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Kinetic evaluation of photocatalytic decoloration of Synozol Red K3BS dye using TiO_2-anatase and direct solar radiation

Evaluación cinética de la decoloración fotocatalítica del colorante Synozol Red K3BS utilizando TiO_2-anatasa y radiación solar directa

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Abstract
The intense solar radiation of the city of Arequipa has been used as an activation factor for TiO_2 anatase to evaluate the decoloration kinetics of the Synozol Red K3BS textile dye. For this purpose, a factorial design (2^3) was developed to optimize reaction time values, pH and TiO_2 doses for 200 mL of solution. The optimal factors for the study were: a 60 min duration, a pH of 3 and 0.1 g of photocatalyst. The first-order kinetic model adequately explained the decoloration of a solution at a concentration of 40 mg/L, showing an excellent reaction rate constant (k=0,0333 min^{-1}) and a decoloration percentage of 86.15%.
Keywords: Solar radiation, decoloration, anatase, Synozol Red K3BS, kinetics.

Resumen
La intensa radiación solar de la ciudad de Arequipa ha sido utilizada como factor de activación del TiO_2 anatasa para evaluar la cinética de decoloración del colorante textil Synozol Red K3BS, para tal fin se desarrolló un diseño factorial (2^3) para optimizar los valores de tiempo de reacción, pH y dosis de TiO_2 para 200 mL de solución. Los factores óptimos para el estudio fueron un tiempo de 60 min, un pH de 3 y 0.1 g de fotocatalizador, donde el modelo cinético de primer orden explica de forma apropiada la decoloración de una solución a 40 mg/L de concentración, registrando una excelente constante de velocidad (k=0,0333 min^{-1}) y un porcentaje de decoloración de 86.15 %.
Palabras clave: Radiación solar, decoloración, anatasa, Synozol Red K3BS, cinética.

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1 Introduction

Wastewater from paper, food and textile industries contains different colorant types that are difficult to biodegrade using conventional treatments, which causes major negative pollution issues (Ambati and Gogate, 2017; Kalikeri *et al*., 2018).

Non-thermal plasma in a liquid medium is used to degrade different types of dyes such as AB52 an azo dye (Alarcón-Hernández *et al*., 2022). Furthermore, different advanced oxidation processes (AOP) are feasible treatment alternatives. In this study, light sources that provide specific radiation for activating photocatalysts are crucial.

Heterogeneous photocatalysis is one of the most efficient advanced oxidation processes. In this AOP, hydroxyl radicals (·OH) that rapidly oxidize different types of compounds are generated (Andriantsiferana *et al*., 2014; Priyanka *et al*., 2019). Semiconductors, which are activated by sunlight or artificial light such as titanium dioxide (TiO_2), zinc oxide (ZnO), tungsten trioxide (WO_3), strontium peroxide (SrO_2), iron (III) oxide (Fe_2O_3), cerium (IV) oxide (CeO_2) and zirconium dioxide (ZrO_2), whose properties have been studied as an alternative for the degradation of pollutants, are used (dos Santos *et al*., 2017; Sai Saraswathi & Santhakumar, 2017; Zhao *et al*., 2018; Tahir *et al*., 2019; Pei *et al*., 2020).

TiO_2 is a promising semiconductor material for wastewater treatment. It has a low operating temperature, is insoluble in water, chemically stable, photoactive, and has a low level of toxicity (Al-Mamun *et al*., 2019; Ibukun & Jeong, 2020; Thomas *et al*., 2016). This catalyst has three main phases: anatase, brookite and rutile. In its anatase crystalline phase, TiO_2 has a higher photocatalytic activity and can use only UV light (<390 nm) from solar irradiation due to its wide band gap (3.2eV) (Byrne *et al*., 2018). TiO_2 modified with different transition metals was analyzed for the photocatalytic decomposition rate of methyl orange and methylene blue using the visible light region. Results showed a % of decoloration of 80% and 44%, for both dyes respectively demonstrating that TiO_2 doped with Cu had the highest catalytic activity under visible irradiation (Kerkez-Kuyumcu *et al*., 2015). Furthermore, TiO_2 nanoparticles were synthesized and evaluated for the degradation of three of the most used dyes in the textile industry such as malachite green, methylene blue, rhodamine B exposed to a UV light source, showing a removal percentage of 95% (Soni *et al*., 2015). Solar light irradiation and TiO_2 were used to study the photodegradation of rhodamine B and methyl orange demonstrating the effectiveness of this binary system for wastewater treatment system (Ariyanti *et al*., 2018).

According to the Peruvian National Meteorology and Hydrology Service, SENAMHI, the city of Arequipa is subject to a high level of solar radiation throughout the year, with quite high UV-B radiation peaks. This peculiarity can be used to develop a bleaching treatment using TiO_2 anatase, which can be easily activated with radiation below 390 nm (Byrne *et al*., 2018). Other studies have also taken advantage of the high solar radiation of the city to produce photovoltaic solar energy in order to implement a water treatment system. (Ramírez-Revilla, 2021).

The aim of this research was to evaluate the degradation kinetics of the Synozol Red K3BS textile dye using TiO_2 in its anatase crystalline phase and direct solar radiation in the city of Arequipa, using a full factorial design to determine the optimal degradation conditions.

2 Materials and methods

2.1 Colorant and photocatalyst

The dye used for the decoloration study was Synozol Red K3BS, provided by the Proyecto Mercurio Research Laboratory of the Universidad Católica Santa María de Arequipa (UCSM). The TiO_2 anatase crystalline phase used for the study was acquired from Sigma Aldrich with a degree of purity of 99.8% without any prior treatment.

2.2 Analytical equipment

The concentration of the dye was determined using a Thermo Fisher Scientific Genesys 150 UV-VIS spectrophotometer; a Mettler Toledo ME204 analytical scale for weighing and a HANNA HI2211 pH / mV equipment for the measurement of pH levels.

2.3 Experimental procedure

A 1000 mg/L stock solution of Synozol Red K3BS dye was prepared using distilled water. Then, standard solutions of 2.5, 5, 10, 20, 30, 40 and 50 mg/L were obtained. All readings were made at a wavelength of 541 nm. The maximum absorption graph is presented in Figure 1.

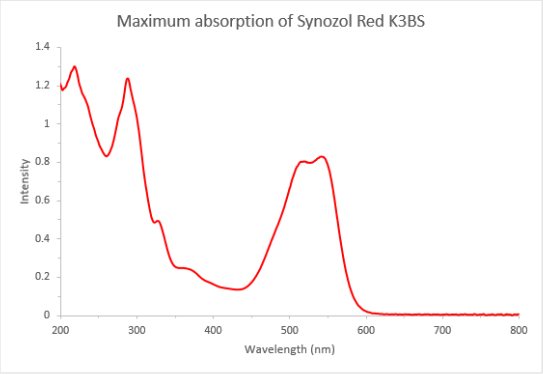

Figure 1. Maximum absorption of Synozol Red K3BS dye.

Table 1. Factors and levels of the factorial design.

Factor	Low level (-1)	High level (+1)
Time (min)	30	60
pH	3	11
TiO_2 dose (g/200 mL)	0.1	0.3

Figure 2. Magnetic stirring reactors under solar radiation.

To evaluate photocatalytic decoloration, a full 2^3 factorial design was performed three times for each point. The factors studied were exposure time, pH and TiO_2 doses in g/200 mL. The pH adjustment was carried out with concentrated H_2SO_4 and NaOH at 10% concentration. Table 1 shows the assigned values for each factor.

The decoloration tests were carried out in magnetic stirring reactors, which were directly exposed to solar radiation between 11:00 and 12:00 on July 15, 16 and 17, 2020 in Arequipa, Peru. (Longitude: W 71°32'32.15", Latitude: S 16°24'29.47", Average altitude: 2312.00 m ASL) using an initial dye concentration of 40 mg/L. The average solar radiation was 632 W/m^2 and the average temperature was 25 ºC. Figure 2 shows the configuration of the system used for the photocatalysis experiments. The average solar radiation data was obtained from the National Meteorology and Hydrology Service of Peru (SENAMHI) website.

Once the factorial design tests were carried out, the optimal conditions to evaluate the decoloration kinetics were identified. Then, the optimal test was performed three times to evaluate the reaction rate constant using a pseudo first order kinetic model.

$$\%Decoloration = \frac{C_0 - C_f}{C_0} \times 100 \quad (1)$$

$$C_f = C_0 e^{-kt} \quad (2)$$

Where: C_f is the dye concentration (mg/L) at the end of the experiment, C_0 is the initial dye concentration (mg/L), k is the reaction rate constant (min^{-1}) and t is the reaction time (min).

3 Results and discussion

Easy-development and implementation analytical methods such as ultraviolet visible spectrophotometry, have been widely studied in photocatalysis processes (Ambati and Gogate, 2017). In order to quantify the dye, a calibration graph was constructed, which corresponded to a linear model with a determination coefficient equal to 0.9999, which suggests a good explanation of the variability in the linear equation.

$$Absorbance = 0.0106 + 0.0228 Concentration \quad (3)$$

Likewise, to determine the best conditions for the decoloration study, a full 2^3 factorial design was developed. The decoloration results obtained using the different combinations of factor levels are shown in Table 2.

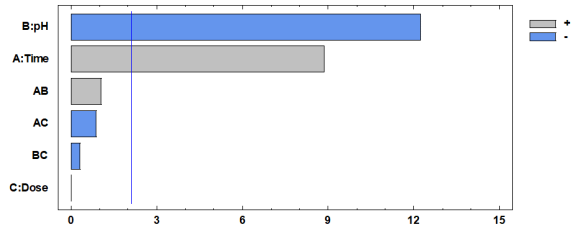

Figure 3. Pareto graph for Synozol Red K3BS decoloration.

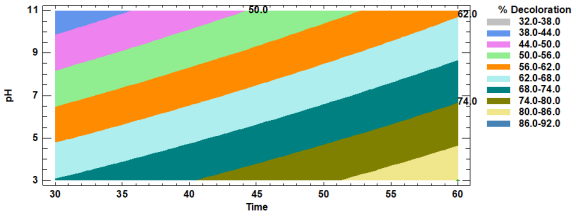

Figure 4. Isovalue plot for Synozol Red K3BS decoloration.

The Pareto chart shown in Figure 3 suggests that the reaction time and the pH are the factors with significant positive and negative influence on the decoloration, respectively. The dose of the photocatalyst in this design does not show a significant effect, as well as the double interactions of the studied factors. Therefore, the reaction time is a key factor in the decoloration process. This statement was verified with the data obtained from the analysis of variance that showed a p-value <0.05.

The multiple linear regression model that describes the decoloration process shows the most relevant interactions between the three evaluated factors. The coefficient of determination explains 93.11% of the variability of the photocatalytic process.

$$\%Decoloration = 57.13 + 0.62 Time - 3.93 pH + 34.06 Dose + 0.02 Time\ pH - 0.63 Time\ Dose - 0.79 pH\ Dose \quad (4)$$

Figure 4 shows the isovalue graph, which indicates that, in order to achieve the maximum decoloration of the Synozol Red K3BS solution (85.46%), the conditions should be the following: a pH equal to 3, a period of approximately 60 minutes and a dose of 0.1 g per 200 mL of solution.

Table 2. Results of the combination of factor levels.

Time (min)	pH	Dose (g/200 mL)	Decoloration 1 (%)	Decoloration 2 (%)	Decoloration 3 (%)
30	3	0.1	66.35	71.1	63.19
60	3	0.1	84.54	88.5	83.64
30	11	0.1	32.61	46.52	39.25
60	11	0.1	61.45	68.43	56.82
30	3	0.3	63.78	75.31	69.8
60	3	0.3	85.58	83.54	83.26
30	11	0.3	32.38	47.75	41.5
60	11	0.3	56.78	66.36	56.65

Table 3. Results for the decoloration process at a pH value of 3 and a dose of 0.1 g of TiO_2 per 200 mL of solution.

Time (min)	Concentration 1 (mg/L)	Concentration 2 (mg/L)	Concentration 3 (mg/L)	Average Concentration	Standard Deviation
0	40.76	40.57	40.8	40.71	0.13
10	31.27	31.15	31.08	31.16	0.09
20	24.96	24.44	24.78	24.73	0.26
30	13.47	13.32	13.08	13.29	0.2
40	9.58	10.02	9.71	9.77	0.23
50	7.5	8.09	7.43	7.67	0.36
60	5.45	5.85	5.61	5.64	0.2

With the optimal values for photocatalytic evaluation, tests were performed three times to determine the decoloration kinetics of Synozol Red K3BS dye. Table 3 presents the results for the photocatalytic test.

The decoloration kinetics of Synozol Red K3BS are presented in Figure 5. A comparison between the experimental values and those simulated by the first order kinetic equation, which reports a reaction rate constant (k = 0.0333 min^{-1}), is shown as well. Similar constants have been reported in the photocatalytic degradation of Rhodamine B (Varadavenkatesan *et al.*, 2019). Also, the concentrations calculated with this model were obtained using the pseudo first order kinetic model with equation 2 already shown above.

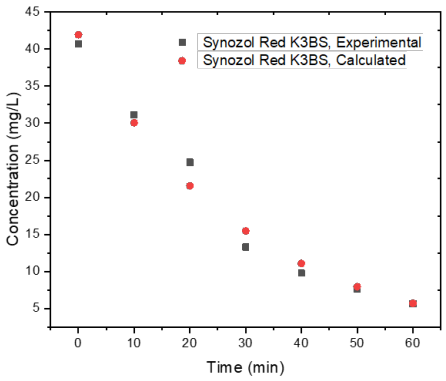

Figure 5. Experimental and calculated kinetics for Synozol Red K3BS.

Considering the variation of the concentration for different test durations, it was determined that the percentage of decoloration after 60 minutes was 86.15%. Other studies report the same reaction time for the evaluation of the degradation of different aqueous pollutants such as dyes and microorganisms (Dos Santos *et al.*, 2017).

Furthermore, the reactive oxygen species (O_2,O_2^-,HOO·/($^-$OH), formed by the activation of TiO_2 with high solar radiation, are responsible for the degradation of Synozol Red K3BS. This behavior produces a large number of active sites that facilitate the degradation of the dye (Priyanka *et al.*, 2019). Likewise, photocatalysts such as ZnO report the achievement of similar degradations of azoic dyes and have a similar radical formation mechanism (Ortiz-Romero *et al.*, 2018).

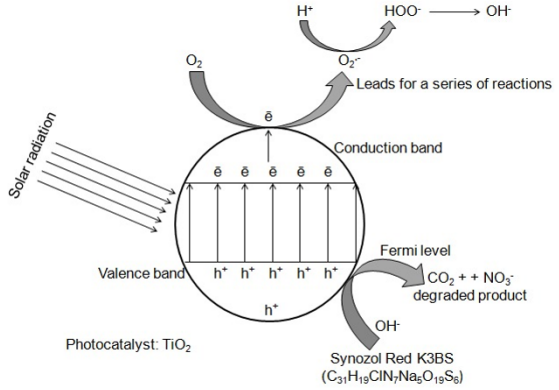

Figure 6. Schematic diagram of the decoloration mechanism of Synozol Red K3BS with TiO_2.

Figure 6 shows the schemata of the degradation mechanism of Synozol Red K3BS using TiO_2 as a photocatalyst.

Conclusions

The high ultraviolet radiation registered in the city of Arequipa constitutes a key factor for the activation of TiO_2 anatase as a photocatalyst for the decoloration of Synozol Red K3BS in aqueous solution at an initial concentration of 40 mg/L. The optimal factors for the test were 60 min of exposure, a pH of 3 and a TiO_2 dose of 0.1 g per 200 mL of solution. The colored solution was decolorized by 86.15% showing a reaction rate constant k=0.0333 min^{-1} that follows the pseudo first order kinetic mechanism.

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