

Environmental implications of hexenuronic acid removal from *Eucalyptus globulus* kraft pulp using peroxymonosulfuric acid.

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SUMMARY

Hexenuronic acid (HexA) formed in alkaline pulping is known to react with bleaching agents, leading to increased production costs, and affecting product quality and environmental performance. This article focuses on environmental implications of HexA removal from *Eucalyptus globulus* kraft pulp using peroxymonosulphuric acid (Ps), before bleaching. The experimental work was conducted at laboratory scale and bleaching effluents were obtained using an ECF sequence (D₀-E₀-D₁). Results show that Ps effectively removed HexA, leading to significant reductions in the kappa number. Moreover, ClO₂ consumption was reduced by 42-77% as a result of such pre-treatment, with a proportional reduction in AOX generation and phenolic compounds release. Finally, effluent TOC concentrations seem to be a function of the Ps load during pretreatment.

SUMÁRIO

É sabido que o ácido hexenurónico formado no processo de polpa alcalina reage com os reativos de branqueio gerando importantes repercussões nos custos de produção, qualidade do produto e nos impactos ambientais

O trabalho experimental foi conduzido na escala de laboratório, consistiu na remoção do HexA de polpas deslignificadas de *Eucalyptus globulus* em uma etapa previa à sequencia de branqueio com utilização do ácido peroxymonosulfúrico (Ps). Os efluentes obtidos no branqueio com uma sequencia D₀-E₀-D₁ foram analisados em base a COD, TOC, DBO₅, AOX, fenóis totais e coloração.

Os resultados mostram que Ps removeu eficazmente HexA, com às reduções significativas no número do kappa. Ademais, se determinou que a remoção do HexA é lineal com a carga do Ps e exponencial com a temperatura.

Além disso, o consumo ClO₂ foi reduzido por 42-77% em consequência de tal pre-tratamento, com uma redução proporcional na geração de AOX e compostos fenóis. Finalmente, as concentrações do TOC no effluent parecem ser uma função da carga do Ps durante o pre-tratamento.

KEYWORDS

Hexenuronic acid removal, *Eucalyptus* pulp, peroxymonosulphuric acid, bleaching effluents, AOX.

INTRODUCTION

During the last decades, bleached kraft cellulose production has undergone important technological innovations, in order to reduce environmental impacts, particularly, due to the generation of toxic organic chlorinated compounds. Consequently, efforts have been made to reduce the chlorine load in bleaching, and important modifications in both pulping and bleaching processes have been introduced. Recently, the presence of hexenuronic acid has been found to increase the consumption of bleaching chemicals, such as ClO_2 and ozone, increasing production costs and affecting product quality and environmental performance. .

As illustrated in Figure 1, HexA is formed during alkaline pulping, due to beta elimination of methylglucuronic acid, which are randomly distributed on both sides of xylane main chain, both in hardwood and softwood pulps [1]. Such reaction rapidly takes place during the heating phase at early stages of pulping, between 110 y 150°C at pH 12 -13, [2].

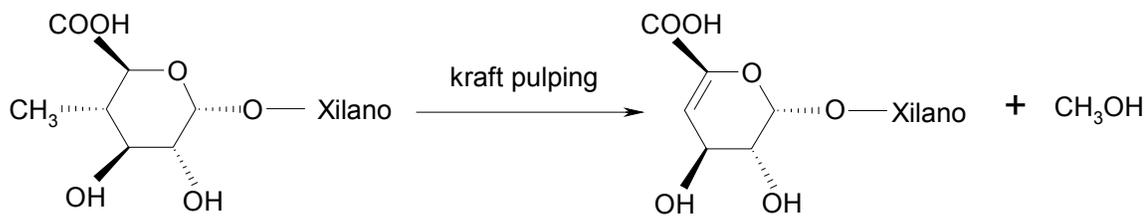


Figure 1 Formation of hexenuronic acid

HexA rapidly reacts with permanganate, thus affecting the kappa number determination. Indeed, about 3-7 kappa units are reported to be accounted for by the presence of HexA in hardwood pulps [3, 4, 5, 6]. Moreover, HexA reacts with ClO_2 and ozone, forming undesirable organic by-products (see Figure 2). Those reactions lead to oxalic acid formation, which later precipitates affecting pulp brightness.

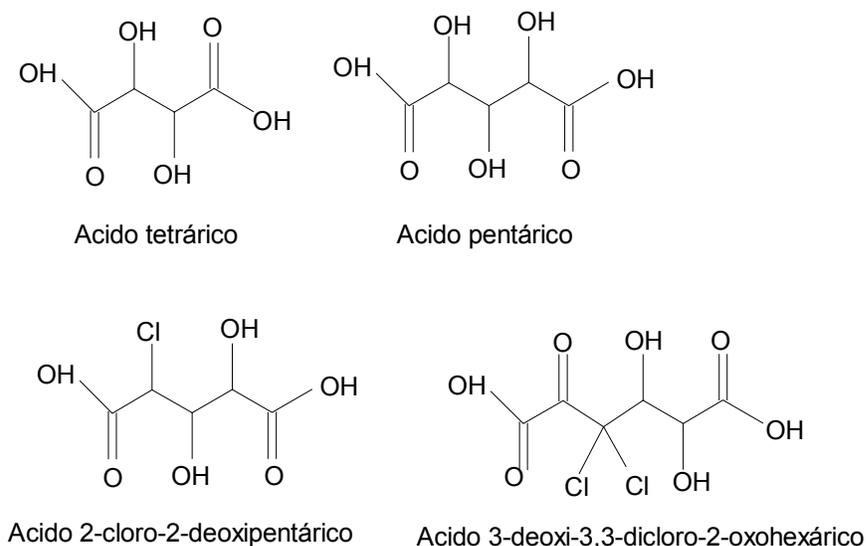


Figure 2 HexA and ClO_2 reaction by-products (Vuorinen et al., 1997)

HexA features enol-ether and unsaturated carboxylic functional groups, presenting both nucleophilic and electrophilic reactivity [7]. Those groups are relatively stable under mild acid conditions; however, HexA undergoes hydrolysis in the presence of strong acids, forming furans derivatives [8].

Jiang (2000) suggested that HexA protects xilans from terminal depolymerisation and, therefore, early removal of HexA during pulping could lead to a significant reduction in yield [7].

On the other hand, HexA elimination before bleaching could be attained using appropriate agents. Henricson (1997) showed that 80% of HexA was removed by acid hydrolysis with sulphuric acid at pH

3-4, 90-110°C, and 2 a 4 h treatment. Unfortunately, significant cellulose degradation may occur due to sulphuric acid poor selectivity.

In the search for low cost and selective agents for HexA removal, peroximonosulphuric acid (Ps) has been identified as a potential alternative at industrial scale since it does not require pressurization. Ps is a peracid derived from hydrogen peroxide when a hydrogen atom is replaced by a SO₃H group. Unfortunately, there is little published information on its HexA removal capacity. In this context, the aim of this work is to present experimental information on the Ps HexA removal capacity and its effect on bleaching chemical consumption and environmental performance.

MATERIALS AND METHODS

Peroximonosulphuric treatment.

Oxygen predelignified *Eucalyptus globules* pulp with kappa 9.7 was used here. Predelignified pulp was washed with distilled water, pelletised and stored at 4°C. Then, 200 g pulp samples were fed into a 5L reactor and treated with peroximonosulphuric acid at set load (0.2-1.0 % w/w, based on dried pulp weight), 10% consistency, and controlled temperature (20-107°C), for 1 h. After Ps treatment, the pulp was washed with distilled water until all acid was removed, characterized and stored for further use.

Preparation of peroximonosulphuric acid (Ps)

A 2:1 molar ratio H₂SO₄ and H₂O₂ solution was prepared and allowed to rest for 2 h. The peracid concentration was determined by the method proposed by Greenspan and McKellar (1948) [9].

Bleaching sequence

An ECF (D₀ - E₀ - D₁) sequence was used in this study. Both D₀ and D₁ stages were conducted at 70°C for 40 min, using a kappa factor of 2.2. Alkaline extraction was carried out using 2% w/w NaOH (based on dry pulp weight), at 2 kgf O₂/cm², and 70°C during 1 h. All bleaching stages were carried out at 10% consistency.

Analytical methods

- *HexA Analysis*; the spectrophotometric technique reported by Chai *et al* (2001) [10] was used here. The pulp was hydrolysed using a sodium acetate and mercury chloride solution at 65°C for 30 min. The absorbance was measured at 255 nm. A calibration curve was built based on HUT procedure reported by Alison *et al* (1999) [8] and by Tenkanen *et al* (1996) [11] on the basis of 2-furoic acid, which is the main hydrolysis by-product. This method considers an acid hydrolysis with formic acid/sodium formate buffer at pH 3, for 6 h at 110°C. Under those conditions, HexA is fully removed and 2-furoic acid accounts for 90% of hydrolysis products.

- *Pulp properties*: Klason Lignin on (insoluble); Klason lignin, Kappa Index, and ISO brightness were determined by standard Tappi methods T 222, T 236 cm-85, and T 525 om-92, respectively.

- *Bleaching effluents composition*: Bleaching effluents were obtained from D₀ and E₀ stage washing corresponding to a 4% consistency. Effluents were characterised on the basis of colour, total phenols, total organic carbon, biological oxygen demand (BOD₅), chemical oxygen demand (COD), and organochlorinated compounds (AOX). Pt-Co colour, total phenols, TOC, BOD₅, and COD were determined using Standard Methods 2120, 5550B, 5310B, 5210B, and 5220C, respectively [12]. Adsorbable organic halogens (AOX) were determined by Method AOX Bin/38409 H14 under Norm ISO 9562-1989, using a MicroCoulombmetric Euroglas ECS 1000.

RESULTS AND DISCUSSIONS

Table 1 and Figures 3-5 summarize the main results of HexA removal by peroximonosulphuric acid (Ps) treatment. As seen in Table 1, HexA was effectively removed by Ps treatment of unbleached pulp under conditions used here. Temperature was an important variable as shown in Figures 3 and 4, where the % removal increased exponentially with temperature. Moreover, HexA removal was far more sensitive to temperature than to Ps load. In all cases, bleached pulps reached above 90% ISO brightness. However, pulps pretreated with high Ps load presented very poor mechanical properties after bleaching.

TABLE 1 PEROXIMONOSULPHURIC ACID TREATMENT OF UNBLEACHED KRAFT PULP

Ps load % (w/w dpb)	T (°C)	Kappa	HexA (mmol/kg)	HexA % reduction	Lignin (mmol/kg)	Lignin % reduction
Untreated pulp		9.7	43	-	53	-
0.20	93	5.3	21	51	19.3	64
0.20	100	3.8	9	80	24.5	54
0.20	107	3.5	7	84	13.8	74
0.36	65	7.2	26	39	-	-
0.36	85	6.7	25	43	-	-
0.36	100	3.9	9	80	-	-
0.53	20	7.0	34	20	-	-
0.53	60	6.3	30	31	-	-
0.53	100	3.3	8	81	-	-
0.60	93	4.8	19	57	13.9	74
0.60	100	3.3	8	82	16.0	70
0.60	107	2.2	2	95	-	-
1.00	93	4.1	14	68	2.7	95
1.00	100	2.8	6	87	-	-
1.00	107	2.0	0	100	8.2	85

As seen in Table 1, Ps treatment also led to lignin removal as depicted by a significant reduction in kappa number and Klason lignin content. Results shown in Figure 5 indicate that the extent of HexA removal was proportional to the reduction in kappa number, with 12% reduction in HexA content per unit decrease in kappa number. These results agree with those published in the literature by other authors [3, 4, 5, 6].

It must be emphasized that Ps attack on lignin appears to occur via a free radical mechanism, leading to the formation of soluble aromatic fractions. Unfortunately, cellulose may also be affected by acid hydrolysis as a result of Ps action. Viscosity of pretreated unbleached pulps were found to decrease sharply at Ps load 1% w/w, reflecting the strong acid attack on cellulose during pretreatment. Indeed, intrinsic viscosities below 540 (ml/g) were obtained under those conditions, as compared with 1012 (ml/g) in the case of untreated pulp.

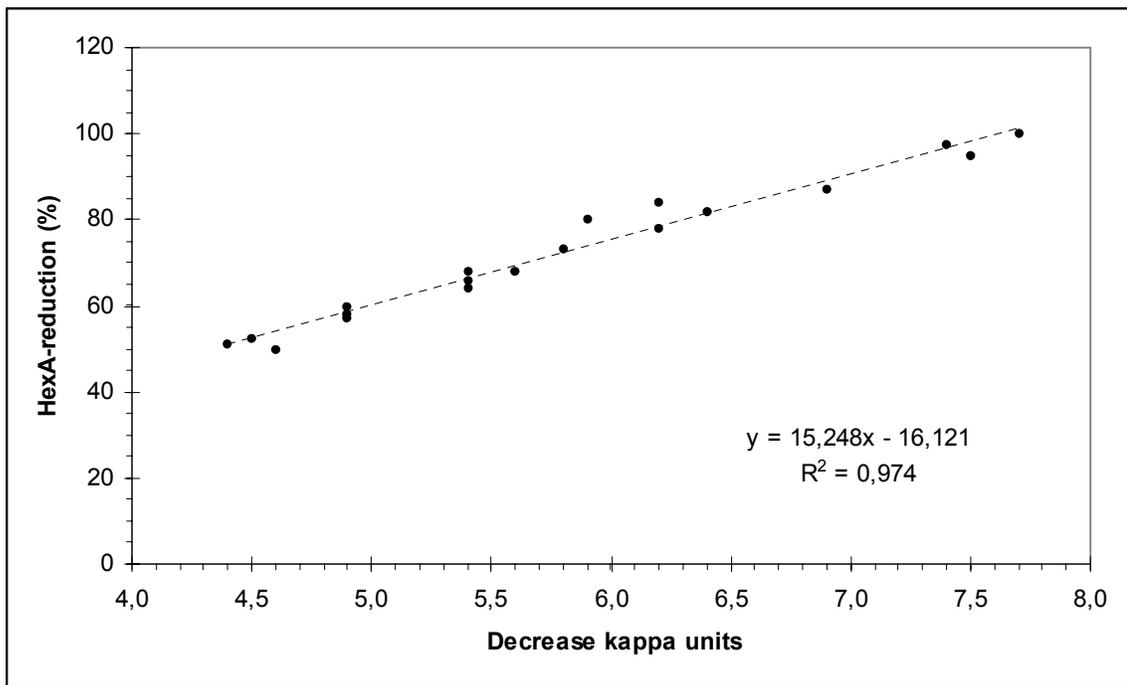


Figure 3. Relationship between HexA removal and kappa reduction due to peroximonosulphuric acid pretreatment.

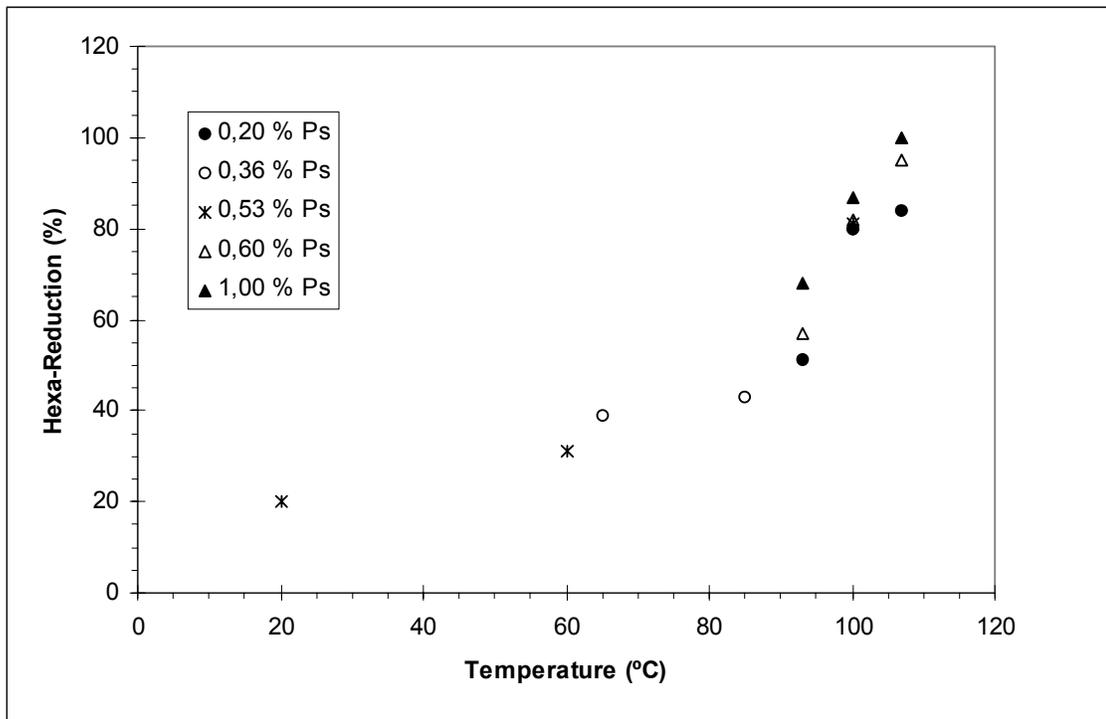


Figure 4. Effect of temperature on HexA removal during peroximonosulphuric acid pretreatment.

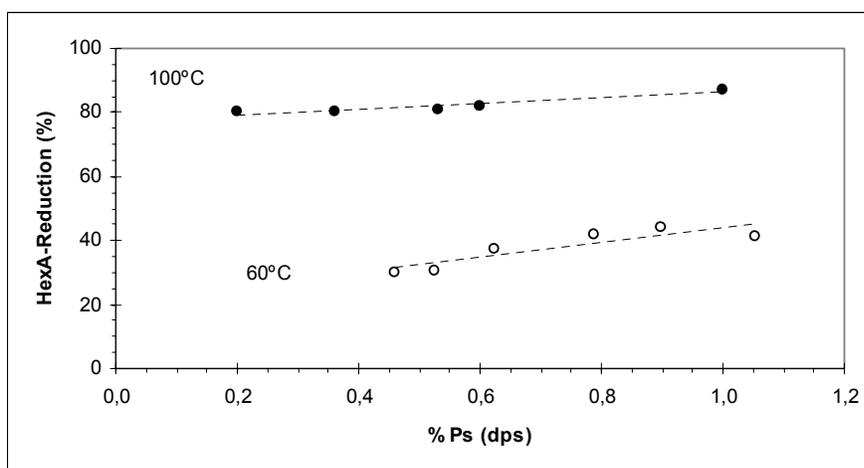


Figure 5. Effect of temperature and peroximonosulphuric acid (Ps) on HexA removal

Table 2 shows that Ps treatment before bleaching led to a 42 - 77% reduction in the ClO_2 consumption in bleaching. This is a direct consequence of the significant decrease in kappa number due to Ps treatment. Apart from the obvious positive impact on production costs, a lower demand of ClO_2 leads to a reduction in the generation of organic chlorinated compounds during bleaching. Indeed, Figure 6 shows that reductions in AOX concentration in bleaching effluents were inversely proportional to ClO_2 loads used in bleaching. Moreover, as seen in Figure 7, AOX generation in bleaching was proportional to the extent of HexA removal in Ps pretreatment, featuring a 57% AOX reduction when all HexA had been previously removed.

TABLE 2 EFFECT OF PEROXIMONOSULPHURIC ACID PRETREATMENT ON EFFLUENT BLEACHING COMPOSITION

Ps Treatment conditions			Bleaching Effluent Composition				
%Ps (dps)	T (°C)	Colour (ppm)	Phenol (ppm)	AOX (ppm)	COD (ppm)	TOC (ppm)	ClO_2 Savings in Bleaching
Untreated pulp		167	6.3	2.1	413	153	
0.2	93	142	4.3	1.4	300	162	42%
0.2	100	127	3.8	-	335	-	57%
0.2	107	135	3.5	1.3	324	123	60%
0.6	93	129	3.9	-	268	182	44%
0.6	100	185	5.3	-	304	189	57%
0.6	107	165	4.3	-	304	-	76%
1.0	93	185	-	1.5	444	506	54%
1.0	100	135	4.0	-	357	468	68%
1.0	107	173	4.7	0.93	321	461	77%

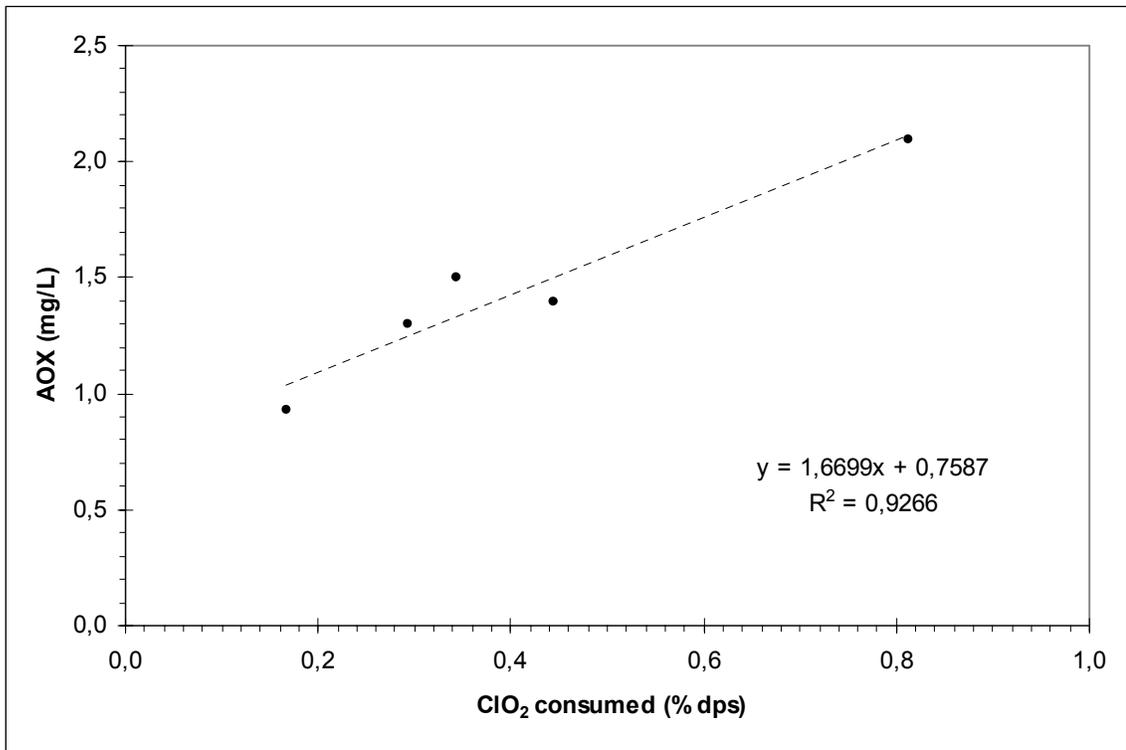


Figure 6. Effect of ClO₂ load on AOX generation during pulp bleaching

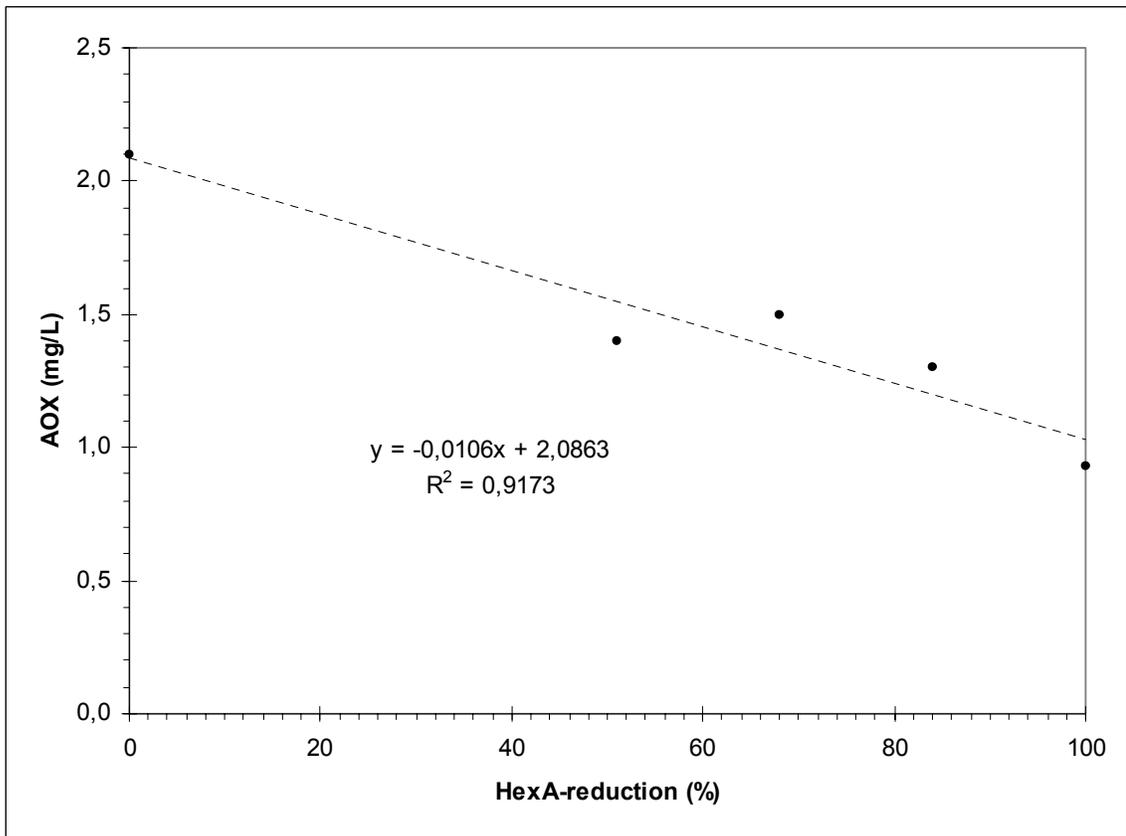


Figure 7. Effect of HexA removal on AOX generation during pulp bleaching

In all cases, Ps pretreatment led to a slight decrease in total phenols concentrations in bleaching effluents, although these did not correlate with either HexA removal yields or Ps loads. On the other hand, a reduction in COD concentrations in bleaching effluents due to Ps pretreatment could be observed.

However soluble organic carbon in bleaching effluents increased at higher Ps loads. Indeed, TOC concentrations in bleaching effluents show a sharp rise at 1% Ps load in pretreatment. It would appear that cellulose suffered acid hydrolysis at high Ps loads, increasing its vulnerability to oxidative and alkaline actions during bleaching. This hypothesis is supported by the low viscosity values showed by pulps pretreated at high Ps loads.

Bleaching effluent colour was not affected by HexA removal and detected variations were not statistically significant.

Given that cellulose may undergo considerable degradation during Ps treatment, appropriate optimization of operating conditions is required. According to results obtained here, pretreatment around 0.5% Ps at 100°C yield acceptable pulp properties and effluent pollution load.

CONCLUSIONS

This work shows that peroximonosulphuric acid (Ps) effectively removes HexA even at low concentrations, and such effect is enhanced at higher temperature. Ps acts both on lignin and on HexA, leading to reductions in unbleached pulp lignin content, and a reduction on the ClO₂ bleaching demand. However, at high Ps load, cellulose could be degraded resulting in poor mechanical properties after bleaching. Reductions in ClO₂ consumption reduced AOX generation during pulp bleaching. Moreover, total phenols concentrations in bleaching effluents also dropped as a result of Ps pretreatment.

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