

Single Stage Peroxide Bleaching of ASAM Bagasse Pulp.

Part I: Effect of Some Bleaching Parameters on Pulp Properties.

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ABSTRACT

The effect of some bleaching parameters on the properties of ASAM pulp from bagasse was studied. A chelation stage (Q) with DTPA prior to peroxide bleaching (P) is very useful for removing transition metal ions that cause catalytic decomposition of the peroxide. Different charges of H₂O₂, MgSO₄ and NaOH were used for bleaching in the presence of DTPA or / and DTPMPA. Pulps having brightness above 80% ISO could be obtained in a single peroxide bleaching treatment using 4% H₂O₂, 2.5% NaOH, and 0.1-0.3% MgSO₂ in the presence of 0.1% DTPMPA.

Key words

H₂O₂ bleaching, TCF bleaching, ASAM pulp, chelation, DTPA, DTPMPA,

INTRODUCTION

The demand for totally chlorine free TCF bleached pulps has been rapidly growing during the last years. This indicates increased awareness and concern about environmental problems arising from the pulp and paper industry. TCF bleaching sequences contribute to decreased pollution parameters such as AOX, BOD, COD and colour and can eventually lead to totally effluent free (TEF) pulp production (1). Successful TCF bleaching requires a low kappa number of the unbleached pulp to start with because the common chlorine free bleaching agents are less efficient than chlorine {2,3}.

The present study aims at optimizing one-stage H₂O₂ bleaching of bagasse pulp obtained by the ASAM process (alkaline sulfite pulping with addition of

anthraquinone and methanol). Unbleached ASAM pulps are characterized by very low kappa number at high pulp yield and viscosity, which facilitate TCF bleaching. The necessity of a chelation stage prior to peroxide bleaching as well as the effects of some bleaching parameters, such as H₂O₂, NaOH and MgSO₄ charges, and the type of chelant used within the P stage were studied.

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EXPERIMENTAL

Pulping

Bagasse was pulped as follows: chemical charge (as NaOH o.d. bagasse) =16%, alkali ratio (Na₂SO₃/total alkali) =0.7, AQ (o.d. bagasse) =0.1%, methanol charge (on total liquor, v/v) = 15%, liquor ratio = 4:1, heat up time 45 min, cooking time at maximum temperature of 170°C = 60 min. Pulping was conducted with charges of 600 g o.d. bagasse in a rotating autoclave at the Institute of Wood Chemistry, University of Hamburg, Germany. The pulping conditions applied represent the optimum conditions obtained after a series of experiments carried out at our laboratory in Egypt. Our experiments were performed on a small scale with 100 g o.d. bagasse. The small autoclaves were rotating in a temperature controlled oil bath. Different chemical charges (14,16,18,20%), alkali ratios (0.6,0.7,0.8), and methanol concentrations (0.5,10,15, 20, 25, 30, 35% v/v of liquor) were investigated applying different cooking times (30-170min) at 165°C.

PULP PRETREATMENT

A chelation stage with DTPA (diethylenetriaminepentaacetic acid) was carried out to remove transition metals ions. The pulp was mixed with the amount of deionized water of 60°C necessary to adjust 3% pulp consistency. The pulp slurry was acidified to pH 4.5 -5.5 before adding the chelant (0.2% DTPA based on o.d. pulp). After 30 min at 60°C, the pulp suspension was washed on a Buchner funnel, pressed and centrifuged to about 30-35% consistency.

BLEACHING EXPERIMENTS

The peroxide stage was carried out for 120 min at

80°C and 10% consistency. The chemical charges applied are given in the corresponding tables. The order of addition of the chemicals was standardized as follows: First MgSO₄ with chelant, then NaOH and finally H₂O₂. At first the pulp was placed in a plastic bag and the chemicals were added. The pulp was kneaded by hand and the initial pH measured. The plastic bag was then sealed and immersed in a water bath. At the end of the bleaching, the plastic bag was cooled and the liquid was squeezed from the pulp for measuring final pH and residual peroxide. The bleached pulp was then washed thoroughly with dionized water and centrifuged to 30-35% consistency. The residual peroxide in the filtrate was determined iodometrically.

ANALYSIS OF THE PULP

Kappa number Tappi 236 - cm for the unbleached pulp and Tappi UM 246 for bleached pulp

Brightness ISO units measured on pulp sheets prepared according to Scan C 11.75

Viscosity modified method based on Zellcheming Merkblatt IV /36/61 and Scan -CM 15:88

RESULTS AND DISCUSSION

Effect of chelation (Q stage) before peroxide bleaching

A chelation stage with DTPA was performed on four unbleached ASAM pulps Table 1 shows transition metal ions content, brightness, kappa number and viscosity of the pulps before (B) and after this pretreatment (Q). The amount of Mn, Mg, Cu and Fe

TABLE 1. Metal ions content and properties of four ASAM bagasse pulps before (B) and after chelation with 0.2 % DTPA (Q)

Sample	Mn ppm	Mg ppm	Cu ppm	Fe ppm	Brightness (% ISO)	Brightness gain (% ISO)	Kappa number	Viscosity ml/g
B ₁	15	205	57	129	51.4		4.9	789
Q ₁	5.0	141	5.7	111	59.3	7.9	4.5	801
B ₂	10	215	23	110	49.9		4.7	823
Q ₂	5.0	154	5.7	101	54.3	4.4	4.2	837
B ₃	10	208	29	128	48.7		4.8	795
Q ₃	5.0	150	5.8	100	53.2	4.5	4.4	797
B ₄	9.9	341	54	198	56.8		5.2	856
Q ₄	5.0	191	9.2	164	61.8	5.0	4.6	819

TABLE 2. Results of peroxide stages carried out on pretreated (P_{1,2,3,4}) and untreated (P_{1*,2*,3*,4*}) ASAM Pulps.

Sample	MgSO ₄ %	DTPA %	DTPMPA %	Kappa number	Residual H ₂ O ₂ (% of charge)	Brightness (% ISO)	Brightness gain (%ISO)
B ₁	-	-	-	4.9	-	51.3	
Q ₁	-	-	-	4.5	-	59.3	8.0
P ₁	0.1	0	0.1	2.3	17.8	81.1	29.8
P ₁ *	0.1	0	0.1	2.3	0.4	74.2	22.9
P ₂	0.3	0	0.1	2.3	24.9	80.3	29
P ₂ *	0.3	0	0.1	2.4	0.3	73.6	22.3
P ₃	0.3	0.1	0.2	2.3	32.4	80.9	29.6
P ₃ *	0.3	0.1	0.2	2.4	1.9	76.3	25.0
P ₄	0.3	0.2	0.4	2.4	46.5	81.5	30.2
P ₄ *	0.3	0.2	0.4	2.4	10.9	78.4	27.1

Bleaching conditions: Temperature = 80°C, Time = 120 min. H₂O₂ = 4%, NaOH=2.5%

ions in the pulps before and after chelation were determined by AAS. About 60% of Mn ions, 40% of Mg ions, 85% of Cu ions, and 15% of Fe ions were removed from the pulp by the DTPA treatment. Brightness gains ranging from 4.5 - 7.9 ISO units were obtained after the Q stage slight drops in the kappa number and times in the viscosity were attained.

The necessity of a chelation stage before bleaching could be proven by peroxide bleaching tests on pretreated and untreated pulp samples. DTPA and/or DTPMPA (diethylenetriaminepentamethylene-phosphonic acid) were added in the P stage (Tab.2). As a result of partly removing the harmful metal ions in the Q stage, the peroxide decomposition was

restricted and the pulp brightness was significantly improved compared to peroxide bleaching without pretreatment. The use of a chelant or even two chelants only with the P stage was not sufficient. Even at high charges, the chelants were not able to stabilize the peroxide. The much lower brightness gain achieved indicates excessive catalytic decomposition of the peroxide.

EFFECT OF H₂O₂ CHARGE AND NaOH: H₂O₂ RATIO ON PULP PROPERTIES

It is obvious from Table-3 that 1% H₂O₂ is not sufficient to delignify and brighten the pulp. By increasing the charge of H₂O₂ to 2% the delignification

TABLE 3. Effect of different H₂O₂ and NaOH charges on ASAM pulp properties

Sample	H ₂ O ₂ %	NaOH %	Residual H ₂ O ₂ (% of charge)	Kappa number	Viscosity (ml/g)	Brightness (% ISO)	Brightness gain (%ISO)
Q ₁	-	-	-	4.5	801	59.3	-
P ₅	1	1.75	3.4	3.1	775	69.1	9.8
P ₆	2	2.0	8.1	2.7	751	73.1	13.8
P ₇	3	2.25	16.2	2.6	768	76.2	16.9
P ₈	4	2.5	22.3	2.6	761	78.7	19.4
P ₉	5	3.0	5.1	2.3	728	79.3	20.0
P ₁₀	6	3.5	3.68	2.2	716	78.9	19.6

Bleaching conditions: Temperature = 80°C, Time = 120 min, MgSO₄ = 0.3%, DTPA = 0.1%

TABLE 4. Effect of NaOH charge at constant H₂O₂ charge on ASAM pulp properties.

Sample	H ₂ O ₂ %	NaOH %	pH		Residual H ₂ O ₂ (% of charge)	Brightness (% ISO)	Brightness gain (%ISO)
			initial	final			
P ₁₁	4	1.5	11.6	11.8	48.9	76.6	17.3
P ₁₂	4	2.0	11.5	11.8	20.2	77.1	17.8
P ₈	4	2.5	11.3	11.7	22.3	78.7	19.4
P ₁₃	4	3.0	11.3	11.5	6.4	76.4	17.1
P ₁₄	4	3.5	11.3	11.5	5.9	75.8	16.5

Bleaching conditions: Temperature = 80°C, Time = 120 min, MgSO₄ = 0.3%, DTPA = 0.1%

TABLE 5. Effect of MgSO₄ charge at constant H₂O₂ charge on ASAM pulp properties.

Sample	MgSO ₄ %	DTPA %	DTPMPA %	Kappa number	pH		Residual H ₂ O ₂ (% of charge)	Brightness (% ISO)	Brightness gain (%ISO)
					initial	final			
Q ₁	-	-	-	4.5	-	-	-	59.3	-
P ₁₅	0	0	0	2.4	11.3	12.2	0.2	77.4	18.1
P ₁₆	0	0.1	0	2.4	11.3	12.3	0.1	76.5	17.2
P ₁₇	0	0	0.1	2.2	11.4	12.2	4.7	80.7	21.4
P ₁	0.1	0	0.1	2.3	11.3	12.0	17.8	81.1	20.8
P ₁₈	0.2	0	0.1	2.3	11.4	12.0	20.8	80.5	21.2
P ₂	0.3	0	0.1	2.3	11.3	11.7	24.9	80.3	21.0
P ₁₉	0.5	0	0.1	2.3	11.3	11.6	33.2	75.6	16.3

Bleaching conditions: Temperature = 80°C, Time = 120 min, H₂O₂ = 4%, NaOH = 2.5%

and brightening processes were considerably improved. Further increase of the peroxide charge up to 4% improved only the brightness, whereas the kappa number was not further reduced at higher charges of hydrogen peroxide (5-6%) the carbohydrates were attached more intensively. The drop in the viscosity caused by raising the peroxide charge from 4 to 6% was 45 ml/g, whereas the drop in viscosity affected by increasing the peroxide from 1 to 4% was only 14 ml/g. Therefore, 4% H₂O₂ was considered as the optimum peroxide charge.

Table 4 and figure 1 show the effect of increasing the NaOH charge at 4% H₂O₂ on the properties of the ASAM bagasse pulp. Up to a charge of 2.5% (0.625 NaOH: H₂O₂) the brightness increases steadily. A higher alkali charge, however, leads to a too high peroxide consumption and the brightening effect decreases due to alkaline darkening.

EFFECT OF MgSO₄ AND THE CHELANTS ON THE STABILIZATION OF H₂O₂

The amount of MgSO₄ added to the bleach system was varied, while the peroxide and NaOH charges were kept constant at 4 and 2.5% respectively. Table-5 shows the results.

Experiment no.15 was carried out without addition of any stabilizer. The detrimental effect on the stabilization of H₂O₂ is very obvious, the peroxide was almost totally consumed. Addition of 0.1% DTPA did not improve the bleaching result (experiment no.16). The use of 0.1% DTPMPA instead of DTPA (experiment no.17) resulted in a somewhat better peroxide stabilization and an increased brightness. However, the rather low amount of residual peroxide indicates a not optimal bleach performance, since the H₂O₂ residual

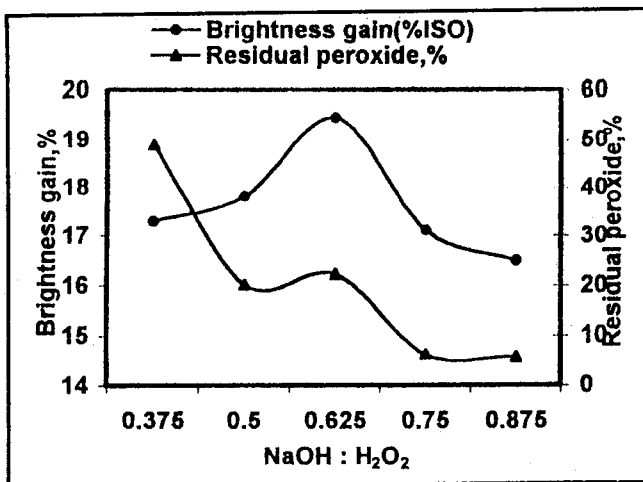


Figure 1: Effect of NaOH: H₂O₂ ratio on brightness gain and residual peroxide of ASAM

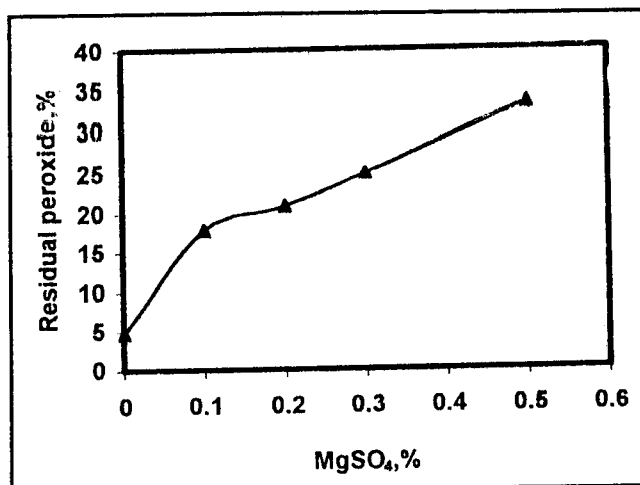


Figure 2: Effect of MgSO₄ charge on residual peroxide of ASAM pulp.

TABLE 6. Bleach results obtained by using DTPA and DTPMPA in the P stage.

Sample	MgSO ₄ %	DTPA %	DTPMPA %	pH		Kappa number	Residual H ₂ O ₂ (% of charge)	Brightness gain ISO units (%ISO)
				initial	final			
P ₂₀	0.1	0.1	0	11.3	12.5	2.4	0.5	20.2
P ₂₁	0.2	0.1	0	11.4	12.5	2.3	1.8	19.1
P ₈	0.3	0.1	0	11.3	11.7	2.6	22.	19.5
P ₁	0.1	0	0.1	11.3	12.0	2.4	17.	21.9
P ₁₈	0.2	0	0.1	11.4	12.0	2.3	20.8	21.2
P ₂	0.3	0	0.1	11.3	11.7	2.3	24.9	21.00
P ₃	0.3	0.1	0.2	11.3	11.7	2.3	32.4	21.7
P ₄	0.3	0.2	0.4	11.3	11.3	2.4	46.5	22.3

Bleaching conditions: Temperature = 80°C, Time = 120 min, H₂O₂ = 4%, NaOH = 2.5%.

should not be lower than 15-20 {4}. By introducing MgSO₄ to the bleaching system (experiments 1,18,2,19) a substantially improved stabilization of the peroxide was observed, as expressed by the increased amount of residual H₂O₂. The extent of stabilization was proportional to the MgSO₄ charge (Fig.2). In case of absence of MgSO₄ the amount of residual peroxide was 4.7%. With increase of the MgSO₄ charge from 0.1 to 0.5 the residual peroxide increased from 17.8 to 33.2%. This result confirms the important role of MgSO₄ in deactivating the transition metals still present in the bleaching system (5). It was also found that the presence of MgSO₄ in amounts ranging from 0.1-0.3 (based on o.d. pulp) is beneficial, but an increase of the charge to 0.5% had an adverse effect on the brightness gain, which indicates that the brightening effect is suppressed by a too high amount of Mg. Our results are in accordance with those obtained by Desprez et al. {6} and van Lierop et al {7}. As given in Tab. 5 the initial

pH of the bleaching system was 11.3 and the final pH was higher, which means that during bleaching the pH increases due to the consumption of peroxide. Such an increase of the pH is favourable in some cases, because final pH of 11.7 to 12 can be considered as optimal with respect to peroxide decomposition reactions. It can also be concluded that the final pH should not exceed 12, otherwise the peroxide decomposition is accelerated (cf. experiments 15-17).

EFFECT OF THE TYPE OF CHELANT ADDED IN THE P STAGE ON PULP PROPERTIES

In another set of experiments it was tested if DTPA or DTPMPA is more appropriate to stabilize the peroxide in combination MgSO₄ added in different quantities (Tab.6).

At a DTPA charge of 0.1% based on o.d. pulp, an

increased charge of MgSO_4 from 0.1 to 0.3 resulted in an increase of the residual peroxide from 0.5 to 22.3%, but the better peroxide stability was not associated with an improved brightening effect (experiments 20,21,8). On the other hand DTPMPA stabilized the peroxide very efficiently even at low MgSO_4 charge and a better bleaching effect was obtained (experiments 1,18,2). It can be concluded that, applied with the P stage, DTPMPA is superior to DTPA, especially at low MgSO_4 charges. The use of both chelants in different quantities enables an even better peroxide stabilization but the achieved improvement in brightness was negligible (experiments 3 and 4). From the economic point of view it is advisable to use 0.1% DTPMPA together with 0.1% MgSO_4 for peroxide stabilization.

CONCLUSION

ASAM pulping of bagasse results in easily bleachable pulps with low kappa number and high initial brightness. A single P stage is sufficient to reach a target brightness of 80% ISO. However, a preceding chelation stage is necessary to remove transition metal ions which catalyze the decomposition of H_2O_2 in the subsequent P stage. The importance of this pretreatment could be proven by comparison with reference bleaching tests performed with the untreated pulp. The pretreatment resulted in higher peroxide stability and in significantly higher pulp brightness. It was also found that charges of 4% H_2O_2 and 2.5% NaOH (based on o.d. pulp) give optimum results. Moreover, the presence of MgSO_4 and a chelant in the bleach system is a must in order to stabilize the peroxide. However, too high MgSO_4 charges (>0.3%) suppress the bleaching process. DTPA stabilizes the system only at high MgSO_4 charges, whereas DTPMPA shows a good stabilizing effect even at a low MgSO_4 charge.

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