Photocatalysis of Orange - 84 Reactive dye using a sunlight collector

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Fotocatálisis del colorante Naranja Reactivo 84 utilizando un colector de luz solar

Fotocatálisis do corante Laranja Reativo 84 utilizando um recolhedor de luz solar

Resumen

Introducción. El Naranja Reactivo 84 es un colorante utilizado en la industria textil que al ser aplicado en la tela de algodón, sólo el 65% de éste queda impregnado y el 35% restante se hidroliza en el agua, generando un agua residual altamente coloreada. **Objetivo.** Estudiar la fotocatálisis del Naranja Reactivo 84 utilizando colector solar y dióxido de titanio como catalizador. **Materiales y métodos.** Se utilizó un colector solar, el cual constaba de tres módulos, cada módulo estaba compuesto por ocho tubos de vidrio (Schott-Duran) de 48 mm de diámetro externo y 150 cm de largo y lámina de aluminio, ya que permite la reflectancia de la radiación ultravioleta de la luz solar, todo el conjunto tenía una bomba de recirculación y un tanque; el colector solar tenía una inclinación de 6º con respecto al suelo, de frente al Norte, ya que debe coincidir con la posición geográfica del lugar. Se varió una sola condición en cada experimento con el objetivo de estudiar su influencia en la degradación del colorante; en esta investigación se presentan diferentes combinaciones de peróxido de hidrógeno, dióxido de titanio y aire utilizados en la fotocatálisis del Naranja Reactivo 84. **Resultados.** Se encontró que las concentraciones óptimas para la degradación del naranja reactivo 84 en una concentración de 340 mg/L son: 40 mg/L de dióxido de titanio y 2mL/L de peróxido de hidrógeno sin inyección de aire. **Conclusión.** Con una cantidad de dióxido de titanio y una concentración de peróxido de hidrógeno adecuados, se puede obtener muy buenos porcentajes de degradación del naranja reactivo 84 y aguas residuales coloreadas y altos porcentajes de mineralización.

Palabras clave: Fotocatálisis. Colorante. Dióxido de Titanio. Naranja Reactivo 84. Agua Residual Abstract

Abstract

Introduction. Reactive Orange 84 is a dye used in the textile industry, specifically in cotton clothing, which generates a hightly colored residual water, because only 65% of this water is impregnated and the 35% remaining hydrolyses in water, generating a highly colored waste water **Objective.** To study photocatalysis of Reactive Orange 84 by the use of a sunlight collector and titanium oxide as a catalyst. **Materials and methods.** A sunlight collector made up by three modules (each one made up by eight glass Schott-Duran pipes) was used. Each glass pipe is 48 cm of external diameter and 150 cm long and also contains an aluminum sheet, which allows the reflection of sunlight. The whole device had a re-circulation bomb and a tank. The sunlight collector had an inclination of 6 degrees in comparison with the floor and was facing north because it must be located according to the geographic position of the place. Only one condition was modificated for each experiment with the objective of studying its influence in the dye's degradation. In this research work we show different combinations of hydrogen peroxide, titanium dioxide and air, used in the photo catalysis of the 84 Orange reactive and waste water samples from textile industry. **Results.** The optimal concentrations found for 84 orange reactive in a 340 mg/lL concentration are: 40 mg/L of titanium dioxide and 2 mL/L of hydrogen peroxide

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with no air injection. **Conclusion:** With an appropriate quantity of titanium dioxide and a well calculated concentration of hydrogen peroxide, very good concentration percentages of the 84 orange reactive and colored waste waters are obtained, besides of high mineralization percentages.

Key words: Extraction. Oleoresin. Chili pepper. Capsaicin. Dihydrocapsaicin.

Resumo

Introdução. O Laranja Reativo 84 é um corante utilizado na indústria têxtil que ao ser aplicado na tela de algodão, somente o 65% deste fica impregnado e o 35% restante se hidrolisa na água, gerando uma água residual altamente colorida. **Objetivo.** Estudar a fotocatálisis do Laranja Reativo 84 utilizando recolhedor solar e dióxido de titânio como catalisador. **Materiais e métodos.** Utilizou-se um recolhedor solar, o qual constava de três módulos, cada módulo estava composto por oito tubos de vidro (Schott-Duram) de 48 mm de diâmetro externo e 150 cm de longo e lâmina de alumínio, já que permite a refletância da radiação ultravioleta da

Luz solar, todo o conjunto tinha uma bomba de recirculação e um tanque; o recolhedor solar tinha uma inclinação de 6º com respeito ao solo, de frente ao Norte, já que deve coincidir com a posição geográfica do lugar. Variou-se uma só condição em cada experimento com o objetivo de estudar sua influência na degradação do corante; nesta investigação se apresentam diferentes combinações de peróxido de hidrogênio, dióxido de titânio e ar utilizados na fotocatálisis do Laranja Reativo 84. **Resultados.** Encontrou-se que as concentrações ótimas para a degradação do laranja reativo 84 numa concentração de 340 mg/L são: 40 mg/L de dióxido de titânio e 2ML/L de peróxido de hidrogênio sem injeção de ar. **Conclusão.** Com uma quantidade de dióxido de titânio e uma concentração de peróxido de hidrogênio adequada, podem-se obter boas porcentagens de degradação do laranja reativo 84 e águas residuais coloridas e altas porcentagens de mineração.

Palavras chaves: Fotocatálisis. Corante. Dióxido de Titânio. Laranja Reativo 84. Água Residual.

Introducción

Medellín has a lot of textile industries, and, therefore, a high number of dye factories. The city is located at 6º of north latitude, at 1.632 meters above sea level with an average temperature of 28ºC (12 m). The application of solar energy brought the interest of researchers back in the 1970´s. The solar energy was used to eliminate pollutants in waste waters by using an appropriate photocatalyzer.

This system takes advantage of the solar energy that arrives to the earth to cause a series of chemical reactions (redox) that eliminates organic compounds in urban, industrial and agricultural waters, changing the oxidation state of heavy metals from a dissolved to an insoluble form[1-4].

One of the technologies that seems to be attractive to decontaminate waste waters is the photo catalytical degradation based on the use of titanium dioxide (TiO_2) as photo catalyzer, and a low energy ultraviolet light (320-390 nm). The method has been proved in laboratories since the middle 80´s in hydrocarbons, chlorinated organic and phosphorated compounds contained in pesticides and herbicides, dyes and surfactants. This fact has become even more interesting recently due to its potential application with the use of solar energy, despite the fact that only 5% of the sunlight that arrives to the troposphere contains the necessary energy to activate the titanium dioxide[5-7].

Orange - 84 dye is used in the textile industry, specifically in cotton clothing, which generates a highly colored residual water, because only 65% of this water is impregnated and the 35% remaining hydrolyses in water, generating a highly colored waste water. The concentration that will be used to prepare the synthetic samples for this study will have the same average concentration found in the waters after the dyeing process has been accomplished (340 mg/L)[8,9].

Solar detoxification of waste waters with dyes used in the textile industry, by using photo sensitizers, will avoid the arrival of organic compounds of difficult degradation to the water resources (many of them are toxic as it is the case of some dyes); this will allow the water utilities to get less contaminated water to treat, and, for the fauna and the aquatic flora, to diminish the danger of extinction. This treatment is a clean technology because it takes advantage of the solar energy which is not a pollutant. Non pollutants photo sensitizers are used because they do not produce toxicity by-products, nor sludge, due to the organic composition, which is mineralized. Besides, the photo sensitizers can be recovered and used again[9-12].

Materiales y métodos

The solar collector used in the study has three modules, each one made with eight glass Schott-Duran pipes. Each glass pipe has 48 cm of external diameter and is 150 cm long. It also contains an aluminium sheet, which allows the reflection of ultraviolet radiation from the sunlight. The whole set has a recirculation pump and a tank; the solar collector has an inclination of 6 degrees, facing North, because it must be located with the geographical position of the place where it is being accomplished, to avoid the daily adjustment of the position according to the solar elevation, and to have the highest efficiency of radiation. The glass pipes are joined with PVC connections. (Photo 1)

Table 1 shows the experiments carried out for the degradation process of the reactive Orange - 84. Only one condition was changed on each experiment with the aim of studying its influence in the dye's degradation.

Photo 1. Solar collector used in the study

Table 1. Experiments for the degradation of the reactive Orange - 84

Experiment No	Experiment Descriptionn	Dye concentration (mg/L)	TiO_2 concentration (mg/L)	H_2O_2 amount (mL/L)	Aeration
F	Photolysis	340	0	0,0	No
E1	H_2O_2 Oxidation	340	0	4,0	No
E2		340	0	6,0	No
E3	Heterogeneous photocatalysis	340	40	2,0	No
E4		340	40	4,0	No
E5		340	80	2,0	No
E6		340	80	3,0	No
E7		340	80	4,0	No
E8		340	100	4,0	No
E9		340	100	0,0	No
E10		340	40	2,0	Yes
E11		340	80	3,0	Yes
E12		340	80	0,0	Yes

A not balanced three Levels (4x5x2), Factorial Experiment was the model used for the analysis at a not balanced status, with interaction between the photo catalyzer and the oxidizing agent. The dependent variable is the degradation percentage for eight hours of solar irradiation. The statistical model proposed for the degradation of this dye is the following, analyzed by the statistical package SAS:

$$y_{ijkl} = \mu + \alpha_i + \beta_j + \gamma_k + (\alpha\beta)_{ij} + \varepsilon_{ijkl}. \quad (1)$$

Where: μ: is the mean (half degradation), α_i: is the effect of the TiO_2 in the degradation process, β_j: is the effect of the H_2O_2 in the degradation process, γ_k: is the effect of the Air in the degradation process, $\alpha\beta_{ij}$: is the interaction effect between the TiO_2 and the H_2O_2 in the degradation process, ε_{ijkl}: is the aleatory error.

Each experiment was carried out three times. From the experiments at table 1, we chose three of them, which were the ones with the best percentages of degradation of the reactive Orange - 84 to be carried out again three times; to determine the mineralization degree, monitored with the DQO. These experiments were E3, E6 and E11.

Results

Orange - 84 was not very degraded in the photolysis (10.68%), after 32 hours of solar radiation (figure 1).

The percentage of degradation of Orange - 84 using 4 mL/L of H_2O_2 (E1) was very low (32,25%). The dye was degraded much faster in the experiment E1 than in the photolysis. The percentage of degradation of the dye using 6 ml/L of H_2O_2

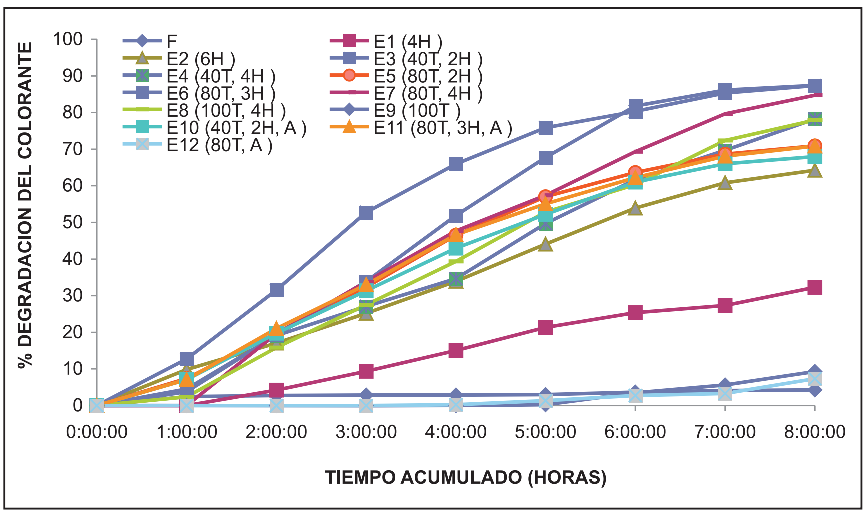

Figure 1. Results of the experiments for the degradation of Orange - 84

(E2) was 64,25%, corroborating that hydrogen peroxide oxidizes Orange - 84.

In the photocatalysis with 40 mg/L of TiO_2 and 2 mL/L of H_2O_2 (E3), the amount of peroxide added was smaller than in the experiments with only hydrogen peroxide; the average percentage of degradation of the dye increased (87,34%), because in this case the oxidizing agent is the radical hydroxyl and not the H_2O_2. When we repeated the experiment E3, the average percentage of degradation of Orange - 84 was 88.70% and in the previous experiments it was 87,34%. The degradation percentages were similar. The mineralization percentage reached 45,32%.

It was not corroborated that, at a higher dose of H_2O_2 (with 40 mg/L of TiO_2 and 4 ml/L of H_2O_2 [E4]), the degradation percentage is higher as well. Comparing with E3, it can be explained that with higher amounts of H_2O_2, in the case of the dye, the radical hydroxyl can pass through a recombination.

The photo catalysis with 80 mg/L of TiO_2 and 2 ml/L of H_2O_2 (E5), degraded the Orange - 84 in 70,3%. Comparing with experiment E3, which had a degradation of 87.34%, the percentage was smaller, indicating that when incrementing TiO_2, the percentage of degradation of the dye decreases. Nevertheless, there could have remained some TO_2 particles inside the pipe which were not photo activated.

The experiment with 80 mg/L of TiO_2 and 3 ml/L of H_2O_2 (E6) degraded Orange-84 in 87,42%. Comparing with E3, which degraded 87,34%, we could observe that the effects of the TiO_2 or the H_2O_2 did not have much difference between them.

If the E6 is compared with the E5 we can observe that the increase of the H_2O_2 increased the percentage of degradation of the dye. The experiment E6 was done again. The mineralization percentage was 45.36%. The new experiment degraded the dye in 76,77%, while the previous experiment's degradation was 87.42%. This decrease could be caused by the characteristics of the day the three repetitions were carried out, because it was less sunny.

The experiment with 80 mg/L of TiO_2 and 4 ml/L of H_2O_2 (E7) degraded the RO84 in 84,74% and, comparing it with the experiment E6 (87.42%), it is observed that the degradation of the Orange-84 decreased in 2,68%; therefore, when we increased the amount of H_2O_2, the degradation percentage did not increase. If it is compared with the E5, 70,93%, the positive effect of the H_2O_2 is noticed. It means that when we have a concentration of 80 mg/L of TiO_2, the percentage of degradation of the dye does not increase (previously discussed).

The degradation of the dye with 100 mg/L of TiO_2 and 4 ml/L of H_2O_2 (E8) was 77,96%, which is lower compared with the photo catalysis experimented in E7. It is corroborated that the increase of the TiO_2 above 40 mg/L does not produce an increment in degradation of the Orange - 84.

In the experiment E9 (100 mg/L of TiO_2), the non-use of the hydrogen peroxide reduced almost completely the degradation of the dye. Therefore, it is imperative for us to use it. For this experiment, the percentage of degradation was 9,30% and for E8 the degradation was 77,96%.

The experiment with 40 gm/L of TiO_2, 2 ml/l H_2O_2 and Air (E10), compared with the results of the experiments with TiO_2 and H_2O_2 (without using air), showed us that the air does not improve the percentage of degradation of the dye, at contrary, it reduces that rate. This happens because, when there are enough free radicals, there is a competition among them for the dye and the interaction reduces the effective amount of free radicals.

Also the percentage of degradation of Orange-84 got reduced when 80 gm/L of TiO_2 were used with 3 ml/l H_2O_2 and air (E11). This E11 was carried out again to evaluate the mineralization obtained, which was 52,77% (one of the highest values obtained in this work). In the previous experiments, as well as in the repetition, different percentages of degradation were obtained. The first one was 70,84% and the second one was 81,85%. This was caused by the days when the previous experiments took place, that were less sunny.

In the experiment with 80 mg/L TiO_2 and air (E12), the degradation percentage was as low as the one obtained with 100 mg/L of TiO_2 without using hydrogen peroxide or air. This corroborates that the hydrogen peroxide is needed to carry out the photo catalysis of the Orange-84. This is proved if it is compared with the best results of the experiments of the oxidation with hydrogen peroxide only.

The ANOVA was calculated for the statistical model of this analysis, with the aim of checking if the model used was good enough to explain the degradation of the dye. For the ANOVA model of this analysis it is significant ($p < 0,0001$), therefore, the proposed model is valid or acceptable to explain the degradation of the Orange 84, according to the factors.

The variation coefficient ($R2=0,9446$), means that 94,46% of the variation in the degradation of the reactive Orange - 84 is explained by the model proposed that includes the effects of the TiO_2, H_2O_2, air and the interaction among them.

The significance analysis of effects shows that the TiO_2, H_2O_2, the air and the interaction among them, is significant ($p < 0,001$); the change in the concentration of each one of them and its interaction affect the degradation.

Figure 2 shows the percentage of degradation of the Orange - 84 versus the combination of the TiO_2 and H_2O_2. This figure indicates that, without hydrogen peroxide and with concentrations of titanium dioxide of 0,80 and 100 mg/L, low levels of degradation are obtained, as well as very small differences among them. It can be deduced that the highest degradation of the dye is obtained when the TiO_2 is combined in a range of 40 - 80 mg/L with the H_2O_2 in the range of 2 - 4 mg/L. The air reduces the efficiency of this procedure. It had already been affirmed that it was statistically significant, therefore it is proved that the highest degradations in the reactive dye Orange - 84 appeared in experiments E3, E4, E6 and E7. The best concentrations of degradation of the reactive Orange - 84 in a concentration of 340 mg/L were: 40 mg/L of titanium dioxide and 2mL/L of hydrogen peroxide without injection of air.

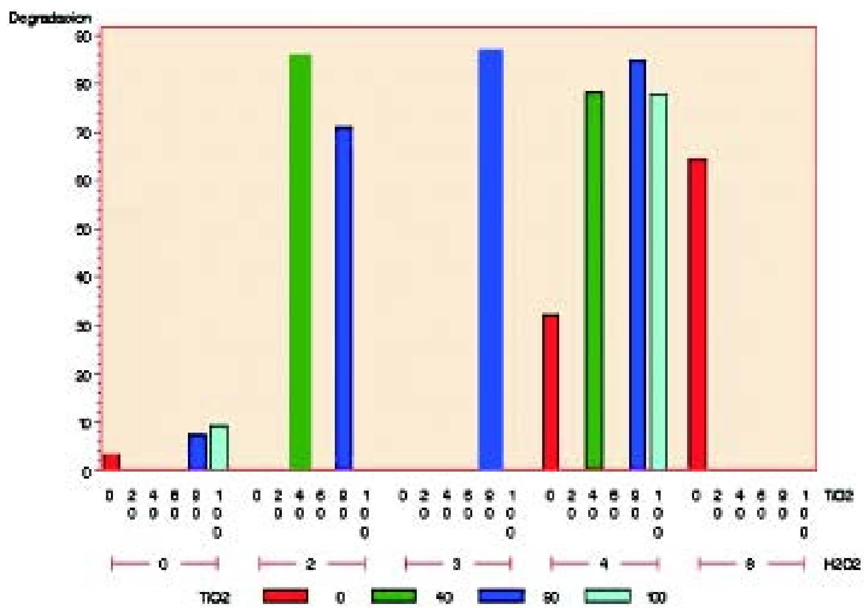

Figure 2. Interaction between the titanium dioxide and hydrogen peroxide for the degradation of the Orange - 84

It was graphically proved that the residuals of the model are homogeneous and the variability was low. Besides, the Kolmogorov test, with a significance of 5%, confirms that the remainders have a normal distribution, showing this that the model fulfills the suppositions of normality and the validity of the model (normality in errors and homogeneous variance).

Discussion

In the study of Reactive Orange 84 dye photo catalysis, it was found that in the dye´s photolysis very low percentages of degradation resulted after 32 hours of sun radiation; therefore, Reactive Orange 84 is photo stable before sun radiation. The optimal concentrations of photo catalyzer and oxidant agent for the degradation of Orange 84 (340mg/L) found in this research work are: 40 mg/L of TiO_2 and 2 mL/L of H_2O_2, without air injection because it diminishes the percentage of final degradation of the dye. In scientific literature we could not find articles from to compare the findings of this research, due to the fact that this dye has not been studied.

Conclusions

In the photolysis of the reactive Orange - 84, the percentages of degradations of the dye obtained were very low, and the average percentages of the three repetitions carried out were 10,68%, in 32 hours.

In the experiment with 80 mg/l of TiO_2 and 3 ml of H_2O_2/L we obtained the highest percentage of degradation of the dye: 87,42%. The highest degradation percentages and rates were reached when the combinations of titanium dioxide and hydrogen peroxide were used.

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