Application of central composite design for the optimization of photo-destruction of a textile dye using UV/S₂O₈²⁻ process

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The photooxidative destruction of C.I. Basic Red 46 (BR46) by UV/S₂O₈²⁻ process is presented. Central Composite Design (CCD) was employed to optimize the effects of operational parameters on the photooxidative destruction efficiency. The variables investigated were the initial dye and S₂O₈²⁻ concentrations, reaction time and distance of the solution from UV lamp. The predicted values of the photo-destruction efficiency were found to be in good agreement with the experimental values ($R^2 = 0.9810$, Adjusted $R^2 = 0.9643$). The results of the optimization predicted by the model showed that the maximum decolorization efficiency (>98%) was achieved at the optimum conditions of the reaction time 10 min, initial dye concentration 10 mg/l, initial peroxydisulfate concentration 1.5 mmol/l and distance of UV lamp from the solution 6 cm. The figure-of-merit electrical energy per order (E_{eo}) was employed to estimate the electrical energy consumption and related treatment costs.

Keywords: Experimental design, Response surface methodology, Decolorization, C. I. Basic Red 46, K₂S₂O₈.

INTRODUCTION

Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger. About 1 – 20% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents. Most of these dyes are toxic and potentially carcinogenic in nature and their removal from the industrial effluents is a major environmental problem^{1–3}. Among the various methods to handle the dye removal from water, the advanced oxidation processes (AOPs) appears to be a promising method, which has been reported to be effective for the near ambient degradation of soluble organic contaminants from waters and soils^{4–6}. AOPs to improve the removal performance are always of interest and the photochemical oxidant, UV/S₂O₈²⁻ process, could be a good candidate for such a purpose.

Peroxydisulfate (S₂O₈²⁻) is a strong oxidant (E^0 2.05 V) which has been used widely in the petroleum industry for the treatment of hydraulic fluids or as a reaction initiator⁷. It has also been reported to be effective for degrading organics in hazardous waste-waters in acidic or basic media through direct chemical oxidation, where peroxydisulfate is used as a sacrificial reagent^{7–9}. However, since the reactions of S₂O₈²⁻ are generally slow at normal temperature, the thermal or photochemical activated decomposition of S₂O₈²⁻ ion to SO₄^{•-} radical has been proposed as a method of accelerating the process^{9–12}.

S₂O₈²⁻ is normally available as a salt associated with ammonium, sodium, or potassium. The comparative performance of K₂S₂O₈ (KPS) and (NH₄)₂S₂O₈ (APS) as the oxidant under the irradiation of UV light for removal of butylated hydroxyanisole⁹ and a textile dye (Basic yellow 2)¹², indicated that KPS gave a more rapid photooxidative removal than APS at neutral pH. The difference in the removal efficiency is apparently due to the presence of the ammonium ion. The aqueous ammonium can undergo photooxidation leading to nitrate and/or nitrite by the available oxidants in the solution, such as, S₂O₈²⁻, and its

related intermediates H₂O₂ or O₂^{9,12}. Furthermore, the reaction of NH₄⁺/NH₃ with UV/S₂O₈²⁻ process are proved to be able to convert it to nitrate under the 254 nm photolysis¹³, thereby making the ammonium a competitor of the organic pollutants. In view of this, and the general unsuitability of adding ammonia to waters and wastewaters, APS is not recommended to be used in the UV/S₂O₈²⁻ oxidation process. Therefore, UV/KPS combination was chosen for further investigation throughout this study.

As it has been reported previously^{9–12}, UV/S₂O₈²⁻ oxidation process is dependent on various parameters such as initial dye concentration, reaction time, UV light intensity and the amount of peroxydisulfate. In most of the previous reports, conventional methods used to determine the influence of each one of these parameters. In the conventional methods, experiments were carried out varying systematically the studied parameter and keeping constant the others. This should be repeated to all the influence parameters, resulting in an the combined effect of the effective parameters. In order to optimize the effective parameters with the minimum number of experiments, application of the experimental design methodologies can be useful^{14–16}. Response surface methodology (RSM) is an experimental design technique that uses mathematical and statistical techniques to analyze the influence of independent variables on a specific dependent variable (response)¹⁷. Using RSM, it is possible to estimate linear interaction and the quadratic effects of the factors and a prediction model for the response. In this way, RSM designs could be used to find improved or optimal process settings in an efficient use of the resources. The experimental data required are dependent on the chosen design, Central Composite or Box-Behnken designs¹⁸. These are different in the number of runs required and in the combinations of the levels used in the experiments. The central composite design gives almost as much information as a multilevel factorial, requires much fewer experiments than a full factorial and has been shown to be sufficient to describe the majority of steady-state process responses^{19,20}.

RSM methodology has been applied to model and optimize several wastewater treatment processes including adsorption¹⁷, Fenton's oxidation^{21,22}, electrochemical oxidation²³, electrocoagulation²⁴ and photocatalytic decolorization processes^{20,25}. However, to the best of my knowledge, the efficiency of treatment and the effect of interaction of various parameters using central composite design during UV/S₂O₈²⁻ oxidation process have not been reported.

In this work, the central composite design has been applied to optimize the UV/S₂O₈²⁻ process for the decolorization of the dye solution containing BR46. The factors (variables) investigated were the reaction time, initial dye concentration, initial S₂O₈²⁻ concentration and the distance of the UV lamp from the solution. The electrical energy consumption and related treatment costs were also estimated.

EXPERIMENTAL

Materials

Potassium peroxydisulfate (K₂S₂O₈), sulfuric acid and sodium hydroxide were of laboratory reagent grade (Merck Co., Germany) and used without further purification. The mono azo dye, C.I. Basic Red 46, (C₁₈H₂₄N₆O₄S, Mw=420 g mol⁻¹, λ_{max} =530 nm)²⁶ which commonly used as a textile dye was obtained from Boyakhsaz Co. (Iran). Its chemical structure is shown in Figure 1.

Figure 1. Chemical structure of C.I. Basic Red 46

General Procedure

For UV/S₂O₈²⁻ process, irradiation was carried out with a 30W (UV-C) mercury lamp (Philips, the Netherlands), which was put above a batch photoreactor of 500 ml in volume. The desired concentration of BR46 and K₂S₂O₈ were fed into the Pyrex reactor. The distance between the solution and UV source was adjusted according to the experimental conditions. On the surface of the solution, the light intensity was measured by Cassy Lab (Germany). The pH of the solution was measured by a pH meter (Metrohm 654 pH-meter, Switzerland). Then, the UV

lamp was switched on to initiate the reaction. During irradiation, agitation was maintained to keep the solution homogeneous. At regular time intervals, samples were taken and the remaining BR46 was determined using UV/Vis spectrophotometer (WPA lightwave S2000, England) at λ_{max} =530 nm and calibration curve. Using this method, the conversion percent of BR46 could be obtained at different intervals. The efficiency of color removal (CR (%)) was expressed as the percentage ratio of decolorized dye concentration to that of the initial one.

Experimental design

In the present study, central composite design, which is a widely used form of RSM was employed for the optimization of biological color removal efficiency. In order to evaluate the influence of operating parameters on the decolorization efficiency of BR46, four main factors were chosen: reaction time (min) (X₁), initial dye concentration (mg/l) (X₂), initial S₂O₈²⁻ concentration (mmol/l) (X₃) and distance of the solution from UV lamp (cm) (X₄). A total of 31 experiments were employed in this work, including 2⁴=16 cube points, 7 replications at the center point and 8 axial points. Experimental data were analyzed using the Minitab 15 software. For statistical calculations, the variables X_i were coded as x_i according to the following relationship:

$$x_i = \frac{X_i - X_0}{\delta X} \quad (1)$$

where X₀ is the value of X_i at the center point and δX presents the step change^{27,28}. The experimental ranges and the levels of the independent variables for BR46 removal are given in Table 1. It should be mentioned that preliminary experiments was performed to determine the extreme values of the variables.

RESULTS AND DISCUSSION

CCD model and analysis of variance

The 4-factor CCD matrix and experimental results obtained in the photooxidative color removal runs are presented in Table 2. The second-order polynomial response equation (Eq. (2)) was used to correlate the dependent and independent variables.

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{34}x_3x_4 + b_{111}^2 + b_{222}^2 + b_{333}^2 + b_{444}^2 \quad (2)$$

where Y is a response variable of decolorization efficiency. The b_i are regression coefficients for linear effects; b_{ik} the regression coefficients for quadratic effects; x_i are coded experimental levels of the variables.

Based on these results, an empirical relationship between the response and independent variables was attained and expressed by the following second-order polynomial equation:

Table 1. Experimental ranges and levels of the independent test variables

Variables	Ranges and levels				
	-2	-1	0	+1	+2
Reaction time (min) (X ₁)	2	4.5	7	9.5	12
Initial dye concentration (mg/l) (X ₂)	5	10	15	20	25
Initial S ₂ O ₈ ²⁻ concentration (mmol/l) (X ₃)	0.4	0.8	1.2	1.6	2
Distance from UV lamp (cm) (X ₄)	4	6.5	9	11.5	14

Table 2. The 4-factor central composite design matrix and the value of response function (CR(%))

Run	Initial dye concentration (mg/l)	Initial $\text{S}_2\text{O}_8^{2-}$ concentration (mmol/l)	Distance from UV lamp (cm)	Reaction time (min)	Decolorization efficiency (%)	
					Experimental	Predicted
1	-1	1	1	1	87.6	85.9
2	-1	1	1	-1	61.0	58.5
3	0	-2	0	0	22.4	20.7
4	-1	-1	1	1	65.7	65.2
5	1	1	1	-1	29.7	28.5
6	0	0	0	0	56.2	57.2
7	1	1	-1	1	70.9	68.4
8	1	-1	-1	-1	24.2	24.7
9	0	0	0	-2	21.4	24.1
10	0	0	-2	0	74.0	70.2
11	0	0	0	2	76.4	74.7
12	-1	-1	1	-1	38.0	39.3
13	1	-1	1	-1	16.4	11.2
14	0	0	0	0	54.8	57.2
15	-1	1	-1	-1	69.8	67.4
16	2	0	0	0	31.9	34.4
17	1	1	-1	-1	43.0	43.6
18	0	0	0	0	54.7	57.2
19	0	0	0	0	57.2	57.2
20	1	1	1	1	53.7	51.6
21	-1	-1	-1	-1	44.4	46.7
22	-2	0	0	0	92.2	90.7
23	-1	-1	-1	1	74.3	74.3
24	1	-1	-1	1	45.4	48.0
25	0	0	2	0	41.3	46.1
26	0	2	0	0	57.6	60.3
27	1	-1	1	1	31.6	32.8
28	0	0	0	0	65.2	57.2
29	-1	1	-1	1	91.2	96.5
30	0	0	0	0	56.8	57.2
31	0	0	0	0	55.5	57.2

$$Y = 57.2 - 14.0708x_1 + 9.8875x_2 - 6.0375x_3 + 12.6625x_4 + 1.3427x_1x_2 - 4.1698x_1x_3 + 0.2427x_1x_4 - 1.9448x_2x_3 - 0.4687x_2x_4 - 1.5438x_3x_4 - 1.0813^2_1 - 0.3938^2_2 + 0.3688^2_3 - 0.4312^2_4 \quad (3)$$

The photooxidative decolorization efficiencies (CR(%)) have been predicted by Eq. (3) and presented in Table 2. These results indicated good agreements between the experimental and predicted values of decolorization efficiency. The regression coefficient (R^2) quantitatively evaluates the correlation between the experimental data and the

predicted responses (Figure 2). Two lines were used to show the success of the prediction. The one is the perfect fit (predicted data equal to the experimental data), on which all the data of an ideal model should lay. The other line is the line that best fits on the data of the scatter plot with equation $Y = ax + b$ and it is obtained with regression analysis based on the minimization of the squared errors. The correlation coefficient of this line is also presented (R^2). The closer to 1 this factor is and the closer the coefficients of the line to 1 and 0, respectively, are the better the model is. As it can be seen, the predicted values match the experimental values reasonably well with R^2 of 0.9810. This implies that 98.10% of the variations for dye removal efficiency are explained by the independent variables and this also means that the model does not explain only about 1.90% of variation. Adjusted R^2 (Adj- R^2) is also a measure of goodness of a fit, but it's more suitable for comparing models with different numbers of independent variables. It corrects the R^2 -value for the sample size and the number of terms in the model by using the degrees of freedom on its computations, so if there are many terms in a model and not very large sample size, adjusted R^2 may be visibly smaller than R^2 ^{17, 29}. Here, adjusted R^2 value (0.9643) was very close to the corresponding R^2 value (see Table 3).

In addition to regression coefficient, the adequacy of the models was also evaluated by the residuals (the difference between the observed and the predicted response value). Residuals are thought as elements of variation unexplained by the fitted model and then it is expected that they occur according to a normal distribution. Nor-

Figure 2. Comparison of the experimental results of photooxidative destruction efficiency with those calculated via central composite design resulted equation

Tablg 3. Analysis of variance (ANOVA) for fit of decolorization efficiency from central composite design

Source of variations	Sum of squares	Degree of freedom	Adjusted Mean square	F-value
Regression	12573.0	14	898.07	58.87
Residuals	244.1	16	15.25	
Total	12817.1			

$R = 0.9810^2$; Adjusted $R = 0.9643^2$

Figure 3. Residual plots for photooxidative destruction efficiency of BR46

mal probability plots are a suitable graphical method for judging the normality of the residuals. The observed residuals are plotted against the expected values, given by a normal distribution (see Figure 3). Trends observed in Figure 3, reveal reasonably well-behaved residuals.

Table 3 indicates the results of the quadratic response surface model fitting in the form of analysis of variance (ANOVA). ANOVA is required to test the significance and adequacy of the model^{28, 29}. ANOVA subdivides the total variation of the results in two components: variation associated with the model and variation associated with the experimental error, showing whether the variation from the model is significant or not when compared with the ones

associated with residual error^{17, 29, 30}. This comparison is performed by the F-value, which is the ratio between the mean square of the model and the residual error. If the model is a good predictor of the experimental results, F-value should be greater than the tabulated value of the F-distribution for a certain number of degrees of freedom in the model at a level of significance α . F-value obtained, 58.87, is clearly greater than the tabulated F (2.352 at 95% significance) confirming the adequacy of the model fits.

The student t distribution and the corresponding values, along with the parameter estimate, are given in Table 4. The P-values were used as a tool to check the significance of each of the coefficients, which, in turn, are necessary to

Table 4. The estimated regression coefficients and the corresponding t and P values from the data of central composite design experiments

Coefficient	Parameter estimate	Standard error	t-value	P-value
b_0	57.2000	1.4762	38.748	0.000
b_1	-14.0708	0.7972	-17.650	0.000
b_2	9.8875	0.7972	12.402	0.000
b_3	-6.0375	0.7972	-7.573	0.000
b_4	12.6625	0.7972	15.883	0.000
b_{12}	1.3427	0.7304	1.838	0.085
b_{13}	-4.1698	0.7304	-5.709	0.000
b_{14}	0.2427	0.7304	0.332	0.744
b_{23}	-1.9448	0.7304	-2.663	0.017
b_{24}	-0.4687	0.9764	-0.480	0.638
b_{34}	-1.5438	0.9764	-1.581	0.133
b_{11}	-1.0813	0.9764	-1.107	0.285
b_{22}	-0.3938	0.9764	-0.403	0.692
b_{33}	0.3688	0.9764	0.378	0.711
b_{44}	-0.4312	0.9764	-0.442	0.665

understand the pattern of the mutual interactions between the test variables. The larger the magnitude of the *t*-value and smaller the *P*-value, the more significant is the corresponding coefficient^{27, 28}.

Optimization of the operational variables

In order to gain insight into the effect of each variable, the three dimensional (3D) and contour (2D) plots for the predicted responses were formed, based on the model polynomial function to analyze the change of the response surface. The surface and contour plots of the quadratic model with two variables kept constant and the other two varying within the experimental ranges are shown in Figures^{4–8}.

The response surface plots provide a method to predict the photooxidative decolorization efficiency for different values of the tested variables and the contours of the plots help in identification of the type of interactions between these variables³¹.

In Figure 4, the response surface and contour plots were developed as a function of initial dye concentration and reaction time while the initial $K_2S_2O_8$ concentration and distance of UV lamp from the solution were kept constant at 1.2 mmol/l and 9 cm, respectively, being the central levels. The decrease in photooxidative decolorization efficiency with increasing initial BR46 concentration has been observed (see Figures 4 and 5). The presumed reason is that the higher the dye concentration, the more the absorption of UV light. Indeed, the extinction coefficient

(ϵ) of BR46 at UV range is high, so that an increase in BR46 concentration induces a rise of the internal optical density. The solution becomes more and more impermeable to UV radiation. Peroxydisulfate can then only be irradiated by a smaller portion of UV light to form lower free active radicals and the decolorization efficiency decreases^{12, 32}. Also Figures 4 and 5 showed that the color removal efficiency increased with increasing the reaction time.

UV irradiation decomposes $S_2O_8^{2-}$ to generate the sulfate and hydroxyl radicals required for the degradation of organic matters (Eqs. (4) and (5)). The overall energy input to a photochemical process is related to the light intensity. The photo-destruction efficiency increases with increase in the light intensity. Figures 5 – 7 show the color removal efficiency increased with decreasing the distance between the UV lamp and the solution. The reason of this observation is that the light intensity increased, from 12 to 33.4 W/m², with decreasing the distance between the UV lamp and the dye solution from 14 to 4 cm. Therefore, color removal efficiency enhanced. The finding was in agreement with literature reports where higher light intensities would result in higher photooxidative decolorization efficiency^{33, 34}.

To study the effect of initial $K_2S_2O_8$ concentration as a function of the distance of UV lamp from the solution and reaction time on photooxidative decolorization efficiency, the experiments were carried out with initial $K_2S_2O_8$ concentration varying from 0.4 to 2 mmol/l. The

Figure 4. The response surface and contour plots of the photooxidative destruction efficiency (%) as the function of reaction time (min) and initial dye concentration (mg/l)

Figure 5. The response surface and contour plots of the photooxidative destruction efficiency (%) as the function of initial dye concentration (mg/l) and distance of UV light from the solution (cm)

Figure 6. The response surface and contour plots of the photooxidative destruction efficiency (%) as the function of reaction time (min) and distance of UV lamp from the solution (cm)

results were displayed in Figures 7 and 8. These figures show that photooxidative decolorization efficiency increased with an increase in the initial amount of $K_2S_2O_8$, but once it exceeded a certain level, it was accompanied by a decrease in decolorization efficiency. It is reasonable, since as the concentration of $S_2O_8^{2-}$ is increased, more sulfate and hydroxyl radicals are available to attack the aromatic rings (RH) and rate of reaction increases (Eqs. (4) and (6)). However, at higher $S_2O_8^{2-}$ dosages, excessive generated hydroxyl radicals (Eqs. (4) and (5)) would be recombined to form less reactive H_2O_2 (Eq. (7)), which is a known quencher of $OH^\bullet$ radical (Eq. (8)). Therefore, the rate increment of BR46 photooxidative decolorization is slightly slowed down at higher $S_2O_8^{2-}$ dosages. However, such a recombination effect of the radical is likely not very effective due to the low steady-state concentrations of the radicals; higher decay rates of BR46 at higher $S_2O_8^{2-}$ dosages are still expected. The finding was in agreement with literature reports where optimal concentration of $S_2O_8^{2-}$ would result in higher photooxidative removal efficiency^{9-12, 32}.

Figure 7. The response surface and contour plots of the photooxidative destruction efficiency (%) as the function of initial $K_2S_2O_8$ concentration (mmol/l) and distance of UV lamp from the solution (cm)

As it can be seen in the above reactions, sulfate ion will be generated as the end-product, which is practically inert and is not considered to be a pollutant. The USEPA has listed it under the secondary drinking water standards with a maximum concentration of 250 mg/l (1.43 mmol/l), based on aesthetic reasons^{9, 12}.

The main objective of the optimization in this work is to determine the optimum values of variables for photooxidative decolorization using UV/ $S_2O_8^{2-}$ process, from the CCD model obtained using the experimental data. The desired goal in terms of decolorization efficiency was defined as "maximize" to achieve highest treatment performance. The optimum values of the process variables for >98% decolorization efficiency are shown in Table 5. After verifying by a further experimental test with the predicted values, the result indicated that the maximal decolorization efficiency was obtained when the values of each parameter were set as the optimum values, which was in good agreement with the value predicted from the model. It implies that the strategy to optimize

Table 5. Optimum operating conditions of the process variables for >98% decolorization efficiency

Variable	Optimum value
Reaction time (min)	10
Initial dye concentration (mg/l)	10
Initial $S_2O_8^{2-}$ concentration (mmol/l)	1.5
Distance from the UV lamp (cm)	6

Figure 8. The response surface and contour plots of the photooxidative destruction efficiency (%) as the function of initial $K_2S_2O_8$ concentration (mmol/l) and reaction time (min)

the decolorization conditions and to obtain the maximal decolorization efficiency by CCD for the photooxidative decolorization of BR46 solution using UV/ $S_2O_8^{2-}$ process is successful.

Since the photochemical treatment of aqueous organic pollutants is an electric-energy intensive process, and electric energy can represent a major fraction of the operating costs, simple figures-of-merit based on electric energy consumption can be very useful and informative. In the case of low pollutant concentrations, which applies here, the appropriate figure-of-merit is the electrical energy per order (E_{EO}), defined as the number of kW h of electrical energy required to reduce the concentration of a pollutant by 1 order of magnitude in 1 m^3 of contaminated water. The EEO ($kW\ h\ m^{-3}\ order^{-1}$) can be calculated from the following equations^{35–37}:

$$E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log(C_i / C_f)} = \left(\frac{38.4 \times P}{V \times k} \right) \quad (9)$$

where P is the lamp power (kW) of the AOP system, t is the irradiation time (min), V is the volume (l) of the water in the reactor, and C_i and C_f are the initial and final pollutant concentrations and k is the pseudo-first-order rate constant (min^{-1}) for the decay of the pollutant concentration. Pseudo-first-order rate constants were estimated from the slope of $\ln[Dye]$ versus time.

The electric energy ($kW\ h\ m^{-3}\ order^{-1}$) required to photooxidative decolorization of 10 mg/l of the dye from 100 ml dye solution in the optimized conditions, described in Table 5, was $29.43\ kW h\ m^{-3}\ order^{-1}$. It is useful to relate the E_{EO} value found in this study to treatment costs. If the cost of the electricity, in Iran, is \$ 0.023 per kWh, the contribution to treatment cost from electrical energy will be \$ 0.68 per m^3 , for photooxidative treatment of BR46. In addition there will be small cost factors for the oxidant ($K_2S_2O_8$) used and for UV lamp replacement. The electric energy consumption and related cost required to photooxidative decolorization of 10 mg/l of the dye from 100 ml dye solution in the optimized conditions was calculated.

CONCLUSIONS

The results of this study demonstrate that CCD methodology could efficiently optimize the photooxidative decolorization of BR46 using UV/ $S_2O_8^{2-}$ process. The optimum values of the reaction time, initial dye concentration, initial $S_2O_8^{2-}$ concentration and distance of UV lamp from the solution were found to be 10 min, 10 mg/l, 1.5 mmol/l and 6 cm, respectively. Under optimal value of the process parameters, high color removal (>98%) was obtained for the dye solution containing BR46. The results showed that the addition of proper amount of $S_2O_8^{2-}$ could improve the photooxidative decolorization efficiency. Analysis of variance showed a high coefficient of determination value ($R^2 = 98.10\%$ and $Adj-R^2 = 96.43\%$), thus ensuring a satisfactory adjustment of the second-order regression model with the experimental data. Effect of experimental parameters on the decolorization efficiency was established by the response surface and contour plots of the model-predicted responses. The residuals follow a normal distribution.

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LITERATURE CITED

1. Rauf, M.A. & Ashraf S. (2009). Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution. *Chem. Eng. J.* 151, 10 – 18. DOI: 10.1016/j.cej.2009.02.026.
2. Khataee, A.R., Vatanpour, V. & Amani, A. (2009). Decolorization of C.I. Acid Blue 9 solution by UV/Nano-TiO₂, Fenton, Fenton-like, electro-Fenton and electrocoagulation processes: A comparative study. *J. Hazard. Mater.* 161, 1225 – 1233. DOI: 10.1016/j.jhazmat.2008.04.075.
3. Konstantinou, I.K. & Albanis, T.A. (2004). TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations. *Appl. Catal. B: Environ.* 49, 1 – 14. DOI: 10.1016/j.apcatb.2003.11.010.
4. Liu, Z., Kanjo, Y. & Mizutani S. (2009). Removal mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment-physical means, biodegradation, and chemical advanced oxidation: A review. *Sci. Total Environ.* 407, 731 – 748. DOI: 10.1016/j.scitotenv.2008.08.039.
5. Brodzik, K., Walendziewski, J. & Stolarski M. (2007). Photodegradation of organic compounds in water. *Pol. J. Chem. Technol.* 9, 130 – 133. DOI: 10.2478/v10026-007-0072-1.

6. Morawski, A.W., Janus, M., Tryba, B., Toyoda, M., Tsumura, T. & Inagaki, M. (2009). Carbon modified TiO₂ photocatalysts for water purification. *Pol. J. Chem. Technol.* 11, 46 – 50. DOI: 10.2478/v10026-009-0023-0.
7. Kurechi, T., Aizawa M. & Kunugi A. (1983). Studies on the antioxidants XVIII: Oxidation product of tertiary butyl hydroquinone (TBHQ) (I). *J. Am. Oil Chem. Soc.* 60, 1878 – 1882. DOI: 10.1007/BF02901542.
8. Hepel, M. & Luo, J. (2001). Photoelectrochemical mineralization of textile diazo dye pollutants using nanocrystalline WO₃ electrodes. *Electrochimica Acta* 47, 729 – 740. DOI: 10.1016/S0013-4686(01)00753-8.
9. Lau, T.K., Chu, W. & Graham, N.J.D. (2007). The aqueous degradation of butylated hydroxyanisole by UV/S₂O₈²⁻: study of reaction mechanisms via dimerization and mineralization, *Environ. Sci. Technol.* 41, 613 – 619. DOI: 10.1021/es061395a.
10. House, D.A. (1962). Kinetics and mechanism of oxidations by peroxydisulfate, *Chem. Rev.* 62, 185 – 203. DOI: 10.1021/cr60217a001.
11. Gara, P.M.D., Bosio, G.N., Gonzalez, M.C. & Mártire, D.O. (2007). Kinetics of the sulfate radical-mediated photooxidation of humic substances, *Int. J. Chem. Kinet.* 40, 19 – 24. DOI: 10.1002/kin.20287.
12. Salari, D., Niaei, A., Aber, S. & Rasoulifard, M.H. (2009). The photooxidative destruction of C.I. Basic Yellow 2 using UV/S₂O₈²⁻ process in a rectangular continuous photoreactor, *J. Hazard. Mater.* 166, 61 – 66. DOI: 10.1016/j.jhazmat.2008.11.039.
13. Roig, B., Gonzalez, C. & Thomas, O. (1999). Measurement of dissolved total nitrogen in wastewater by UV photooxidation with peroxodisulphate, *Anal. Chim. Acta* 389, 267 – 274. DOI: 10.1016/S0003-2670(99)00212-3.
14. Box, G.E.P. & Wilson, K.B. (1951). On the experimental attainment of optimum conditions, *J. R. Stat. Soc., Ser. B Stat. Methodol.* 13, 1 – 45. DOI:
15. Box, G.E.P. & Hunter, W.G. (1961). The 2k-p fractional factorial designs, *J. Technometrics* 3, 311 – 458. DOI: 10.2307/1271430.
16. Obeng, D.P. Morrell, S. & Napier, T.J.N. (2005). Application of central composite rotatable design to modeling the effect of some operating variables on the performance of the three-product cyclone, *Int. J. Miner. Process.* 769, 181 – 192. DOI: 10.1016/j.minpro.2005.01.002.
17. Santos, S.C.R. & Boaventura, R.A.R. (2008). Adsorption modelling of textile dyes by sepiolite. *Appl. Clay Sci.* 42, 137 – 145. DOI: 10.1016/j.clay.2008.01.002.
18. Box, G.E.P. & Behnken, D.W. (1960). Some new three level designs for the study of quantitative variables. *J. Technometrics* 2, 455 – 475. DOI:
19. Zhang, X. Wang, R. Yang, X. & Yu, J. (2007). Central composite experimental design applied to the catalytic aromatization of isophorone to 3,5-xyleneol. *Chemometr. Intell. Lab. Sys.* 89, 45 – 50. DOI: 10.1016/j.chemolab.2007.05.006.
20. Lewandowski, G. & Cwirko, J. (2007). Uncommon applications of statistical methods of the design of experiments in chemical technology and environment protection. *Pol. J. Chem. Technol.* 9, 63 – 67. DOI: 10.2478/v10026-007-0092-x.
21. Ahmadi, M. Vahabzadeh, F. Bonakdarpour, B. Mofarrah, E. & Mehranian, M. (2005). Application of the central composite design and response surface methodology to the advanced treatment of olive oil processing wastewater using Fenton's peroxidation. *J. Hazard. Mater.* 123, 187 – 195. DOI: 10.1016/j.jhazmat.2005.03.042.
22. Catalkaya, E.C. & Kargi, F. (2007). Effects of operating parameters on advanced oxidation of diuron by the Fenton's reagent: a statistical design approach. *Chemosphere* 69, 485 – 492. DOI: 10.1016/j.chemosphere.2007.04.033.
23. Gurses, A., Yalcina, M. & Dogar, C. (2000). Electrocoagulation of some reactive dyes: a statistical investigation of some electrochemical variables. *Waste Manage.* 22, 491 – 494. DOI: 10.1016/S0956-053X(02)00015-6.
24. Ölmez, T. (2009). The optimization of Cr(VI) reduction and removal by electrocoagulation using response surface methodology. *J. Hazard. Mater.* 162, 1371 – 1378. DOI: 10.1016/j.jhazmat.2008.06.017.
25. Cho, H. & Zoh, K.D. (2007). Photocatalytic degradation of azo dye (Reactive Red 120) in TiO₂/UV system: Optimization and modeling using a response surface methodology (RSM) based on the central composite design. *Dyes Pigments* 75, 533 – 543. DOI: 10.1016/j.dyepig.2006.06.041.
26. Khataee, A.R. (2009). Photocatalytic removal of C.I. Basic Red 46 on immobilized TiO₂ nanoparticles: artificial neural network modeling. *Environ. Technol.* 30 (11), 1155 – 1168. DOI: 10.1080/09593330903133911.
27. Aleboyeh, A., Daneshvar, N. & Kasiri, M.B. (2008). Optimization of C.I. Acid Red 14 azo dye removal by electrocoagulation batch process with response surface methodology. *Chem. Eng. Process.* 47, 827 – 832. DOI: 10.1016/j.ccep.2007.01.033.
28. Kasiri, M.B., Aleboyeh, H. & Aleboyeh, A. (2008). Modeling and optimization of heterogeneous photo-Fenton process with response surface methodology and artificial neural networks. *Environ. Sci. Technol.* 42, 7970 – 7975. DOI: 10.1021/es801372q.
29. Liu, H.L. & Chiou, Y.R. (2005). Optimal decolorization efficiency of Reactive Red 239 by UV/TiO₂ photocatalytic process coupled with response surface methodology. *Chem. Eng. J.* 112, 173 – 179. DOI: 10.1016/j.cej.2005.07.012.
30. Harrelkas, F., Azizi, A., Yaacoubi, A., Benhammou, A. & Pons, M.N. (2009). Treatment of textile dye effluents using coagulation-flocculation coupled with membrane processes or adsorption on powdered activated carbon. *Desalination* 235, 330 – 339. DOI: 10.1016/j.desal.2008.02.012.
31. Li, Y., Chang, C. & Wen, T. (1996). Application of statistical experimental strategies to H₂O₂ production on Au/Graphite in alkaline solution. *Ind. Eng. Chem. Res.* 35, 4767 – 4771. DOI: 10.1021/ie960286+.
32. Khataee, A.R. & Mirzajani, O. UV/peroxydisulfate oxidation of C. I. Basic Blue 3: Modeling of key factors by artificial neural network. *Desalination* In press. DOI: 10.1016/j.desal.2009.09.142.
33. Behnajady, M. & Modirshahla, N. (2006). Evaluation of electrical energy per order (EEO) with kinetic modeling on photooxidative degradation of C. I. Acid Orange 7 in a tubular continuous-flow photoreactor. *Ind. Eng. Chem. Res.* 45, 553 – 557. DOI: 10.1021/ie050111c.
34. Zang, Y. & Farnood, R. (2005). Photocatalytic decomposition of methyl tert-butyl ether in aqueous slurry of titanium dioxide. *Appl. Catal. B: Environ.* 57, 275 – 282. DOI: 10.1016/j.apcatb.2004.11.005.
35. Bolton, J.R., Bircger, K. Tumas, G. & Tolman, W.C. A. (2001). Figure-of merit for the technical development and application of advanced oxidation technologies for both electric and solar-derived systems. *Pure Appl. Chem.* 73, 627 – 637. DOI: 10.1351/pac200173040627.
36. Khataee, A.R. Pons, M.N. & Zahraa, O. (2009). Photocatalytic degradation of three azo dyes using immobilized TiO₂ nanoparticles on glass plates activated by UV light irradiation: influence of dye molecular structure. *J. Hazard. Mater.* 168, 451 – 457. DOI: 10.1016/j.jhazmat.2009.02.052.
37. Khataee, A.R., Aleboyeh, H. & Aleboyeh, A. (2009). Crystalline phase-controlled preparation, characterization and photocatalytic properties of titanium dioxide nanoparticles. *J. Experiment. Nanosci.* 4, 121 – 137. DOI: 10.1080/17458080902929945.