



Acute ecotoxicity on *Daphnia magna* to evaluate effluent samples of Kraft pulp mill treated by UV/H₂O₂ process

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Joicy Micheletto^{1*}; Naiara Mariana Fiori Monteiro Sampaio²
Henrique Zavattieri Ruiz³; Lucia Regina Rocha Martins¹
Marcus Vinicius de Liz¹; Adriane Martins de Freitas¹

¹Universidade Tecnológica Federal do Paraná (UTFPR), Curitiba, PR, Brasil
Departamento de Química e Biologia (DAQBi). E-mail: joicymicheletto@hotmail.com,
luciaregi@utfpr.edu.br, marcusliz@utfpr.edu.br, adrianefreitas@utfpr.edu.br

²Universidade Federal do Paraná (UFPR), Curitiba, PR, Brasil
Departamento de Química (DQUI). E-mail: naiaramfms@gmail.com

³Universidade Federal do Paraná (UFPR), Curitiba, PR, Brasil
Centro Mesorregional de Excelência em Tecnologia do Leite (CMETL).

E-mail: henriquezr@hotmail.com

*Corresponding author

ABSTRACT

The pulp and paper industry is one of world's largest water consumers, generating high volumes of effluents. The Kraft process produces effluents with high BOD, COD, suspended solids, lignin and a myriad of potentially toxic compounds, which require treatment before discharge into the aquatic environment. Advanced oxidation processes, such as UV/H₂O₂, have been applied as treatment alternatives because they can destroy many compounds before they mineralize. However, when the oxidation process is incomplete, occurs could be produced by products with high toxicity. This study evaluated the acute toxicity on *Daphnia magna* of two effluent samples of Kraft pulp mill (KE1 and KE2) treated by UV/H₂O₂ process. The effects of the pH variation and oxidant concentration on the removal of DOC, total UV-vis spectral area and apparent color were considered to adjust the experiments' conditions with diluted effluent KE1. Both samples were treated at pH 4.0 and 70 mg L⁻¹ of H₂O₂ for 40 min, achieving removals of up to 69.4% in apparent color, 73.7% of phenolic compounds and 68.9% of lignin compounds. When the reaction was applied in undiluted effluent samples, the acute toxicity for *Daphnia magna* decreased for KE1 after 780 min of treatment, whereas KE2 became four times more toxic. The data showed that although the treatment had been efficient considering physics and chemicals parameters, it is necessary follow the oxidative processes with ecotoxicological bioassays to guarantee their safety, since different effluents of the Kraft pulp mill could present different levels of organic compound mineralization.

Keywords: advanced oxidation process, ecotoxicology bioassays, industrial effluent.



Ecotoxicidade aguda em *Daphnia magna* para avaliação de amostras de efluente de celulose Kraft tratadas por processo UV/H₂O₂

RESUMO

A indústria de papel e celulose está entre as que mais consome água no mundo, gerando grandes volumes de efluentes. O processo Kraft produz efluentes com elevada DBO, DQO, sólidos suspensos, teor de lignina e uma mistura complexa de compostos potencialmente tóxicos, os quais necessitam de tratamento para posterior descarte no meio ambiente. Os processos oxidativos avançados, dentre eles o processo UV/H₂O₂, têm sido aplicado como alternativa de tratamento pois é capaz de degradar os mais diversos compostos até sua mineralização. No entanto, quando o processo oxidativo é incompleto, podem ser formados produtos intermediários com elevada toxicidade. Este estudo avaliou a toxicidade aguda em *Daphnia magna* de duas amostras de efluente Kraft (KE1 e KE2) tratadas por processo UV/H₂O₂. Os efeitos da variação de pH e da concentração do oxidante sobre a redução de COT, área espectral UV-vis e cor aparente foram utilizados para ajustar as condições experimentais com a amostra KE1 diluída. Ambas as amostras foram tratadas em pH 4.0 e com 70 mg L⁻¹ de H₂O₂ por 40 min, alcançando remoções de até 69,4% na cor aparente, 73,7% de compostos fenólicos e 68,9% de compostos lignínicos. Quando a reação foi aplicada nas amostras não diluídas de efluentes, a toxicidade aguda para *Daphnia magna* diminuiu para KE1 após 780 min de tratamento, enquanto KE2 tornou-se três vezes mais tóxica. Os dados mostraram que embora o tratamento tenha sido eficiente, considerando os parâmetros físicos e químicos, é necessário acompanhar os processos oxidativos por ensaios ecotoxicológicos para garantir sua segurança, uma vez que cada efluente kraft pode apresentar diferentes níveis de mineralização de seus compostos orgânicos.

Palavras-chave: bioensaio ecotoxicológico, efluente industrial, processos oxidativos avançados.

1. INTRODUCTION

The pulp and paper industry consumes a large amount of water (Ashrafi *et al.*, 2015) and is one of the largest polluters due the variety of chemicals that are released into the environment (Savant *et al.*, 2006). One of common pulping technologies is the Kraft process, which is applied for wood delignification with alkaline solutions at high pressures and temperatures (Kamali and Khodaparast, 2015). Kraft effluent has high biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids, lignin and its derivatives and a variety of toxic compounds (Ali and Sreekrishnan, 2001). If these effluents are poorly treated, toxic substances are released into the aquatic environment, affecting many ecosystems (Oller *et al.*, 2011).

In order to mitigate these negative effects, studies have evaluated options of treatments; the application of advanced oxidation processes (AOPs) is a promising alternative (Rueda-Márques *et al.*, 2015; Merayo *et al.*, 2013). In wastewater treatment of the pulp and paper industry, the AOPs most used are those wherein a source of radiation is applied (UV, visible or solar light), such as UV/H₂O₂, photo-Fenton and TiO₂ photocatalysis (Catalkaya and Kargi, 2008). These processes are based on the generation of hydroxyl radicals *in situ* that exhibit high oxidizing power, low selectivity and in many cases result in complete degradation of organic matter (Del Moro *et al.*, 2013). In the UV/H₂O₂ process, the hydroxyl radicals are formed by the homolytic break of H₂O₂ according to Equation 1:



The hydroxyl radicals ($\bullet\text{OH}$) are capable of mineralizing organic contaminants by three different routes of oxidation: hydrogen abstraction, electron transfer and radical addition (Malato *et al.*, 2009). The efficiency of these processes have been applied to different matrices such as urban wastewater (Silva *et al.*, 2018), petroleum refinery effluent (Moser *et al.*, 2018) and pharmaceutical substances (Alharbi *et al.*, 2017). There are many advantages in the application of AOPs compared with other treatment systems, such as non-phase transfer, high solubility of H_2O_2 in water, no sludge formation and relatively low operational cost; but despite these, its application in the treatment of pulp and paper mill effluent is still incipient (Rizzo, 2011).

Some studies show that if the amount of hydroxyl radicals generated in AOPs was insufficient to the complete mineralization the partial oxidation of organic contaminants may result in formation of toxic byproducts (Rizzo, 2011; Rueda-Márquez *et al.*, 2015). In order to avoid this issue, toxicity tests could be used as important tools for the monitoring of the effectiveness of the treatment process (Oller *et al.*, 2011). The main objective of this study was to evaluate the acute ecotoxicity of two effluent samples of a Kraft pulp mill submitted to treatment with the UV/ H_2O_2 process, using the *Daphnia magna* as a test organism.

2. MATERIALS AND METHODS

2.1. Kraft effluent samples

Two effluent samples (named KE1 and KE2) were collected in different days in a kraft pulp mill of *Pinus taeda* and *Pinus elliottii*. These samples were collected before primary treatment (raw effluent) in plastic vessels (5 L) and stored at 4°C. After filtration (7-11 μm , Quantity) the samples were characterized by standardized methods for pH, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD_5), Dissolved Organic Carbon (DOC), turbidity, apparent color (440 nm), alkalinity, total phenolics and UV-Vis spectral area (200-800 nm) (APHA *et al.*, 2012). Lignin compounds were analyzed by absorbance measured at 280 nm, according to Çeçen (1999). All analyses were performed in triplicate.

2.2. Experimental design

The effects of two variables (pH and H_2O_2 concentration) were evaluated by 2^2 factorial design with triplicate of the central point. The levels for each variable were pH 4.0 and 8.0 and for the H_2O_2 concentrations 50 and 70 mg L^{-1} . The performance of experiments was measured by color, UV-Vis spectral area and DOC and the results were expressed as percentage of reduction. The end of the reaction was determined as the time when consumption of hydrogen peroxide was above 95%. Residual H_2O_2 was determined by the spectrophotometric method based on reaction with ammonium metavanadate (Nogueira *et al.*, 2005).

The effluent samples (500 mL) were filtered (7-11 μm , Quantity), diluted with demineralized water (fifteen times) and the pH was adjusted before treatment by the UV/ H_2O_2 process. The experiments were conducted in a borosilicate bench photoreactor equipped with a water-cooler and a magnetic stirrer. Artificial radiation was provided by a high-pressure mercury vapor lamp (125W, $\lambda_{\text{max}} = 254 \text{ nm}$, Philips) immersed in the solution through a quartz bulb. Before the addition of oxidant and at the end of the treatment, an aliquot of each sample was collected for the measurements indicated in Item 2.1.

The significance of the variables effect was evaluated by the Pareto graph (95% confidence level, Statistica 7.0). The treatment condition chosen was applied to the other sample.

2.3. Bioassays with *Daphnia magna*

Acute toxicity tests were conducted with effluent samples (KE1 and KE2) before (initial time) and after the UV/ H_2O_2 treatment, which was performed with filtered and undiluted

effluent samples, after adjusting the pH (4.0). The hydrogen peroxide added was fifteen times more (1050 mg L^{-1}) than in the factorial design because the samples were not diluted. For this reason, the reaction time was 780 min (hydrogen peroxide consumption above 95%). Before the tests the samples had the pH adjusted (~ 6.5) and catalase bovine solution (1%, Sigma) added before and after the treatment for removal of residual H_2O_2 . The bioassays with *D. magna* were performed in triplicate with 20 neonates organisms (6-24h) that were exposed to effluent samples at concentrations of 100, 50, 25, 12.5 and 6.25% (v/v) diluted in standard medium, that was used also for the control experiments. All tests were maintained at 20°C by 48h of exposure and after that the number of immobile organisms was recorded (ABNT, 2016). The results were expressed by 50% effective concentration (EC_{50}) that was calculated through the Probit method and by toxic units (TU), defined as $100/\text{EC}_{50}$. The sensitivity of the organism batches was evaluated monthly with KCl solutions (Panreac; purity 99%) in concentrations between $570\text{-}840 \text{ mg L}^{-1}$. In this work, the organisms used for the bioassays presented $\text{EC}_{50, \text{KCl}} = 710 \pm 15 \text{ mg L}^{-1}$.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of the effluent samples

The physical and chemical properties of the effluent samples (KE1 and KE2) reveal that although they originated from the same pulping process there were differences among them (Table 1). In both samples, the COD were quite similar; but there was a wide variation in the BOD_5 values. The most adopted method used to quantify biodegradability is the assessment of the BOD_5/COD ratio (Sarria *et al.*, 2002). According to this, the KE2 sample ($\text{BOD}_5/\text{COD} = 0.905$) was more biodegradable than the KE1 sample ($\text{BOD}_5/\text{COD} = 0.395$) which may be related to the low phenolic content and the turbidity of KE2.

Table 1. Chemical and physical properties of Kraft effluent samples.

Parameter	KE1	KE2
pH	10.5 ± 0.1	9.7 ± 0.1
Turbidity (FTU)	129 ± 0	73.4 ± 1.2
True color (440 nm)	0.4144 ± 0.0005	0.4560 ± 0.0007
Apparent color (440 nm)	0.7261 ± 0.0001	0.6070 ± 0.0002
BOD_5 ($\text{mg L}^{-1} \text{O}_2$)	414 ± 39	971 ± 93
COD ($\text{mg L}^{-1} \text{O}_2$)	1047 ± 21	1073 ± 1
DOC ($\text{mg L}^{-1} \text{C}$)	316 ± 7	308 ± 15
Total phenolics (mg L^{-1} gallic acid)	83.6 ± 2.8	75.8 ± 1.7
Lignin compounds (280 nm) *	0.4944 ± 0.0001	0.4811 ± 0.0003
Spectral area (200-800 nm) *	106.40 ± 3.56	108.89 ± 5.45
Alkalinity ($\text{mg L}^{-1} \text{CaCO}_3$)	40.1 ± 0.9	46.4 ± 1.1

* values obtained from diluted sample (factor = 15).

3.2. Experimental design

The effect of pH variation and hydrogen peroxide concentration on the performance of the UV/ H_2O_2 process was initially evaluated on the KE1 sample (Table 2). The central point (exp. 5) was assayed in triplicate and demonstrated a satisfactory repeatability among experiments (mean SD = 2.67). The results indicated low reduction of the apparent color in all conditions tested, except for the DOC and UV-vis spectral area best results were reached in acidic media and with high peroxide concentration.

Table 2. Factorial design data for UV/H₂O₂ process for the KE1 sample (reaction time = 40 min).

Exp	Variable			Reduction (%)		
	H ₂ O ₂ / (mg L ⁻¹)	pH	Apparent Color	DOC	UV-vis Spectral area	
1	50	4	23.12	62.85	56.76	
2	70	4	41.33	77.45	71.04	
3	50	8	21.43	28.44	45.44	
4	70	8	22.49	45.58	45.88	
5*	60	6	24.06 ± 3.72	48.70 ± 2.17	52.14 ± 2.12	

*triplicate of central point, mean ± standard deviation estimative (SD).

The Pareto chart (Figure 1) confirmed that an increase in the dosage of oxidant contributes significantly ($p = 0.95$) to the decrease of DOC. The pH variation had a significant effect over the reduction of DOC and UV-vis spectral area; its increase interfered negatively in all studied parameters. This effect was not expected, since H₂O₂ have a higher absorptivity at 254 nm in basic pH (HO₂⁻), generating more hydroxyl radicals.

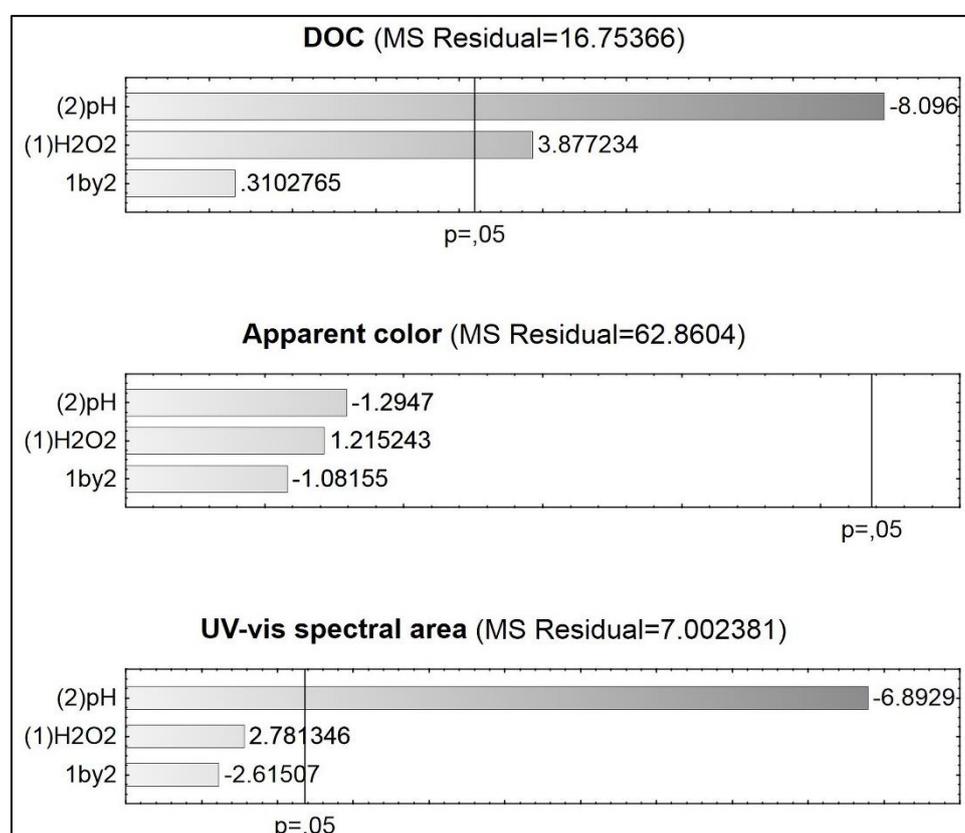


Figure 1. Main effect Pareto charts for apparent color, DOC and spectral area reductions obtained from 2² factorial design (Standardized Effect Estimate for absolute values - 95% confidence interval).

For color removal, the low efficiency of the process can be explained by the presence of some recalcitrant compounds, such as condensed tannins which contribute to the coloration of the sample (Kamali and Khodaparast, 2015). During the oxidative process, these recalcitrant compounds are broken down into smaller chromophore fractions, reaching less-expressive results in the removal of color (Kemeny and Benerjee, 1997). No linear response explain the low correlation ($R^2 = 0.59032$) and adjustment (0.1864) for this parameter in comparison to DOC ($R^2 = 0.96415$ and adjustment = 0.9283) and UV-vis spectral area ($R^2 = 0.95391$ and

adjustment = 0.90782). Based on these data, the best treatment condition for KE1 was an oxidant concentration of 70 mg L⁻¹ and pH 4.0, which was then applied to the treatment of the two samples (KE1 and KE2).

3.3. Effluent treatment by UV/H₂O₂ process

The adjusted conditions of the UV/H₂O₂ reactions were applied in both effluent samples, and the process performance was evaluated through analytical parameters (Table 3). The variations in the results are probably correlated with the different chemical properties of the samples. Although the treatment was conducted under the same pH and oxidant concentration conditions, it is not possible to predict how the hydroxyl radicals formed will interact with the organic matter in the effluent. Such interactions are critical for color reduction as a consequence of the breakdown of conjugated double bonds, but the non-selectivity of the hydroxyl radical could affect the samples in different ways (Lee and Von Gunten, 2010). Besides that, the difference in DOC removal between the samples can be explain by the higher biodegradability of KE2 (Table 1). This indicates that this sample had a great amount of labile compounds.

Table 3. Percentual reduction of the parameters after treatment of Kraft effluent samples ([H₂O₂] = 70 mg L⁻¹, pH = 4.0, reaction time = 40 min).

Parameter	Removal (%)	
	KE1	KE2
Turbidity	-41.8	0.91
True color (440 nm)	19.4	69.4
Apparent color (440 nm)	35.0	34.2
DOC	18.8	50.7
Total phenolics	79.3	73.7
Lignin compounds (280 nm)	40.5	68.9
UV-vis spectral area (200-800 nm)	49.4	69.9

The best result was expected in the DOC removal in the KE1 sample (18.8%), since in the literature COD reductions between 45% and 74% have been reported with AOPs applied for the treatment of pulp and paper effluents, although the largest reduction was described by combining a coagulation-flocculation process followed by heterogeneous photocatalysis (Catalkaya and Kargi, 2008; Rodrigues *et al.*, 2008).

Satisfactory reductions of lignin compounds and total phenolics can be attributed to aromatic content in the start of the process; above those occur the electrophilic addition of hydroxyl radicals, generating new phenols in the media. Once the oxidative process continues, these formed compounds undergo the breakdown of the aromatic rings, lose their chromophoric groups and afterwards would mineralize (Tiburtius *et al.*, 2009; Kamali and Khodaparast, 2015). Theses results indicate that higher H₂O₂ doses should be implemented to mineralize of the organic compounds.

3.4. Acute ecotoxicity on *Daphnia magna*

The bioassay with *Daphnia magna* is one of the most broadly used in the laboratory routine of industries to evaluate the ecotoxicity of effluent samples. The bioassays data for non-treated samples showed acute toxicity to *Daphnia magna*. However, for treated samples the results were quite variable for KE1 and KE2 (Table 4), once the toxicity of KE2 increased after UV/H₂O₂ treatment.

Table 4. Acute toxicity of Kraft effluent samples on *D. magna* before and after UV/H₂O₂ process (pH = 4.0; [H₂O₂] = 1050 mg L⁻¹; reaction time = 780 min).

Sample	KE1		KE2	
	Before UV/H ₂ O ₂	After UV/H ₂ O ₂	Before UV/H ₂ O ₂	After UV/H ₂ O ₂
48h -EC ₅₀ ^a (% v/v)	132.90	Non-toxic ^b	183.51	50.05
TU	0.752	Non-toxic ^b	0.545	1.998

^aconcentration that cause immobilization in 50% of the test organisms; for results before treatment the values correspond to extrapolation because the effluent did not reach the EC₅₀ index. ^bno organism presented immobility at the concentrations tested.

The increase of KE2 acute toxicity after treatment could be at least partially explained by the formation of byproducts once complete mineralization has not been achieved. Previous studies suggested that the degradation of high molecular weight compounds can generate highly toxic compounds (Fernandez-Alba *et al.*, 2002; Pereira *et al.*, 2009). The literature suggests that lignins, tannins and resin acids are some of the major compounds in this complex kind of effluent that are responsible for the toxicity in untreated samples (Peitz and Xavier, 2017). Carvalho *et al.* (2009) described the production of some compounds such as p-hydroxy-phenyl, guaiacyl and syringyl when oxidation process are carried out in degradation of wood. The electrophilic addition of the hydroxyl radical to the aromatic rings of these subunits can lead to the formation of quinone and catechol derivatives (Azevedo *et al.*, 2006). Some of similar molecules such as phenol and hydroquinone have been demonstrated high toxicity to *D. magna* (48 h-EC₅₀ = 6.6 mg L⁻¹ and 0.15 mg L⁻¹, respectively) (Guerra, 2001). Considering that almost same removal of total phenolics were achieved for both samples, the higher toxicity may have been caused by compounds in a more advanced stage of oxidation. Once the KE2 was a more biodegradable sample, the byproducts formed in the oxidation process grew abundant enough to increase the toxicity after treatment.

4. CONCLUSIONS

This study demonstrates that the physical and chemical measures are not sufficient to evaluate the effectiveness of the oxidative treatment of effluent samples of a Kraft pulp mill. Moreover, it was possible to verify that each batch of these complex effluents should be considered a particular case and require additional performance criteria, such as toxicity monitoring. In the same way as in this study, the application of reactional parameters obtained by factorial planning in a preliminary sample on other similar effluent can result in an increase of toxicity due to the partial oxidation of organic compounds.

5. ACKNOWLEDGEMENTS

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