Homogeneous degradation of the Remazol Black B dye by Fenton and photo-Fenton processes in aqueous medium

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Degradación homogénea del colorante Remazol Black B mediante procesos Fenton y foto-Fenton en medio acuoso

Degradació homogènia del colorant Remazol Black B mitjançant processos Fenton i foto-Fenton en medi aquós

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RESUMEN

En esta investigación, se han empleado diseños factoriales para estudiar la influencia de tres factores importantes ([H₂O₂], [Fe²⁺] y el tiempo de la reacción) en la decoloración y la degradación del colorante Remazol Black B mediante procesos Fenton y foto-Fenton. Para los experimentos de foto-Fenton se utilizaron dos fuentes de radiación: luz UVA y visible. Esta investigación revela la importancia de la radiación en la reacción de decoloración y de degradación de Remazol Black B. Basado en las condiciones experimentales optimas, la eficacia de eliminación del colorante siguió el orden: Foto-Fenton luz UVA > Foto-Fenton luz visible > Fenton. Los valores del Carbono Orgánico Total (COT) fueron de 36%, 27% y 16%, para los procesos foto-Fenton luz UVA, foto-Fenton luz visible y Fenton, respectivamente, obtenidos para la degradación del colorante a partir también de las condiciones experimentales optimas. Los resultados constataron que la luz visible puede ser empleada como una fuente de radiación económicamente viable en comparación con la luz UVA visible.

Palabras clave: Decoloración. Diseño factorial. Fenton. Foto-Fenton. Remazol Black B. Luz UVA. Luz visible.

ABSTRACT

In this research, factorial designs have been employed to study the influence of three important factors $([H_2O_2], [Fe^{2+}]$ and the reaction time) on the discoloration and the degradation of Remazol Black B dye by Fenton and photo-Fenton processes. For the photo-Fenton experiments, two different sources of radiation were used: UVA and visible light. This investigation reveals the importance of irradiation on the discoloration reaction and the degradation of the Remazol Black B. Based on the optimum experimental conditions the more efficient dye removal followed the sequence: UVA light photo-Fenton > Visible light photo-

Fenton > Fenton. Total organic carbon (TOC) values of 36%, 27% and 16%, for the UVA light photo-Fenton, visible light photo-Fenton and Fenton processes, respectively, were obtained for the dye degradation also at the optimum experimental conditions. Based on the observed data it was found that the visible light can be employed as an economically viable source of irradiation in comparison to the UVA light.

Keywords: Discoloration. Factorial design. Fenton. Photo-Fenton. Remazol Black B. UVA light. Visible light.

RESUM

En aquesta investigació, s'empren dissenys factorials per estudiar la influència de tres factors importants ([H2O2], [Fe2+] i el temps de la reacció) en la decoloració i la degradació del colorant Remazol Black B mitjançant processos Fenton i foto-Fenton. Per als experiments de foto-Fenton, s'utilitzen dues fonts de radiació: Ilum UVA i visible. Aquesta investigació revela la importància de la radiació en la reacció de decoloració i de degradació de Remazol Black B. En les condicions experimentals òptimes, l'eficàcia d'eliminació del colorant segueix l'ordre: Foto-Fenton llum UVA > Foto-Fenton Ilum visible > Fenton. Els valors del Carboni Orgànic Total (COT) són de 36%, 27% i 16%, per als processos foto-Fenton Ilum UVA, foto-Fenton llum visible i Fenton, respectivament, obtinguts per a la degradació del colorant a partir també de les condicions experimentals òptimes. Els resultats constaten que la llum visible pot ser emprada com una font de radiació econòmicament viable en comparació amb la llum UVA.

Mots clau: Decoloració. Disseny factorial. Fenton. Foto-Fenton. Remazol Black B. Llum UVA. Llum visible.

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INTRODUCTION

Dyes are important compounds employed in several industries, such as textile, pharmaceutical, cosmetics, plastics, photographic, paper and food. Since they are a key factor for the success of many textile products, a great amount of different dyes are commercially available⁽¹⁾. Widely used textile synthetic dyes may be of acidic or basic character, and display different reactivity and dispersivity. They may be also have different chemical functionalities (azo, diazo, antraquinone-based and metal-complex dyes)⁽²⁾. In spite of their importance, azo dyes and their breakdown products, in particular, have been found to be toxic, mutagenic/carcinogenic and genetoxic, to aquatic life (3).

Textile industries are one of the largest water consumers, producing 50-100 L of wastewater per kilogram of finished product. Textile dyeing constitutes therefore a major environmental pollution problem, due to the variety and complexity of the required chemicals (dyes, sequestering agents, tannins, dye carriers, leveling agents, dispersing agents, etc.)⁽⁴⁾. Over 700 000 tons of approximately 10 000 kinds of dyes and pigments are annually produced worldwide for dyeing and printing. About 20% of this output is discharged in wastewaters causing a huge environmental problem⁽⁵⁾.

Colored dye effluents are conventionally treated by various chemical and physical methods, such as coagulation, reverse osmosis and adsorption. These methods, however, are not destructive. They merely concentrate the polluting agents, which need further processing before disposal. Biological processes, on the other hand, do not work efficiently, because of the high solubility of the synthetic dyes and their resistance to aerobic degradation^(6,7).

Advanced oxidation processes (AOP), which include Fenton, Fenton-like, H_2O_2/UV , and photo-Fenton reactions, might prove to be effective alternatives to remove textile industrial dyes, as they may have the ability to completely discolor and partially mineralize them, in relatively short reaction times^(B-10). AOP are considered chemical treatment methods based on the generation of hydroxyl radicals (*OH), which contain a high oxidative power. These radicals are capable of rapidly attacking organic substrates and causing decomposition of these compounds by H-abstraction and addition to C–C unsaturated bonds^(10,11).

For the Fenton reaction, or dark Fenton, the ${}^{\bullet}OH$ radicals are generated by the iron-catalyzed decomposition of $H_{2}O_{2}$, where the overall reaction usually accepted is⁽¹²⁾:

$$Fe^{2+} + H_2O_2 \rightarrow {}^{\bullet}OH + Fe^{3+} + OH^-$$
 (1)

While in the case of photo-Fenton reaction, more hydroxyl radicals are formed in addition to reaction (1), due to the UV or UV-visible irradiation, according to the following reactions⁽¹³⁻¹⁵⁾:

$$H_2O_2 + h_U \rightarrow {}^{\bullet}OH + {}^{\bullet}OH$$
 (2)

$$Fe^{3+} + H_2O + h_{\mathcal{U}} \rightarrow {}^{\bullet}OH + Fe^{2+} + H^+$$
 (3)

The aim of the present work is to optimize the color removal of synthetic aqueous solutions of Remazol Black B, an azo dye employed in the textile local industries, by Fenton and UVA light photo-Fenton processes. Additional photo-Fenton experiments were carried out employing visible light, in order to propose a color removal process of lower cost. The dye degradation was determined by the total carbon analysis (TOC) for selected conditions. Full two-level factorial designs were employed to estimate the influence of three factors on the discoloration of the Remazol Black B: H₂O₂ concentration, Fe²⁺ concentration, and reaction time. The use of factorial design allows more efficient and economical removal treatment conditions to be found with a relatively small number of experiments, as compared to traditional one-variable-at-a-time experimentation. Moreover, the results straightforward to analyze and interpret, taking into account all experimental parameters and yielding estimates of the main effects of the most significant factors and their possible interactions⁽¹⁶⁾.

MATERIALS AND METHODS

Chemicals

Remazol Black B dye (RB5, Color Index 20505, $C_{26}H_{21}O_{19}N_5S_6Na_4$, Molecular weight = 991.8 g mol⁻¹) was provided by DyStar and used as received. The molecular structure of Remazol Black B in its non-hydrolyzed form is illustrated in Fig. 1. H_2O_2 (Degussa) was standardized with KMnO₄ (Reagen) in an acidic medium⁽¹⁷⁾. FeSO₄·7H₂O (Carlo Erba), H_2SO_4 (Quimex) and Na_2SO_3 (F. Maia) were all of reagent grade. The dye aqueous solutions (100 mg L⁻¹) were prepared daily. The pH of the reaction solutions was adjusted with a 0.5 M H_2SO_4 solution.

Fenton experiments

The experiments were performed in the dark, using erlenmeyer flasks covered with aluminum foil. A 100 mgL⁻¹ Remazol Black B aqueous solution was prepared and acidified to pH 3.0 with H_2SO_4 . In the sequence, 20 mL of the dye solution were added to erlenmeyer flasks, followed by the addition of appropriate volumes of 0.008 mol L⁻¹ FeSO₄·7H₂O and 1.47 mol L⁻¹ H₂O₂ solutions. The mixtures were homogenized and the starting time recorded. After the prescribed reaction time had elapsed, the analytical measurements were carried out immediately, to avoid further reaction.

Photo-Fenton experiments

The UVA light photo-Fenton experiments were carried out in a batch photo-reactor fitted with three UVA blacklightblue fluorescent lamps (XELUX T10 BL B). For the visible

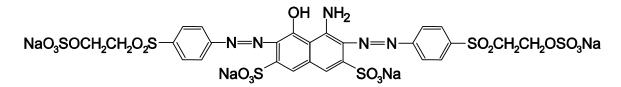


Figure 1. Molecular structure of Remazol Black B.

light photo-Fenton experiments three daylight fluorescent lamps (Daylight Special – OSRAM Universal Brazil k 828) were used. The two kinds of lamp were 60 cm long and had a 20 W nominal output, and their spectral energy distribution are exhibited in Fig. 2. The Remazol Black B 100 mg L⁻¹ aqueous solution was prepared and acidified as before. Then, 50 mL dye solution aliquots were added to petri dishes, and transferred to the reactor, where appropriate volumes of 0.01 mol L⁻¹ FeSO₄·7H₂O and 1.47 mol L⁻¹ H₂O₂ solutions were added and the system homogenized. The reactor was switched on and after the prescribed the time, the solutions were analyzed.

The photon flow entering each petri dish was evaluated to be 17 μ Einstein s⁻¹ (UVA light) and 21 μ Einstein s⁻¹ (visible light).

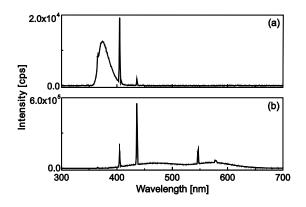


Figure 2. Spectral energy distribution of the two fluorescent lamps: (a) Blacklight-blue (XELUX T10 BL B) (UVA light); (b) Daylight (Daylight Special – OSRAM Universal Brazil k 828) (Visible light).

Statistical design

The first statistical design was performed for the Fenton process, which used a full 2³ design to specify the factor level combinations for the experimental runs, as given in Table 1. This table shows the actual and coded values of each factor level. The experiments were carried out in random order, to prevent any statistical distortion. In addition, the basic two-level factorial was augmented with a central point run in triplicate. The experiments 1 to 8 were run in duplicate, and experiment 9 (central point) in sextuplicate, allowing an estimate of experimental error with 13 degrees of freedom. The statistical significance of the main effects and interactions of the three factors on the two responses were evaluated by an analysis of variance (ANOVA), based on the pure error mean square estimated from the variance of the replicate response values. All calculations and graphical analysis were performed with the Statistica software⁽¹⁸⁾. The choice of iron levels also took into account CONAMA's resolution(19), which restricts environmental iron levels to a maximum of 15 mg L⁻¹.

A second statistical design was made for the UVA light photo-Fenton process based on the results of the first factorial design.

Analysis

Remazol Black B concentrations were determined using an UV-Vis Spectrophotometer (Aquamate - Thermo Spectronic) at the 597 nm wavelength with a 10 mm quartz cuvette (3.0 mL) by means of a calibration curve.

Factor	Level			
	-1	0	+1	
A - H ₂ O ₂ (mg L ⁻¹)	100	200	300	
B - Fe ²⁺ (mg L ⁻¹)	1	2	3	
C - Reaction time (min)	30	60	90	

 Table 1 Factors and levels of the full 2³ factorial design for the Fenton experiments. The digits -1, 0 and +1 represent the coded values of the actual levels given in the table

Dye degradation was quantified on basis of total organic carbon contents measurements (TOC) only after the prescribed reaction time had elapsed. For this determination, aliquots of a 0.1 M Na₂SO₃ solution were added immediately to the samples in a 1:1 (v/v) proportion, to quench the residual H₂O₂^(20,21) before the analysis. The measurements were performed with a total organic carbon analyzer, TOC - V_{CSH} Shimadzu.

The spectral emission range of the UVA blacklight-blue and daylight fluorescent lamps utilized in this study were obtained using an ISS K2 Spectrophotometer, with spectral resolution: 0.5 nm.

RESULTS AND DISCUSSION

Remazol Black B removal by the Fenton process

Remazol Black B percent removal observed in the Fenton process are shown in Table 2. The percent removal varied from 66.65 (run 1) to 99.92 (run 8). The best overall results, 99.92 and 99.69%, were observed when the three factors were set at their corresponding higher levels, as in run no. 8; while the worst percent removal were observed in run no. 1 when three factors are fixed at corresponding lower levels. However, the results for the central point run, which represent intermediate levels, showed high percentage removals, i.e., 98.91%, on average. It means that increasing the levels of the factors from lower to intermediate values a high removal is reached.

The t test results for the effect estimates are shown in Table 2. The pure error of an effect was estimated as 0.71%.

The statistical model for a full 2^3 design allows the calculation of three main effects, three two-factor interactions, and one three-factor interaction, which is usually assumed negligible. The values of the main effects and their interactions are presented in Table 3, most of them are statistically significant at the 95% confidence level.

		Factor	•	
Run	Α	в	С	Remazol Black B removal (%)
1	-1	-1	-1	66.65; 72.14
2	+1	-1	-1	79.68; 81.69
3	-1	+1	-1	98.62; 99.05
4	+1	+1	-1	98.74; 99.46
5	-1	-1	+1	86.23; 83.04
6	+1	-1	+1	94.63; 91.90
7	-1	+1	+1	99.59; 99.27
8	+1	+1	+1	99.92; 99.69
9	0	0	0	98.95; 98.82
				99.04; 98.83
				99.09; 98.75

 Table 2 Remazol Black B percent removal values for the experiments run at all possible combinations of the levels given in Table 1, using a Fenton process

Main effects	Effect estimate (%)
A - H ₂ O ₂ (mg L ⁻¹)	5.14
B - Fe ²⁺ (mg L ⁻¹)	17.30
C - Reaction time (min)	7.28
Two-factor interactions	
AB	- 4.82
AC	- 0.64
BC	- 6.63
Three-factor interaction	
ABC	0.69

Table 3 Estimates of the main and interaction effectscalculated from the response values in Table 2.Statistically significant values are shown in boldface

All main effects are positive, which means that raising the level of any factor from lower to higher value tends to increase Remazol Black B removal, on average. The single largest main effect, 17.30%, is that associated with factor **B**, the Fe²⁺ concentration. Moreover, factor **B** has two significant interaction effects with the other two factors. Since these interactions are negative, they reflect an antagonistic effect between the three factors. In other words, although raising the level of any factor improves Remazol Black B removal, the effect obtained by raising simultaneously the levels of two factors is less than the sum of the individual effects.

Since run no. 9 yielded a percent removal over 98%, and it required only intermediate values of the three factors (200 mg L⁻¹ H₂O₂, 2 mg L⁻¹ Fe²⁺ and 60 min reaction time), therefore being more economical, it was selected as the best condition for the discoloration study and TOC removal.

Remazol Black B removal by the photo-Fenton processes

The second full 2³ design was prepared for the UVA light photo-Fenton experiment. The levels were chosen based on the Fenton level combinations yielding a Remazol removal in the 98-100% range. Moreover, for economical reasons, the higher levels selected for the three factors were those of the central point in the Fenton experiments. Table 4 shows the actual and coded values of each factor. The results obtained for this second experiment design are presented in Table 5. This time only three replicates were run at the central point, which yields an estimate of the error of an effect with just two degrees of freedom. The percent removal values are very high, ranging from 97.07% (run 6) to 99.88% (run 9).

In comparison with the Fenton process, the lower values for percent removal found in Table 5 for the photo-Fenton process, are much higher even in the runs that used lower levels for the three factor investigated.

The effects calculated from the responses in Table 5 are presented in Table 6. Almost all effects now appear to be statistically significant, but this probably is a consequence

		Level	
Factor	-1	0	+1
A - H ₂ O ₂ (mg L ⁻¹)	150	175	200
B - Fe ²⁺ (mg L ⁻¹)	1.5	1.75	2
C - Reaction time (min)	40	50	60

Table 4 Factors and levels of the full 2³ facto-rial design for the UVA light photo-Fenton experi-ments. The digits -1, 0 and +1 represent the codedvalues of the actual levels given in the table.

		Factor		
Run	Α	В	С	Remazol Black B removal (%)
1	-1	-1	-1	97.82
2	+1	-1	-1	98.87
3	-1	+1	-1	99.79
4	+1	+1	-1	99.82
5	-1	-1	+1	99.56
6	+1	-1	+1	97.07
7	-1	+1	+1	99.32
8	+1	+1	+1	99.26
9	0	0	0	99.88; 99.48
				99.83; 99.76
				99.83; 98.73

Table 5 Remazol Black B percent removal values for the experiments run at all possible combinations of the levels given in Table 4, using a UVA light photo-Fenton process

of the extremely high reproducibility of the replicates run at the central point. The Fe^{2+} concentration effect, associated with factor **B**, is again the single most important main effect. In contrast to the Fenton process, this is the unique positive effect, meaning that only its increase can enhance Remazol Black B removal.

Additionally, it should be pointed out that in the experiments using UVA light the effects are much smaller than those observed with the Fenton's reaction. This is of course due to the similarity of the responses at all level of the three factors, which may be a result of the UVA light effect on the reaction.

Run no. 3 was selected for the discoloration study and the TOC removal, because its percent removal was almost 100%, which employed the lower values for H_2O_2 concentration (150 mg L⁻¹) and for the reaction time (40 minutes). These conditions were also used as the basis for the visible light photo-Fenton experiments, which were run in triplicate. The UVA light experiments were repeated at the same conditions, for comparison purposes (see Table 7).

The percent removals for the three triplicates run under UVA light were all 100%. For the visible light process, the removal was a little less (97.32%, on average). When the UV light ($\gamma = 200$ to 400 nm) is absorbed directly by H₂O₂, photolysis of this molecule occurs⁽²²⁾, with generation of two hydroxyl radicals according to the Eq. 2. Since the highest $^{\circ}OH$ radicals yields are obtained when short-wave ultraviolet radiation are used^(23,24), this could explain the higher dye removal percentage observed in the UVA light photo-Fenton experiment.

Main effects	Effect Estimate (%)
A - H₂O₂ (mg L⁻¹)	- 0.37
B - Fe ²⁺ (mg L ⁻¹)	1.22
C - Reaction time (min)	- 0.28
Two-factor interactions	
AB	0.35
AC	- 0.91
BC	- 0.24
Three-factor interaction	
ABC	0.86

Table 6 Estimates of the main and interaction effectscalculated from the response values in Table 5. Sta-
tistically significant values are shown in boldface

For comparative purpose, Table 7 also includes an estimate of the percent dye removal that could be expected (based upon a regression analysis of the data presented in Tables

	Remazol Black B	
Process	removal (%)	
Fenton	88.90ª	
Photo-Fenton (visible light)	97.38; 97.09; 97.50	
Photo-Fenton (UVA light)	100; 100; 100	
^a Estimated value from	regression analysis	

Table 7 Remazol Black B percent removal for Fenton, photo-Fenton (visible light) and photo-Fenton (UVA light) processes. The experimental conditions were: $[H_2O_2] =$ 150 mg L⁻¹, $[Fe^{2+}] = 2$ mg L⁻¹ and time reaction = 40 min

2 and 3) for the Fenton process, if it were carried out at the same experimental conditions of the photo-Fenton experiments. This table shows that the percent dye removal follows the sequence UVA light photo-Fenton > Visible light photo-Fenton > Fenton.

Since dye removal with visible light showed good efficiency, we suggest that it may replace UVA light, with economical, occupational and environmental advantages.

Remazol Black B discoloration by the Fenton and photo-Fenton processes

The effect of discoloration of the Remazol Black B by the Fenton process can be observed in Fig. 3, which shows the dye electronic absorption spectra before and after the reaction. Before the process, there are two characteristic absorption bands: one centered at 310 nm, assigned to the two adjacent rings, and another at 597 nm, assigned to the -N=N- groups, which are the chromophores mainly responsible for the dye's characteristic color^(25,26). A comparison of the two UV-visible spectra in Fig. 3 shows that all the characteristic bands disappeared completely after the reaction. The disappearance may be explained by the breakage of the -N=N- bonds and the aromatic rings of the dye molecule by the hydroxyl radical⁽²⁷⁾, implying that theses groups were degraded.

The UV-visible Remazol Black B spectra after the photo-Fenton processes with UVA and visible light were very similar for the Fenton reaction. The two characteristic dye absorption bands disappeared completely. This similarity may be an indication that the three AOP follow analogous reaction mechanisms.

TOC removal by the Fenton and photo-Fenton processes

As previously mentioned, the remaining total organic carbon concentration (TOC) for the Remazol Black B degradation was quantified by measurements after the prescribed reaction time had elapsed. These results are presented in Table 8.

Process	TOC removal (%)
Fenton	16.22
Photo-Fenton (visible light)	28.34
Photo-Fenton (UVA light)	36.39

Table 8 Total organic carbon percent removal for Remazol Black B after AOP treatments. The experimental conditions were: Fenton - $[H_2O_2] = 200 \text{ mg } L^{-1}$, $[Fe^{2+}] = 2 \text{ mg}$ L^{-1} and time reaction = 60 min; Photo-Fenton - $[H_2O_2] =$ 150 mg L^{-1} , $[Fe^{2+}] = 2 \text{ mg } L^{-1}$ and time reaction = 40 min

TOC removal is larger when the AOP are carried under UVA light. The higher efficiency of the UVA light may be due to the larger number of hydroxyl radicals formed, as

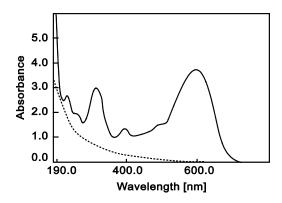


Figure 3. UV-visible absorption spectra of Remazol Black B (starting concentration: 100 mg L⁻¹). Full line: Before reaction; Dotted line: After treatment with the Fenton process. The experimental conditions were: $[H_2O_2] = 200$ mg L⁻¹, $[Fe^{2+}] = 2$ mg L⁻¹ and reaction time = 60 minutes.

already mentioned. The attack of dye molecule by ${}^{\bullet}OH$ radicals can be described by Eqs. (4) and (5)⁽²⁸⁾, leading, upon a complete dye oxidation, to CO₂, H₂O and mineral species, all of which have structures much smaller than the dye's^(29,30):

•OH + dye
$$\rightarrow$$
 dye intermediate (4)

•OH + dye intermediate \rightarrow CO₂ + H₂O + mineral species (5)

A comparison of the three AOP again shows the efficiency of the irradiation effect for the two photo-Fenton processes. According to the data in Table 8, the visible and UVA light photo Fenton process yielded about twice TOC removal (27% and 36%, respectively) than the Fenton process (16%). On the other hand, the Remazol removal data presented in Tables 2 (runs 9-11 - Fenton process) and 7 (photo-Fenton processes), showed almost complete removal (above 97%) in all cases. This is a clear indication that, although dye decomposition is easily obtained, dye mineralization is difficult to achieve, and that the use of light (either visible or UVA) may improve dye mineralization.

CONCLUSIONS

To evaluate the Remazol Black B dye removal efficiency, both the Fenton and the UVA light photo-Fenton processes were considered. The factorial designs have been carried out with three factors: H_2O_2 concentration, Fe²⁺ concentration, and reaction time. According to the ANOVA results, Fe²⁺ concentration is the most significant factor for the factor levels considered.

At the optimum experimental conditions, an additional experiment was carried out with a Daylight Special – Universal Brazil k 828 lamp (visible light), manufactured by OSRAM®. As expected, Remazol Black B removal is higher for the UVA light photo-Fenton process. However, the white light photo-Fenton process also yields very good removal efficiency. The Fenton process is the least efficient.

The dye mineralization, as quantified with TOC, was about two times higher for the photo-Fenton processes, as compared to the Fenton process. The UVA light is also more efficient than the visible light in this mineralization process. Considering that the visible light source is much cheaper than UVA light, circa 70% cheaper. From the economical point of view, this is an interesting result since it was shown that dye removal, leading to mineralized products, using visible light, was almost as good as with UVA light. So, the cheaper lamp can be successfully used for the Remazol Black B dye removal and mineralization, leading to application of this technology in large scale.

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