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Removal of Brilliant Green from Wastewater by Heat Activated Persulfate Oxidation : Modeling and Optimization.

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Abstract:

The present paper aims to investigate the effect of various operational parameters on the degradation efficiency of the toxic dye “Brilliant Green (BG)” using temperature-activated persulfate (T/SP). The study was carried out by varying the concentration of Brilliant Green (BG) from 5 to 50 mg/L, the concentration of persulfate from 0.42 to 4.2 mM, and the agitation speed from 250 to 350 rpm under a temperature range from 25 to 50°C. Statistical approaches, such as Plackett-Burman Design (PBD) and Response Surface Methodology (RSM), were used in the optimization process. The Plackett-Burman design was carried out using twelve trials, identifying significant parameters such as the Brilliant Green (BG) concentration, the persulfate concentration [SP], and the temperature T. The RSM was used to determine the optimal parameters for degradation. The maximum degradation efficiency (100%) was achieved under the following optimal conditions: T = 25 °C, [SP] = 3.7165 mM, and [BG] = 50 mg/L. Despite a strong correlation between theoretical and practical returns ($R^2 = 93.89\%$). Finally, a confirmatory study using optimized parameter levels showed a good response to the predicted model. The results revealed that the T/SP oxidation system is an effective and promising process for the degradation of BG at room temperature.

Keywords: Brilliant Green (BG) dye, thermally activated persulfate, design of experiments, Plackett-Burman screening, and Box-Behnken design.

1. Introduction

The critical scarcity of potable water sources and high levels of water resource pollution exacerbate the problem. The textile, leather, beverage, food processing, paper, and cosmetics

industries, as well as other sectors, discharge toxic synthetic dyes into surface water, which is one of the main organic pollutants among water pollutants. Dyes are the only organic compounds that lend color to water due to their ability to absorb visible light. This property is attributable to their chromophore, which consists of an associated system, as well as to electronic resonance, giving them remarkable thermal, visual, and chemical stability (Zhang et al. 2011). A cationic dye, Brilliant Green (BG), is widely used as a biological dye, dermatological treatment, and veterinary medicine, as well as in poultry feeding to prevent the growth of mold, intestinal parasites, and fungi (Nandi et al. 2009). Furthermore, this substance is utilized in the rubber and paper industries, as well as in the formulation of disinfectant products, due to its effectiveness in inhibiting the reproduction of gram-positive bacteria. However, due to its confirmed carcinogenic nature and harmful effects on the respiratory tract, the BG dye must be disposed of from industrial liquid waste before being released into aquatic environments (Bose et al. 2021; Mukhopadhyay et al. 2021).

A number of methods, such as coagulation–flocculation (Obiora-Okafo and Onukwuli 2018), chemical treatment (Gao et al. 2007), oxidation (Ahmadi et al. 2018), adsorption (Igwegbe et al. 2016, 2017, 2018), and photocatalytic degradation (Saravanan et al. 2015, 2016a, b), have been used to remove dyes from contaminated waters. Adsorption is the most used method due to its ease of use, affordability, and ability to collect pollutants (Ahmadi et al. 2017). In order to remove dyes, adsorption is often carried out using an adsorbent, such as activated carbon; however, this method just moves contaminants from one phase to another (Ikehata et al. 2008).

Over the years, various treatment techniques have been considered for the removal of BG dye from wastewater, in particular adsorption, electrocoagulation, advanced oxidation processes (AOPs) such as UV/TiO₂, sonolysis, and microwave (MW)-persulfate (PS) oxidation (Aleboyeh et al. 2008; Sohrabi and Ghavami 2008; Tripathy et al. 2020; Yadav et al. 2021).

An effective, promising, and cost-effective wastewater treatment technique involves alternative persulfate-based AOPs. This method is advantageous for being more "environmentally friendly" compared to other physical, chemical, and biological processes, since persulfate-based AOPs do not transfer pollutants from one phase to another or create a large amount of hazardous sludge (Habache and Bechiri 2024).

Persulfate (S₂O₈²⁻) activation can be achieved by heat, UV light, transition metals, and severe alkaline conditions, leading to the production of sulfate radicals (Chen et al. 2017; Dong et al.

2017; He et al. 2014; Ji et al. 2015; Lu et al. 2015; Manz and Carter 2017; Waldemer et al. 2006; Wang et al. 2017; Zhou et al. 2017; Zrinyi and Pham 2017).

In situ thermal activation of persulfate was one of the earliest techniques developed. Despite requiring a lot of energy, it is better than a number of alternatives since it does not require costly or unusual catalysts or be constrained by radiation-related size scaling. Furthermore, the procedure is straightforward to use and apply, requiring minimal supplies. This characteristic makes it highly suitable for industrial applications requiring the utilization of steam or combined heat and power. Moreover, integrating this approach with renewable energy sources has the potential to significantly reduce energy consumption and minimize environmental impact throughout the treatment process (Arvaniti et al. 2022).

The main objective of this study was to evaluate the effectiveness of the temperature-activated persulfate system (T/SP) in the degradation of Brilliant Green (BG) and to examine the effects of key operational parameters such as temperature (T), stirring speed (SS), persulfate concentration ([SP]), and Brilliant Green concentration ([BG]) using a fractional Plackett-Burman factorial design. The secondary objective was to use the response surface methodology (RSM) to improve the most important parameters found during the preliminary selection. A Box-Behnken plan was then used to establish the best circumstances and improve the effectiveness of the degradation.

2. Materials and methods

2.1. Chemicals

The Brilliant green (BG) ($C_{27}H_{33}N_2 \cdot HO_4S$) and Sodium Persulphate ($Na_2S_2O_8$) were purchased from Sigma-Aldrich (USA) and were used as received at Biochem-Chimopharma (France). The molecular structure of BG is shown in Fig. 1. All reagents used in the present study were purchased from high purity (analytical grade) products. All the experiments were carried out using distilled water.

2.2 Experimental procedures

A batch reactor with a capacity of 500 mL was employed to oxidize BG using heat-activated persulfate. As a starting point for each manipulation, a BG solution with concentrations ranging from (5–50 mg/L) was prepared by diluting a stock solution (100 mg/L). For all experiments, a volume of 100 mL of this solution was used. Persulfate was

added at concentrations between (0.42– 4.2 mM). The reaction mixture was homogenized using a magnetic stirrer at a speed between (250 - 350 rpm). The treatment was carried out at temperatures of 25 and 50 ° C for 120 minutes under neutral pH. Sample analyses were performed by a UV-visible spectrophotometer at $\lambda_{max} = 625 \text{ nm}$ (Soltani-nezhad et al. 2020). The degradation efficiency (DE) was calculated according to Equation 1(Burgot and Burgot 2011).

$$DE(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Where DE is the degradation efficiency, C_i is the initial dye concentration, and C_f is the final dye concentration.

3. Results and discussion

3.1. Screening design PBD

The statisticians R.L. Plackett and J.P. Burman, aiming at providing information mainly on the individual effect of factors without taking into account their interactions (Plackett and Burman 1946), developed a screening plan in 1946. A two-level fractional factorial design, allowing the analysis of N-1 factors (where N is a multiple of 4), is designated as the Plackett-Burman (P-B) plan. The Plackett-Burman Design (PBD) is thus a two-level experimental design. It is widely used due to its effectiveness and low cost, despite certain limitations, in particular the lack of consideration of interactions between factors (Narendran et al. 2019). According to the PBD methodology, each parameter is considered independent and follows a first-order model:

$$Y = \beta_0 + \sum \beta_i + X_i \quad (2)$$

Where Y is the predicted target response, β_0 is the model intercept, β_i is the regression coefficient, and X_i is an independent parameter.

The BG degradation was accomplished by simultaneously varying four parameters, as indicated in Table 1. Following an exhaustive review of the literature and the carrying out of preliminary tests, the minimum and maximum levels of each parameter have been defined. The various operating conditions for the degradation by thermal activation of persulfate, established according to an experimental Plackett-Burman design, are presented in Table 2. Moreover, the experimental results relating to the efficiency of the degradation

are presented. During the twelve tests carried out, the degradation efficiency varied between 2% and 100% at temperatures of 25°C and 50 °C, respectively. These experimental data form the basis for all subsequent statistical analyses.

3.1.1. Pareto chart and half-normal plots

The most crucial elements can be found using the Pareto effects diagram. For easier comparison, the effects are standardized using the value (F-value). More precisely, the effect of each factor is divided by the error associated with the estimation of this factor to obtain a standardized value (Habache et al. 2021).

According to Fig. 2, when the value F of a factor is greater than 2.365 and for a confidence interval fixed at 95%, the effect is considered significant. The increase in the production of sulfate radicals as a function of the persulfate concentration ([SP]), the temperature (T), and the Brilliant Green concentration ([BG]) clearly indicates that the persulfate concentration constitutes the most influential factor. On the other hand, the stirring speed was considered not significant for the two degradation responses (DE) because its effect does not exceed the reference line drawn on the graph. Moreover, since the factors furthest from the noise line ([SP], T, and [BG]) are the most significant, the graph of standardized effects (Fig. 3) confirms the observations obtained from the Pareto diagrams.

3.1.2 Main effects

The variation in the reaction response induced by a modification in the amount of a factor is designated by the term “effect.” The main effects of the various variables on the degradation efficiency of brilliant green (BG) are illustrated in Fig. 4. It clearly appears that, while the pollutant concentration and the stirring speed exert a negative impact on the degradation efficiency, the persulfate concentration as well as the temperature have a positive effect on the reaction. Therefore, an increase in these two parameters is likely to significantly improve the degradation efficiency of the BG. When using activated persulfate for the degradation of contaminants, temperature is a determining factor. The results obtained are in agreement with previous work, indicating that the degradation efficiency of BG increases with increasing temperature. This improvement is attributed to the increase in the fission of O–O bonds in persulfates (SPS) under the effect of temperature, which leads to an acceleration of the degradation rate of AB92 (Luo 2014; Rahmani et al. 2016). The high temperature favors the elimination of pollutants by providing

the energy necessary for the rupture of the O–O bonds within the persulfate, thus generating active species such as $\text{OH}^\bullet$ and $\text{SO}_4^{\bullet-}$ (Gao et al. 2015). In addition, it is important to note that high temperatures also facilitate the degradation of non-organic chemical compounds through activated SPS.

The sodium persulfate concentration is considered a critical and determining factor in the thermally activated oxidation of persulfate since it directly influences the balance of sulfate radicals. Therefore, the effect of the sodium persulfate concentration on the degradation of the dye has been thoroughly studied. Increasing the SP concentration from 0.42 to 4.2 mM resulted in a significant degree of BG elimination, as shown in Fig. 4. In comparison to the persulfate anion, the sulfate radical exhibited enhanced reduction and oxidation capabilities and had the capacity to break down a significant quantity of organic compounds. Higher concentrations of persulfate favor the formation of an increased number of sulfate radicals, which act as reactive species that effectively degrade contaminants, following the reactions described in equations 3 and 4 (Pokhalekar and Chakraborty 2016). Moreover, the persulfate ions can be regenerated by the reaction of these sulfate radicals (Soubh and Mokhtarani 2016).



Degradation efficiency decreases with the increase in the pollutant concentration, which is explained by the substantial and adverse impact of BG concentration on the degradation process. This phenomenon can be attributed to the fact that the number of persulfate radicals remains constant. In contrast, the number of BG molecules increases in proportion to the dye's initial concentration. Consequently, both the degradation efficiency and the kinetics of the degradation response are reduced (Habache and Bechiri 2024).

3.1.3. Analysis of variance

In order to definitively examine the impact of the factors on the variations of a given response, the analysis of variance (ANOVA) is used to compare the variances of the values determined by the model with the variances of the residuals. The probability that an effect is statistically significant is considered high when the confidence level reaches 95%, 99% or 99.9% (Loukas 2001; Ryan 1989). The P-value (Table 3) is a statistical metric that can be used to identify the most significant elements. This value is compared with a threshold α , representing the risk of model error, generally set at 5%. Table 4 shows the coefficients relating to the various parameters studied. The average amplitude of the variation in the efficiency of the degradation,

when the parameters evolve from the level (-1) to the level (+1), is quantified by the algebraic values of these coefficients.

3.1.4. Polynomial regression

By using a mathematical model that considers all the variables using polynomial equations, the experimental design method maximizes the system's response, namely the efficiency of the degradation. The regression equations are presented in the forms (5) and (6), corresponding respectively to the parameters expressed in non-coded and coded values:

Uncoded Units

$$DE = 15.5 - 0.633[BG] + 13.47[SP] - 0.030SS + 1.302 T \quad (5)$$

Coded Unit

$$DE = 69.05 - 14.24[BG] + 25.46[SP] - 1.49SS + 16.27 T \quad (6)$$

Furthermore, the comparison of the measured and calculated responses presented in Table 5 reveals a high coefficient of determination ($R^2 = 84.10\%$). The adjusted R-squared value ($R_{adj}^2 = 75.01\%$) confirms that it shows a good connection.

3.2. Optimization of factors using Box-Behnken Design (BBD)

The concentrations of persulfate [SP] and Brilliant Green [BG], along with the temperature T, were determined to be significant for the dye degradation based on the results of screening various parameters using the Plackett-Burman design. Meanwhile, the stirring speed was fixed at a minimum of 250 rpm. Following the PB screening design, the three significant variables were further optimized and validated using the Box–Behnken Design (BBD) (Table 6), comprising 12 experimental runs and 3 center points (Table 7). This approach allowed for the evaluation of the main, interaction, and quadratic effects of the significant factors on the selected response (degradation efficiency). Furthermore, Box–Behnken has been shown to be among the most effective response surface designs compared to other designs (Ferreira et al. 2007). The following quadratic equation described the system's behavior:

$$Y = b_0 + \sum b_i X_i + \sum b_{ij} X_i X_j + \sum b_{ii} X_i^2 \quad (7)$$

Where Y was the predicted response (degradation efficiency); b_0 was the offset term; b_i was the linear effect; b_{ii} was the squared effect, and b_{ij} was the interaction effect. The coded independent variables are denoted by X_i and X_j . The coefficients of second-order polynomials were computed and examined using Minitab 19. To assess the analysis of variance (ANOVA), a statistical study of the model was conducted.

The Response Surface Methodology (RSM), a set of statistical and mathematical methods, was used to optimize degradation efficiency using experimental Box-Behnken (BBD) designs (El-Naggar et al. 2018; Jabeen et al. 2015). Specifically, the effects of temperature T and persulfate [SP] and Brilliant Green [BG] concentrations were investigated through this approach (Tables 6 and 7).

3.2.1 Main effects plot and interactions for DE (%)

The impact of the factors studied in the selected field on the degradation efficiency of Brilliant Green (BG) is illustrated in Fig. 5. According to the latter, the degradation efficiency of the BG increases with the increase in the persulfate concentration ([SP]), the maximum efficiency being reached for [SP] = 4.2 mM after one minute of reaction time. Since the generation of sulfate radicals $SO_4^{\bullet-}$ in the oxidation system comes exclusively from the persulfate anion; the increase in the SP concentration strengthens the oxidizing capacity of the system to degrade organic substances (Liu et al. 2018).

From a practical point of view, it was essential to determine the optimal temperature for the oxidation process in order to maximize the efficiency of degradation of the pollutant by activation of the persulfate. Moreover, the persulfate can be thermally activated to produce $SO_4^{\bullet-}$ (Hu et al. 2018), therefore making the rise in temperature, from 25°C to 50°C, particularly beneficial.

An interaction diagram illustrates the influence of variation in one factor on another. It is generally used as a complement to an analysis of variance (ANOVA) and is particularly useful for assessing the existence of interactions between factors. When the lines of an interaction diagram are parallel, this indicates the absence of interaction. Conversely, the more the lines deviate from parallelism, the more significant the degree of interaction between the factors (Habache et al. 2021).

In Figure 6, the adjusted mean degradation efficiency is plotted against different combinations of persulfate concentration ([SP]), temperature (T) and Brilliant Green concentration (BG). Observation of this figure reveals that the lines drawn are not all parallel, indicating that the relationship between each factor and degradation efficiency depends on the value of the other factors. This highlights the existence of significant interaction effects.

3.2.2. Analysis of variance and polynomial regression

Table 8 presents the results of the statistical analysis. Variance analysis (ANOVA) is a method for designing experiments to refine the definition of objective function by evaluating the influence of each parameter studied. Indeed, it should be stressed that not all factors have an equivalent influence; some have a significant effect while others are negligible (Habache et al. 2021).

The value of $P = 0.015$ obtained for the global model indicates that it is statistically significant. Furthermore, the linear effects taken individually, with a value of $p = 0.005 (< 0.05)$, also demonstrate the existence of significant linear effects for the main factors studied, namely the persulfate concentration [SP], Brilliant Green [BG], and temperature (T).

Persulphate concentration [SP], temperature T, and Brilliant Green concentration [BG] are the three quadratic terms included in the model. All the interactions and quadratic effects associated with these parameters have p-values greater than 0.05. Consequently, no significant variation in degradation efficiency is observed when the quadratic and interaction effects of these three factors are modified, suggesting that there is no significant curvature in the response surfaces.

The regression coefficients were calculated from the coded data using MINITAB version 19 software, as shown in Table 9. By using a mathematical model incorporating all the variables, the experimental design method makes it possible to optimize the system response, in this case the degradation efficiency. Polynomial equations (8) and (9), for the coded and uncoded parameters, respectively, formalize the regression models obtained.

$$\begin{aligned}
 DE = & -46.5 - 0.54 [BG] + 52.1 [SP] + 3.26 T - 0.0034 [BG] * [BG] - 5.07[SP] * [SP] \\
 & - 0.0088 T * T + 0.258[BG] * [SP] - 0.0032 [BG] * T - 0.661 [SP] * T \quad (8)
 \end{aligned}$$

$$\begin{aligned}
 DE = & 95 - 5.69 [BG] + 20.74 [SP] + 12.3 T - 1.77 [BG] * [BG] - 18.11 [SP] * [SP] \\
 & - 1.37 T * T + 10.96 [BG] * [SP] - 0.90 [BG] * T - 15.62 [SP] * T \quad (9)
 \end{aligned}$$

The results of the analysis of variance (ANOVA) presented in Table 9 indicate that the model is predictable with a confidence interval of 95%, associated with a coefficient of determination (R^2) of 0.9389. These results attest to the reliability of the equation obtained, thus confirming the suitability of the model for prediction within the range of the variables studied. Therefore, the model can be considered of satisfactory quality, insofar as it explains 93.89% of the observed variations in the response. The studied phenomenon is correctly described by the established model. The results from the modeled equations, expressed in terms of theoretical degradation efficiency, are compared with the experimental degradation efficiency in Table 7.

3.2.3. Response surface and contour

The three-dimensional representation of the response surface from the regression model is a valuable tool for clarifying and interpreting the results of statistical and mathematical analyses (Li et al. 2022). To test experimental data from the Box–Behnken design, response surface plots and contour plots were created. These plots allow the relationship between two variables to be studied simultaneously, while the other variables are held constant. These plots graphically represent the response over a range of relevant factor levels, illustrating the magnitude of factor interactions and the sensitivity of the response to changes in the levels of each factor.

Furthermore, these plots made it possible to determine optimal response values and the expected operating conditions. In addition, it was observed that the orientation of the response surface varied depending on the operational parameters studied, namely persulfate ([SP]) and Brilliant Green ([BG]) concentrations, as well as temperature (T). At the conditions of $T = 50\text{ }^{\circ}\text{C}$ (Fig. 7), $[\text{SP}] = 4.2\text{ mM}$ (Fig. 8) and $[\text{BG}] = 50\text{ mg/L}$ (Fig. 9), the maximum degradation efficiency was achieved.

3.2.4. Desirability Plots

The primary goal of this research is to optimize the operating parameters to obtain the intended objective response. Utilizing the desirability function for multi-objective response optimization is a particularly suitable and effective approach for this purpose (Chaabouni et al. 2012). It should be emphasized that achieving a 100% degradation efficiency is particularly challenging when using costly reagents and greater pollutant concentrations. Therefore, this study aims to optimize the degradation efficiency (DE) by determining the ideal operating settings. The parameters subject to optimization include temperature T, Brilliant Green concentration [BG], and persulfate concentration [SP].

The optimal combination of factors was obtained at a temperature of $25\text{ }^{\circ}\text{C}$, [SP] of 3.7165 mM, and [BG] of 50 mg/L, as indicated by a desirability value of around 1.0000. The desirability plot for DE is presented in Fig. 10. With all parameters optimized, the degrading efficiency may be determined from the theoretical model with a value of 100%. To validate these optimal conditions, a double experimental verification was performed under identical settings, achieving 100% degradation efficiency of BG. Thus, the model proved adequate to depict the procedure.

Conclusion

This article focused on the study of the oxidation of the Brilliant Green dye (BG) by thermally activated persulfate. In order to identify the most decisive operational parameters for the degradation of the BG, an initial screening strategy was implemented. An experimental plan by Plackett-Burman made it possible to simultaneously modulate several operating variables, in particular the temperature, the stirring speed, the persulfate concentration, and the Brilliant Green concentration, in order to evaluate their influence on the degradation efficiency. An in-depth statistical analysis was thus carried out to quantify the relative impact of each of these factors, leading to the identification of the optimal levels associated with the best performance.

The results revealed that the three most significant variables for the efficiency of the degradation of BG were the temperature, the persulfate concentration, and the Brilliant Green concentration. These major effects were confirmed by a Box-Behnken plan, based on the response surface methodology (RSM), which made it possible to deepen the study of these parameters. The optimal conditions were established at 25°C and a persulfate concentration of 3.7165 mM, leading to a complete degradation (100%) of the BG at an initial concentration of 50 mg/L.

Obtaining maximum efficiency with a minimum of consumables testifies to the high potential of the advanced oxidation process by thermally activated persulfate. These results strongly encourage the application of this technology in industrial and technological contexts, with a view to an efficient and economical treatment of effluents contaminated with synthetic dyes.

References

Ahmadi S, Banach A, Mostafapour FK, Balarak D (2017) Study survey of cupric oxide nanoparticles in removal efficiency of ciprofloxacin antibiotic from aqueous solution: adsorption isotherm study. *Desalin Water Treat* 89:297-303.

<https://doi.org/10.5004/dwt.2017.21362>

Ahmadi S, Mohammadi L, Igwegbe CA, Rahdar S, Banach AM (2018) Application of response surface methodology in the degradation of Reactive Blue 19 using H₂O₂/MgO nanoparticles advanced oxidation process. *Int J Ind Chem* 9:241-253.

<https://doi.org/10.1007/s40090-018-0153-4>

Aleboyeh A, Daneshvar N, Kasiri MB (2008) Optimization of C.I. Acid Red 14 azo dye removal by electrocoagulation batch process with response surface methodology. *Chem Eng Process: Process Intensif* 47:827-832.

<https://doi.org/10.1016/j.cep.2007.01.033>

Arvaniti OS, Ioannidi AA, Mantzavinos D, Frontistis Z (2022) Heat-activated persulfate for the degradation of micropollutants in water: A comprehensive review and future perspectives. *J Environ Manage* 318:115568.

<https://doi.org/10.1016/j.jenvman.2022.115568>

Bose S, Kumar Tripathy B, Debnath A, Kumar M (2021) Boosted sono-oxidative catalytic degradation of Brilliant green dye by magnetic MgFe_2O_4 catalyst: Degradation mechanism, assessment of bio-toxicity and cost analysis. *Ultrason Sonochem* 75:105592.

<https://doi.org/10.1016/j.ultsonch.2021.105592>

Burgot G, Burgot J-L (2011) Méthodes instrumentales d'analyse chimique et applications: Méthodes chromatographiques, électrophorèses, méthodes spectrales et méthodes thermiques. Lavoisier, France.

Chaabouni M, Ayedi H, Kamoun A (2012) Plans d'expériences et traitements de surface—Etude quantitative des effets et interactions. *Techniques De L'ingénieur* 1428.

Chen Y, Deng P, Xie P, Shang R, Wang Z, Wang S (2017) Heat-activated persulfate oxidation of methyl- and ethyl-parabens: Effect, kinetics, and mechanism. *Chemosphere* 168:1628-1636.

<https://doi.org/10.1016/j.chemosphere.2016.11.143>

Dong H, Qiang Z, Hu J, Sans C (2017) Accelerated degradation of iopamidol in iron activated persulfate systems: Roles of complexing agents. *Chem Eng J* 316:288-295.

<https://doi.org/10.1016/j.cej.2017.01.099>

El-Naggar NE-A, Hamouda RA, Mousa IE, Abdel-Hamid MS, Rabei NH (2018) Biosorption optimization, characterization, immobilization and application of *Gelidium amansii* biomass for complete Pb^{2+} removal from aqueous solutions. *Sci Rep* 8:13456.

<https://doi.org/10.1038/s41598-018-31660-7>

Ferreira SLC, Bruns RE, Ferreira HS, Matos GD, David JM, Brandão GC, da Silva EGP, Portugal LA, dos Reis PS, Souza AS, dos Santos WNL (2007) Box-Behnken design: An alternative for the optimization of analytical methods. *Anal Chim Acta* 597:179-186.

<https://doi.org/10.1016/j.aca.2007.07.011>

Gao B-Y, Yue Q-Y, Wang Y, Zhou W-Z (2007) Color removal from dye-containing wastewater by magnesium chloride. *J Environ Manage* 82:167-172.

<https://doi.org/10.1016/j.jenvman.2005.12.019>

Gao Y-q, Gao N-y, Deng Y, Yin D-q, Zhang Y-s, Rong W-l, Zhou S-d (2015) Heat-activated persulfate oxidation of sulfamethoxazole in water. *Desalin Water Treat* 56:2225-2233.

<https://doi.org/10.1080/19443994.2014.960471>

Habache N, Bechiri O (2024) Thermally activated persulfate oxidation of Basic Fuchsin dye: Effect of different operating parameters, kinetic, and thermodynamic study. *Int J Chem Kinet* 56:30-42.

<https://doi.org/10.1002/kin.21690>

Habache N, Bechiri O, Djaghout I, Djenouhet M (2021) Modelling and optimizing Orange G removal by heat-activated persulfate using two-step statistical strategies: Plackett–Burman and Box–Behnken designs. *Desalin Water Treat* 244:291-301.

<https://doi.org/10.5004/dwt.2021.27904>

He X, Mezyk SP, Michael I, Fatta-Kassinos D, Dionysiou DD (2014) Degradation kinetics and mechanism of β -lactam antibiotics by the activation of H_2O_2 and $Na_2S_2O_8$ under UV-254nm irradiation. *J Hazard Mater* 279:375-383.

<https://doi.org/10.1016/j.jhazmat.2014.07.008>

Hu X, Yue Y, Peng X (2018) Release kinetics of vanadium from vanadium titano-magnetite: The effects of pH, dissolved oxygen, temperature and foreign ions. *J Environ Sci* 64:298-305.

<https://doi.org/10.1016/j.jes.2017.07.001>

Igwegbe CA, Onyechi PC, Onukwuli OD, Nwokedi IC (2016) Adsorptive treatment of textile wastewater using activated carbon produced from *Mucuna pruriens* seed shells. *World J Eng Technol* 4:21-37.

<https://doi.org/10.4236/wjet.2016.41003>

Igwegbe CA, Onukwuli OD, Nwabanne JT (2017) Adsorptive Removal of Vat Yellow 4 on Activated *Mucuna pruriens* (Velvet Bean) Seed Shells Carbon. *Asian J Chem Sci* 1:1-16.

<https://doi.org/10.9734/ajocs/2016/30210>

Igwegbe CA, Banach AM, Ahmadi S (2018) Adsorption of Reactive Blue 19 from aqueous environment on magnesium oxide nanoparticles: kinetic, isotherm and thermodynamic studies. *Pharm Chem J* 5:111-121.

Ikehata K, Gamal El-Din M, Snyder SA (2008) Ozonation and Advanced Oxidation Treatment of Emerging Organic Pollutants in Water and Wastewater. *Ozone: Sci Eng* 30:21-26.

<https://doi.org/10.1080/01919510701728970>

Jabeen H, Iqbal S, Anwar S, Parales RE (2015) Optimization of profenofos degradation by a novel bacterial consortium PBAC using response surface methodology. *Int Biodeterior Biodegrad* 100:89-97.

<https://doi.org/10.1016/j.ibiod.2015.02.022>

Ji Y, Dong C, Kong D, Lu J, Zhou Q (2015) Heat-activated persulfate oxidation of atrazine: Implications for remediation of groundwater contaminated by herbicides. *Chem Eng J* 263:45-54.

<https://doi.org/10.1016/j.cej.2014.10.097>

Li Q, Chai C, Du Y, Cai J, Zhao L (2022) Recombinant Laccase Production Optimization in *Pichia pastoris* by Response Surface Methodology and Its Application in the Biodegradation of Octyl Phenol and 4-Tert-Octylphenol. *Catal Lett* 152:1086-1099.

<https://doi.org/10.1007/s10562-021-03682-w>

Liu L, Lin S, Zhang W, Farooq U, Shen G, Hu S (2018) Kinetic and mechanistic investigations of the degradation of sulfachloropyridazine in heat-activated persulfate oxidation process. *Chem Eng J* 346:515-524.

<https://doi.org/10.1016/j.cej.2018.04.068>

Loukas YL (2001) A Plackett–Burnam screening design directs the efficient formulation of multicomponent DRV liposomes. *J Pharm Biomed Anal* 26:255-263.

[https://doi.org/10.1016/S0731-7085\(01\)00419-8](https://doi.org/10.1016/S0731-7085(01)00419-8)

Lu J, Wu J, Ji Y, Kong D (2015) Transformation of bromide in thermo activated persulfate oxidation processes. *Water Res* 78:1-8.

<https://doi.org/10.1016/j.watres.2015.03.028>

Luo Q (2014) Oxidative treatment of aqueous monochlorobenzene with thermally-activated persulfate. *Front Environ Sci Eng* 8:188-194.

<https://doi.org/10.1007/s11783-013-0544-x>

Manz KE, Carter KE (2017) Investigating the effects of heat activated persulfate on the degradation of furfural, a component of hydraulic fracturing fluid chemical additives. *Chem Eng J* 327:1021-1032.

<https://doi.org/10.1016/j.cej.2017.06.168>

Mukhopadhyay A, Tripathy BK, Debnath A, Kumar M (2021) Enhanced persulfate activated sono-catalytic degradation of brilliant green dye by magnetic CaFe_2O_4 nanoparticles: Degradation pathway study, assessment of bio-toxicity and cost analysis. *Surf Interfaces* 26:101412.

<https://doi.org/10.1016/j.surfin.2021.101412>

Nandi BK, Goswami A, Purkait MK (2009) Adsorption characteristics of brilliant green dye on kaolin. *J Hazard Mater* 161:387-395.

<https://doi.org/10.1016/j.jhazmat.2008.03.110>

Narenderan ST, Meyyanathan SN, Karri VVSR (2019) Experimental design in pesticide extraction methods: A review. *Food Chem* 289:384-395.

<https://doi.org/10.1016/j.foodchem.2019.03.045>

Obiora-Okafo I, Onukwuli O (2018) Characterization and optimization of spectrophotometric colour removal from dye containing wastewater by Coagulation-Flocculation. *Green Sci* 20:49-59.

<https://doi.org/10.2478/pjct-2018-0054>

Plackett RL, Burman JP (1946) The Design of Optimum Multifactorial Experiments. *Biometrika* 33:305-325.

<https://doi.org/10.1093/biomet/33.4.305>

Pokhalekar P, Chakraborty M (2016) Degradation of bisphenol A and 4-tert-octylphenol: a comparison between ultrasonic and photocatalytic technique. *Desalin Water Treat* 57:10370-10377.

<https://doi.org/10.1080/19443994.2015.1041053>

Rahmani AR, Rezaeivahidian H, Almasi M, Shabanlo A, Almasi H (2016) A comparative study on the removal of phenol from aqueous solutions by electro-Fenton and electro-persulfate processes using iron electrodes. *Res Chem Intermed* 42:1441-1450.

<https://doi.org/10.1007/s11164-015-2095-1>

Ryan TP (1989) Statistical methods for quality improvement. Wiley, New York.

Saravanan R, Mansoob Khan M, Gupta VK, Mosquera E, Gracia F, Narayanan V, Stephen A (2015) ZnO/Ag/CdO nanocomposite for visible light-induced photocatalytic degradation of industrial textile effluents. *J Colloid Interface Sci* 452:126-133.

<https://doi.org/10.1016/j.jcis.2015.04.035>

Saravanan R, Khan MM, Gracia F, Qin J, Gupta VK, Arumainathan S (2016) Ce³⁺-ion-induced visible-light photocatalytic degradation and electrochemical activity of ZnO/CeO₂ nanocomposite. *Sci Rep* 6:31641.

<https://doi.org/10.1038/srep31641>

Saravanan R, Sacari E, Gracia F, Khan MM, Mosquera E, Gupta VK (2016) Conducting PANI stimulated ZnO system for visible light photocatalytic degradation of coloured dyes. *J Mol Liq* 221:1029-1033.

<https://doi.org/10.1016/j.molliq.2016.06.074>

Sohrabi MR, Ghavami M (2008) Photocatalytic degradation of Direct Red 23 dye using UV/TiO₂: Effect of operational parameters. *J Hazard Mater* 153:1235-1239.

<https://doi.org/10.1016/j.jhazmat.2007.09.114>

Soltani-nezhad F, Saljooqi A, Mostafavi A, Shamspur T (2020) Synthesis of Fe₃O₄/CdS–ZnS nanostructure and its application for photocatalytic degradation of chlorpyrifos pesticide and brilliant green dye from aqueous solutions. *Ecotoxicol Environ Saf* 189:109886.

<https://doi.org/10.1016/j.ecoenv.2019.109886>

Soubh A, Mokhtarani N (2016) The post treatment of composting leachate with a combination of ozone and persulfate oxidation processes. *RSC Adv* 6:76113-76122.

<https://doi.org/10.1039/c6ra09539a>

Tripathy BK, Kumar S, Kumar M, Debnath A (2020) Microwave induced catalytic treatment of brilliant green dye with carbon doped zinc oxide nanoparticles: Central composite design, toxicity assessment and cost analysis. *Environ Nanotechnol Monit Manag* 14:100361.

<https://doi.org/10.1016/j.enmm.2020.100361>

Waldemer RH, Tratnyek PG, Johnson RL, Nurmi JT (2006) Oxidation of Chlorinated Ethenes by Heat-Activated Persulfate: Kinetics and Products. *Environ Sci Technol* 41:1010-1015.

<https://doi.org/10.1021/es062237m>

Wang Q, Lu X, Cao Y, Ma J, Jiang J, Bai X, Hu T (2017) Degradation of Bisphenol S by heat activated persulfate: Kinetics study, transformation pathways and influences of co-existing chemicals. *Chem Eng J* 328:236-245.

<https://doi.org/10.1016/j.cej.2017.07.041>

Yadav AA, Hunge YM, Kang S-W (2021) Porous nanoplate-like tungsten trioxide/reduced graphene oxide catalyst for sonocatalytic degradation and photocatalytic hydrogen production. *Surf Interfaces* 24:101075.

<https://doi.org/10.1016/j.surfin.2021.101075>

Zhang L, Liu X, Guo X, Su M, Xu T, Song X (2011) Investigation on the degradation of brilliant green induced oxidation by NiFe_2O_4 under microwave irradiation. *Chem Eng J* 173:737-742.

<https://doi.org/10.1016/j.cej.2011.08.041>

Zhou L, Ferronato C, Chovelon J-M, Sleiman M, Richard C (2017) Investigations of diatrizoate degradation by photo-activated persulfate. *Chem Eng J* 311:28-36.

<https://doi.org/10.1016/j.cej.2016.11.066>

Zrinyi N, Pham AL-T (2017) Oxidation of benzoic acid by heat-activated persulfate: Effect of temperature on transformation pathway and product distribution. *Water Res* 120:43-51.

<https://doi.org/10.1016/j.watres.2017.04.066>

Table 1 : Parameters and levels

Factor	Symbol	Unit	Level	
			Low (-1)	High (+1)
Brilliant Green concentration	[BG]	mg/L	5	50
Persulfate concentration	[SP]	mM	0.42	4.2
stirring speed	SS	Rpm	250	350
Temperature	T	°C	25	50

Table 2: Results of experiments using the Plackett-Burman design

Run	[BG]	[SP]	SS	T	DE (%)
1	5	0.42	250	25	35.03
2	50	0.42	250	25	8.90
3	50	0.42	350	25	2.76
4	5	4.20	350	50	100
5	5	4.20	250	50	90.18
6	50	0.42	350	50	28.85
7	5	0.42	250	50	92.06
8	50	4.20	250	50	99.48
9	50	4.20	350	25	91.25
10	5	0.42	350	50	93.95
11	50	4.20	250	50	97.58
12	5	4.20	350	25	88.52

Table 3: Analysis of Variance (ANOVA).

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	4	13414.5	3353.63	9.25	0.006
Linear	4	13414.5	3353.63	9.25	0.006
[BG]	1	2434.5	2434.47	6.72	0.036
[SP]	1	7775.5	7775.48	21.45	0.002
SS	1	26.7	26.70	0.07	0.794
T	1	3177.9	3177.86	8.77	0.021
Error	7	2537.0	362.43		
Lack-of-Fit	6	2535.2	422.53	234.09	0.050
Pure Error	1	1.8	1.81		
Total	11	15951.5			

Table 4 : Effects and coefficients of the estimated efficiency (coded units)

Term	Effect	Coef	SE Coef	T-Value	P-Value
Constant		69.05	5.50	12.56	0.000
[BG]	-28.49	-14.24	5.50	-2.59	0.036
[SP]	50.91	25.46	5.50	4.63	0.002
SS	-2.98	-1.49	5.50	-0.27	0.794
T	32.55	16.27	5.50	2.96	0.021

Table 5: Comparison between estimated and experimental efficiency

Run	DE _{exp} (%)	DE _{est} (%)
1	35.03	43.05
2	8.90	14.577
3	2.76	11.58
4	100	123.527
5	90.18	93.96
6	28.85	44.13
7	92.06	75.60
8	99.48	98.02
9	91.25	62.49
10	93.95	72.62
11	97.58	98.02
12	88.52	90.980

Table 6: Parameters and levels in the Box-Behnken design .

Factor	Symbol	Unit	Levels		
			Low (-1)	Medium (0)	High (+1)
Brilliant concentration	Green [BG]	mg/L	5	27.5	50
Persulfate concentration	[SP]	mM	0.42	2.31	4.2
Temperature	T	°C	25	37.5	50

Table 7: Box-Behnken plan with experimental responses.

Run order	[BG]	[SP]	T	DE _{exp} (%)	DE _{est} (%)
1	5	0.42	37.5	47.77	39.11
2	5	4.2	37.5	88.63	76.82
3	50	0.42	37.5	5.11	16.92
4	50	4.2	37.5	27.55	36.20
5	27.5	0.42	25	2.82	1.53
6	27.5	4.2	25	5.48	7.34
7	27.5	0.42	50	48.28	46.42
8	27.5	4.2	50	96.27	97.85
9	5	2.31	25	26.53	36.48
10	50	2.31	25	4.89	-5.63
11	5	2.31	50	82.82	93.34
12	50	2.31	50	82.59	72.464
13	27.5	2.31	37.5	29.44	27.60
14	27.5	2.31	37.5	27.31	27.60
15	27.5	2.31	37.5	26.06	27.60

Table 8: Analysis of Variance (ANOVA).

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	4	13414.5	3353.63	9.25	0.006
Linear	4	13414.5	3353.63	9.25	0.006
[BG]	1	2434.5	2434.47	6.72	0.036
[SP]	1	7775.5	7775.48	21.45	0.002
SS	1	26.7	26.70	0.07	0.794
T	1	3177.9	3177.86	8.77	0.021
Error	7	2537.0	362.43		
Lack-of-Fit	6	2535.2	422.53	234.09	0.050
Pure Error	1	1.8	1.81		
Total	11	15951.5			

Table 9: Regression coefficients estimated for efficiency DE (%) of BG.

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	95.00	5.73	16.57	0.000	
[BG]	-5.69	3.51	-1.62	0.166	1.00
[SP]	20.74	3.51	5.91	0.002	1.00
T	12.30	3.51	3.50	0.017	1.00
[BG]*[BG]	-1.73	5.17	-0.33	0.752	1.01
[SP]*[SP]	-18.11	5.17	-3.50	0.017	1.01
T*T	-1.37	5.17	-0.27	0.801	1.01
[BG]*[SP]	10.96	4.97	2.21	0.078	1.00
[BG]*T	-0.90	4.97	-0.18	0.863	1.00
[SP]*T	-15.62	4.97	-3.15	0.026	1.00

$$R^2 = 93.89\% \quad , \quad R^2_{adj} = 82.90\%$$

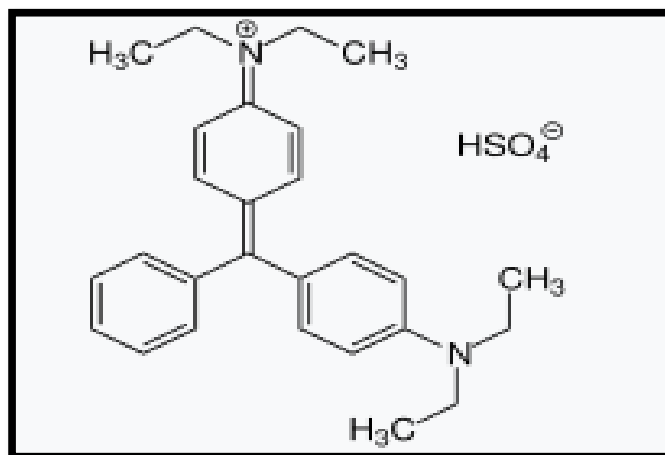


Figure 1: Molecular structure of BG.

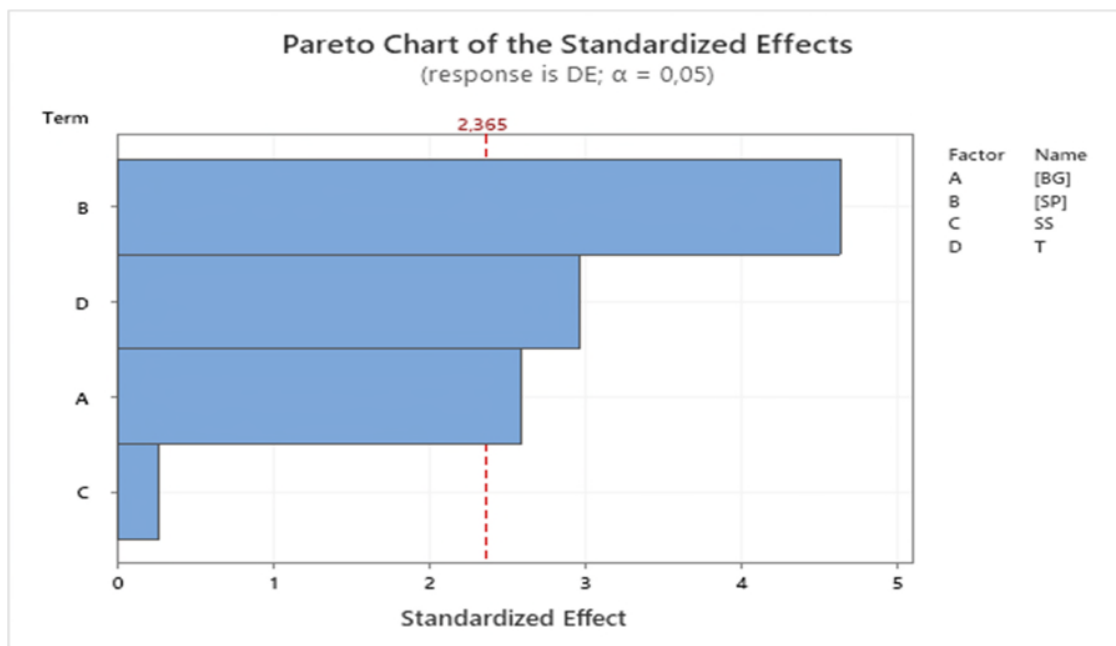


Figure2: Pareto chart of the standardized effects for DE (%) as response (Alpha=0,05).

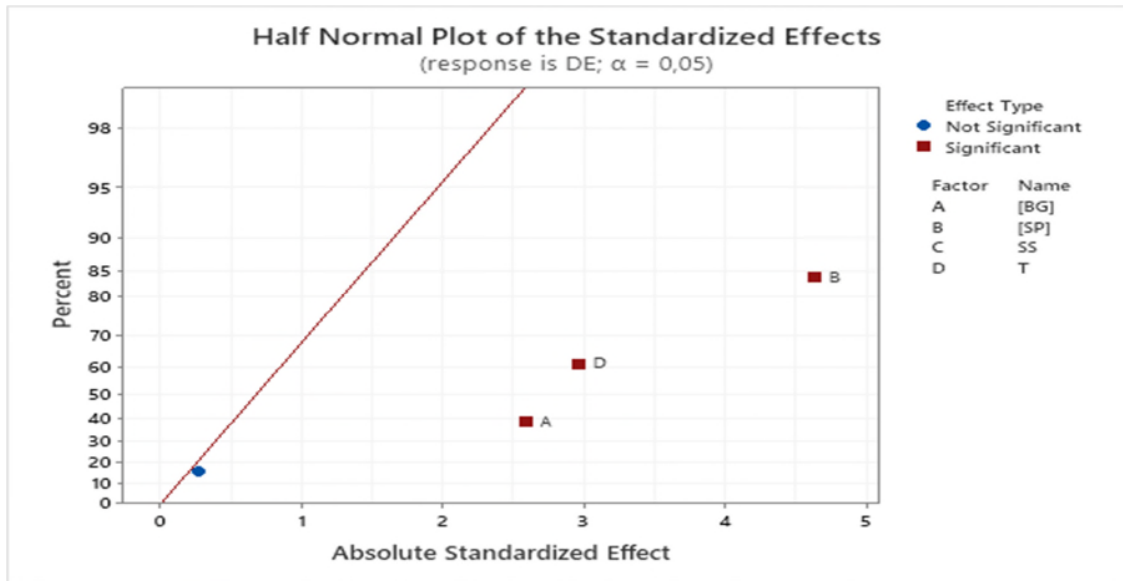


Figure 3: Half-normal plots of the standardized effect for DE (%).

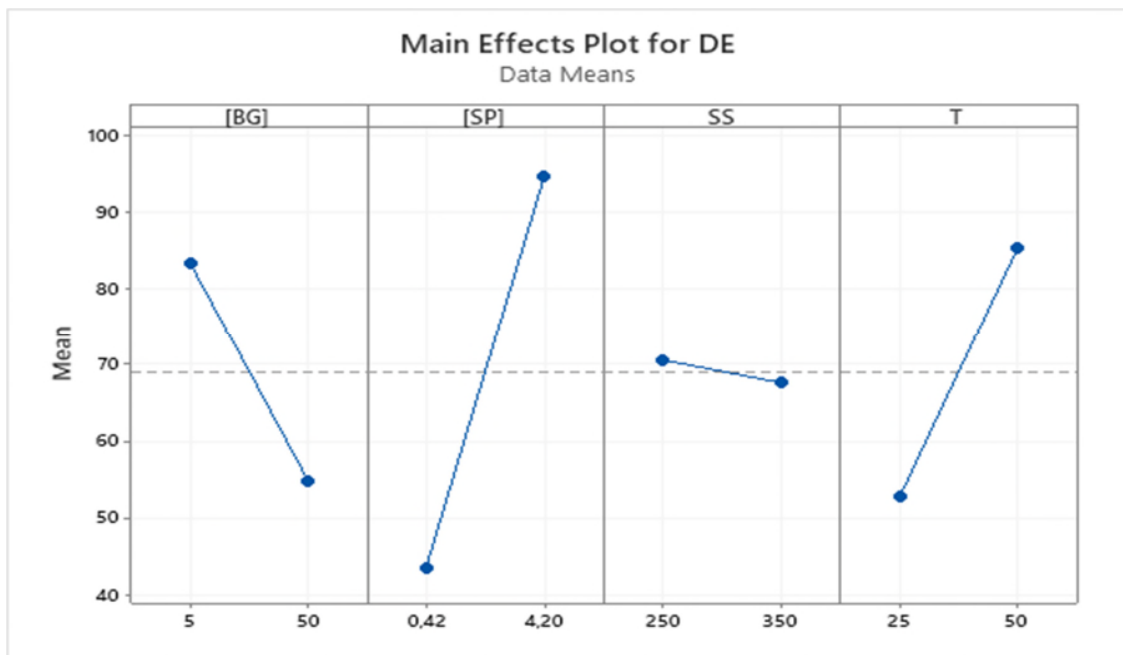


Figure 4 : Main effects plot of parameters for DE (%).

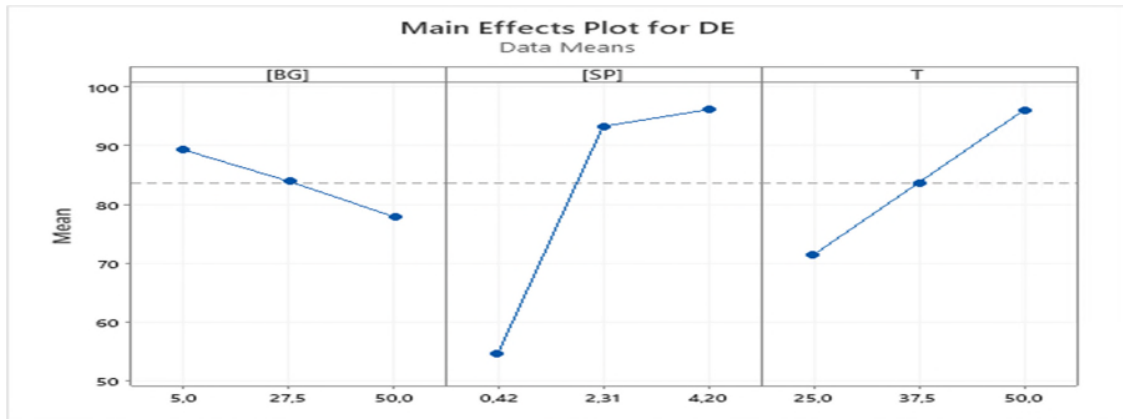


Figure 5 : Main effect plot for DE (%).

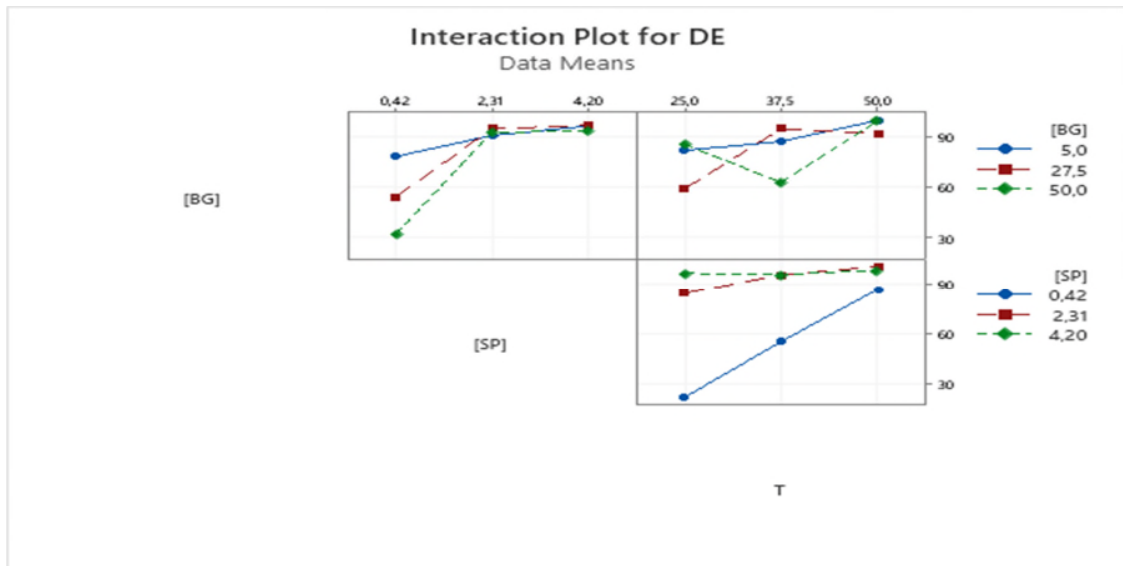


Figure 6: Interaction plot for DE (%).

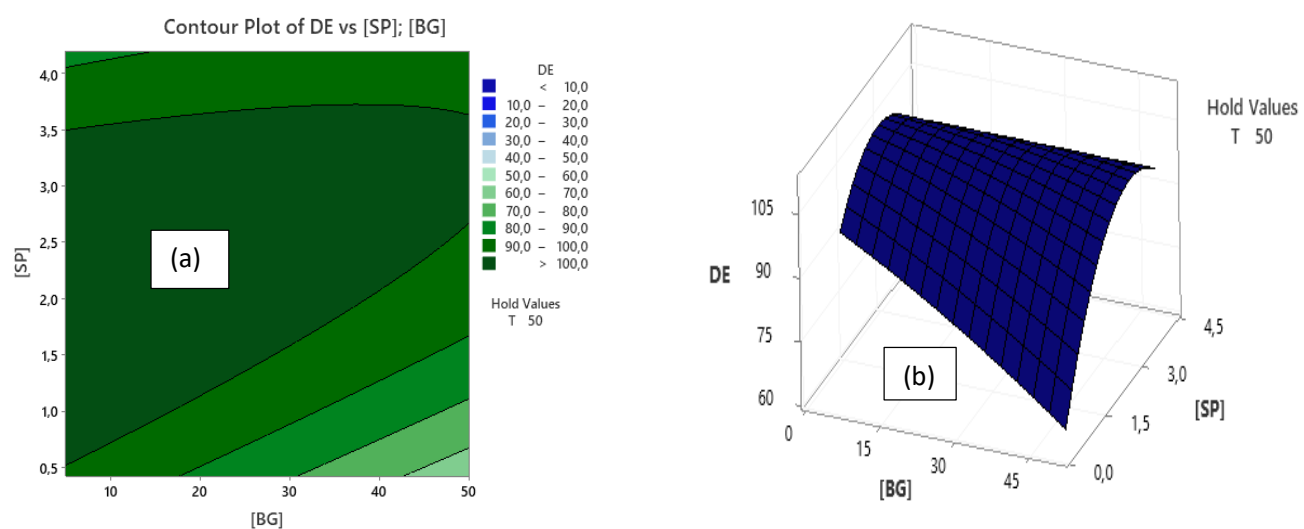


Figure 7: Contour plots (a) and Response surface (b) of the degradation efficiency according [BG] and [SP] High levels of T.

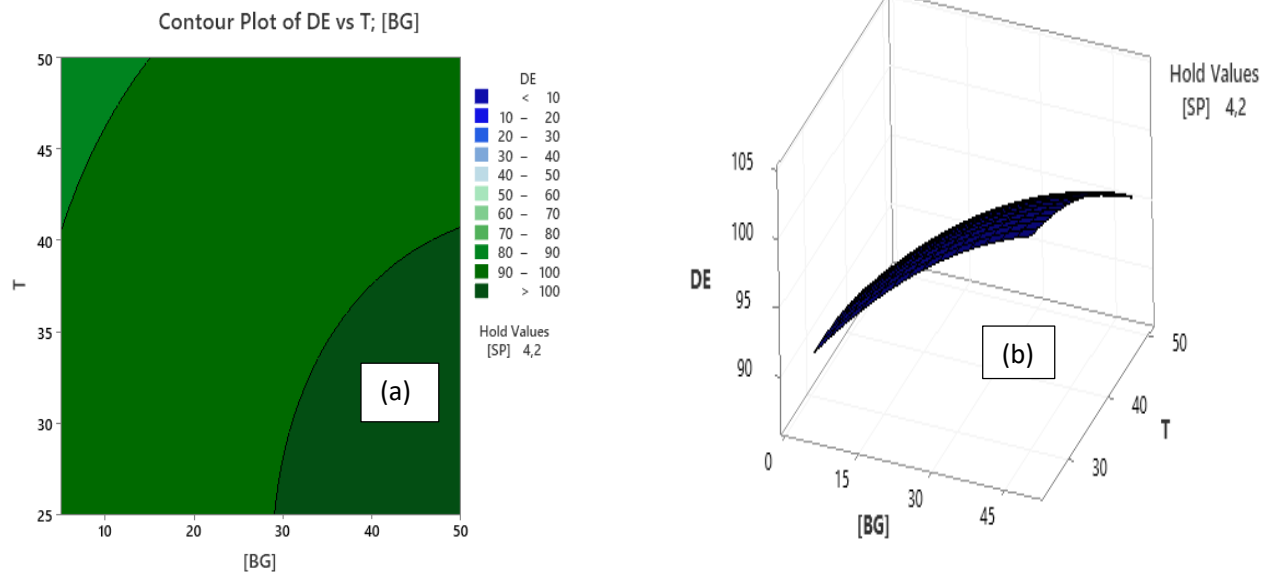


Figure 8: Contour plots (a) and Response surface (b) of the degradation efficiency according [BG] and T at High levels of [SP].

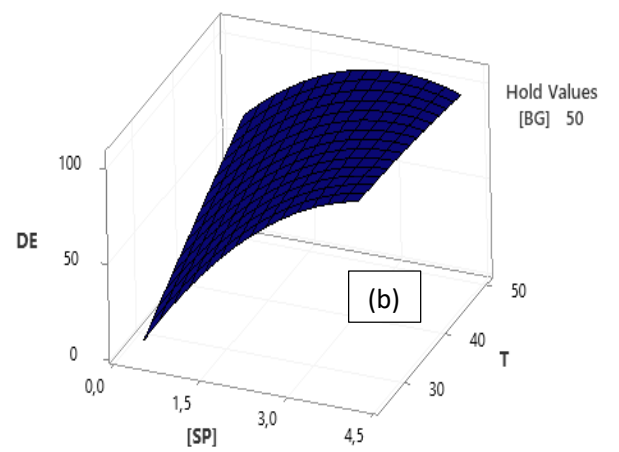
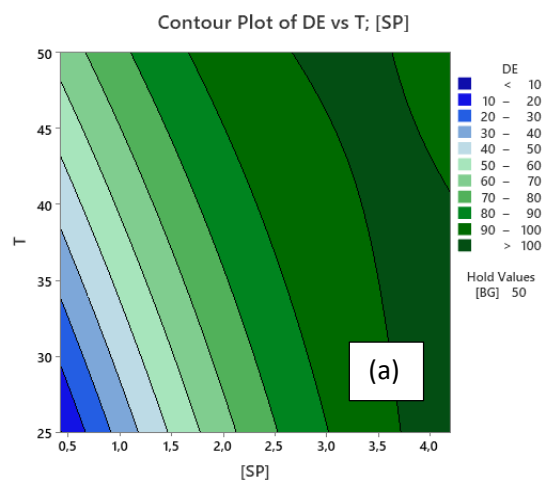


Figure 9: Contour plots (a) and Response surface (b) of the degradation efficiency according [SP] and T at High levels of [BG].

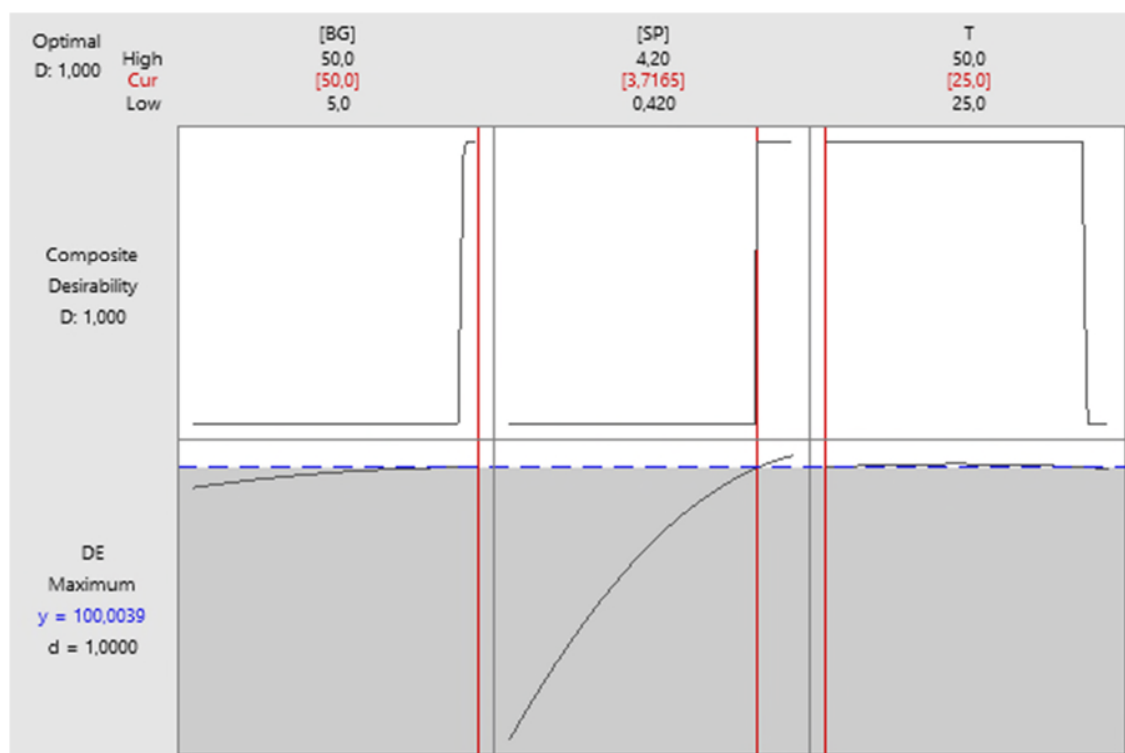


Figure 10: Optimization response for degradation the BG at 50 mg/L.