Improvement in optical properties of paper using Molybdate Catalyst during alkaline H_2O_2 bleaching

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ABSTRACT

Effect of Na_2MoO_4 catalyst for improving brightness and post colour number of bamboo, subabul and their mixed pulps has been studied. The bleaching sequence followed is conventional CEH sequence with H_2O_2 at pH=10 5. The catalytic effect of Na_2MoO_4 has been examined on addition of EDTA and $K_2Cr_2O_7$. The kappa number and brightness of the catalyst treated pulps after extraction stage have been determined. Viscosity and FS factor of bleached pulp are also reported.

Introduction

Delignification optimisation using hydrogen peroxide has evoked enormous interests recently (1-5) as the bleaching process involved requires little capital investment and effluent having lesser pollutant chloroorganic compounds (6, 7). Hydrogen peroxide is added normally in the extraction stage of bleaching process Higher the delignification efficiency, lower will be the hypo consumption. Ever since the introduction of use of H_2O_2 in 1943 in bleaching process, (8) attempts for optimising efficiency of H_2O_2 for delignification are going on. The delignification rate is indirectly determined from the following relationship with kappa number (7 :

Lignin content = 0.15 × kappa number.

It is now widely accepted that because of catalytic decomposition of H_2O_2 added by the metal ions (Fe, Cu, Mn) initially present, the efficiency of H_2O_2 is reduced (8-10). One third of H_2O_2 is reported to be going on waste because of the Fe-catalysed reaction with H_2O_2 (11). Five mechanisms have been advanced for H_2O_2 decomposition (11).

1. A base catalysed ionic mechanism.
2. A base catalysed free radical mechanism.
3. A transition metal-catalysed free radical mechanism.
4. A transition metal reaction with perhydroxyl ions to form unstable peroxides or complexes.
5. A heterogenous surface-catalysed reaction caused by colloidal transition metal oxides/hydroxides.

A new innovation in peroxide bleaching process is through using catalysts such as Na-molybdate and tungstates (2). In the recent work of kubelka (2) where Na-molybdate catalyst was used was on acidic medium on O_2-delignified soft wood pulp which are quite different from average Indian mill conditions. Our work is carried out in alkaline medium with common raw materials, namely bamboo, subabul and bamboo-hard wood mixed pulp without being subjected to oxygen treatment.

Improvement o optical properties, namely brightness and post colour number, is the primary objective of this work. Any improvement in reduction of kappa number of the extracted pulp using Na-molybdate can be subsequently for not only hypo chemical saving but more important is, reduction in formation of COC. In fact, if the delignification level is enhanced, with H_2O_2, use of ClO_2 can be eliminated where capital investment can be quite high.

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Experimental

The pulp used here are as follows :

a) Bamboo : Daba bamboo (local name), Bambusa Arundinacea.

b) Hard wood : Subabul (local name), Leucaena Leucocephala.

Both the samples were collected from the nearby mill and digested in the laboratory in a 17 lt Rotary digester having following conditions :

Bath ratio	:	1 : 2 7
Cooking temperature	:	165° C
Time to temperature	:	2 hrs.
Time at temperature	:	1 5 hrs
Sulphidity of active alkali, %	:	18±1.

The unbleached pulp was taken for bleaching experiment Quality of chemicals used were :

Na-molybdate (Qualigens fine chemicals), EDTA (BDH)—E. Merk (India) Ltd.,

H_2O_2 (30%)—E. Merk (India) Ltd., $MgSO_4$—LOBACHEMIE.

Bleaching experiment was carried by following conditions :

	Chlorination (C)	Extraction (E)	Hypo stage (H)
Consistency, %	3	10	10
Temperature, °C	Ambient	55	40
Retention, hrs	0.75	1.5	2.5

The brightness was measured in Elrepho brightness tester and the FS factor in pulmac trouble shooter (Model—TS 100).

Results and Discustion

1. Chemical dosing

In the chlorination stage, 4.5-5 5% Cl_2 was added having consumption of 4.5-4 75% with final pH of 1.65 to 2. The % of available chlorine in $Ca(OCl)_2$ added during hypo stage was 2 showing consumption of 1.5 to 1.9% with final pH of 7.8 to 8.9. The extraction stage consisted of adding 1.6 to 1.8% of NaOH (1/3rd of Cl_2 dose at chlorination stage) along with 0 3% of H_2O_2 (30% concentration). Na_2MoO_4, $MgSO_4$, EDTA and $K_2Cr_2O_7$ were added in the extraction stage in the following concentrations :

Na_2MoO_4	=	100—250 ppm
EDTA	=	20—200 ppm
$MgSO_4$	=	50 ppm
$K_2Cr_2O_7$	=	50—200 ppm.

The pH in the extraction stage was 11–11.5. The blank experiment consisted of adding only H_2O_2. Na_2MoO_4 has been added in 16 sets of experiments conducted Two sets had $MgSO_4$ and $MgSO_4$+EDTA, while in the remaining EDTA was used as complexing agent. $K_2Cr_2O_7$ has been employed in only 4 sets of experiments.

2. Kappa number

The three pulp samples used; bamboo, subabul and bamboo (80%) + hard wood (20%) mixed mill pulp had kappa number of 16.7, 17.8 and 22.3 respectively. The mill hard wood was comprised of eucalyptus + casuarina and therefore, higher kappa number of 22.3 was found The other two pulps had been cooked in the laboratory.

Kappa no. Vs Na_2MoO_4 concentrations graph is shown in Fig. 1 EDTA had been added in all these experiments. Kappa nos of bamboo and subabul are in similar range; 5.8 and 5.5 in average. Increase of molybdate concentration from 100 to 250 ppm showed little variation in kappa number.

However, in bamboo-hard wood mixed pulp, the kappa number is found to be on the higher side In Fig. 1, it can be seen that the lowest kappa number is achieved at 100-150 ppm. Increasing concentration of the catalyst does not have any positive effect beyond 150 ppm. Some experiments were conducted by adding $K_2Cr_2O_7$ helps to the system at 150 ppm of Na_2MoO_4 to see whether the kappa number can be further brought down (Table 2). It was reported previously that addition of $K_2Cr_2O_7$ in improving delignification because of oxygen liberation. According to the results

shown in Table 2 where $K_2Cr_2O_7$ concentration was varied from 50-200 ppm, marginal improvement was observed at 50 ppm; 5.6 instead of 5.9–6.5 without $K_2Cr_2O_7$.

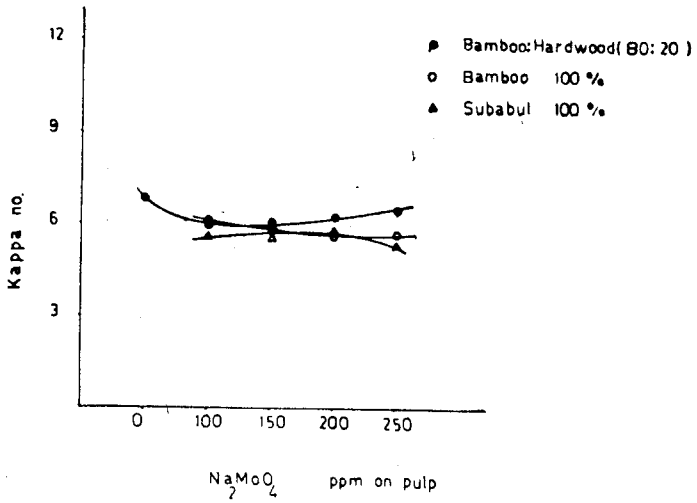

Fig. 1

In Table 3, $MgSO_4$ was added without the catalyst or $K_2Cr_2O_7$ and the kappa number increased to 6.7-6 9. Addition of EDTA had no effect on reducing the kappa number. $MgSO_4$ is added for stabilising hydrogen peroxide and retardation of carbohydrate degradation (12). It is reported that $MgSO_4$ was more efficient than Na_2SiO_3 for chelation.

The reduction of kappa number from 22.3 to 5.6 with Na_2MoO_4 (150 ppm) + $K_2Cr_2O_7$ (50 ppm) or to 5 9 with only 100 ppm of Na_2MoO_4 is quite significant. Kubelka et al (2) have observed minimum kappa number of 6 from initial value of 30 in soft wood using system of acidic H_2O_2 activated by molybdate catalyst on oxygen delignified pulp. Therefore, the values of 5.6 kappa number without oxygen delignification is important. It is worth mentioning that there can be improvement of 1.3 unit of kappa number. Na_2MoO_4 is used instead of $MgSO_4$ alone with H_2O_2 in the same pH range of extraction.

3. Viscosity property

The viscosity values (Fig. 2) of bamboo is better than the other two bleached pulp samples. Because of the fibre characteristics, bamboo pulp results in higher viscosity than subabul. The fibre dimensions are as follows -

	Length, mm	Diameter, micron
Bamboo	1.9	24.8
Subabul	0 79	12 0
Eucalyptus	0.82	14.06

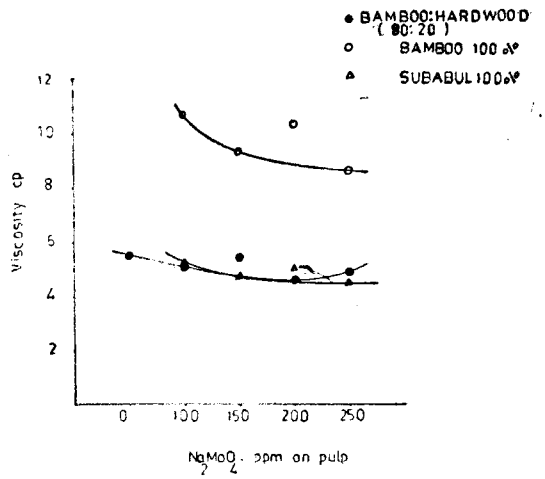

Fig 2

Increasing Na_2MoO_4 concentration again deteriorates the viscosity parameter. 100 ppm of Na_2MoO_4 is adequate for having optimum viscosity value of 10.7 cP for bamboo, 5 2cP for subabul and 5.1 cP for bamboo hard wood mixed mill pulp. The viscosity value of the mixed pulp can not be improved on addition of $K_2Cr_2O_7$ (Table 4) or with $MgSO_4$ (Table 5). It can be assumed that Na-molybdate does not have any adverse effect on viscosity property; it does not cause degradation.

4 Fibre strength (FS) Factor

The effect of Na-molybdate catalyst is again not very important for FS factor of all the three bleached pulps. Bamboo has average FS factor of 22, 21 for subabul and 19-20 for the mill pulp which are again based on the initial fibre length as shown above. It can be seen in Table 4 that addition of $K_2Cr_2O_7$ marginally brings in deterioration in FS factor but make no change when only $MgSO_4$ was added (Table 5) in the mill pulp.

5 Optical properties

a) Brightness

Brightness of extracted pulp samples were also found to be little varying similar to the kappa no.

TABLE—1

Chemical dosing in bleaching stage

		Blank	A	B	C	D	E
Cl_2 added	(%)	5.5	4.5	5.0	5 5	5.5	5.5
Cl_2 consumed	(%)	4.75	4 5	4.6	4.75	4.6	4 75
NaOH added	(%)	1.8	1.6	1.6	1.8	1.8	1.8
H_2O_2 added	(%)	0.3	0.3	0 3	0.3	0.3	3 3
Na_2MoO_4	(ppm)	—	100–250	100–250	100–250	150	Nil
EDTA	(ppm)	—	150	150–200	50–200	—	20

Blank : Bamboo:Hard wood mixed pulp; A : Bamboo pulp; B : Subabul pulp; C, D and E : Bamboo:Hard wood mixed pulp.

TABLE—2

Kappa no. and brightness with Na_2MoO_4 and $K_2Cr_2O_7$

Na_2MoO_4 (ppm)	$K_2Cr_2O_7$ (ppm)	Kappa no. (no.)	Brightness (% El)
150	50	5.6	48.0
150	100	5.8	47.0
150	150	6.2	46.8
150	200	6 0	46.9

TABLE—3

Kappa no and brightness with $MgSO_4$ and EDTA

$MgSO_4$ (ppm)	EDTA (ppm)	Kappa no. (no)	Brightness (% El)
50	—	6.9	40.7
50	20	6.7	44.3

TABLE—4

Properties of bleached pulp with $K_2Cr_2O_7$ and Na_2MoO_4

Na_2MoO_4 (ppm)	$K_2Cr_2O_7$ (ppm)	Brightness (% El)	PC No. (no)	Viscosity (cP)	FS Factor
150	50	85.2	10.9	4 5	19 9
150	100	84 0	10 7	4.9	19.0
150	150	84 2	10 8	5 2	19 4
150	200	84 4	10.3	4 8	19.2

TABLE—5

Properties of bleached pulp with $MgSO_4$ and EDTA

$MgSO_4$ (ppm)	EDTA (ppm)	Brightness (% El)	PC No (no.)	Viscosity (cP)	FS Factor
50	—	83 0	10.7	5.7	21 2
50	20	83 8	10 0	4 5	20 5

values It is important to mention that the bamboo-hard wood mill pulp not treated with catalyst, has low brigtness of 40 7% El instead of 47-48% El in other catalyst treated samples Thus, the catalytic effect of a Na-Molybdate for delignification in pulp, causing improvement of brightness is evident. An increase in brightness to the level of 6-7% at the extraction stage will naturally reduce hypo dose which will have notable improvement in effluent quality also. Lesser amount of hypo dose will also cause lesser deterioration in FS factor of the bleached pulp.

Brightness of the bleached pulp samples is shown in Fig. 3. The brightness values of bamboo is 84.5% EI and 84% El in subabul and 84-85 in the mill pulp. The catalyst having $K_2Cr_2O_7$ presents (Table 4) marginally higher brightness (85.2% El with 50 ppm of $K_2Cr_2O_7$+150 ppm of Na-molybdate) than the pulp without $K_2Cr_2O_7$ (83-84% El). The pulp without treatment (Table 5) or Na-molybdate or $K_2Cr_2O_7$ has (83% El) low brightness. Thus, there is gain of(2%El) brightness due to these additives.

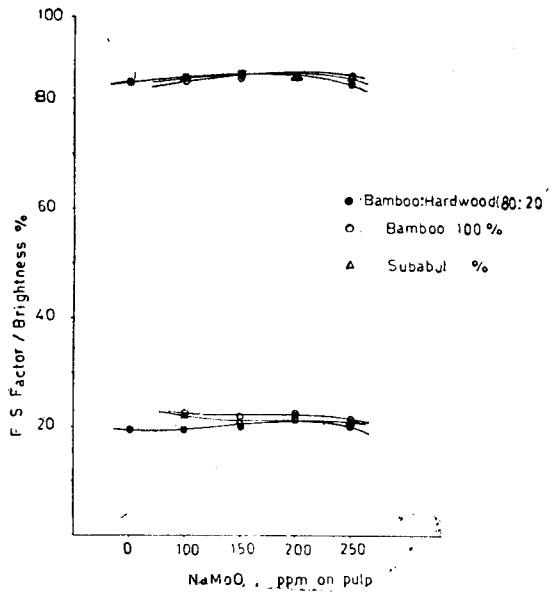

Fig. 3

b) Post colour (PC) number

The most impo tant contribution of the molybdate catalyst has been for improvement in colour reversion property PC no. of the three pulp samples shown in Fig. 4 indicate that 150 ppm of Na-molybdate causes the least PC no. The PC no. of bamboo is comparatively higher than the other two samples, least being in case of subabul. The results with $K_2Cr_2O_7$ show high PC no of 10.9 for the mill pulp which is 6 5 with 100 ppm of Na-molybdate. Therefore, though the brightness properties were marginally better when $K_2Cr_2O_7$ is added, it is not ideal for colour reversion property. It is again interesting to compare the PC no. values of pulp samples without catalyst (Table 5)which is 10.7. Thus addition of molybdate catalyst can retard colour reversion equivalent to PC no. unit of 4,2 which is quite significant.

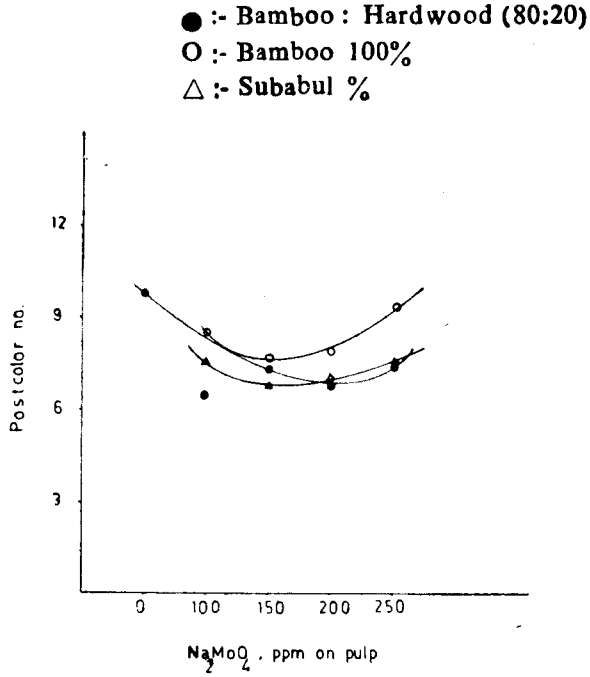

Fig. 4

Conclusion :

The kappa number of bamboo–hard wood mixed pulp decreases from 22.3 to 5 9 on addition of Na–molybdate catalyst, which was 8.7 without catalyst treatment. Brightness of catalyst–incorporated pulp is ~ 4% El more than pulp without catalyst treatment (47 2% El and 43 4% El). The bleached pulp brightness can be enhanced by ~ 2% El because of Na_2MoO_4 addition. The PC No. is improved by 3 5 while viscosity and FS factor is marginally improved on addition of the molybdate.

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