



## Influence of pH and concentration on the decolorization and degradation of BR red azo dye by ozonization

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**ABSTRACT.** Ozone application has been generally reported based only on the oxidation of textile dyes. In this study, a central composite design and surface response methodology were applied to optimize operational parameters pH and concentration of the dye in the decolorization process. The oxidation of Corafix BR Red Azo dye in aqueous solutions was carried out in a semi-batch bubble column reactor with ozone production at 0.702 g hour<sup>-1</sup>. Tests were performed at pH 4, 7 e 10 and initial dye concentration of 50, 100 and 150 mg L<sup>-1</sup>. The maximum removal efficiency was 98% for pH 10 and initial dye concentration of 50 mg L<sup>-1</sup> with pseudo-first order constant rate ( $k_1$ ) of 0.0595 min<sup>-1</sup>. Statistical analysis determined the influence of pH and dye concentration in the decolorization process. The pH presented a positive effect on the decolorization while the variation in dye concentration had a negative effect on the same variable, indicating the higher the pH and the lower the initial concentration of dye, the higher the efficiency. Toxicity tests performed before and after ozonization showed acute toxicity for the test organism *Daphnia similis* with higher percentage of mortality after ozonization.

**Keywords:** dye removal; AOP; ozone; textile effluent.

## Influência do pH e concentração na descoloração e degradação do azo corante vermelho BR por ozonização

**RESUMO.** A aplicação do ozônio tem sido, geralmente, reportada com base apenas na oxidação de corantes têxteis. Neste estudo o delineamento composto central rotacional e a metodologia de superfície de resposta foram aplicados para otimizar os parâmetros operacionais pH e concentração do corante no processo de descoloração. A oxidação do corante Azo Corafix Red BR em solução aquosa foi realizada em uma coluna de ozonização semibatelada com produção de ozônio de 0,702 g h<sup>-1</sup>. Os testes foram realizados em pH 4, 7 e 10 e concentração inicial do corante de 50, 100 e 150 mg L<sup>-1</sup>. A eficiência de remoção máxima alcançada foi de 98% para pH 10 e concentração inicial de corante de 50 mg L<sup>-1</sup> com constante cinética de pseudo-primeira ordem ( $k_1$ ) de 0,0595 h<sup>-1</sup>. Análises estatísticas determinaram a influência do pH e concentração do corante no processo de descoloração. O pH apresentou efeito positivo na descoloração, enquanto a variação do corante apresentou efeito negativo na mesma variável, indicando que quanto maior o pH e menor a concentração inicial de corante maior a eficiência. Os testes de toxicidade, realizados antes e após a ozonização, mostraram toxicidade aguda para o organismo teste *Daphnia similis* com maior percentual de mortalidade após a ozonização.

**Palavras-chave:** remoção de corante; POA; ozônio; efluente têxtil.

### Introduction

Agricultural and industrial sectors are the main water consumers in the world, with the textile sector presenting higher volume ratio of water consumed by processed textile material. In the dyeing processes, water consumption can range from 80 to 400 L kg<sup>-1</sup> fibers (cotton or synthetic mesh) (Garg, Amita, Kumar, & Gupta, 2004). This large water consumption has become unbearable in many countries where potable water is scarce.

The composition of textile effluents depends on the different organic-based compounds, chemicals and dyes used in industrial processes. The dyes characterize the textile effluents as highly colored and are responsible for many problems in water bodies, like prevent the entry of light that impairs photosynthetic activity and interfere with the development of aquatic biota, therefore making regulatory agencies increasingly concerned, especially about the possible carcinogenicity of some

compounds (Rauf & Ashraf, 2009; Sulak & Yatmaz, 2012).

The main processes applied for textile wastewater treatment are biological and physical-chemical (flocculation, coagulation, sedimentation, adsorption on activated carbon) (Amorim, Kato, Florencio, & Gavazza, 2013; Amaral, Kato, Florencio, & Gavazza, 2014). Biological treatment systems are known for their economic feasibility and capability in removing organic matter (Khelifi, Gannoun, Touhami, Bouallagui, & Hamdi, 2008). Although the activated sludge has been the most used biological process (Khandegar & Saroha, 2013), anaerobic processes, with emphasis on the UASB-type reactors, have also been investigated (Amaral et al., 2014).

Microorganisms such as algae, fungi, bacteria and yeasts are able to degrade certain type of dyes. However, their application is limited because some dyes are not easily degraded and some microorganisms are sensitive to toxicity (Shao et al., 2012).

Studies have been published showing the ozonation as one of the most promising alternatives to treat recalcitrant compounds (chlorinated hydrocarbons, phenols, pesticides, aromatic hydrocarbons) and remove color in textile effluents. In fact, ozone breaks the conjugated chains of dyes molecules that provide color thus making them degradable (Santana et al., 2009; Tabrizi, Glasser, & Hildebrandt, 2011; Sharma, Buddhdev, Patel, & Ruparelia, 2013).

According to these authors, this process presents the additional advantage of not producing sludge and inorganic ions, as in chlorine oxidation. However, it has the disadvantage of its short half-life time (approximately 20 min). This time can be further reduced if stability is affected by the presence of salts, pH and temperature.

Usually the studies are based only on the oxidation analysis of textile dyes, in the present study there was a concern to optimize the operational parameters pH and concentration of the dye by applying a central composite design (CCD).

However, ozonation of dyes may result in the formation of toxic by-products (Paraskeva & Graham, 2005), which can cause disturbances in some living organisms. Thus, ecotoxicological tests are very useful for identifying environmental effects (Mendonça et al., 2009).

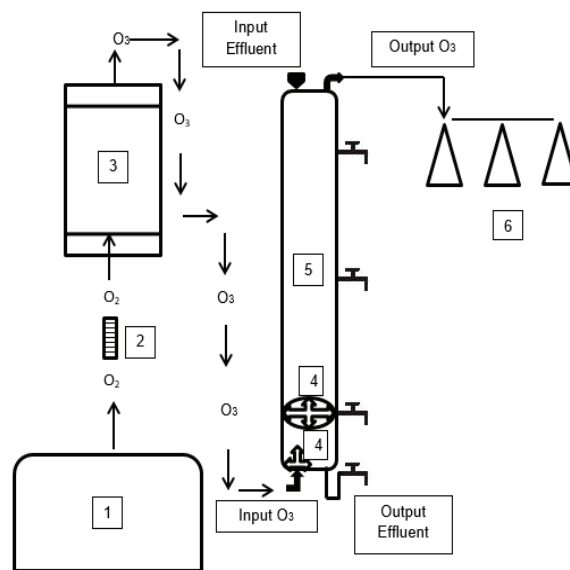
In the present study, an ozonation system consisting of air compressor, ozone generator, gas flow meter and bubble column reactor was operated to evaluate the behavior of removing color from an aqueous solution containing the reactive Corafix BR Red azo dye. The influence of parameters solution initial pH and initial dye concentration on the

ozonation was investigated in order to optimize the operational conditions. The effects of these parameters on the efficiencies of decolorization and ozone utilization were also analyzed.

## Material and methods

Corafix BR Red Azo - Reactive (ARR) was purchased from Coratex Siebert Chemical Factory (Brazil) and used without further purification to prepare the simulated wastewater. The dye solution was prepared by dissolving ARR in tap water in concentrations of 50, 100 and 150 mg L<sup>-1</sup>, and the natural pH of the dye solution varied from 7.5-7.8. The initial pH of dye solutions was adjusted using 1 M H<sub>2</sub>SO<sub>4</sub> (98%, Neon Comercial, Brazil) and 1 M NaOH (Vetec Química Fina, Brazil).

Ozonation studies were carried out using an experimental setup consisting of air compressor, ozone generator, gas flow meter, bubble column reactor (100 mm diameter and 2 m height) and flasks to trap the unreacted ozone (Figure 1). Samples were collected in a first control valve located at 50 cm above the bottom of the reactor.



**Figure 1.** Experimental apparatus: 1) air compressor, 2) gas flow meter, 3) ozone generator, 4) air diffusers, 5) bubble column reactor, 6) flasks to trap the unreacted ozone.

Ozone was generated from air by Corona Discharge Ozone generator. The air flowrate into the generator was controlled and adjusted at 5, 10 and 15 L min<sup>-1</sup> using a gas flow meter to establish the optimum ratio between air flowrate and ozone generation.

Three sampling time profiles were carried out with the solution containing 50, 100 and 150 mg L<sup>-1</sup> for each pH 4.0, 7.0 and 10.0 at room

temperature. Approximately 12 L of the aqueous solution containing the reactive dye were initially subjected to ozonation. Ozonation was performed to remove at least 90% of the concentration of the dye or for a maximum period of five hours in each profile.

Each sample was withdrawn at intervals of 15 min and the parameters analyzed were temperature, pH (4500\_H+), dye concentration and the concentrations of ozone consumed (4500\_B), ozone dissolved (4500\_B) and off-gas (4500\_B) in accordance with the methodologies described in American Public Health Association (Apha, 2012).

Dye concentration was determined by measuring the absorbance of the solution in 150 mg L<sup>-1</sup> at the wavelength in the visible range of a spectrophotometer (Hach UV-Vis, DR 5000 model), where maximum absorbance obtained was 583 nm.

All analyses were done in duplicate and samples were centrifuged at 2,500 rpm for 5 min in a Sislab centrifuge, twister model. The analytical curve method for the Azo dye Reactive Red resulted in the equation  $y = 1.8918x - 0.0041$  ( $R^2 = 0.9978$ ), where  $x$  corresponds to dye concentration and  $y$  to absorbance.

The response surface methodology (RSM) was applied to improve this process achieving the optimal values of pH and initial concentration of dye. Besides that, the factorial planning provided significant results with a fewer number of tests performed. A central composite design (CCD) was prepared to check the influence of initial pH and initial concentration of dye ([ ] i Dye) factors in the removal of dye, comprising factorial ( $2^2$ ) with levels (-1 and +1), three replicates at the central point (0) for aqueous solutions of synthetic wastewater, at 95% confidence level. The experiments were conducted in random order to not introduce systematic analysis of data errors. The response variable assessed was the removal of dye concentration. The levels of the factors analyzed are presented in Table 1.

The determination of the effects of independent variables and the obtainment of the graphics of response surface, at 5% significance level, were performed on a computational tool.

**Table 1.** Levels of the experimental factors applied in the experimental delineation.

Factorial experiments/Unit	Coded variables		
	-1	0	1
Factor 1 pH	4	7	10
Factor 2 [ ] i Dye (mg L <sup>-1</sup> )	50	100	150

Acute toxicity tests were performed before and after ozonation to pre-established conditions of pH

and dye concentration, in which higher dye removal efficiencies were verified. These assays were carried out according to procedures described in NBR 12713 - Aquatic Ecotoxicology acute-toxicity - Test method with *Daphnia spp.* (Cladocera, Crustacea) (Associação Brasileira de Normas Técnicas [ABNT], 2004). *Daphnia* is commonly used for the evaluation of water toxicity due to its important position in the aquatic food chain, sensitivity to many pollutants, easy to culture and have a short life cycle (Park & Choi, 2007).

Acute toxicity bioassays were performed to obtain the concentration in which mortality and/or immobility of 50% or more of the test organisms ( $LC_{50}$ ) were noted. In this study,  $LC_{50}$  was considered as acute toxic ( $LC_{50} > 50\%$ ), slightly toxic ( $LC_{50} > 0$ ) and non-toxic ( $LC_{50} = 0$ ).

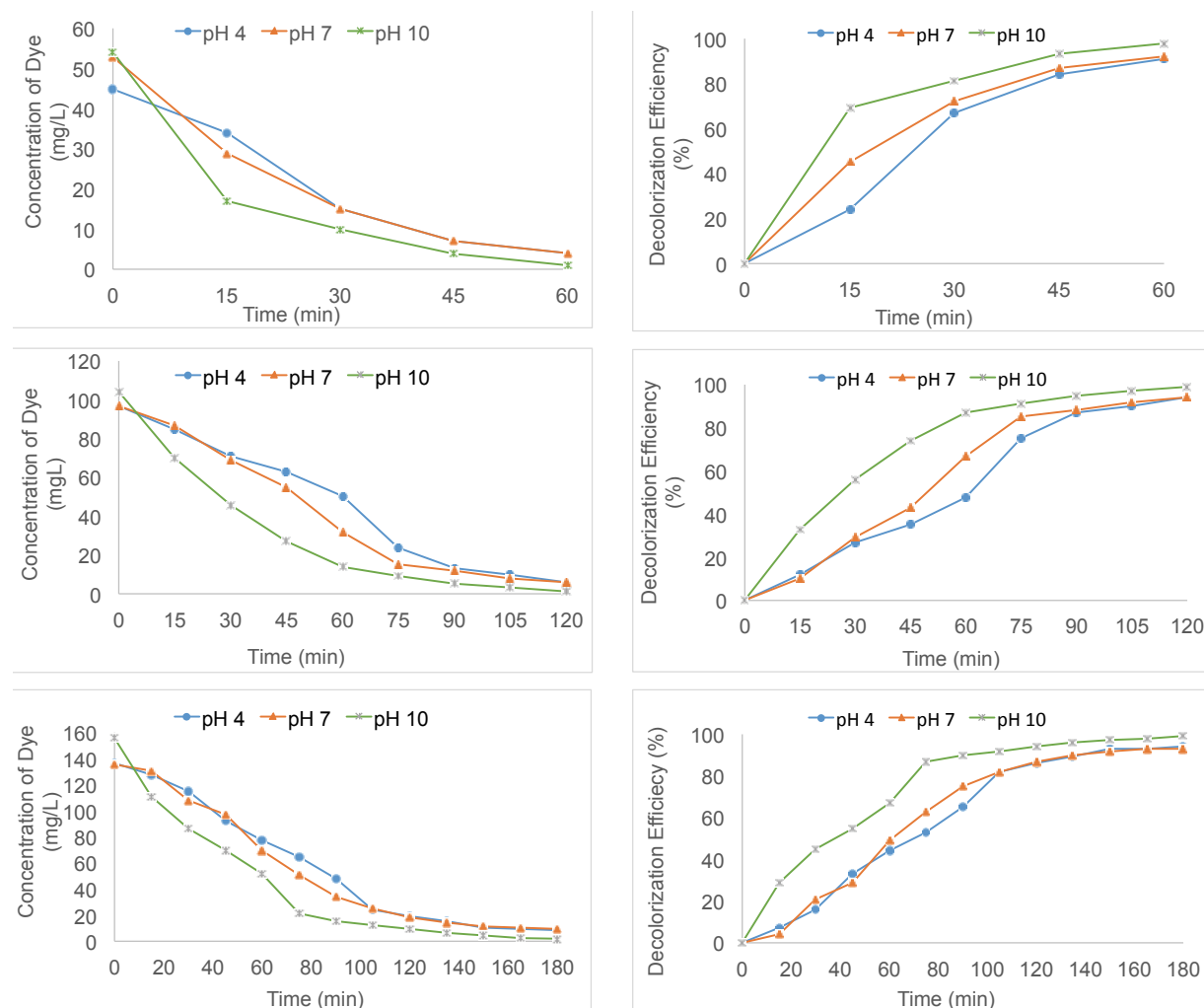
## Results and discussion

The increase in ozone production was from 0.402 to 0.702 g hour<sup>-1</sup> over the increase of air flowrate from 5 to 15 L min<sup>-1</sup>, being this maximum value adopted in this study. Ozone production rate and air flowrate were already reported in the literature by Silva, Pic, Sant'Anna, and Dezotti (2009), who obtained ozone production rate of 0.26 g hour<sup>-1</sup> and air flowrate varying from 5 to 20 L min<sup>-1</sup> and Santana et al. (2009) that noted 0.25 g hour<sup>-1</sup> ozone application rate.

Figure 2 illustrates the influence of pH (4, 7 and 10) on the removal of dye from the aqueous solution with initial concentration in the range of 50, 100 and 150 mg L<sup>-1</sup> and ozone application rate of 0.702 g hour<sup>-1</sup>.

As shown in Figure 2a-c, the time required for the complete decolorization gradually increased from 60 to 180 min with increase in the initial concentration from 50 to 150 mg L<sup>-1</sup>. These findings are in accordance with the literature (Tabrizi et al., 2011; Gao et al., 2012; Sharma et al., 2013) thus confirming that ozonation is a very efficient process for color removal and the time required for the complete decolorization gradually increase with increase in the initial concentration.

Sharma et al. (2013) observed an increase of 19 min (48 to 67 min) in the time required for the decolorization of Reactive Red 135 dye, increasing the initial concentration in 1000 mg L<sup>-1</sup> (500 to 1500 mg L<sup>-1</sup>). Gao et al. (2012) noted a decrease in the removal efficiency from 98 to 67% by increasing the concentration of Acid Red 14 azo dye from 50 to 800 mg L<sup>-1</sup>. Tabrizi et al. (2011) achieved near 100% removal of reactive red dye after 60 min ozonation, but detected a higher efficiency with the concentration of 250 mg L<sup>-1</sup> compared to the concentrations of 500 and 1000 mg L<sup>-1</sup>.



**Figure 2.** Influence of the solution pH and ozonization time on ARR dye removal - 50 (a), 100 (b) and 150 mg L<sup>-1</sup> (c).

Figure 2a shows that total decolorization of AAR dye solution (98% color removal) is achieved in alkaline conditions (pH 10), followed by 93% in neutral conditions (pH 7) and 90% in acid conditions (pH 4) after 60 min of ozonation with 50 mg L<sup>-1</sup>.

Figure 2b indicates the average decolorization of ARR dye solution of 90, 93 and 94% for pH 4, 7 and 10, respectively, after 120 min ozonation with 100 mg L<sup>-1</sup>. At pH 10, the decolorization is higher with an average efficiency of 86% after the ozonation time of 60 min, while this efficiency decreases to 49 and 67% at the same time for pH 4 and 7, respectively.

Figure 2c shows removal efficiency of 94% at pH 4, 93% at pH 7 and 99% at pH 10 after 180 min ozonation with 150 mg L<sup>-1</sup>. In 60 min ozonation, dye removal efficiency was 67% at pH 10, 48% at pH 7 and 44% at pH 4, indicating the highest removal efficiency in alkaline conditions.

The ozonation of the ARR dye solution shows effective decolorization in all pH variations, with a faster removal dye at pH 10.

Gao et al. (2012) verified an increase of 18% in the efficiency decolorization of azo dye Acid Red 14 (from 64 to 82%) to the pH variation from 2 to 12, with ozone application of 10 mg L<sup>-1</sup>. Santana et al. (2009) achieved removal of reactive dye Orange 122 of 99.9% after a short ozonation time (< 15 min) in both alkaline (pH 12) and acidic (pH 4.5) conditions with constant ozone application rate of 0.25 gO<sub>3</sub> hour<sup>-1</sup>.

Kusvuran, Gulnaz, Samil, and Erbil (2010) obtained higher removal efficiencies of 86 and 95% in the decolorization of Basic Yellow dye 28 with ozone, increasing pH from 2 to 11, respectively.

No significant variation in temperature was detected in the ozonation of the aqueous solution in the conditions studied. The highest temperature variation was 0.3°C (18.9 ± 2.4°C before the

ozonization and  $19.2 \pm 2.1^\circ\text{C}$  after the ozonation) to the initial concentration of  $100 \text{ mg L}^{-1}$  and pH 10. The same behavior was observed by Silva, Daniel, Bruning, and Rulkens (2010), who obtained temperature of  $14.55^\circ\text{C}$  before ozonation and  $14.83^\circ\text{C}$  after ozonation in coliform inactivation and the formation of byproducts through ozonation.

Table 2 lists the results obtained for dissolved ozone, absorbed ozone, off gas and efficiency of ozone transfer obtained with initial concentration in the range of 50, 100 and  $150 \text{ mg L}^{-1}$ , pH of 4, 7 and 10 and input ozone of  $0.72 \text{ mgO}_3 \text{ L}^{-1}$ .

**Table 2.** Results of dissolved ozone, off gas, absorbed ozone and efficiency of ozone transfer to the conditions of dye concentration and pH.

Dye concentration ( $\text{mg L}^{-1}$ )	pH	Dissolved ozone ( $\text{mg L}^{-1}$ )	Off-gas ozone ( $\text{mg L}^{-1}$ )	Absorbed ozone ( $\text{mg L}^{-1}$ )	Ozone transfer efficiency (%)
50	4	0.10	0.44	0.19	40
	7	0.10	0.40	0.23	45
	10	0.04	0.28	0.40	61
100	4	0.10	0.41	0.21	44
	7	0.10	0.36	0.26	50
	10	0.05	0.28	0.40	62
150	4	0.10	0.34	0.29	53
	7	0.09	0.27	0.35	62
	10	0.04	0.22	0.47	70

No significant changes in ozone concentration were found for variations in pH and dye concentration due to the constant air flowrate ( $15 \text{ L min}^{-1}$ ) and input ozone dose ( $0.72 \text{ mg L}^{-1}$ ) during ozonation. During the ozonation, the amount of dissolved ozone was practically the same in all conditions analyzed (average of  $0.08 \pm 0.02 \text{ mg L}^{-1}$ ).

The same behavior, even though not very significant, was noted for the off gas (average of  $0.33 \pm 0.07 \text{ mg L}^{-1}$ ) and absorbed ozone ( $0.31 \pm 0.09 \text{ mg L}^{-1}$ ), thus indicating the greater the amount of absorbed ozone, the lower the amount released in the off gas.

The most significant efficiency of ozone transfer occurred in alkaline conditions with maximum of 70% to pH 10 and dye concentration of  $150 \text{ mg L}^{-1}$ , proving the higher the concentration of ozone absorbed, the higher the ozone transfer.

Table 3 shows the results obtained for pseudo-first-order and pseudo-s-order kinetics to the decolorization of the ARR dye as function of pH and initial dye concentration. A rather good linear behavior ( $R^2 \cong 1$ ) was verified using the pseudo-first-order kinetic model, thus rejecting the pseudo-s-order. Turhan, Durukan, Ozturkcan, and Turgut (2012) and Gao et al. (2012) reported that dye ozonation is a first-order kinetics reaction in relation

to ozone and dye concentration. The ozonation rate increases with both dye concentration and ozone concentration. In this study, the ozone injecting concentration is fixed. Therefore, the degradation kinetics can be treated as a pseudo-first-order reaction with respect to the dye concentration.

**Table 3.** Pseudo-first and second-order kinetic profiles for discoloration of the ARR dye.

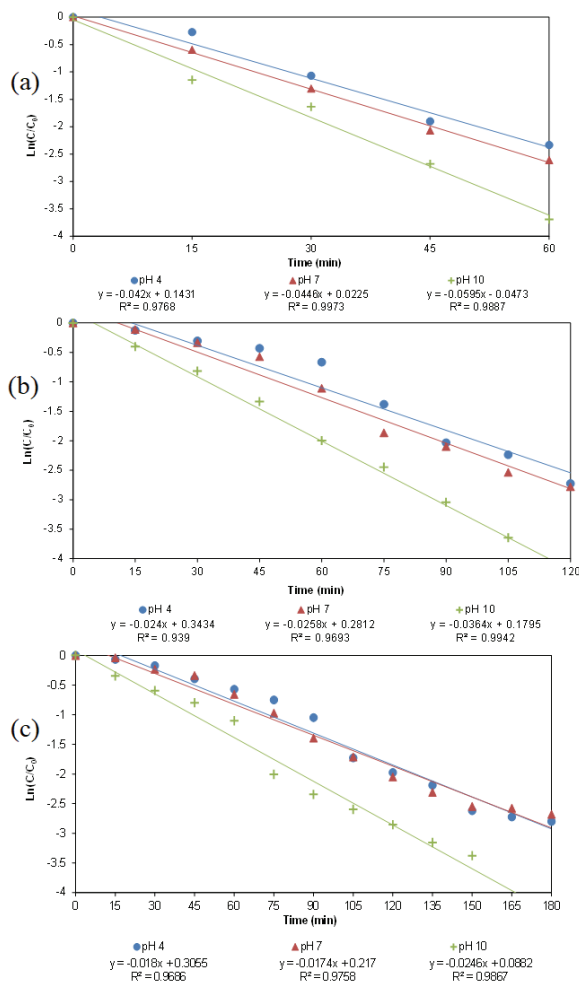
Pseudo-first-order kinetics				Pseudo-s-order kinetics			
pH	Concentration ( $\text{mg L}^{-1}$ )	$k_1$ ( $\text{min}^{-1}$ )	$R^2$	pH	Concentration ( $\text{mg L}^{-1}$ )	$k_2$ ( $\text{min}^{-1}$ )	$R^2$
4	50	0.0420	0.9768	4	50	0.0360	0.9073
	100	0.0240	0.9300		100	0.0011	0.7893
	150	0.0180	0.9686		150	0.0007	0.8615
7	50	0.0446	0.9973	7	50	0.0039	0.9028
	100	0.0258	0.9693		100	0.0013	0.8636
	150	0.0174	0.9758		150	0.0006	0.9116
10	50	0.0595	0.9887	10	50	0.0112	0.7728
	100	0.0364	0.9942		100	0.0050	0.6862
	150	0.0246	0.9867		150	0.0022	0.7326

However, Peng and Fan (2005) reported that the reaction kinetic order of dye discoloration via ozonation may not be constant for the duration of the ozonation process, since it can change with the variation of the ozone to dye ratio during the progress of the ozonation process.

Figure 3 shows the correlation between  $\ln(C/C_0^{-1})$  and the linear reaction time. The highest kinetic constant rate ( $k_1$ ) was  $0.0595 \text{ hour}^{-1}$  for pH 10 and initial concentration of  $50 \text{ mg L}^{-1}$ , coinciding with the optimum color removal efficiency of 98% at 60 min of ozonation. The lowest kinetic constant rate ( $k_1$ ) of  $0.0174 \text{ hour}^{-1}$  was obtained at pH 7 and initial concentration of  $150 \text{ mg L}^{-1}$  for removal efficiency of 93% at 180 min of ozonation.

According to Santana et al. (2009), Kusvuran et al. (2010) and Gao et al. (2012), the decolorization process via ozonation is rapid in both alkaline and acid conditions due to the electrophilic nature of the direct (attack by  $\text{O}_3$  molecules) and indirect (attack via  $\text{HO}\cdot$  radicals) ozonation process, which considerably facilitates the reaction with the azo-groups (chromophore centers).

A comparison of the  $k$  as functions of pH supports that both the direct and indirect oxidative pathways play a similar role during decolorization. This behavior can be understood considering that both  $\text{O}_3$  and  $\text{HO}\cdot$  present a strong electrophilic nature, which considerably facilitates the attack at the chromophore centers. However, hydroxyl radicals exhibit a much higher reaction rate than molecular ozone, thus the direct oxidation is slower than the indirect oxidation.

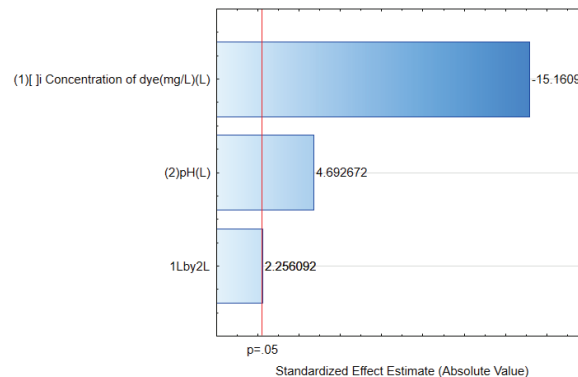


**Figure 3.** Pseudo-first-order kinetic correlation and time reaction for decolorization of the ARR dye according to the solution pH and initial dye concentration.

To determine the influence of pH and initial dye concentration in the removal of dye, it was necessary to adopt a single treatment time. Statistical tests were performed with results of removal efficiency after 60 min of ozonization, common time for all analyses.

In Pareto charts are shown the linear (L) and quadratic (Q) effects of the factors and their interaction. The effects with values located to the right of the red line were significant at 5% level of significance (Figure 4).

pH and initial dye concentration had significant effects at 5% level to decolorization process ( $p < 0.05$ ). The pH factor presented a positive effect on discoloration while the variation in the dye concentration presented a negative effect on the same variable, thus, the higher the pH and the lower the initial concentration of dye, the higher the efficiency. The effect of initial concentration of dye was greater than the effect of the pH, as observed in Figure 4 by the interaction of these variables.

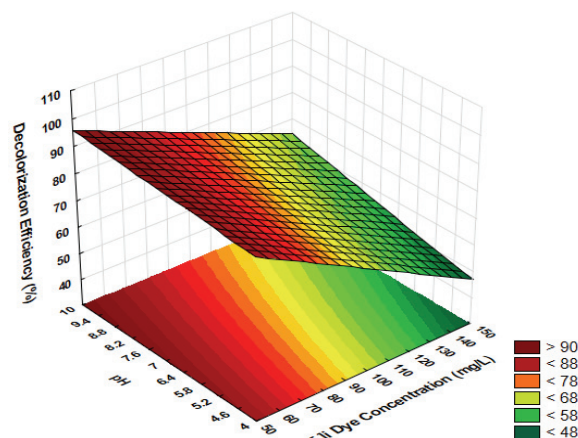


**Figure 4.** Pareto chart for the color removal.

Figure 5 shows the results regarding the behavior of the process for initial dye concentration and pH in the decolorization (%) through the contour graphics. It was possible to ascertain the existence of an optimal range for each factor and the combination of these ranges. The increase in pH and decrease of the initial concentration of dye resulted in greater efficiency in removal of dye concentration.

Therefore, the optimum point (> 90%) occurred with approximately 100% removal efficiency at pH 10 and initial dye concentration of 50 mg L<sup>-1</sup>. For all trials and statistical tests performed, it can be seen that the change in the initial concentration of dye exerted more significant influence than pH on the removal of dye.

Toxicity tests were performed before and after the ozonization with the samples obtained with the best removal conditions: 98% removal efficiency at 60 min of treatment with initial dye concentration of 50 mg L<sup>-1</sup> and pH 10. Table 4 shows the toxicity data before and after 60 min of ozonation for the test organism *Daphnia similis*.



**Figure 5.** Graphic of the surface response to the decolorization efficiency (%) with the variation in pH and initial dye concentration.

**Table 4.** Results of acute toxicity before and after ozonization.

Before Ozonization				After Ozonization			
EO	TE	E (%)	R	OE	TE	E (%)	R
20	13	65	AT	20	20	100	AT

EO = Exposed organisms, TE = Total Effect (immobility or dead organisms), E = (percentage of immobility or dead organisms). R = Results according to LC.

Higher percentage of mortality was found after ozonation, which may be related with the by-products formed in the oxidation of organic molecules present in the dye. Mortality or immobility of 50% or more of the test organisms ( $LC_{50}$ ) was observed in all samples. In this study,  $LC_{50}$  was considered as acute toxic ( $LC_{50} > 50\%$ ), slightly toxic ( $LC_{50} > 0$ ) and non-toxic ( $LC_{50} = 0$ ), both conditions (before and after ozonation) showed acute toxicity (AT) for the test organism *Daphnia similis*.

## Conclusion

Discoloration was rapidly achieved, thus revealing that direct and indirect oxidative pathways are efficient for color removal.

The maximum ARR decolorization (98%) occurred within 60 min for concentration of 50 mg L<sup>-1</sup> and pH 10, with adjustment of the results by pseudo-first order kinetics ( $k_1$  of 0.0595 min<sup>-1</sup>).

The initial dye concentration had more influence than pH on the ARR removal according to the statistical tests.

Samples showed acute or evidence of acute toxicity, being higher percentage of *Daphnia similis* mortality for ozonated samples.

More studies are necessary to evaluate the by-products generated in the oxidation of the dye chemical chains.

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