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Analysis of the optimal conditions for the mineralization and degradation of Novactive Red F6BS in waste water*

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Análisis de las condiciones óptimas para la mineralización y degradación del Rojo Novactive F6BS en aguas residuales

Análise das condições ótimas para a mineralização e degradação do vermelho novactive F6BS em águas residuais

ABSTRACT

Introduction. The research work consisted of an analysis of the conditions to treat waste waters with Novactive Red F6BS dye by the use of advanced oxidation processes with artificial light to eliminate persisting substances from the water. **Objective.** To evaluate the optimal conditions to remove the Novactive Red F6BS dye in waste waters by the use of an artificial light source. **Materials and methods.** A MIGTHY PURE 60 Hz ultraviolet light lamp was used with a glass bucket that stores 15 liters of sample. This sample was re-circulated with a pump with a 0.047 L/s flow. **Results.** The best results for the Novactive Red F6BS dye were 76.2% of degradation and 49.4% of mineralization in two hours, with the E7 test (60 mg/L of $FeCl_3$ and 1 mL/L of H_2O_2). **Conclusions**. The dye is faster degraded and mineralized with the $FeCl_3$; this took place in the E7 test (60 mg/L of $FeCl_3$ and 1 mL/L of H_2O_2).

Key words: Photodegradation, UV lamp, mineralization, Novactive Red.

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RESUMEN

Introducción. La investigación consistió en analizar las condiciones para el tratamiento de aguas residuales con el colorante Rojo Novactive F6BS, por procesos de oxidación avanzada empleando luz artificial para la eliminación de sustancias persistentes en el agua. **Objetivo**. Evaluar las condiciones óptimas para la remoción del colorante Rojo Novactive F6BS en aguas residuales utilizando una fuente de luz artificial. **Materiales y métodos.** Se utilizó una lámpara de luz ultravioleta marca MIGTHY PURE de 60 Hz, con una cubeta de vidrio que almacena 15 L de muestra; la muestra se recirculó con bomba que manejó un flujo de 0.047 L/s. **Resultados.** Los mejores resultados obtenidos para el colorante Rojo Novactive F6BS fueron de 76.2% de degradación y un 49.4% de mineralización en dos horas, con el ensayo E7 (60 mg/L de $FeCl_3$ y 1 mL/L de H_2O_2). **Conclusiones**. El colorante degrada y mineraliza más rápidamente con el $FeCl_3$; esto sucedió en el ensayo E7 (60 mg/L $FeCl_3$ y 1.0 mL/L de H_2O_2).

Palabras clave: fotodegradación, lámpara UV, mineralización, Rojo Novactive.

RESUMO

Introdução. A investigação consistiu em analisar as condições para o tratamento de águas residuais com o corante Vermelho Novactive F6BS, por processos de oxidação avançada empregando luz artificial para a eliminação de substâncias persistentes no água. **Objetivo.** Avaliar as condições ótimas para a remoção do corante Vermelho Novactive F6BS em águas residuais utilizando uma fonte de luz artificial**. Materiais e métodos.** Utilizou-se um lustre de luz ultravioleta marca MIGTHY PURE de 60 Hz, com uma cuba de vidro que armazena 15 L de mostra; a mostra se re-circulou com bomba que manejou um fluxo de 0.047 L/s. **Resultados.** Melhores resultados obtidos para o corante Vermelho Novactive F6BS foram de 76.2% de degradação e um 49.4% de mineralização em duas horas, com o ensaio E7 (60 mg/L de FeCl3 e 1 mL/L de H2Ou2). **Conclusões.** O corante degrada e mineraliza mais rapidamente com o FeCl3; isto sucedeu no ensaio E7 (60 mg/L FeCl3 e 1.0 mL/L de H2Ou2).

Palavras importantes: fotodegradação, lustre UV, mineralização, Vermelho Novactive.

INTRODUCTION

The photodegradation sensibilized with TiO_2 or $FeCl_3$ is a technique that can be used as a depuration system by itself or as a tertiary process, especially to treat industrial waste with recalcitrant compounds. Photocatalytic techniques are considered as very promising to be applied for their application in solving waste water problems. These technologies are very attractive to be used worldwide. The use of these techniques in order to degrade and mineralize dyes can become an alternative more adequate than other traditional oxidation processes[1, 2].

The acceleration of a photoreaction by the presence of a catalyst is called photocatalysis[3-10]. The catalyst activated by the absorption of the light, accelerates the reaction with the reactive through an excited state or, also, by the appearing of electron-hole pairs, if the catalyst is a semiconductor (e- and h+). In the latter case, the excited electrons are transferred to the reducible species, at the same time that the catalyst accepts electrons from the oxidizable species, which will fill the holes. This way, the net flow of electrons will be null and the catalyst will stay unaltered[11-19].

MATERIALS AND METHODS

To dye clothes from textile industries, one of the most commonly used dyes is Novactive Red F6BS. The average concentration in the water was 300 mg/L for each one, which is the typical average concentration of the effluents from textile industries that contain these dyes. Table 1 shows the tests performed. Each test was performed in triplicate in order to reduce the experimental error. For the experiments, hydrogen peroxide was used as oxidation agent (H_2O_2). The tests lasted two hours.

Table 1. Conditions of the experiments for the Novactive Red F6BS

Experiment	Novactive Red F6BS (mg/L)	TiO_2 (mg/L) or $FeCl_3$ (mg/L)	H_2O_2 (mL/L)
E1	300	0	0
E2	300	30	0
E3	300	30	0.5
E4	300	30	1.0
E5	300	60	0
E6	300	60	0.5
E7	300	60	1.0
E8	300	0	0.5
E9	300	0	1.0

Source: proprietary production

The degradation of the dye was evaluated by measuring the concentration of the pollutant by monitoring the color (photometry) and the mineralization, by the use of the total organic carbon (TOC).

The experiments were performed with the following procedure:

- 15 L of water were measured and stored in the glass bucket.
- The dye was added in the bucket, and a 300 mg/L was obtained.
- The solution was shaken, initially by hand and then recirculated by the use of the pump and the lamp.
- A sample was taken in order to measure the color and the initial TOC..
- The chemical substances were added in accordance with the experiments of Table 1 (hydrogen peroxide, titanium dioxide, ferric chloride and their respective mixtures).
- The pH was continuously measured in order to adjust it at 4 when $FeCl_3$ was being used; H_2SO_4 or NaOH were added in accordance with the values. With TiO_2 the pH values were measured with no necessity of adding acids or bases, due to the fact that they are more stable (pH near 7).
- The samples were taken in order to be analyzed in the laboratory. They were taken every 20 minutes to measure the color and the TOC was measured every 40 minutes.
- After finishing every experiment the lamp was washed with a diluted chromo-sulfuric solution and plenty of water, having it clean for the next experiment.
- The color and TOC analysis were immediately performed in the laboratory.
- The R.2.7.2 program was used to process the information, and the methods were: variance analysis (ANOVA) of three factors, with a confidence level of 95% and a power level to detect significant differences of 100%, and factorial analysis 3^3, to optimize the response variables: degradation percentage and mineralization percentage.

RESULTS

Table 2 shows the results for the degradation and the mineralization of wáter with the Novactive Red F6BS dye.

Table 2. Results for the degradation and mineralization of the Novactive Red F6BS dye

Test	Results with $FeCl_3$				Results with TiO_2			
	% degradation		% mineralization		% degradation		% mineralization	
	%	D.E.	%	D.E.	%	D.E.	%	D.E.
E1	19.5	0.4	3.9	0.5	19.5	1.2	3.9	0.4
E2	43.8	0.5	20.8	1.2	37.7	1.4	15.9	0.9
E3	52.8	0.9	26.7	1.3	43.9	1.0	20.8	0.9
E4	62.0	1.2	32.2	1.0	49.5	1.3	26.2	0.8
E5	55.3	1.0	29.3	0.9	44.5	0.9	26.1	0.8
E6	68.4	0.3	41.0	0.8	52.4	0.7	30.3	1.3
E7	76.2	0.3	49.4	0.4	68.3	0.4	39.4	0.6
E8	33.8	0.7	12.5	1.2	33.8	0.8	12.5	0.4
E9	41.1	0.6	15.7	1.0	41.1	0.6	15.7	0.2

Source: proprietary production

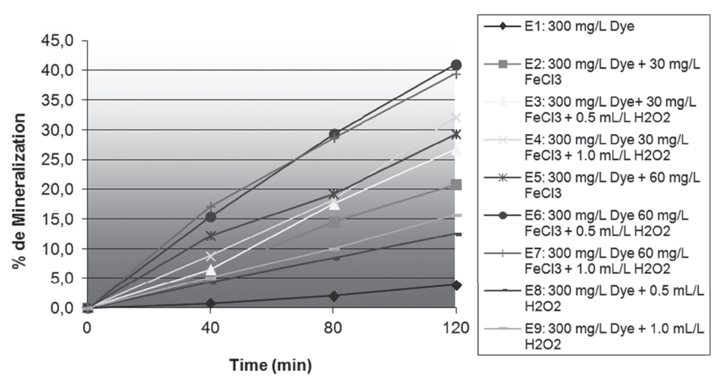

Figure 1. Degradation percentage of the Novactive Red F6BS dye with $FeCl_3$ in the different tests
Source: proprietary production

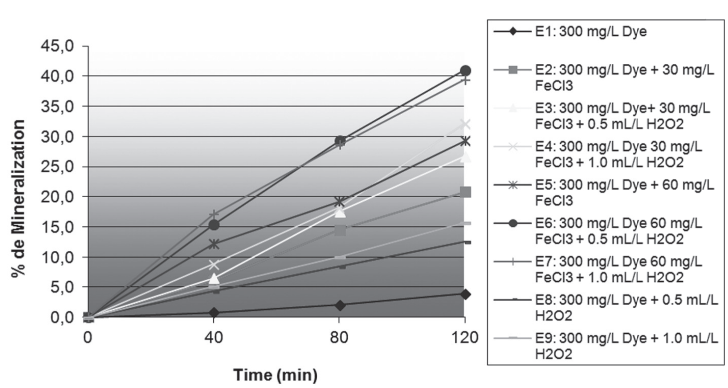

Figura 2. Mineralization percentage of the Novactive Red F6BS dye with $FeCl_3$ in the different tests
Source: proprietary production

Table 2 and figures 1and 2 show the degradation and mineralization percentages for the tests with $FeCl_3$ of the Novactive Red F6BS dye. It can be inferred that in the photolysis (E1) the degradation and mineralization percentages had the lowest results found for this dye, 19.5 and 3.9%, respectively.

The use of 30 mg/L of $FeCl_3$ (E2) increased the degradation and mineralization percentages of the dye in 43.8 y 20.8%, respectively. This test was performed in order to know if photo activated $FeCl_3$ is able to generate enough hydroxyl free radicals from water to degrade and mineralize the Novactive Red F6BS dye. Therefore, the photocatalysis was performed without hydrogen peroxide.

Compared with the sole use of $FeCl_3$, the use of 30 mg/L of $FeCl_3$ and 0.5 mL/L of H_2O_2 (E3) increased the degradation and mineralization percentages of the dye in 52.8 and 26.7%, respectively. This can be explained by the fact that in this experiment the oxidation agent is the hydroxyl radical. With the increase of hydrogen peroxide from 0.5 mL/L to 1.0 mL/L (E4) an increase of the degradation velocity of the Novactive Red F6BS dye was intended, because this is a source of hydroxyl radicals. Comparing E3 and E4 tests, it was proved that the higher hydrogen peroxide content is, the higher degradation and mineralization of the dye is, too (the quantity of $FeCl_3$ was constant). For the E4 test the degradation and mineralization percentages were 62.0 y 32.2%, respectively.

The increase of the $FeCl_3$ from 30 mg/L to 60 mg/L, using only the photosensitizer (tests E2 and E5, respectively), increased the degradation and mineralization percentages in 55.3% and 29,3%, respectively. The test with 60 mg/L of $FeCl_3$ and 0.5 mL/L (E6) increased the degradation and mineralization percentages in 68.4% and 41.0%, thus being one of the best tests for this dye. By increasing the hydrogen peroxide quantity in 1 mL/L (E7), 76.2% of degradation and 49.4% of mineralization were obtained in two hours. This I the best test obtained for the Novactive Red F6BS dye.

In order to verify the importance of chemical oxidation with hydrogen peroxide in this research work, the E8 and E9 tests were performed with 0.5 mL/L and 1.0 mL/L respectively; 33.8 and 41.1% of degradation were obtained, respectively, and so were 12.5 and 15.7% of mineralization. The degradation and mineralization percentages of the dye increased as the hydrogen peroxide did too, a very probable fact because H_2O_2 has a great oxidation potential.

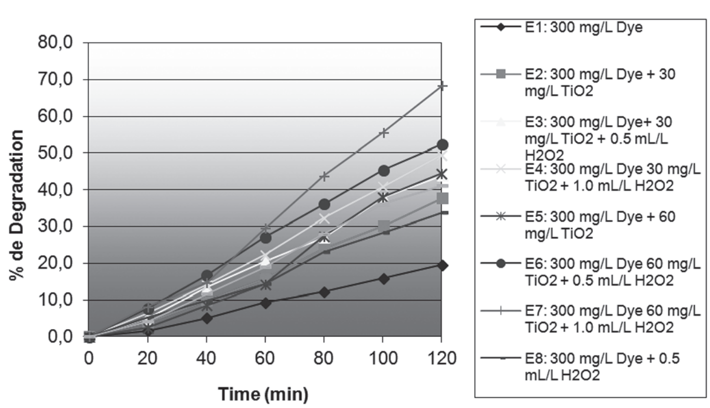

Figure 3. Degradation percentage of the Novactive Red F6BS dye with TiO_2 in the different tests

Source: proprietary production

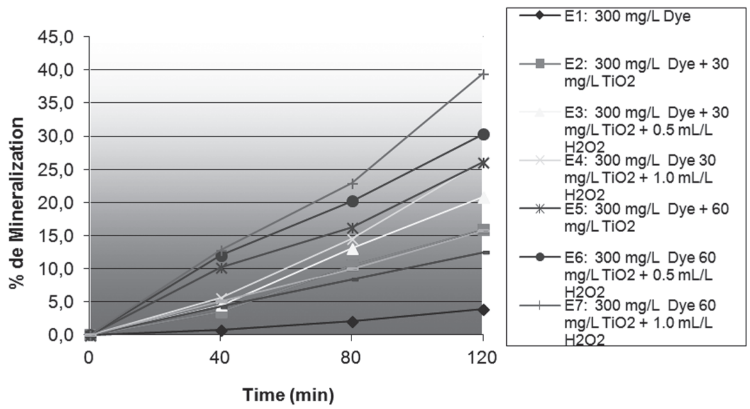

Figure 4. Mineralization percentage of the Novactive Red F6BS dye with TiO_2 in the different tests
Source: proprietary production

Table 16 and figures 3 and 4 show the degradation and mineralization percentages for the tests performed with TiO_2. For the photolysis (E1) the degradation and mineralization percentages were the lowest results obtained for this dye, 19.65 and 3.9 % respectively. The use of 30 mg/L of the TiO_2 (E2) increased the degradation and mineralization percentages of the dye in 37.7 and 15.9%, respectively. This test was performed to verify if photo activated TiO_2 is able to generate enough hydroxyl radicals from water to degrade and mineralize the Novactive Red F6BS dye. This is why the photocatalysis was performed without hydrogen peroxide.

In comparison to the sole use of TiO_2, the use of 30 mg/L de TiO_2 and 0.5 mL/L of H_2O_2 (E3) increased the degradation and mineralization percentages in 43.9 and 20.8 % respectively. This can be explained by the fact that in this test the oxidation agent is the hydroxyl radical, with a great oxidation power. The hydroxyl radical is easily formed from the hydrogen peroxide given the presence of titanium dioxide, when this is photo activated by ultra violet light.

By increasing hydrogen peroxide from 0.5 mL/L to 1.0 mL/L (E4) a velocity increase of the degradation of the Novactive Red F6BS dye was intended, because this is a source of hydroxyl radicals. Comparing E3 and E4 tests it was proved the fact that the higher the quantity of hydrogen peroxide is, so are the degradation and mineralization percentages of the dye (the TiO_2 quantity was constant).

It was interesting to check if photocativated TiO_2 is able to generate enough hydroxyl radicals from water to degrade and mineralize the Novactive Red F6BS dye. Therefore, a photocatalysis without hydrogen peroxide was performed. The TiO_2 increase from 30 mg/L to 60 mg/L, using only the photosensitizer (tests E2 and E5 respectively), increased the degradation and mineralization percentages in 44.5% y 26.1%, respectively, although the degradation increase between both tests was not significant.

The test with 60 mg/L of TiO_2 and 0.5 mL/L (E6), increased the degradation and mineralization percentages in 52.4% and 30.3%. This test is one of the best ones for this dye with TiO_2. By increasing the quantity of hydrogen peroxide 1 mL/L (E7), a 68.3% of degradation and a 39.4% of mineralization were obtained in two hours. This is the best test obtained for the Novactive Red F6BS dye with TiO_2.

CONCLUSION

By comparing the photocatalysts used for the Novactive Red F6BS dye ($FeCl_3$ y TiO_2), it can be concluded that the dye is more rapidly degraded and mineralized with $FeCl_3$. This happened in the E7 test

(60 mg/L $FeCl_3$ and 1.0 mL/L of H_2O_2), in which a degradation percentage of 76.2% and a mineralization percentage of 49.4% were obtained.This is the same experiment in which the best results for the degradation and the mineralization of the dye with TiO_2 were obtained.

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