Photocatalytic degradation of a diazo-dye in artificial seawater matrix: Optimization of UV/H₂O₂ process on the Ponceau S decolorization by using central composite design

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ABSTRACT

The photocatalytic oxidation using the highly reactive hydroxyl radical from UV/H₂O₂ system is one of the advanced oxidation processes (AOPs) that destroy or even mineralize organic pollutants, which are harmful to the environment. However, certain costs must be controlled by taking into account influencing factors such as the dose of irradiance, oxidant dosage, and the complexity of the background matrix, among others. The objective of this work was to optimize Ponceau S (PS) degradation efficiency by UV/H₂O₂ process in artificial seawater by using central composite design (CCD). The three selected factors were the hydrogen peroxide concentration, the irradiated volume and the PS dosage. The regression analysis showed good fit of the experimental data to the second-order polynomial model with a correlation coefficient (R^2) of 0.9612. The optimal conditions were found to be: $C_{(PS)} = 50.91$ mg/L, $[H_2O_2] = 2.24$ mM, and irradiated volume = 600 mL. Under these conditions, the PS decolorization efficiency was equal to 72.47%.

Keywords: Advanced oxidation process, Artificial seawater, Central composite design, Photocatalytic decolorization, Ponceau S, UV/H₂O₂ process

1. Introduction

The increased demand for the synthetic dyes for various uses such as printing, cosmetic, pharmaceutical and textile industries in particular [1], has resulted in discharging of the dye effluents into watercourses and /or salt water. However, these chemically complex substances cause damage to the environment in terms of a serious threat to human health by causing allergic reactions, cancer and eye irritation, and to aquatic ecosystems even at low concentrations [2, 3]. Among these synthetic dyes, the azo dyes class is the most widely marketed (50-70%), it known to be able to alter the physical and chemical properties of the soils as well as intoxicating the flora and fauna of the waters [4].

The treatment of the saline or fresh water, downstream or upstream, used for the various activities mentioned above, becomes necessary [5]. The deployed and conclusive efforts of researchers on the water treatment have covered all areas, physical, biological

and chemical, and have resulted in some limitations being encountered, such as high costs, sludge formation, time consuming treatment, among others [6].

Meanwhile, it has been reported that the chemical or physical treatment of waters containing azo dyes, known by their stability and low-biodegradability, leads in addition to the constraints mentioned above, to the formation of toxic by-products when these waters are treated by uncontrolled oxidative reactions [7].

The growing need for an alternative solution that can, to a large extent, alleviate the constraints of the conventional processes and achieve satisfactory results, has been satisfied by the coming of advanced oxidation processes (AOPs) [7, 8].

These new technologies can be grouped into processes using homogeneous phase chemical oxidation (H₂O₂/Fe²⁺ and H₂O₂/O₃), homogeneous and/or heterogeneous phase photocatalysis (H₂O₂/UV, O₃/UV, Fe²⁺/H₂O₂/UV and TiO₂/UV), sonochemical oxidation and electrochemical oxidation, allowing more reactive oxidants to be

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generated under softer conditions than conventional oxidants. These powerful oxidants designated by highly reactive radicals which include the oxygen superoxide radical ($O_2^{\bullet-}$), the hydroperoxyl ion radical ($HO_2^{\bullet-}$) and especially the hydroxyl radical ($HO^\bullet$) which, when compared to the others, has a greater non-selective reactivity making it responsible for the destruction of organic pollutants and competitive surrounding anionic species. The production rate of hydroxyl radicals depends mainly on various parameters, including the characteristics of the UV lamps (emission spectrum, power) and the physico-chemical properties of the medium (pH, turbidity, H_2O_2 concentration, among others).

Despite the noticeable success of researches conducted on the treatment of simple matrices containing a single compound, these technologies still have limited applicability to the treatment of other matrices including seawater. Currently, most of the reported studies on salt water management have focused more on the disinfection of salt water than on the removal of commonly undesirable organic matter [9]. Among the systems that have been mainly investigated in a water-saline environment to disinfect and/or remove organic matter, were those using UV coupling with ozone or hydrogen peroxide or even titanium dioxide [10].

As known, the complex composition of seawater in several ions has made some of them act as scavengers of active namely chlorides (Eq. (1)), sulphates (Eq. (2)) and carbonates (Eq. (3)) by reducing the degrading efficiency of organic pollutants [11]. It is essential to note that the significant presence of bromides in such media compete with organic matter against hydroxyl radicals especially the ozone, when using the O_3 /UV system, to affect the mineralizing activity and to form by-products such as bromates and trihalomethanes [12]. The global equations of the reactions concerning the formation of hydroxyl radicals from the photolysis of H_2O_2 (Eq. (4)), the action of bromides on $HO^\bullet$ [13] (Eq. (5)), the reduction of ozone by hypobromite ions (Eq. (6)) resulting from the oxidation of bromides by O_3 [14] (Eq. (7)) and the inter-species reactions discussed previously are summarized as follows:

It should be pointed out in this context that the reactive species HOBr or its conjugate base BrO^- are rapidly reduced by the hydrogen peroxide present in the H_2O_2 /UV system, in order to

prevent significant formation of brominated species like bromides (Eq. (8) and Eq. (9)) [14]. Furthermore, chlorides are present in large quantities in a marine environment ($pH > 8$), they are reactive towards $HO^\bullet$ giving rise to an anion radical $ClOH^{\bullet-}$ (Eq. (10)) whose transformation would depend on the pH of the medium (Eq. (11) and Eq. (12)) [15]. The global equations are given below:

Otherwise, the approach adopted by design of experiments (DOE) in the field of water treatments, among other industrial and research areas, has often centered its goals on mathematical modeling and subsequently optimizing the process in question. In order to achieve their purpose and to help in the decision to be taken, the diversity of these published experimental designs has been attributed to their conceptualization, their detailed statistical evaluation of the model used, and their cost.

From the conceptualization stage to the process optimization stage, an approach necessarily involves a mathematical modeling that links the response(s) by a polynomial equation to the factors under study. In this perspective, to understand exceptionally the topography of the response within the range of the variations of the studied factors, the response surface methodology (RSM) has become a powerful mathematical and statistical tool for better executing all the stages of a design.

The most well-known designs used in this methodology are the Box-Behnken (BBD) and the central composite (CCD) designs in order to perform experiments, model the response surface by regression, assess the effects of the factors and search the optimum conditions of the chosen response in only a few experiments [16, 17].

In fact, the CCD consists of a set of mathematical and statistical approaches based on the fit of a polynomial equation to the experimental data, which aims at evaluating the multiple factors and their interactions [18]. In addition, it can be well applied to fit a quadratic response surface with a minimum number of experiments and to optimize the responsive factors and analyze the interaction between them [16].

The present work is undertaken to investigate the optimization of the UV/ H_2O_2 process on PS photocatalytic removal in artificial seawater. The factors retained and which affect the phenomena were the PS concentration, the hydrogen peroxide dose and the irradiated volume. The experiments are planned using the central composite design under the response surface methodology to determine the main effects of the above factors with their interactions and to achieve the combination of the optimum operating conditions.

2. Materials and Methods

2.1. Materials

The salt of the diazo dye Ponceau S (Abbreviation: PS; color index number: 27195; chemical class: Diazo; molecular formula: $C_{22}H_{12}N_4Na_4O_{13}S_4$; molecular weight: 760.6 g/mol) was obtained from REACTIFS RAL. The hydrogen peroxide (H_2O_2 , 50%) was manufactured by PROCHILABO. The ultrapure water with a resistivity of 0.055, obtained using a (VWR PURANITY TU), was used to prepare all stock and working solutions.

All chemicals were of chemically pure grade. The UV-visible spectrum of PS diazo dye in the artificial seawater was recorded from 200 to 800 nm using a UV-Vis spectrophotometer (Rayleigh UV-1800) with a spectrometric quartz cell (1 cm path length).

The hypsochromic and hypochromic effects were observed when the background matrix was changed from the ultrapure water to the artificial seawater. On our part, the kinetic monitoring was conducted at the maximum of the azo band relocated at 510 nm in synthetic seawater. The concentrations of PS dye have been extracted from a calibration curve, which was obtained from six known concentrations.

2.2. Methods

2.2.1. Preparation of the artificial seawater

The artificial seawater was freshly prepared according to the “Lyman and Fleming” formula (Table 1) that has been one of the most widely used recipes for the artificial seawater [19].

To avoid precipitation of $CaCO_3$, $CaSO_4$, $SrCO_3$, or $SrSO_4$, the chloride solution (Table 1. B) and the first solution (Table 1. A) were prepared in two separate containers, after the two solutions were thoroughly mixed, they were combined while stirring.

The salinity and the conductivity of the artificial seawater was measured using (HACH sensION+ EC7) conductimeter. The pH of the artificial seawater was determined using (HACH sensION+PH3) pH-meter. The synthetic seawater prepared accord-

ing to the “Lyman and Fleming” formula, has a salinity and conductivity of 33.3 g/L at 17.9°C and 52.8 $\mu S/cm$ at 17.9°C, respectively and a pH of 8.02 at 17.7°C.

2.2.2. Photocatalytic oxidation experiments

A stock of PS diazo dye was prepared by dissolving the necessary quantity in the artificial seawater. The different hydrogen peroxide doses ranging from 1.46 to 2.24 mM were prepared by diluting the commercial solution in the artificial seawater. The UV doses absorbed by H_2O_2 were expressed as function of the irradiated volume (mL). The reactor was operated with the working volume ranging from 197.73 to 702.27 mL. All the experiments were carried out in an aerated cylindrical reactor with 1L capacity in which we immersed a double walled quartz sleeve containing a high-pressure mercury lamp (250 W, manufactured by Ingelec). The continuous circulation of water through an internal cooling tube in the sleeve was used to keep a constant temperature in the treated solution. The temperature during the experiment was equal to 23°C. The solutions were stirred at the same agitation speed with a magnetic stirrer placed at the reactor base. The lamp has been turned on to initiate the reaction after adding the hydrogen peroxide.

A 5 mL aliquot of the reaction medium was taken after 5, 10 and 15 min of irradiation and immediately analyzed by UV-Vis spectrophotometry. The absorbances, read at 510 nm and retained for this study, are those of the aliquots taken after 10 minutes in order to minimize experimental errors.

The decolorization efficiency was determined by the Eq. (13).

$$\% \text{ Decolorization efficiency} = \left(\frac{A_0 - A_t}{A_0} \right) * 100 \quad (13)$$

Where A_0 is the initial absorption of PS, and A_t is the absorption of PS at reaction time.

2.2.3. Experimental design

In the present work, the central composite design was used to study the effect of operating factors on the PS decolorization effi-

Table 1. The Artificial Seawater Recipes

		Concentration	Purity	Supplier
Dissolved in 500 cm ³ ultra-pure water(A)				
NaCl	23.9 g	0.025 g/mL	99.5%	Scharlau
Na ₂ SO ₄	4 g	4.188 mg/mL	99%	Honeywell
KCl	0.7 g	0.732 mg/mL	99.5%	Scharlau
NaHCO ₃	0.1 g	0.104 mg/mL	99.37%	Riedel-de-Han
KBr	0.2 g	0.209 mg/mL	99.5%	Riedel-de-Han
H ₃ BO ₃	30 mg	0.031 mg/mL	99.8%	SIGMA-ALDRICH
NaF	3 mg	0.003 mg/mL	98.5%	Scharlau
Dissolved in 455 cm ³ ultra-pure water(B)				
MgCl ₂ .6H ₂ O	10.8 g	0.011 g/mL	99%	Carlo Erba Reactifs-sds-
CaCl ₂ .2H ₂ O	1.5 g	1.570 mg/mL	99%	Riedel-de-Han
SrCl ₂ .6H ₂ O	25 mg	0.026 mg/mL	99%	Riedel-de-Han

ciency in the artificial seawater by the UV/H₂O₂ process. The CCD was performed by the Design Expert 7.0 (DX) software to design the trials and analyze the data. The number of experiments required is defined by the Eq. (14) [17].

$$N = 2^k + 2k + C_p \quad (14)$$

Where k is the number of factors and C_p is the number of central points.

The three factors including the hydrogen peroxide concentration (A), the irradiated volume (B) and the PS concentration (C) were adopted in CCD. Each factor was divided in five levels (- α , -1, 0, +1, + α), and the PS decolorization efficiency over 10 min was selected as the dependent response Y. The operating factors and their corresponding levels are shown in Table 2.

Table 2. The Values and Levels of Operating Factors

Operating factors	Levels				
	$-\alpha$	-1	0	+1	$+\alpha$
A: [H ₂ O ₂] (mM)	1.1941	1.46	1.85	2.24	2.5059
B: Irradiated volume (mL)	197.731	300	450	600	702.269
C: C _(PS) (mg/L)	29.7731	40	55	70	80.2269

Table 3. Central Composite Design Matrix

Run	Factors			Coded values			Response
	[H ₂ O ₂] (mM)	Irradiated volume (mL)	C _(PS) (mg/L)	A	B	C	Y
1	1.46	300	40	-1	-1	-1	55.9
2	1.85	450	55	0	0	0	62.54
3	1.85	450	80.23	0	0	$+\alpha$	53.8
4	1.46	300	70	-1	-1	+1	45.42
5	1.19	450	55	$-\alpha$	0	0	42.32
6	2.24	300	70	+1	-1	+1	60.85
7	1.85	450	29.77	0	0	$-\alpha$	57.61
8	2.24	600	70	+1	+1	+1	69.34
9	1.85	450	55	0	0	0	63.08
10	2.24	300	40	+1	-1	-1	67.27
11	2.51	450	55	$+\alpha$	0	0	70.13
12	1.85	450	55	0	0	0	63.12
13	1.85	450	55	0	0	0	62.73
14	1.85	702.27	55	0	$+\alpha$	0	67.29
15	1.85	197.73	55	0	$-\alpha$	0	60.62
16	2.24	600	40	+1	+1	-1	73.35
17	1.46	600	70	-1	+1	+1	50.69
18	1.85	450	55	0	0	0	66.28
19	1.85	450	55	0	0	0	63.34
20	1.46	600	40	-1	+1	-1	59.11

The CCD for three input factors and five levels consists of a standard first order design with eight orthogonal factorial points and six center points, augmented by six axial points. Thus, the total number of experiments becomes 20 experiments that were conducted by the DX software. The factors chosen and their levels as well as the response are presented in Table 3.

The predicted response Y can be obtained from the quadratic model equation as follows [20].

$$Y = b_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j + \sum_{i=1}^n b_{ii} x_i^2 \quad (15)$$

Where Y is the predicted response, b₀ is the constant coefficient, b_{ii} is the quadratic coefficient, b_{ij} is the interaction coefficient and x_i, x_j are the coded values of the factors.

3. Results and Discussions

3.1. Model Fitting and Analysis of Variance (ANOVA)

3.1.1. Mathematical model equation

The CCD was used for fitting in mathematical model that evaluate the interactions among factors and individual contribution of each factor on the experimental response. As no aliases were found for quadratic polynomial model, hence it was selected for optimizing input factors. The equation 16 expresses the obtained correlation between input factors and responses (outputs) which explains the

main effect, the interaction effect and the quadratic effect of the selected independent factors.

$$\begin{aligned} \text{Decolorization efficiency (\%)} = & +62.80 + 7.85A + 2.52B \\ & -3.00C - 0.090AB - 0.042AC - 0.042BC \\ & -2.02A^2 + 0.71B^2 - 2.21C^2 \end{aligned} \quad (16)$$

The effect of a factor is defined as the change in the response resulting by a change in the level of the factor. The above equation represents the second-order polynomial equation (based on coded factor) for the studied response where 62.80 is the model intercept coefficient. The PS decolorization efficiency increases with increasing the hydrogen peroxide concentration (A) and the irradiated volume (B) as clearly appears by the higher coefficient values of 7.85 and 2.52 respectively. While, the PS concentration (C) negatively affects the response with a negative coefficient of 3. The interaction effects of all studied factors are very small. Whereas, only the irradiated volume positively affects the response in terms of its quadratic effect.

The reliability of the aforementioned model was determined by the coefficient of regression R^2 and adjusted- R^2 . In the reported results, R^2 and adjusted- R^2 were equal to 0.9612 and 0.9266 respectively. The R^2 of 0.9612 means that the selected model can describe 96.12 % of the response data. In addition, the predicted- R^2 of 0.7543 completely agree with the adjusted- R^2 that indicates high correlation between the experimental results and the predicted model.

3.1.2. Analysis of variance (ANOVA)

To test the validity of the quadratic model, the effect of factors and the interaction between them, analysis of variance (the regression analysis) was applied. ANOVA has the flexibility to cover a larger number of experimental designs, it aims to compare the variability due to treatment (varying the level of input factors) versus the variability due to residual error. This comparison leads to evaluate the significance of the regression model. It

is important to notice that the regression analysis is valid only if the residues (square of the difference between the response predicted by the mathematical model and the experimental response) present normal distribution and homoscedasticity [21]. Furthermore, the regression analysis was the very useful statistical technique for such kind of engineering or scientific problems [22]. The ANOVA data for the coded quadratic model are shown in Table 4.

The analysis of variance of the data obtained from CCD indicated that the quadratic model significantly explained the factors affecting the response. The high "F-value" of 27.56 and the probability "p-value" less than 0.0001 ensure the quadratic model is highly significant.

In this study A, B, C, A^2 , C^2 are the significant model terms. All the interaction effects (AB, AC and BC), between the studied factors were not significant. The negative effect of the PS concentration on the PS decolorization efficiency makes his interaction with the other factors non-significant. The low interaction between the H_2O_2 concentration and the irradiated volume could be justified by the complex composition of seawater in several ions that act as scavengers of active hydroxyl radicals, such as chlorides, sulphates, carbonates and bromides, thereby reducing the degradation efficiency of PS in the seawater matrix by the UV/ H_2O_2 process.

The "Lack of Fit" test was not significant (low F-value and p-value greater than 0.05) which clearly indicates that this model explains the response very well. In addition, the credibility and accuracy of experimental responses were evaluated using adequate precision that determines a signal to noise ratio, a ratio greater than 4 is desirable. The ratio of 17.77 indicates an adequate signal. According to these results, this model can be used to explore the design space and to find the optimal conditions of this process.

3.2. Model Accuracy Check

To obtain an adequate mathematical model, an accuracy check is necessary. The model accuracy was checked by comparing the

Table 4. Analysis of Variance of the Results Based on CCD

Source	Sum of Squares	df	Mean Square	F value	p-value Prob > F	Significance
Model	1,174.20	9	130.47	27.56	< 0.0001	Significant
A-[H_2O_2] (Mm)	829.90	1	829.90	175.28	< 0.0001	Significant
B-irradiated volume (mL)	85.98	1	85.98	18.16	0.0017	Significant
C- $C_{(PS)}$ mg/L	93.52	1	93.52	19.75	0.0012	Significant
AB	4.64	1	4.64	0.98	0.3457	
AC	8.97	1	8.97	1.89	0.1988	
BC	2.50	1	2.50	0.53	0.4843	
A^2	68.14	1	68.14	14.39	0.0035	Significant
B^2	4.49	1	4.49	0.95	0.3529	
C^2	80.15	1	80.15	16.93	0.0021	Significant
Residual	47.35	10	4.73			
Lack of Fit	37.76	5	7.55	3.94	0.0794	
Pure Error	9.59	5	1.92			
Cor Total	1,221.55	19				

predicted and experimental responses (Fig. 1). In addition, a normal plot of residuals between the normal probability (%) and the internally studentized residuals was also obtained (Fig. 2), to measure the standard deviations separating the experimental and predicted values. If the data points fall fairly close to the straight line, then the data are normally distributed [20].

The Fig. 1 shows the linear relationship between the predicted and experimental responses. The straight line means that there was no apparent problem with normality. Furthermore, it appears from the Fig. 2 that the data points were fairly close to the straight line, which indicates that the normality assumption was satisfied. Thus, the experiments come from a normally distributed population.

Fig. 1. Predicted vs. Actual plot.

Fig. 2. Normal plot of residuals for the PS decolorization efficiency.

3.3. Response Analysis

The three-dimensional (3-D) response surface plots and the contour plots were conspired to measure and interpret the individual and the interaction effect of the independent factors on the response. The responses plotted when two factors changed but the other factor is fixed at its central level [23]. They assist in determining the optimal experimental factors and quantifies the relationship between the input factors and response of interest as shown in Fig. 3 [24]. The form of the contour line illustrates the extent of the interactions between the factors. A negligible effect appears as a circular contour line. While an elliptical line indicates a significant interaction. The 3-D response surface plots permit to visualize the tendency of each factor on the response [25].

Fig. 3(a) showed that the contour plot of the interactions between the hydrogen peroxide concentration and the irradiated volume are found to be elliptical. The PS decolorization efficiency increases with both H_2O_2 concentration and the irradiated volume. In other words, increasing the H_2O_2 concentration from 1.46 mM to 2.24 mM and the irradiated volume from 300 mL to 600 mL has a positive effect on the PS decolorization efficiency.

For the PS decolorization efficiency, increasing the irradiated volume of the dye solution increased the amount of UV radiation absorbed by H_2O_2 . Hence, the formation of plentiful hydroxyl radicals in the treated solution. Similarly, the effect of increasing hydrogen peroxide concentration is positive for efficient PS decolorization. That can be attributed to generation of more hydroxyl radicals since the H_2O_2 concentration increased. However, increasing the PS concentration despite increasing both the hydrogen peroxide concentration and the irradiated volume decreases the PS decolorization efficiency as appears in Fig. 3(b) and 3(c). At a high PS concentration, the dye may inhibit light penetration and minimize the photolysis.

3.4. Process Optimization

After the significance of the factors has been evaluated, the non-significant terms were eliminated and the equation in terms of the actual factors for the PS decolorization efficiency is given as follows:

$$\text{Decolorization efficiency (\%)} = +63.78 + 7.65A + 2.73B - 2.84C + 1.43AC - 1.87A^2 - 2.59C^2 \quad (17)$$

The above model equation helps to find the direction in which the variables should be changed in order to optimize the decolorization yield of PS in the artificial seawater by the UV/ H_2O_2 process. All the statistical indicators were improved, namely: The R^2 that was increased slightly to 0.9654 and the predicted- R^2 of 0.8155 that still in reasonable agreement with the adjusted- R^2 of 0.9294.

The optimization of the process was performed using the numerical optimization function by means of the desirability methodology provided by the DX software. Desirability is an objective function that ranges from zero outside of the limits, to one at the goal. According to this approach, the optimized formulation of the hydrogen peroxide concentration of 2.24 mM, the irradiated volume

Fig. 3. Contour plots and 3-D response surface plots showing the effect of (a) [H₂O₂] and irradiated volume, (b) [H₂O₂] and C_(PS), (c) the irradiated volume and C_(PS) on the PS decolorization efficiency.

of 600 mL and the PS concentration of 50.91 mg/L exhibited a maximum PS decolorization of 72.47%.

4. Conclusions

The present study focused on the application of the CCD associated with the RSM as a convivial tool for the determination of the optimal conditions of the UV/H₂O₂ process using to decolorize the PS in the artificial seawater. The quadratic equation of the

PS decolorization efficiency was evaluated as function of three factors, as follows: the hydrogen peroxide concentration, the irradiated volume and the PS concentration. The coefficient of regression R^2 for the considered equation was equal to 0.9612, showing a good agreement between the independent factors and the output data. The process variables were optimized by using RSM, the hydrogen peroxide of 2.24 mM, the irradiated volume of 600 mL and the PS concentration of 50.91 mg/L exhibited a maximum PS decolorization of 72.47%. The H₂O₂ concentration was determined as the most positive factor affecting the response with

a coefficient of 7.65 followed by the irradiated volume. Nevertheless, the individual effect of the PS concentration has a negative effect on the PS decolorization efficiency.

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Author Contributions

Y.L. (Ph.D student) conducted all the experiments and wrote the manuscript. A.B. (Professor) wrote and revised the manuscript. B.C. (Ph.D student) revised the manuscript (the experimental section). M.H. (Professor), M.E. (Professor) and M.K. (Professor) visualised, reviewed the manuscript (the results section).

References

1. A. Hassaan M, El Nemr A. Health and Environmental Impacts of Dyes: Mini Review. *Am. J. Environ. Sci. Eng.* 2017;1:64-67.
2. Javaid R, Qazi UY. Catalytic oxidation process for the degradation of synthetic dyes: An overview. *Int. J. Environ. Res. Public Health.* 2019;16:1-27.
3. Laftani Y, Boussaoud A, Chatib B, El Makhfouk M, Hachkar M., Khayar M. Comparison of advanced oxidation processes for degrading Ponceau S dye. Application of photo-Fenton process. *Maced. J. Chem. Chem. Eng.* 2019;38:197.
4. Konstantinou IK, Albanis TA. TiO_2 -assisted photocatalytic degradation of azo dyes in aqueous solution: Kinetic and mechanistic investigations: A review. *Appl. Catal. B Environ.* 2014;49:1-14.
5. Penru Y, Guastalli AR, Esplugas S, Baig S. Application of UV and $\text{UV}/\text{H}_2\text{O}_2$ to seawater: Disinfection and natural organic matter removal. *J. Photochem. Photobiol. A Chem.* 2012;233:40-45.
6. A. Hassaan M, El Nemr A, Madkour FF. Advanced oxidation processes of Mordant Violet 40 dye in freshwater and seawater. *Egypt. J. Aquat. Res.* 2017;43:1-9.
7. Chacó JM., Leal MT, Sánchez M, Bandala ER. Solar photocatalytic degradation of azo-dyes by photo-Fenton process. *Dye. Pigment.* 2006;69:144-150.
8. Luo Y, Guo W, Ngo HH, et al. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Sci. Total Environ.* 2014;473-474:619-641.
9. Jones AC, Gensemer RW, Stubblefield WA, Van Genderen E, Dethloff GM, Cooper WJ. Toxicity of ozonated seawater to marine organisms. *Environ. Toxicol. Chem.* 2006;25:2683-2691.
10. Penru Y, Guastalli AR, Esplugas S, Baig S. Disinfection of Seawater: Application of UV and Ozone. *Ozone Sci. Eng.* 2013;35:63-70.
11. Rubio D, Nebot E, Casanueva JF, Pulgarin C. Comparative effect of simulated solar light, UV, $\text{UV}/\text{H}_2\text{O}_2$ and photo-Fenton treatment ($\text{UV-Vis}/\text{H}_2\text{O}_2/\text{Fe}^{2+},^{3+}$) in the *Escherichia coli* inactivation in artificial seawater. *Water Res.* 2013;47:6367-6379.
12. Liao CH, Kang SF, Wu FA. Hydroxyl radical scavenging role of chloride and bicarbonate ions in the $\text{H}_2\text{O}_2/\text{UV}$ process. *Chemosphere.* 2001;44:1193-1200.
13. Von Gunten U. Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. *Water Res.* 2003;37:1469-1487.
14. Haag WR, Holgné J. Ozonation of Bromide-Containing Waters: Kinetics of Formation of Hypobromous Acid and Bromate. *Environ. Sci. Technol.* 1983;17:261-267.
15. Haag WR, Hoigné J. Kinetics and products of the reactions of ozone with various forms of chlorine and bromine in water. *Ozone Sci. Eng.* 1984;6:103-114.
16. Müller A.L.H, De Oliveira JA, Prestes OD, Adaime MB, Zanella R. Design of experiments and method development. *Solid-Phase Extr.* 2019;589-608.
17. Bezerra MA, Santelli RE, Oliveira EP, Villar LS, Escalera LA. Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta.* 2008;76:965-977.
18. Liu T, Wang K, Jiang M, Wan L. Interactions between meso-cellular foam silica carriers and model drugs constructed by central composite design. *Colloids Surfaces B Biointerfaces.* 2019;180:221-228.
19. Grasshoff K, Kremling K, Ehrhardt M. Methods of Seawater Analysis. 3rd ed. Weinheim: WILEY-VCH; 2007.
20. Machrouhi A, Farnane M, Tounsadi H, et al. Activated carbon from thapsia transtagana stems: Central composite design (CCD) optimization of the preparation conditions and efficient dyes removal. *Desalin. Water Treat.* 2019;166:259-278.
21. Fukuda IM, Pinto CFF, Moreira CDS, Saviano AM, Lourenço FR. Design of experiments (DoE) applied to pharmaceutical and analytical quality by design (QbD). *Brazilian J. Pharm. Sci.* 2018;54:1-16.
22. Saha P, Waghmare D. Parametric optimization for autogenous butt laser welding of sub-millimeter thick SS 316 sheets using central composite design. *Opt. Laser Technol.* 2020;122:105833.
23. Laftani Y, Chatib B, Boussaoud A, El Makhfouk M, Hachkar M, Khayar M. Optimization of diazo dye disappearance by the $\text{UV}/\text{H}_2\text{O}_2$ process using the Box-Behnken design. *Water Sci. Technol.* 2019;80(9):1731-1739.
24. Sathyamoorthy N, Magharla D, Chintamaneni P, Vankayalu S. Optimization of paclitaxel loaded poly (ϵ -caprolactone) nanoparticles using Box Behnken design. *Beni-Suef Univ. J. Basic Appl. Sci.* 2017;6:362-373.
25. Qiu P, Cui M, Kang K et al., Application of Box-Behnken design with response surface methodology for modeling and optimizing ultrasonic oxidation of arsenite with H_2O_2 . *Cent. Eur. J. Chem.* 2014;12:164-172.