DISCOLORATION OF WATER CONTAMINATED BY THE TEXTILE DYE RED TS3B UTILIZING ULTRAVIOLET RADIATION AND ZnO AS A PHOTOCATALYST

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ABSTRACT

The current research project consisted of discoloring water contaminated by the textile dye Red TS3B, utilizing ultraviolet radiation and ZnO as a photocatalyst, towards this end, a spectrophotometric method for the quantification of dye was validated, and this method presented an adequate linearity and sensibility. For the discoloration trial run, a factorial design (2^2), in order to optimize the experimental factors of pH and ZnO dosage per 250 mL of solution, was executed. The best discoloration was achieved at 180 minutes of photocatalytic reaction, when it worked with a pH of 11 and a dosage of 0.2 g of ZnO per 250 mL of colored solution, achieving a degradation percentage of 97.5 % of dye in solution.

Keywords: *Discoloration, contaminated water, Red TS3B, ultraviolet radiation, ZnO.*

1. INTRODUCTION

The textile industry is considered one of the biggest consumers of hydraulic resources in the world, generating a great quantity of effluents which end up being harmful to the environment [1].

Dyes are present in these textile effluents, and they often flow directly into different bodies of water, resulting in a dangerous situation because these can interfere with processes of photosynthesis normally carried out by the organisms living in these lakes and rivers [2]. Based on all of these precedents and in accordance with our local and national reality, Processes of Advanced Oxidation (PAO) become an extremely interesting alternative, and among them, photocatalysis with ZnO is appropriate in order to achieve effluent discoloration processes [3].

ZnO is considered a photocatalyst of the highest efficiency due to the fact that it possesses a wide gap of 3.2 eV and a linking energy of great excitation (60 meV). Due to these characteristics, it continues being widely researched for the removal of water and air pollutants and also for microbial disinfection [4]. The general reaction mechanism of ZnO is presented in **Fig. 1** [5].

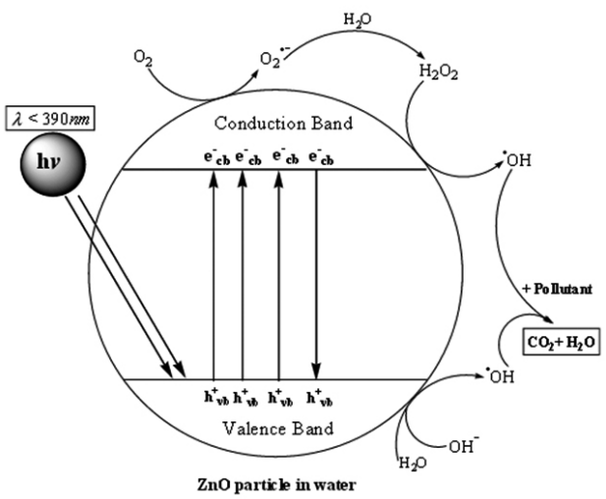

Figure 1. Photolytic reaction mechanism of ZnO in watery conditions.

2. EXPERIMENTAL PROCEDURES

In order to execute the present research project, distilled water (1.0 µS cm^{-1} a 20°C), zinc oxide (ZnO) from Central Drug House, sodium hydroxide, and sulfuric acid, all of which were of experimental and analytical quality, were utilized. The textile dye Red TS3B was provided by Engineer Fredy Molina from the company *Franky & Ricky* in the city of Arequipa.

An ultraviolet light lamp (50 Hz and 30 W) was utilized as a radiation source. In order to conduct the discoloration trial runs, a magnetic agitator CIMAREC was used along with 250 mL Petri dishes.

For the spectrophotometric analysis, a spectrophotometer Cary 60 UV-V from *Agilent Technologies* was utilized. In the same manner, for the pH measurement, a pH-meter from *Metrohm* was employed, and for the measurement of volumes, type A volumetric burettes and pipettes of adequate range were utilized.

The statistical analysis of the data obtained was conducted with the programs *Microsoft Excel 2013*, *Statagraphics Centurion XVI.II*, and *Origin Pro 9.0*.

2.1 Granulometric adaptation of ZnO

In order to achieve a uniform particle size, a sufficient quantity of ZnO went through a rigorous sifting process (size Nº 200), drying it at 120 ºC for 4 hours and keeping it continuously in a desiccator.

2.2 Elaboration of a calibration graphic for the determination of the dye Red TS3B

A stock solution of 100 mg L^{-1} of the dye Red TS3B was prepared in order to obtain standard solutions of 5, 10, 20, 30, 40, 50 and 60 mg L^{-1}. Subsequently, a spectral scan between 800 and 200 nm was conducted in order to determine the wavelength of maximum absorption, using the standard solution of 30 mg L^{-1}. Finally, the reading of the standard solutions was conducted and repeated three times in the spectrophotometer, utilizing distilled water as a target model.

2.3 Evaluation of the method's linearity

Assuming there is a linear relationship, which is directly proportional among absorbance and concentration, a linear regression was calculated for the method of minimal squares, obtaining it as an algebraic form:

$$y = a + bx \quad (1)$$

$$b = \frac{\sum x_i y_i - \frac{\sum x_i \sum y_i}{n}}{\sum {x_i}^2 - \frac{(\sum x_i)^2}{n}} \quad (2)$$

$$a = \frac{\sum y_i - b \sum x_i}{n} \quad (3)$$

Where *y* is absorbance, *x* is concentration, *a* is the intercept and *b* is the slope.

On the other hand, from the independent form to the appearance that the straight line takes, it is convenient to evaluate the correlation coefficient because in analytical practice, *r* must be greater than 0.99.

$$r = \frac{\sum x_i y_i - \frac{\sum x_i \sum y_i}{n}}{\sqrt{\left(\sum {x_i}^2 - \frac{(\sum x_i)^2}{n}\right)\left(\sum {y_i}^2 - \frac{(y_i)^2}{n}\right)}} \quad (4)$$

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However, an indicator which ends up being more trustworthy for the linear correlation evaluation is a statistic test which permits one to find the value *t*.

$$t = \frac{|r|\sqrt{n-2}}{\sqrt{1-r^2}} \qquad 5)$$

2.4 Determination of the detection limit and of method quantification

The detection limit was determined in order to become acquainted with the minimum quantity of analyte, which is possible to detect but not necessarily to quantify utilizing the proposed methodology.

$$\text{LOD} = \frac{y_B + 3S_{y/x}}{b} \cdot \frac{1}{\sqrt{n}} \qquad 6)$$

On the other hand, the quantification limit was determined in order to become acquainted with the minimum concentration of analyte which can be determined by the method in an exact manner.

$$\text{LOQ} = \frac{y_B + 10S_{y/x}}{b} \cdot \frac{1}{\sqrt{n}} \qquad 7)$$

2.5 Factorial design for the discoloration experiments

In order to research the effects of the variables which intervene in a process of photolytic discoloration, a two-level (2^2) factorial design was conducted with only one trial run at each point. The variables under study were dosage of ZnO and pH. Table 1 presents the fixed values for each variable.

Table 1. Variables and levels considered for the study.

Variable	Low level (-1)	High level (+1)
ZnO (g/250 mL)	0.05	0.20
pH	3	11

In order to conduct the discoloration studies, four solutions of the dye Red TS3B were prepared at a concentration of 50 mg L^{-1}, adjusting the pH with solutions of NaOH and H_2SO_4 concentrated in agreement with the requirements presented in Table 2. The solutions were subsequently exposed to intense ultraviolet radiation (UV lamp), with 10 mL samples being taken every 30 minutes for three hours.

Table 2. Discoloration experiments for Red TS3B.

Solution	pH	ZnO (g/250 mL)
1	3	0.05
2	11	0.20
3	3	0.05
4	11	0.20

After having conducted the spectrophotometric determination of the samples obtained by way of the discoloration experiment, the percentage of degradation was calculated using the equation (8):

$$Degradation\ (\%) = \frac{C_0 - C_f}{C_0} \times 100 \qquad 8)$$

Where C_0 is the initial concentration of dye and C_f is the final concentration of dye subsequent to the photolytic process.

3. RESULTS

3.1 Calibration graphic for the determination of the dye Red TS3B

For the evaluation of method linearity, a graphic which related absorbency to concentration was elaborated. The experimental data for absorbency for each standard deviation are presented in Table 3, being read at 541 nm.

Table 3. Absorbance data in order to evaluate method linearity.

Concentration (mg L^{-1})	Abs 1	Abs 2	Abs 3	Average Abs	SD
5	0.0895	0.0892	0.0881	0.0889	0.0007
10	0.1727	0.1736	0.1743	0.1735	0.0008
20	0.3608	0.3613	0.3618	0.3613	0.0005
30	0.5495	0.5484	0.5476	0.5485	0.0010
40	0.7088	0.7322	0.7287	0.7232	0.0126
50	0.9268	0.9239	0.9275	0.9261	0.0019
60	1.1174	1.1158	1.1160	1.1164	0.0009

Fig. 2 illustrates the linear regression obtained for the data presented in Table 3, a correlation coefficient (r^2) of 0.9997, a slope (*b*) equal to 0.0187 and an intercept (*a*) of -0.0115 were obtained, thus yielding the following equation:

$$Absorbance = -0.0115 + 0.0187 \cdot Concentration \qquad 9)$$

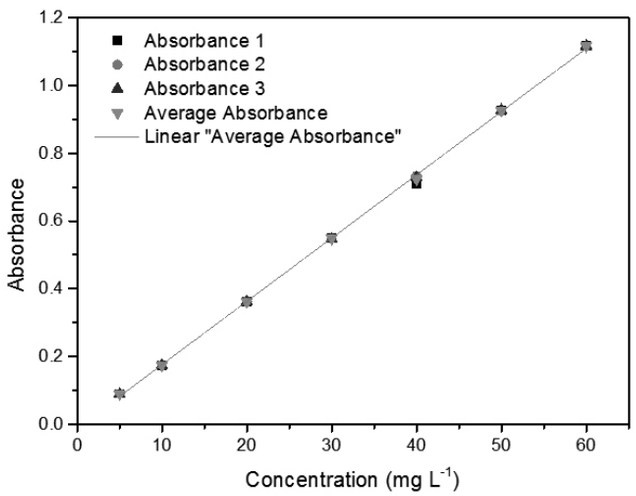

Figure 2. Calibration graphic for the determination of the dye Red TS3B.

Likewise, for the statistical analysis *t*, values of 129.07 and 2.57 for $t_{regression}$ and $t_{theoretical}$ respectively were obtained, with an elevated correlation among absorbance and concentration being observed.

3.2 Detection limit and method quantification

Table 4 presents the required results for the determination of the detection and quantification limits.

Table 4. Values for determining method sensitivity.

Determination of LOD y LOQ		
Result when *x* is zero	Y_{blank}	0.0115
Standard deviation of the result when *x* is zero	S_{blank}	0.0009
Number of data	*N*	7
Slope	*B*	0.0187

After having utilized the data provided en Table 4 in equations (6) and (7), a value of 0.29 mg L^{-1} was determined as the detection limit (LOD) and as a quantification limit (LOQ), a value of 0.41 mg L^{-1} . From these values, it can be deduced that the method is indeed useful in terms of quantifying low concentrations of dye.

3.3 Kinetic study of photocatalytic discoloration

3.3.1. Experiment to pH 3 and 0.05 g of ZnO per 250 mL of solution

Taking as a point of reference the experimentation values proposed in Table 2, the solution to 50 mg L^{-1} was prepared. After having conducted the discoloration trial run, the data presented in Table 5 were obtained.

Table 5. Results obtained for the Red TS3B discoloration process to a pH of 3 and a dosage of 0.05 g of ZnO per 250 mL of solution.

Time (min)	Absorbance	Concentration (mg L^{-1})
0	0.9918	53.65
30	0.8945	48.45
60	0.8540	46.28
90	0.7903	42.88
120	0.7290	39.60
150	0.6536	35.57
180	0.5832	31.80

3.3.2. Experiment to pH 11 and 0.05 g of ZnO per 250 mL of solution

Table 6, presents the data obtained from the photocatalytic discoloration process for the established conditions.

Table 6. Results for the discoloration process to a pH of 11 and a dosage of 0.05 g of ZnO per 250 mL of solution.

Time (min)	Absorbance	Concentration (mg L^{-1})
0	0.9199	49.81
30	0.8266	44.82
60	0.5089	27.83
90	0.3462	19.13
120	0.1697	9.69
150	0.1215	7.11
180	0.0660	4.14

3.3.3 Experiment to pH 3 and 0.2 g of ZnO per 250 mL of solution

In Table 7, the data obtained from the photocatalytic process for established parameters in the factorial design are presented.

Table 7. Results from the discoloration process to a pH of 3 and a dosage of 0.2 g of ZnO per 250 mL of solution.

Time (min)	Absorbance	Concentration (mg L^{-1})
0	0.9411	50.94
30	0.5489	29.97
60	0.2937	16.32
90	0.1331	7.73
120	0.0545	3.53
150	0.0497	3.27
180	0.0483	3.20

3.3.4 Experiment to pH 11 and 0.2 g of ZnO per 250 mL of solution

Finally, in Table 8 the results obtained by way of the photocatalytic discoloration of the dye Red TS3B according to the defined parameters in the experimental design are presented.

Table 8. Results from the discoloration process to a pH of 11 and a dosage of 0.2 g of ZnO per 250 mL of solution.

Time (min)	Absorbance	Concentration (mg L^{-1})
0	0.7995	43.37
30	0.3989	21.95
60	0.1958	11.09
90	0.0802	4.90
120	0.0206	1.72
150	0.0159	1.47
180	0.0088	1.09

Fig. 3, presents a comparison of the different results obtained, according to the established parameters in the factorial design.

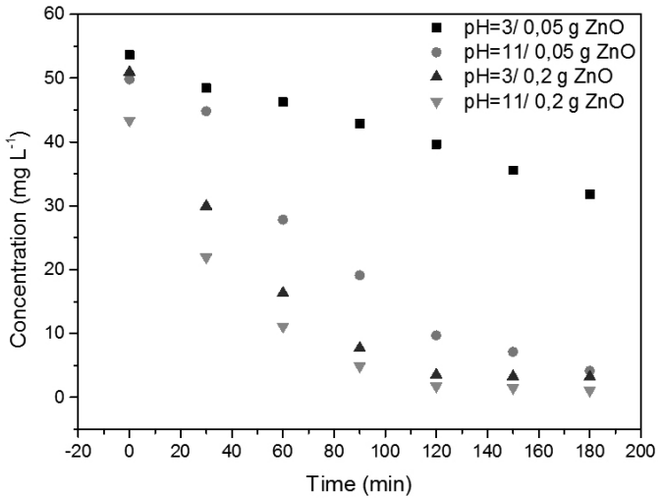

Figure 3. Photocatalytic degradation of the dye Red TS3B to the fixed parameters in the experimental design.

3.4 Evaluation of factorial design

The results obtained in the previous section are summarized in Table 9, after the equation (8) having been applied in each experiment.

Table 9. Degradation percentages obtained with the factorial design experimentation.

Experiment	pH	ZnO (g/250 mL)	Degradation (%)
1	3	0.05	40.73
2	11	0.20	91.68
3	3	0.05	93.72
4	11	0.20	97.50

Upon observing the results, it becomes obvious that the best combination of variables is to work to a pH of 11 and a dosage of 0.2 g of ZnO per each 250 mL of dye solution. Nevertheless, conducting a deeper statistical analysis, Figure 4, presents the repercussion of the factors in the degradation because upon increasing them, an even better degradation is achieved.

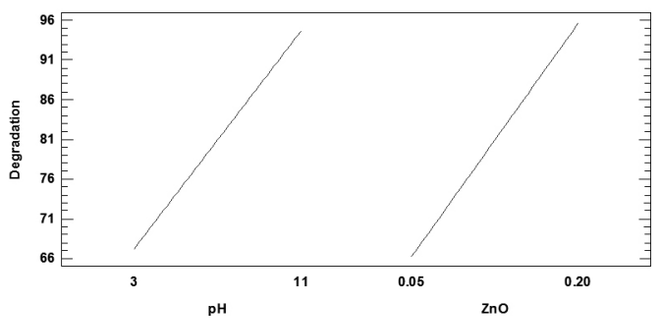

Figure 4. Behavior of the factors for the degradation process.

On the other hand, the representation of the mathematical model obtained by the factorial design is known as the surface-answer graphic. Figure 5 presents the values of pH and dosage of ZnO in order to obtain an adequate percentage of degradation.

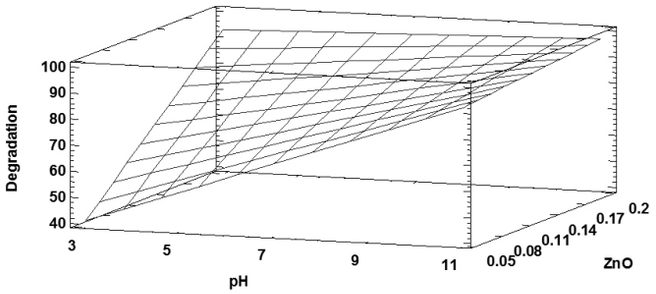

Figure 5. Surface-answer graphic for the discoloration of Red TS3B.

In order to achieve a better visualization, a projection of the solid above the lower plane is effected, achieving what is called the curve of iso-values, which is presented in **Fig. 6** and from which it is deduced that in order to achieve maximum degradation, one must work to a pH of 11 and an dosage increased to 0.2 g of ZnO per 250 mL of solution.

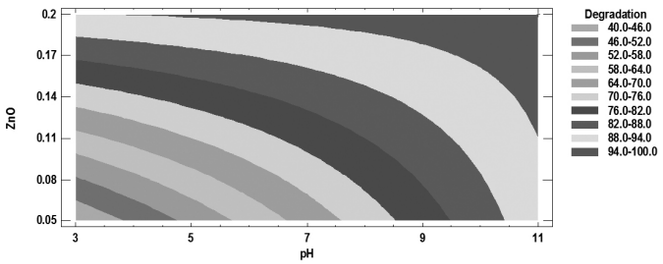

Figure 6. Graphic of iso-values for the degradation of the dye Red TS3B.

Table 10 presents the levels of the experimental factors which guarantee a maximum percentage of degradation, being able to achieve up to 97.5 % degradation.

Table 10. Data for obtaining maximum degradation.

Factor	Low	High	Optimum
pH	3	11	11
ZnO (g/250 mL)	0.05	0.20	0.20

For this photocatalytic degradation process, a mathematical model is proposed, which could include the three components remaining defined in the equation (10).

$$Degradation\ (\%) = -1.94 + 8.33pH + 471.19ZnO - 39.31pH \cdot ZnO \quad 10)$$

The model presents a (r^2) close to 100.00 which means that the results for the most part depend on the pH and the dosage of ZnO. Similarly, **Fig. 7** presents the discoloration obtained a product of the optimization of the photocatalytic process.

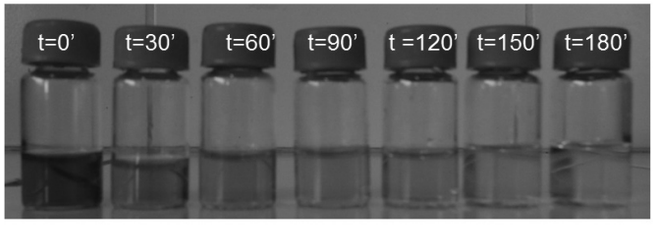

Figure 7. Discoloration of the dye Red TS3B to a pH of 11 and a dosage of 0.2 of ZnO per 250 mL of solution.

4. DISCUSSION

A degradation of 97.5 % was obtained when a pH of 11 and a dosage of 0.2 g of ZnO per 250 mL of solution of the dye Red TS3B were utilized. Rahman et al. [6] has reported an approximately 95% discoloration when a Rhodamine B solution was worked with. While conceding that this is true, this degradation was achieved in a period of 70 minutes of exposure to ultraviolet radiation. It must also be taken into account that ZnO nanostructures were worked with, a technique which upon increasing the contact surface of the photocatalyst, possibly optimizes the degradation time because in our case only sifted ZnO was worked with.

Sakthivel et al. [7] experimented with direct radiation, comparing the efficiency of the TiO_2 versus the ZnO, utilizing acid Brown 14 as a dye, which is characterized by possessing an azo group similar to the dye utilized in the present research project. In a manner analogous to our own research, up to 92.81 % dye degradation was achieved in 180 minutes of reaction. This leaves us with the interesting fact that the ultraviolet radiation inherent in direct solar radiation is not nearly as energetic as the case which Corzo et al. [8] reported, in which degradation results in less reaction time were achieved.

Due to the elevated degradation percentage of azoic dyes, which are widely utilized in the textile industry and which generate a serious problem the moment the water is treated, photocatalysis with ZnO becomes an extremely attractive alternative in order to effect the mineralization of these compounds, such as that which Byrne et al. [3] indicates and proposes upon having catalogued the generation of radicals as the principal source of what are called Advanced Oxidation Processes.

5. CONCLUSIONS

Utilizing a sieve N° 200, a granulometric adaptation of ZnO was realized. The analytic methodology for the quantification of the dye Red TS3B presented an answer directly proportional to the concentration, being linear and sensitive for its determination. The optimal parameters for the discoloration process suggest a pH of 11 and 0.2 g of ZnO per 250 mL of colored solution. A degradation of 97.5 % was achieved when the optimal parameters of the factorial design were worked with.

6. ACKNOWLEDGEMENTS

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