

EFFECTS OF FENTON SYSTEM ON RECYCLED UNBLEACHED PULP IN ABSENCE AND PRESENCE OF *p*-HYDROXYBENZOIC ACID

P. MOCCHIUTTI, M. V. GALVÁN and M. A. ZANUTTINI

*Instituto de Tecnología Celulósica, Facultad de Ingeniería Química
Universidad Nacional del Litoral, Santiago del Estero 2654, S3000AOJ, Santa Fe, Argentina*

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The effects of the Fenton reagent on recycled unbleached pulp in the absence and presence of a model chemical contaminant, the *p*-hydroxybenzoic acid (HBA), were studied. In the absence of HBA, the Fenton system clearly modified the chemical and papermaking properties of the pulp. The kappa number was reduced and the specific light absorption coefficient was increased, indicating lignin modification. The amount of total acid groups increased, suggesting lignin or carbohydrate oxidation. Pulp freeness and wet tensile strength were significantly improved, while short compressive strength was slightly increased. Nevertheless, dry tensile strength decreased. In the presence of HBA, the chemical and papermaking properties of the pulp were less modified. When a higher ferrous ion charge was applied, half of the HBA present in pulp was eliminated while, at a lower ferrous ion charge, a lower reduction in HBA was produced, pulp strength being nevertheless preserved.

Keywords: hydroxyl radicals, oxidation, *p*-hydroxybenzoic acid, papermaking properties

INTRODUCTION

Several studies have shown that the strength of recycled paper can be increased by oxidative chemical or enzymatic treatments. Chen *et al.*¹ showed that the delignification of old corrugated container (OCC) pulp by the application of oxygen subsequently to an alkaline treatment principally improves ring crush and Concora test results; Zanuttini *et al.*² reported strength improvement by the application of ozone treatment on recycled pulp obtained from liner paper and OCC; Mocchiutti *et al.*³ found out that the oxidative action of the laccase-mediator system improves the papermaking properties of the fibrous fraction of recycled unbleached softwood pulp from kraft-liner paper.

The use of an oxidative process, such as the Fenton one, can be considered as another alternative for improving recycled paper. The Fenton reagent is a hydrogen peroxide solution in the presence of ferrous ions (*i.e.* FeSO₄·7H₂O). The ferrous ions catalyze the hydrogen peroxide decomposition to free radicals, after which the ferric ions produced are reduced to ferrous ions by the superoxide

anion or by the other radicals generated in the reaction medium.⁴

As indicated by Peres *et al.*,⁵ the Fenton process presents several advantages: it does not require a complicated apparatus and pressurized systems, the ferrous ion is very abundant and non-toxic and H₂O₂ is safe to handle and environment-friendly.

Several studies have shown that the Fenton process can be useful for improving the mechanical properties of different materials. Thus, Widsten *et al.*⁴ showed that the Fenton reagent can improve the internal bond strength of fiberboards manufactured from spruce and beech fibers. Yelle *et al.*,⁶ who used a chelator-mediated Fenton system (Fenton reagent in the presence of compounds, such as 2,3-dihydroxybenzoic acid) to activate the surface of the thermo-mechanical pulp for fiberboard, found out that the activation of lignin and/or extractives on the surface of wood fibers can give lignin the functionality of a self-bonding adhesive. Qian⁷ studied the oxidative action of the chelator-mediated Fenton system on the fibrous fraction of a bleached hardwood pulp

and found out that such a system improves the tensile strength only under relatively mild reaction conditions. Nevertheless, for beaten pulps, freeness increases and strength properties were not statistically changed.

The oxidative Fenton treatment can be also useful for removing the chemical contaminants that can be present in recycled fibers destined to food packaging.

The p-hydroxybenzoic acid (HBA) is a phenolic compound that can be considered as a model contaminant. It is present in agro-industrial, as well as pulp and paper wastewaters⁸ and also in recycled paper, when the HBA esters are used as preservatives in raw materials or in papermaking additives. The international MERCOSUR GMC Res N° 56/97 Norm establishes the maximum limit of this type of phenolic compounds in paper used for food packaging. HBA is also considered as a model of the humic acids⁹ that can also be present in recycled pulps.

The kinetics of HBA degradation by the Fenton reagent has been studied by several authors.^{5,8}

In the present work, unbleached recycled softwood pulp from kraft-liner paper was treated with different dosages of Fenton reagents, at different reaction time periods, both in the absence and in the presence of HBA. The effects of the treatments on kappa number, total acid groups, freeness, yield and k-absorption coefficient, as well as on the strength properties, were investigated. HBA degradation was also studied.

EXPERIMENTAL

Materials and method

Recycled pulp from kraft-liner paper

Recycled unbleached softwood kraft pulp was used in the study. An industrial liner paper (kappa number – 90) was cut into sheets of approximately 30 g, which were randomly selected and soaked for 12 h. Then, the sheets were repulped in a standard disintegrator for 2 min at 1.5% pulp consistency, using distilled water. The pulp obtained was left under these conditions for 24 h, to ensure fiber wetting, after which the pulp was disintegrated again for 15 min. To remove the metallic ions, the pulp was acid treated (pH 2.4 using H₂SO₄) at 4% pulp consistency for 1 h. Then, it was dewatered to about 30% consistency by centrifugation and neutralized at 4% pulp consistency up to pH 4.5 using NaOH. After 15 min, it was dewatered again and stored at 4 °C until use.

Chemicals

Analytical grade chemicals were used in the experiments. A 50 mM FeSO₄·7H₂O solution in 0.01 N H₂SO₄ was prepared immediately before each experiment, as the solution is unstable. A 50 mM anhydrous Fe₂(SO₄)₃ in 3.6 N H₂SO₄ was prepared as a ferric ion solution.

Experimental design

Table 1 shows the experimental conditions applied in the study. All treatments were randomly done in duplicate and the results were analyzed by one-way ANOVA. The Duncan multiple comparison procedure was applied to determine which means were significantly different from other means (p = 0.05).

Taking into account that, during the Fenton treatments, part of the Fe(II) is oxidized to Fe(III), for the control treatments, both iron oxidation states were considered. A 50% iron was added as FeSO₄·7H₂O solution and the other 50% was added as Fe₂(SO₄)₃ solution.

A pH of 4.0 was adopted for the treatments considering the results of Peres *et al.*,⁵ who found out that the optimal value of pH for converting phenolic acid compounds with Fenton reagents ranged between 2.0 and 4.0.

Pulp treatments

Treatments were carried out in polyethylene bags at 8% pulp consistency, pH 4.0 and 30 ± 1 °C, using a water bath, as recommended by Qian.⁷ Initially, the pH of the pulp slurry was adjusted to 5.5-6.0, using 0.025 N NaOH, and left in that condition for 15 min. Then, it was dewatered in a Büchner funnel to form a wet fiber pad and the filtrate was recirculated once to recover the pulp fines.

The pulp was mixed with a measured amount of 50 mM FeSO₄·7H₂O. When HBA was used, it was added in this stage. Then, the pH was adjusted to 4.0 by the addition of sulfuric acid and the pulp was preheated to the desired temperature. Once the temperature was reached, an aliquot of 1.5 M H₂O₂ was added to trigger the reaction. Every 15 min, a volume of liquor was taken for the determination of H₂O₂ concentration by iodometric titration, while HBA concentration was estimated using UV absorption spectroscopy at 248 nm.

Once the treatment time was reached (30 or 60 min), the reactions were stopped by soaking the pulp bags in ice-water (0 °C) for 2 min. Then, the treated pulp was dewatered and the filtrate was recirculated once, to recover the fines. A small amount of filtrate was passed through a 1.5 µm filter and stored for total organic carbon (TOC) measurements.

The wet fiber pad was washed with 1.5 L distilled water in the same Büchner funnel, dewatered to about 30% pulp consistency and stored at 4 °C until use.

Table 1
Experimental conditions for Fenton treatments on recycled pulp in the absence and presence of *p*-hydroxybenzoic acid

Treatment	Charge of Fe (%/o.d. pulp)	Charge of H ₂ O ₂ (%/o.d. pulp)	Charge of HBA (%/o.d. pulp)	Time (min)
Control treatments	0.015 Fe(II) + 0.015 Fe(III)	–	–	60
	0.03 Fe(II) + 0.03 Fe(III)	–	–	60
	0.03 Fe(II)	0.6	–	30
Fenton treatments	0.03 Fe(II)	0.6	–	60
	0.06 Fe(II)	0.6	–	30
	0.06 Fe(II)	0.6	–	60
Fenton treatments in presence of HBA	0.03 Fe(II)	0.6	1.2	30
	0.06 Fe(II)	0.6	1.2	30

Pulp and paper analyses

The TOC of the liquor was determined according to ISO 8245, using a SHIMADZU TOC-5000A analyzer. Although the TOC results can be associated with the loss of hemicelluloses, lignin and extractives, the percentages of yield loss were estimated here by converting the TOC value (mg of carbon/L of the filtrate) to anhydrous glucose on dried pulp (Eq. 1):

$$\left(\%YL = \frac{TOC \cdot Mw_{ag}}{6 \cdot Aw_c \cdot PulpConsistency \cdot 10^6} \cdot 100 \right) \quad (1)$$

where:

% YL = percentage of yield loss

TOC = total organic carbon (mg of carbon/L of filtrate)

Mw_{ag} = molecular mass of the anhydrous glucose (mg/mol)

Aw_c = atomic mass of carbon (mg/mol)

The total acid groups were determined by the conductimetric titration method described by Katz *et al.*¹⁰ NaHCO₃ was used instead of NaOH, according to Lloyd and Horne.¹¹

The pulp was converted to a calcium form, as previously published,¹² and then handsheets weighing 120 g/m² were prepared from the treated pulps, according to SCAN 26:79 and SCAN P2 techniques. Kappa number and paper properties were determined following the Tappi standard test.¹³ Wet tensile strength was determined according to ISO 3781:1983 and the specific light absorption coefficient, *k*, was calculated according to the Kubelka-Munk theory from *R*₀ and *R*_∞ diffuse reflectance values, with a 557 nm filter of the Elrepho photometer.

RESULTS AND DISCUSSION

Fenton treatments in absence of HBA

Figure 1 shows the hydrogen peroxide consumption during the Fenton treatments.

The higher the Fe(II) charge, the higher was the H₂O₂ consumed. When a higher Fe(II) charge was used (0.06% Fe(II)), the H₂O₂ added was almost totally consumed after 60 min.

Figure 2 shows that the kappa number was reduced by the Fenton treatments. According to the Duncan test, only the Fenton treatment corresponding to 0.03% Fe(II)–0.6% H₂O₂ on dried pulp, for 60 min, showed no difference from the control treatments. The kappa number reduction was low, indicating pulp delignification or lignin modification. The delignifying effect of the hydroxyl radicals has been shown by others. According to Rangar,¹⁴ the hydroxyl radicals delignify indirectly, because they can hydroxylate the aromatic rings, introducing handles for other chemicals to attack.

Figure 3 shows that both specific light absorption and acid group content increased by the Fenton treatments. The increments can be ascribed to oxidative reactions, although by these results it cannot be discriminated whether the acid groups are present in the lignin or in the carbohydrates.

When analyzing the results obtained only by the control treatments, it was observed that the higher was the iron ion charge, the lower the amount of acid groups. Although, during the procedure for determining the amount of acid groups, the pulp was acid-washed twice with 0.1 N HCl, the iron ions were not totally removed. According to atomic absorption spectroscopy measurements, even after two successive acid

washes, only 30 and 34% of the total iron in the control pulps (0.03% Fe(II) and 0.06% Fe(II) on dried pulp, respectively) were removed.

Also, the presence of iron ions probably reduces the amount of acid groups determined for the pulp treated with the Fenton reagent. However, the global result is that the Fenton treatment increases the amount of acid groups.

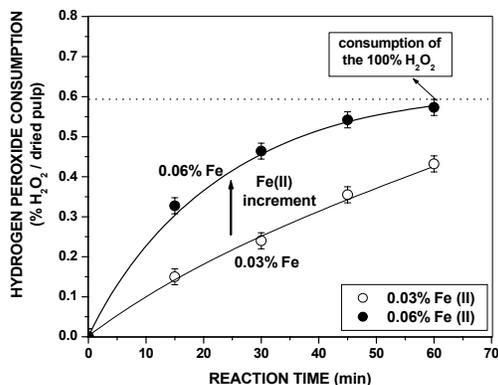


Figure 1: Hydrogen peroxide consumption during Fenton treatments as a function of reaction time for two levels of ferrous ion concentrations applied (the initial H₂O₂ charge was of 0.6% on dried pulp)

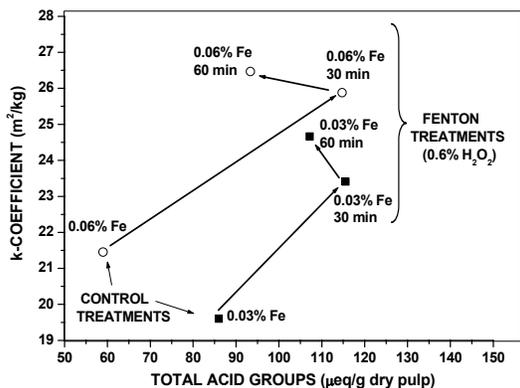


Figure 3: Specific light absorption coefficient (k) as a function of total acid groups content. For Fenton treatments, 0.6% H₂O₂ on dried pulp, two Fe(II) concentrations (0.03 and 0.06% on dried pulp) and two reaction time periods (30 and 60 min) were applied. The ANOVA test indicates significant changes in acid groups content (p = 0.0000) and in k-coefficient (p = 0.0001)

Figure 4 plots tensile strength as a function of freeness. A linear relationship can be established between these parameters. For control treatments, the higher is the iron

TOC analysis showed that the Fenton treatments produced a low yield loss, calculated between 0.7% on dried pulp for the milder treatment (0.03% Fe(II) and 0.6% H₂O₂ on dried pulp for 30 min) and 1.0% on dried pulp for the more severe treatment (0.06% Fe(II) and 0.6% H₂O₂ on dried pulp for 60 min). It can be expected that the application of these treatments at an industrial scale will produce a low organic charge in the effluents.

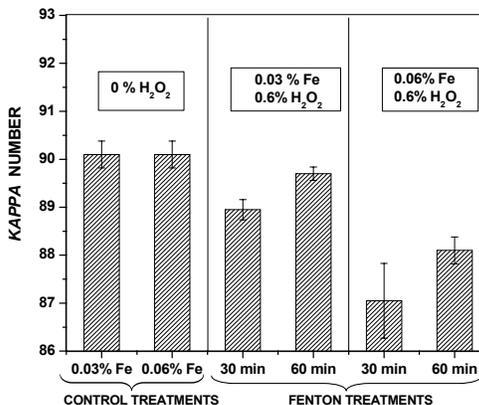


Figure 2: Kappa number results for different treatments. For Fenton treatments, 0.6% H₂O₂ on dried pulp, two Fe(II) concentrations (0.03 and 0.06% on dried pulp) and two reaction time periods (30 and 60 min) were applied. The ANOVA test indicates significant changes in kappa number results (p = 0.0013)

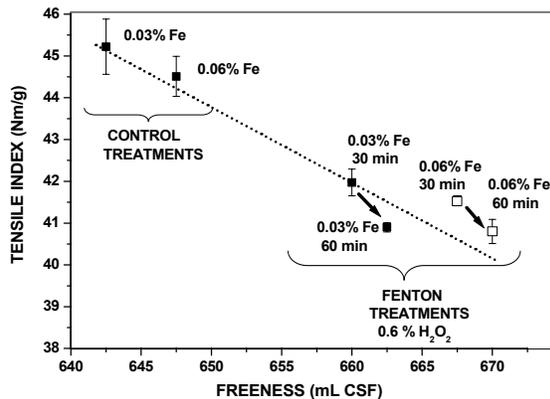


Figure 4: Tensile strength as a function of freeness. For Fenton treatments, 0.6% H₂O₂ on dried pulp, two Fe(II) concentrations (0.03 and 0.06% on dried pulp) and two reaction time periods (30 and 60 min) were applied. The ANOVA test indicates significant changes in freeness (p = 0.0117) and in tensile strength (p = 0.0001)

ion charge, the higher the freeness and the lower the tensile strength. The detrimental effect of the iron ion on paper strength can be ascribed to its known flocculation effect

and to the reduction in the acid groups content, as shown in Figure 3. Scallan¹⁵ and

Barzyk *et al.*¹⁶ showed that the acid groups have an important role on bonding capacity.

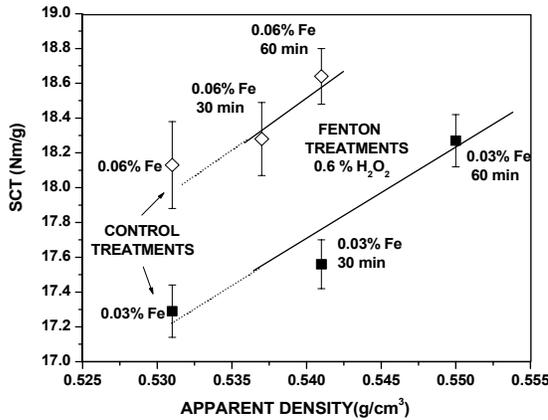


Figure 5: Short compressive strength as a function of apparent density. For Fenton treatments, 0.6% H₂O₂ on dried pulp, two Fe(II) concentrations (0.03 and 0.06% on dried pulp) and two reaction time periods (30 and 60 min) were applied. The ANOVA test indicates significant changes in apparent density ($p = 0.0015$) and in SCT ($p = 0.0020$) for control treatments and 60 min Fenton treatments

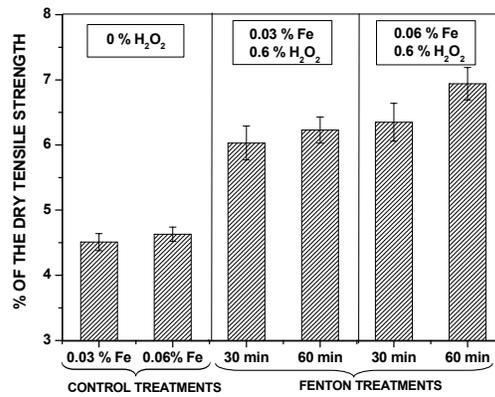


Figure 6: Wet tensile strength as a percentage of dry tensile strength for different treatments, determined on handsheets stored in polyethylene bags and in the dark for 60 days

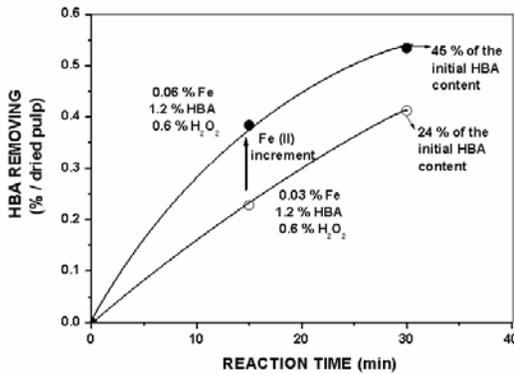


Figure 7: HBA removal as a function of reaction time for 0.03% Fe and 0.06% Fe (the initial charges of H₂O₂ and HBA were of 0.6% and 1.2% on dried pulp, respectively)

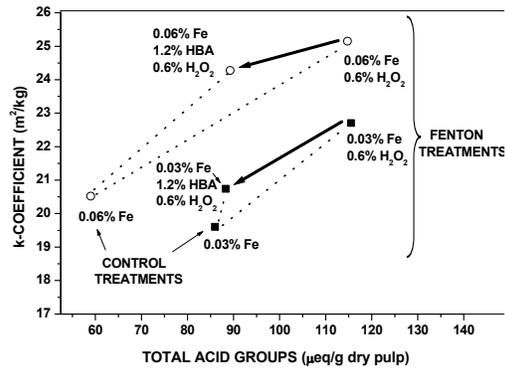


Figure 8: Light absorption coefficient (k) as a function of total acid groups content in the absence and presence of 1.2% HBA on dried pulp after a 30 min treatment. For Fenton treatments, 0.6% H₂O₂ on dried pulp and two Fe(II) concentrations (0.03 and 0.06% on dried pulp) were applied. The ANOVA test indicates significant changes in the amount of acid groups ($p = 0.0000$) and in light absorption coefficient ($p = 0.0000$), due to different treatments. The arrows indicate the effects of HBA presence

Compared to the control treatments, the Fenton treatments increased freeness and decreased tensile strength even more, although the content of acid groups was increased. The beneficial increase in freeness agrees with the results obtained by Qian⁷ for

beaten bleached pulp treated with a chelator-mediated Fenton system. He explained that the hydroxyl radicals may preferentially react with fines and amorphous cellulose, thus increasing freeness.

Figure 5 shows the short span compressive strength as a function of apparent density. A relation can be established for 0.03% Fe and another one for the 0.06% Fe charge. Apparent density increased with all Fenton treatments. The higher was the reaction time, the higher the apparent density. Although the change in density was low, an increase in fiber conformability was evidenced. On the other hand, SCT was slightly increased, which can be ascribed to sheet densification. According to de Ruvo *et al.*,¹⁷ compressive strength is improved by an increase in sheet density, which reduces the length of the free fiber segments in the paper structure, thus reducing the possible inelastic buckling of fibers during stress.

The CMT values were not affected by the Fenton treatments, except for the treatment corresponding to 0.06% Fe(II)–0.6% H₂O₂ at 30 min, for which CMT decreased only by 5% (data not shown).

Figure 6 shows that the Fenton treatments produced a clear increase in wet tensile strength (expressed as percentage of dry tensile strength). This behavior probably indicates that stable bonds are generated in the interfibrillar surface due to lignin-to-lignin reactions. Coupling of phenoxy radicals on lignin associated with adjacent fibers has been suggested by Lund and Felby¹⁸ as an explanation for the improvement in wet strength for high yield unbleached kraft pulps treated with laccase, alone or in the presence of mediators.

In our case, the phenoxy radicals can be generated by the hydroxyl radicals present in a Fenton system. According to Gierer *et al.*,¹⁹ the hydroxyl radicals dehydrogenate the phenolic hydroxyl groups from the lignin model compounds producing phenoxy radicals.

Fenton treatments in presence of HBA

Figure 7 plots HBA degradation as a function of time. After 30 min, 24 and 46% of the HBA present in the pulp were eliminated for low and high ferrous ion charges, respectively. The H₂O₂ consumption as a function of time (data not shown) was similar to that obtained in the absence of HBA (Fig. 1).

Figure 8 shows the specific light absorption coefficient as a function of the amount of acid groups in the pulp treated with Fenton reagents in the absence and presence of HBA. It is clear that the presence of HBA reduces the effects of the free radicals on fibers, especially at low ferrous ion charges.

HBA also reduces the effects of Fenton reagents on tensile strength and freeness after 30 min of treatment (Fig. 9). In the presence of HBA, for a high ferrous ion charge (0.03% Fe/dried pulp), 45% of HBA was eliminated, yet tensile strength was significantly reduced. Nevertheless, for a low ferrous ion charge (0.03% Fe/dried pulp), 24% of HBA was eliminated, freeness was slightly increased and tensile strength was reduced with only 3%.

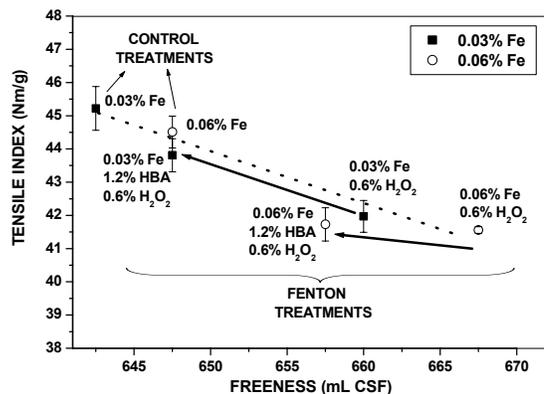


Figure 9: Tensile strength as a function of freeness in the absence and presence of 1.2% HBA on dried pulp after 30 min of pulp treatment. For Fenton treatments, 0.6% H₂O₂ on dried pulp and two Fe(II) concentrations (0.03 and 0.06% on dried pulp) were applied. The ANOVA test indicates significant changes in tensile strength ($p = 0.0004$) and freeness ($p = 0.054$), due to different treatments. The arrows indicate the effects of HBA presence

CONCLUSIONS

The Fenton treatments reduced the content of *p*-hydroxybenzoic acid and clearly modified the chemical and papermaking properties of the recycled unbleached softwood kraft pulp.

In the absence of the *p*-hydroxybenzoic acid, kappa number was reduced and the absorption coefficient, as well as the amount of acid groups increased, indicating that the lignin and/or the carbohydrates were oxidized. Apparent density was increased by inducing positive changes in compressive strength.

Dry tensile strength decreased, yet freeness and wet tensile strength notably increased. The organic charge produced to the treatment liquid was low.

In the presence of the *p*-hydroxybenzoic acid, it was found out that, for a lower ferrous ion charge and a shorter reaction time, the Fenton reagent was useful in reducing the content of this phenolic compound, without significantly changing pulp strength.

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REFERENCES

- ¹ Z. Chen, J. A. Heitmann and H. Chang, *Paper Technol.*, **39**, 45 (1998).
- ² M. A. Zanuttini, T. McDonough, C. Courchene and P. Mocchiutti, *Tappi J.*, **6**, 3 (2007).
- ³ P. Mocchiutti, M. A. Zanuttini, K. Kruus and A. Suurnäkki, *Tappi J.*, **10**, 17 (2008).
- ⁴ P. Widsten, P. Qvintus-Leino, S. Tuominen and J. E. Laine, *Holzforchung*, **57**, 447 (2003).
- ⁵ J. A. S. Peres, L. H. Melo de Carvalho, R. A. R. Boaventura and C. A. V. Costa, *J. Environ. Sci. Health. Part A: Toxic/Hazard. Subst. Environ. Eng.*, **39**, 2897 (2004).
- ⁶ D. Yelle, B. Goodell, D. J. Gardner, A. Amirbahman, P. Winistofer, and S. Shaler, *Forest Prod. J.*, **54**, 73 (2004).
- ⁷ Y. Qian, *Master Thesis*, University of Maine, 139 pp., Maine, USA, 2001.
- ⁸ J. B. De Heredia, J. Torregrosa, J. R. Domínguez and J. A. Peres, *Chemosphere*, **45**, 85 (2001).
- ⁹ D. L. Norwood, J. D. Johnson and R. F. Christman, *Environ. Sci. Technol.*, **14**, 187 (1980).
- ¹⁰ S. Katz, R. P. Beatson and A. M. Scallan, *Svensk Papperstidn.*, **87**, 48 (1984).
- ¹¹ J. A. Lloyd and C. W. Horne, *Nordic Pulp Pap. Res. J.*, **8**, 48 (1993).
- ¹² P. Mocchiutti, M. Zanuttini, M. Citroni and M. C. Inalbon, *Cellulose Chem. Technol.*, **40**, 87 (2006).
- ¹³ Tappi Standard Test 2004-2005, CD version.
- ¹⁴ M. Ragnar, *PhD Thesis*, Royal Institute of Technology, Stockholm, Sweden, 76 pp., 2000.
- ¹⁵ A. M. Scallan, *Tappi J.*, **66**, 73 (1983).
- ¹⁶ D. Barzyk, D. H. Page and A. Ragauskas, *J. Pulp Pap. Sci.*, **23**, 59 (1997).
- ¹⁷ A. de Ruvo, C. Fellers and C. Engman, *Svensk Papperstidn.*, **81**, 557 (1978).
- ¹⁸ M. Lund and C. Felby, *Enzyme Microb. Technol.*, **28**, 760 (2001).
- ¹⁹ J. Gierer, E. Yang and T. Reitberger, *Holzforchung*, **46**, 495 (1992).