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Pulp and Paper Mill Effluent Treated by Combining Coagulation-Flocculation-Sedimentation and Fenton Processes

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Abstract Pulp and paper industries face serious environmental challenges, especially with regard to the conservation of water resources. Chemical thermal mechanical pulping (CTMP) is a process of pulping that combines chemical and mechanical pulping. This reduces the volume of water used in the process. But on the other hand, CTMP generates an effluent with high concentration of organic matter and is difficult to treat. This study evaluated the efficiency in the combination of physicochemical pretreatment by coagulation-flocculation-sedimentation (CFS) process and advanced oxidation process (AOP) by Fenton in sequence to treat CTMP effluent of a Brazilian industry. At first, the best treatment conditions for this type of effluent were determined. To evaluate the efficiency, pH, chemical oxygen demand, biochemical oxygen demand, total organic carbon, lignin contents, color, total phenolic contents, turbidity, and solids were measured before and after treatment. The acute toxicity on *Daphnia magna* was also determined. The treatment with CFS showed better results in the removal of solids and Fenton in the removal of recalcitrant compounds, such as lignin, demonstrating the need to use them in sequence. Combining CFS and Fenton to treat CTMP effluent allowed to achieve a removal efficiency of 95% for TOC, 61% for COD, and 76% for lignin contents.

Keywords Pulp and paper mill effluent · CTMP effluent · Physicochemical treatment · Coagulation-flocculation-sedimentation · Advanced oxidation process · Fenton

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1 Introduction

In 2016, Brazil takes the second position in the world ranking of pulp production, only staying behind the USA. In the production of paper, the country is in the eighth place (Ibá 2017).

The feedstock used by this sector, the wood, has its structure composed by macromolecules of cellulose, hemicellulose, and lignin. There are also low molecular weight substances, as extractives and inorganic compounds (Kamali and Khodaparast 2015).

The pulping process is responsible for separating the fibers from the wood. This process gives rise to a cellulosic mass which is used in paper manufacturing. The pulping processes can be classified into mechanical, chemical, and a combination of these two processes.

The mechanical process includes the separation of fibers by mechanical action. This results in lower pulp quality but a higher than 90% yield. The chemical process promotes the separation of cellulose through chemical action employing alkaline (kraft) or acid media (sulfite). In these cases, the yield is approximately 50%. The chemical thermal mechanical pulping (CTMP) process combines these two pulping methods and results in an 85% yield (Karimi et al. 2009; Sixta 2006; Pokhrel and Viraraghavan 2004).

CTMP is a process that combines chemical by using sodium bisulfite and mechanical pulping. Other chemicals such as sodium hydroxide and peroxide can also be used, replacing the bisulfite. This modified process that uses sodium hydroxide and peroxide is called alkaline peroxide mechanical pulping (APMP). These processes have the characteristic of generating a low volume of effluent when compared with other chemical processes such as kraft pulping. This is positive due to low water consumption. But the effluent generated has a high concentration of color, chemical oxygen demand (COD), and biochemical oxygen demand (BOD_5) (Liu et al. 2011).

Higher chemical concentration in the CTMP effluent also means it has the highest concentrations of inhibitory and recalcitrant organic compounds. Many of these compounds are not water soluble and are resistant to biological degradation. They also can be toxic to aquatic organisms (Orrego et al. 2009; Stephenson and Duff 1996).

The aim of the present work was to asses a physico-chemical method and an advanced oxidation process (AOP) combined to treat CTMP effluent from a pulp and paper Brazilian industry. Biological treatments were not chosen due to their effluent toxicity. The physico-chemical method employed is the coagulation-flocculation-sedimentation (CFS) process that uses aluminum sulfate as coagulant. Samples treated under the best treatment conditions achieved with CSF were also treated by POA Fenton. The best conditions of the relations [COD:H_2O_2] and [H_2O_2]:[Fe^{+2}] were determined to treat the CTMP effluent by Fenton.

2 Material and Methods

The experiments were carried out using effluent from a CTMP plant of a Brazilian cellulose industry. It was collected where the generation is continuous and the flow representative, resulting in two points of collection. One of them was after the pressing processes of the woodchips. The other refers to the washing process of the cellulose pulping, in which the effluent generated is the filtrate extracted from the washing. The effluent samples were mixed in a laboratory following the same proportion generated in the industry (1:4.5). It was stored in plastic bottles and kept at 4 °C in a refrigerator in the dark (APHA 2012).

The analyses carried out to assess the CSF treatment was COD, BOD_5, total organic carbon (TOC), lignin contents, color, total phenolic contents (TPC), turbidity, total suspended solids (TSS), volatile suspended solids (VSS), and toxicity. All are performed in duplicate, and the maximum deviation accepted between the duplicate was 5%. The samples were firstly filtered in 0.45 μm pore-size membrane. The determination of COD, BOD_5, TOC, TPC, TSS, and VSS was performed according to APHA (2012). Lignin contents and color were done according to Çeçen (2003). The acute toxicity factor (TF acute) on *Daphnia magna* was performed based on EC-50 at 48 h, according to ABNT (2016). For Fenton, the same parameters were analyzed, except solids and BOD_5, because this treatment was applied in order to remove recalcitrant compounds. Removal efficiencies ($R\%$) (Eq. 1) were calculated based on the concentrations before (C_0) and after (C_f) treatments

$$R\% = ((C_0 - C_f)/C_0).100 \qquad (1)$$

where C_0 is the initial concentration and C_f is the final concentration.

To determinate the best CSF conditions to treat the samples of CTMP effluent, aluminum sulfate ($Al_2(SO_4)_3$) was tested as coagulant in concentrations of 500 and 750 mg/L, pH 3.0 and 4.0, and settling times of 30 and 60 min. For each test done, the samples were shaken at 120 rpm for 1 min and at 20 rpm for 15 min (Rodrigues et al. 2008; Stephenson and Duff 1996). The settling time was tested next. The samples treated under the conditions that results in the best removals were selected in the application of Fenton.

The Fenton's assays were made with 500 mL of diluted (1:10) samples due to the high consumption of hydrogen peroxide (H_2O_2) required. The variations in COD, H_2O_2, and ferrous ion (Fe^{2+}) concentrations tested to treat CTMP effluent were established based on the literature and are shown in Table 1 (Santos et al. 2010;

Table 1 Three relationships of chemical oxygen demand (COD), hydrogen peroxide (H_2O_2), and ferrous ion (Fe^{2+}) tested to define the best condition to treat the CTMP effluent by Fenton

Variables	Level (−)	Level (+)
[COD]:[H_2O_2]	1:2	1:5.5
[H_2O_2]:[Fe^{2+}]	2:1	5:1

Araujo et al. 2009). The concentration of the hydrogen peroxide solution was 35% (*m*/*v*), and ferrous ions were obtained from a solution of ferrous sulfate ($FeSO_4 \cdot 7H_2O$) with a concentration of 20 g/L.

The pH of the influent was adjusted to 3.0 using 10% sulfuric acid and 10% sodium hydroxide. The addition of Fenton's reagents was done after adjusting the pH and under shaking. During the treatment, the sample was maintained in the dark (Santos et al. 2010; Araujo et al. 2009). The H_2O_2 residual curve was designed according to Nogueira et al. (2005) and the iron curve by the ortho-phenanthroline method (APHA 2012).

3 Results and Discussion

The initial characterization of the CTMP effluent is shown in Table 2. The COD of CTMP effluent is around 9000 mg/L, which is high when compared with other processes. Chamorro et al. (2010) report to effluent originated from kraft processes values around 880 mg/L. The relation BOD_5/COD is approximately 0.6. This indicates that the effluent has good biodegradability. But when the industry sent the CTMP effluent to the biological treatment, negative impacts on treatment were observed. Therefore, it was necessary to study an adequate physicochemical treatment to treat the effluent produced in the CTMP line. The effluent shows concentrations of TSS around 1500 mg/L. This value is three times higher than the reference value indicated by Pokhrel and Viraraghavan (2004) for the CTMP effluent. Comparing TSS with VSS, it was concluded that 87% of solids present had organic origin.

3.1 Physicochemical Treatment by Coagulation-Flocculation-Sedimentation

Figure 1 shows the removal efficiencies achieved on tests to determine the best condition to CFS treatment. The maximum removal of COD was 21% at pH 3.0 at

Table 2 Physicochemical characterization of the CTMP effluent before treatments (influent) given as means ± SDs ($n = 7$ to pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), color, turbidity, total suspended solids (TSS), volatile suspended solids (VSS), lignin contents, total phenolic contents (TPC); $n = 2$ to total organic carbon (TOC) and acute toxicity)

Parameter	Influent
pH	6.10 ± 0.40
COD (mg/L)	9992 ± 2838
BOD_5 (mg/L)	6351 ± 2121
BOD_5/COD	0.65 ± 0.20
Color (VIS_{440}) (1 × 1 cm)	7.8 ± 1.7
Turbidity (UNT)	1439 ± 494
TSS (mg/L)	1570 ± 484
VSS (mg/L)	1370 ± 512
Lignin contents (UV_{280}) (1 × 1 cm)	58.9 ± 9.1
TPC (mg/L)	3002 ± 448
TOC (mg/L)	8203 ± 4207
Acute toxicity (TF)	4–8

settling time of 60 min. Liu et al. (2011) for APMP effluent achieved 81% of COD removal applying coagulation-flocculation-sedimentation. It was achieved using 1000 mg/L of $Al_2(SO_4)_3$ and pH range of 4 to 5. The COD of influent samples used by the author was approximately 300 mg/L, and it is lower than the CTMP effluent used in this study (approximately 10,000 mg/L). This suggests an influence of the initial organic material concentration in the removal efficiency, as also verified by Stephenson and Duff (1996).

The BOD_5 maximum removal efficiency was approximately 30%. Žarković et al. (2011) achieved 65% of BOD_5 removal treating a paper industry effluent by coagulation-flocculation-sedimentation. Their influent sample had an initial BOD_5 concentration of 1372 mg/L. It is a lower load than that used in this study, of approximately 6000 mg/L, repeating the indication of the influence of the initial concentration on the removal efficiency.

The better removal efficiencies for lignin contents and TPC were observed at pH 3.0. It could be explained due the lignin precipitation, which occur under low pH conditions. This was also observed by Liu et al. (2011), Garg et al. (2010), and Stephenson and Duff (1996). And to these two parameters, it was not observed in relation with the coagulant concentration.

The best removal efficiency for color, turbidity, SST, and VSS were 43, 50, 85, and 90%, respectively. These

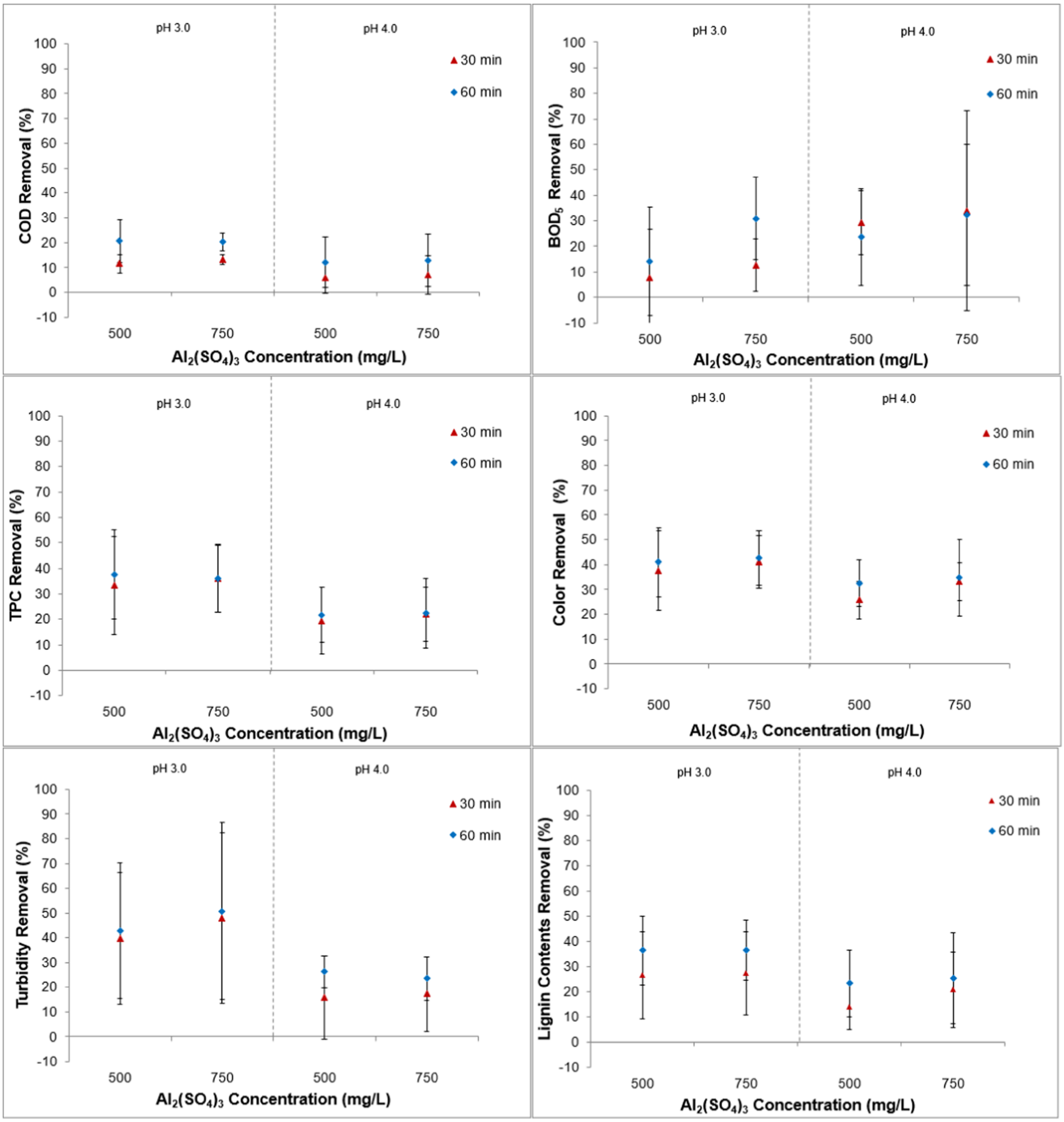

Fig. 1 Removal efficiencies achieved in tests to determine the best conditions to treat CTMP effluent by sedimentation-flocculation-coagulation (CSF). The conditions evaluated were aluminum sulfate ($Al_2(SO_4)_3$) as coagulant in concentrations of 500 and 750 mg/L, pH 3.0 and 4.0, and settling times of 30 and 60 min. The parameters analyzed were chemical

removals were verified at pH 3.0, 750 mg/L coagulant concentration, and settling time of 60 min. Therefore, these parameters were selected as best conditions to treat CTMP effluent by CFT.

TF acute did not indicate changes on effluent toxicity after CFS treatment.

3.2 AOP Treatment by Fenton

The H_2O_2 residual curve for the conditions tested is shown in Fig. 2. Based on this, the time of 1 h was chosen as appropriate for the Fe^{+2} consumption. From that time, it is noted that Fe^{2+} ion concentration had only

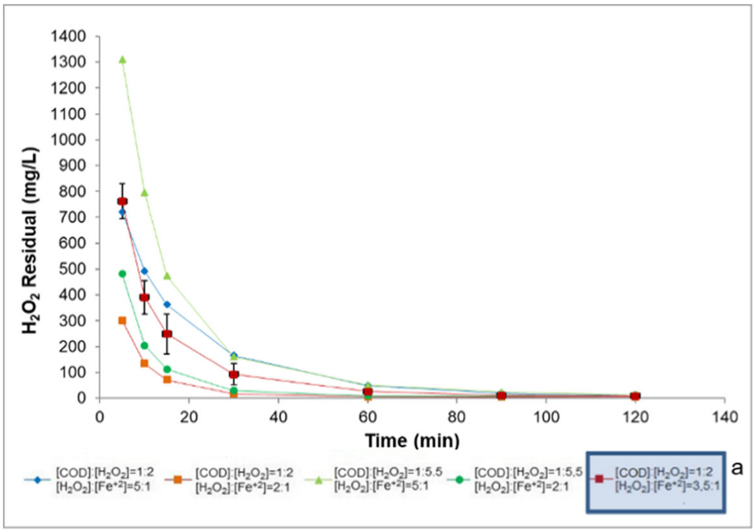

Fig. 2 H_2O_2 residual curve to determine an adequate reaction time for the Fenton treatment

small variations along time. In order to reduce the amount of reagents required, an intermediate condition was chosen to apply in Fenton treatment. This intermediate condition is the central curve in Fig. 2 and corresponds to the relationships of $[COD:H_2O_2] = 1:2$ and $[H_2O_2]:[Fe^{+2}] = 3.5:1$.

The ferrous ion curve (Fig. 3) was designed based on the condition defined. It is noted that at the beginning of the reaction, there is a reduction in Fe^{+2} and an increase in $Fe^{+\ 3}$. This indicates the occurrence of the Fenton reaction. Over the progression of the reaction, the concentration of Fe^{+3} remained constant while Fe^{+2} continues to decrease. This may occur due to the precipitation of $Fe(OH)_3$, which occurs due to the increase of hydroxyl and pH in the reaction media. It was also reported by Araujo et al. (2009).

3.3 Result of Combined Treatments

The efficiency removal obtained by combining both treatments are presented in Table 3. The treatment with CFS showed better results in the removal of turbidity and Fenton in the removal of recalcitrant compounds, such as lignin, demonstrating the benefit of using them in combination.

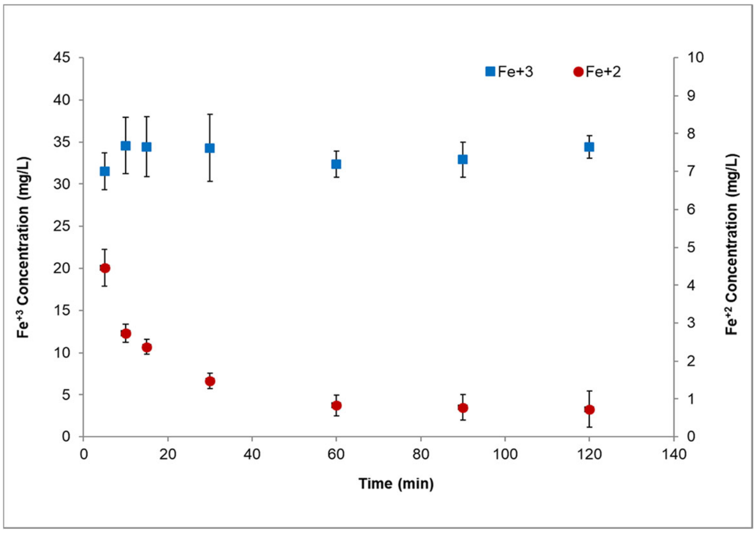

Fig. 3 Ferrous ion curve. The initial variations in the ferrous ion concentration indicate the occurrence of the Fenton reaction

Table 3 Removal efficiency of combined treatments

Parameter	C_0	$R\%_{CFS}$	C_{CFS}	$R\%_{AOP}$	C_F	$R\%_{COMB}$
Turbidity (NTU)	1439	51	708	47	372	74
Color (VIS_{440}) (Abs)	7.8	43	4.5	18	3.7	53
COD (mg/L)	9992	20	7963	52	3850	61
Lignin contents (UV_{280}) (Abs)	58.9	36	37.8	63	13.9	76
TPC (mg/L)	3002	37	1903	32	1298	57
TOC (mg/L)	8203	78	1846	79	389	95

C_0, initial concentration; $R\%_{CFS}$, removal efficiency in the coagulation-flocculation-sedimentation treatment; C_{CFS}, concentration after coagulation-flocculation-sedimentation treatment; $R\%_{AOP}$, efficiency removal by Fenton; C_F, final concentration, after both treatments; $R\%_{COMB}$, total removal efficiency

Color removal efficiency obtained after Fenton was approximately 18%. Santos et al. (2010) reported a 70% efficiency removal for the same parameter, applying Fenton in effluent originated from kraft pulp industry. Such low removal may have occurred by the wavelength on which absorbance color is read using a UV/VIS spectrophotometer, following the methodology used in this study. Color was analyzed at wavelength of 440 nm, according to Çeçen (2003). Fe^{+2} is also absorbed at a near wavelength, and this may have interfered in the color determinations.

The removal of organic matter in Fenton treatment is evidenced by the values obtained in the removal of COD (52%), TOC (79%), and lignin contents (63%), as shown in Table 3. Araujo et al. (2009) achieved 95% of COD removal from the effluent with similar initial COD concentration, and Santos et al. (2010) reported removals between 57 and 74%.

The result obtained on TPC removal efficiency is lower compared with the other values related to organic matter (Table 3). This may have happened because the excess of $NaHSO_3$ is used to eliminate the H_2O_2 residual. According to Burkholder and McKeen (1997), there is an SO_3 absorption in the region of 195–330 nm of the spectrum, and this interference can be closely greater than 200 nm. As the TPC are analyzed at 215 nm wavelength, the results may be influenced by the presence of $NaHSO_3$. Besides that, the low removal of this parameter may result in the breakdown of condensed lignin molecules in the phenolic groups, as reported by Lundquist et al. (2007).

Combining CSF and Fenton, it was possible to achieve removal efficiency of 95% to TOC, 61% to COD, and 76% to lignin contents. Considering the average of all parameters presented in Table 3, the physicochemical treatment by CFS had a removal efficiency of 44% and POA by Fenton had 49%. Using Fenton after CFS improved the removal efficiencies by 25%, and both combined treatments achieved a removal efficiency of around 70%. These results indicate a positive potential for using physicochemical and POA treatments in sequence to treat the CTMP effluent.

4 Conclusions

Several authors have studied coagulation-sedimentation-flocculation and Fenton separately for wastewater from kraft pulp mills. However, the novelty of this research is supported by the treatment of a CTMP pulp mill effluent which has a high organic load compared with a kraft pulp mill. BOD_5/COD ratio of the CTMP effluent indicates good biodegradability potential. But the physicochemical treatment was chosen due to its effluent toxicity, because when industry sent them for biological treatment, negative impacts were observed. The treatment with CFS showed better results in the removal of solids and Fenton in the removal of recalcitrant compounds, demonstrating the need to use them in combination. This treatment combination allowed to obtain an organic matter (TOC) removal efficiency of around 95%, proving to be a suitable treatment for CTMP effluent. Despite the high removal efficiencies achieved, the low pH and the high H_2O_2 consumption make the treatments considerable in cases of water reuse.

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