63.23	76.95
12	69.11	77.43
13	95.15	78.23
14	95.08	79.82
15	97.29	83.01



» **Figure 4:** *Predicted vs. actual values for decolorization efficiency*

The effects of operating variables on response can be illustrated by 3D response surface plots, so the impact of pH value, H_2O_2 concentration and catalysts loading on the decolorization efficincy is presented (Figure 5a,b).



» **Figure 5:** *Decolorization efficiency: a) effect of pH and H_2O_2, b) effect of pH and catalyst loading*

During the photo-Fenton process catalyst CuOFeB showed a good performance at lower pH value and higher concentration of H_2O_2 (Fig. 5a), while catalyst loading was 0.1 g. Namely, at pH above 3, the amount of ·OH radicals decreases due to iron precipitation in the form of iron hydroxide (Huang, et al., 2012). Also, it is well known that the rate of mineralization increases with the availability of H_2O_2 achieving its optimal concentration. Any further increase in the concentration of hydrogen peroxide (>10 mM) has a negligible effect on mineralization, because at high concentrations hydrogen peroxide can act as a very invasive scavenger of hydroxyl radicals. On the other hand, at low concentrations of hydrogen peroxide (<5 mM), sufficient hydroxyl radicals can not be produced to maintain good process performance, and the reaction is much slower or no degradation occurs, since the production of hydroxyl radicals is directly dependent on the concentration of hydrogen peroxide in the solution (Bacardit et al., 2007; Lucas and Peres, 2007; Huang, et al., 2012).

The presence of a catalyst is an important parameter that affects the efficiency of all Fenton processes (Figure 5b). The removal of the dye is directly proportional to the concentration of iron, and depends on the number of active sites, thus directly affecting the efficiency of degradation of the present organic pollutants (Ji et al., 2011). In the heterogeneous Fenton process, increasing the catalyst dose increases the presence of active sites on the surface of the catalysts responsible for the decomposition of hydrogen peroxide and the adsorption of dye molecules (Idel-aouad et al., 2011). Concentration of H_2O_2 remind constant and was 5 mM. Increasing the CuOFeB catalyst loading a higher process efficiency occured. Despite the fact that a higher dose of the catalyst in this type of process can also reduce the sunlight penetration through the suspension (Choi and Sakthivel, 2002; Pardeshi and Patil, 2008; Neppolian, Tanveer and Guyern, 2013), the use of CuOFeB in a given range of catalyst loading in this study did not lead to the screening effect.

Conclusion

In order to achieve a high efficiency of decolorization, the effects of process parameters pH, concentration of H_2O_2 and catalyst loading during photo-Fenton process were investigated using Design Expert software. Based on response surface analysis, H_2O_2 concentration was identified as significant factor for decolorization during the process. Also, maintaining neutral reaction conditions, subsequent water neutralization is reduced before discharge into the recipient, therefore pH 7, 6.8 mM H_2O_2 and 0.2 g of the catalyst can be considered as optimal conditions with acheived decolorization efficiency of 97.95%. Moreover, additional laboratory experiments should be carried out on the original wastewater sample produced in the process of dyeing using the optimal conditions proposed by the Design Expert software, with the aim to confirm the reliability of the model.

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