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Colour and COD Reduction of Bleach Effluents

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SUMMARY

Experiments have been carried out to see the effect of addition of calcium hypochlorite on the colour and chemical oxygen demand of the alkali extraction stage effluents of bamboo and mixed hardwoods. Optimum doses of hypo for maximum colour and COD reduction have been determined. A quick and precise method to measure colour in chloroplatinate units employing UV-visible spectrophotometer has been described. Studies have also been carried out to see the influence of addition of calcium hypochlorite on the concentration of phenolic compounds.

INTRODUCTION

Effluents from the extraction stage of pulp bleaching are highly coloured and have a high chemical oxygen demand (COD). Removal of the coloured substances by massive lime treatment combined with addition of high molecular polyacrylamide is used in some mills (e.g. Oji Paper Mills, Kasugai, Japan) but is complicated and expensive. A report of the Swedish Environmental Care Project (SSVL, 1974) indicated, that the colour of the E. stage effluent can be reduced by adding hypochlorite to the alkali extraction stage. Jauhari and Maheshwari [1] reported effective reduction of colour by adding 1.25% active chlorine as hypochlorite on o.d. pulp basis to E. stage. According to Komarov [2,3] addition of hypochlorite to the extraction stage made it possible to carry out alkaline extraction at 25°C instead of 60–70°C. In the present study the colour and COD reduction using small amounts of hypochlorite in the alkali extraction stage, was investigated. For measuring colour the platinum-cobalt [4] method is most widely used. The unit of colour is taken to be the colour produced by 1 mg/litre of platinum in the form of chloroplatinate ions. A rapid colour determination by spectrophotometry was developed in this study. The destruction of phenolic structures by hypochlorite addition to E. stage was studied by Delta-Epsilon ($\Delta\varepsilon$) curves according to Aulin-Erdtman [5-7] and Goldschmid [8]. This method is based on the fact, that phenolic groups are ionised in alkaline medium and have a deep colour, but are less ionised in neutral medium and thus less coloured. The difference in absorbance indicates the presence of phenolic groups.

EXPERIMENTAL

Laboratory pulp from mixed hardwoods of Bastar area [9] of Kappa number 28 was clhorinated at 3.0% consistency, 30 minutes at 30°C using 7.1% chlorine on o.d. pulp. The pulp was washed and extracted with 1.5% NaOH (on o.d. pulp) at 8.0% consistency, 60 minutes at 60°C. Bamboo pulp from Ashoka Paper Mills of Kappa number 25 was chlorinated at 3.5% consistency, 45 minutes at 28°C with 5.5% chlorine. The chlorinated pulp was washed and extracted with 2.0% NaOH at 10.0% consistency, 90 minutes at 65°C. In both cases 0.2%–1.0% hypochlorite on o.d. pulp was added to the E. stage and for comparison, to the E. stage effluent.

For colour measurements the Pt standard solu-

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tions were prepared according to Tappi Standard Method (4). A Perkin-Elmer UV-visible spectrophotometer model 402 was employed for the measurement of absorbance at 465 nm, as the maxime of standard samples lie at this wavelength Fig. 1. Relationship between absorbance and platinum no. is represented by straight line Fig. 2. (Pt. no. = Absorbance/2.8x 10^{-4}).

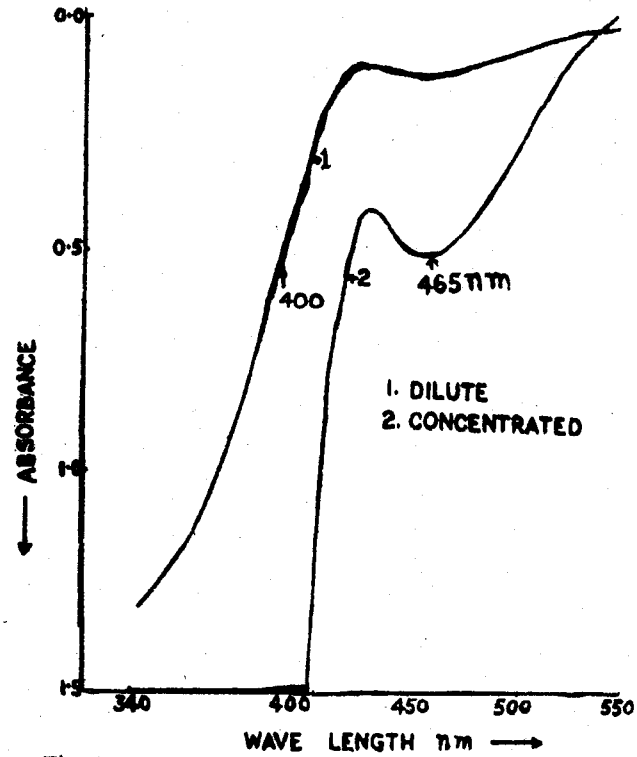

Fig. 1. U.V.-V. Spectra of Standard Pt-Co Solution.

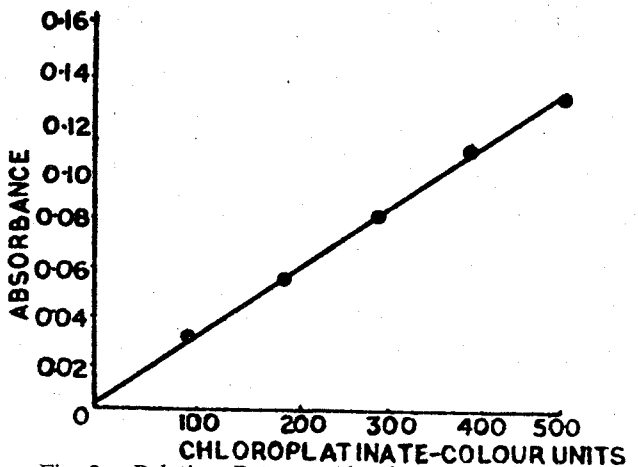

Fig. 2. Relation Between Absorbance at 465 nm & Chloroplatinate Colour Units.

Delta-Epsilon curves were recorded on the above stated spectrophotometer in the range 230–390 nm.

Teh sample of spent caustic extraction liquor after addition of calcium hypochlorite was filtered and pH adjusted to 6 by 1N acetic acid. This sample was equally divided into two portions. The pH of one was brought upto 12 by 1N NaOH (2–3 drops) and to the other equal amount of distilled water was added. Spectra were recorded keeping pH–12 solution in sample beam and pH–6 solution in reference beam. The absorbance values of absorption maximum at 310 nm were taken as measure of phenolic contents.

For COD determination the potassium dichromate method (10) was used.

More details of experimental procedures are given in Research Progress Report (11).

RESULTS AND DISCUSSIONS

COLOUR OF THE EFFLUENTS

From Fig. 3., it is observed that in the case of both bamboo and mixed hardwood pulps, colour of the effluent decreases with an increase in the amount of hypochlorite in the extraction stage. For mixed hardwoods 80% reduction in the effluent colour can be affected by adding 0.4% hypochlorite in the extraction stage. On increasing the amount of hypochlorite beyond 0.4% there is no further significant reduction in the colour. In case of bamboo pulp, 0.6% hypochlorite addition is necessary to obtain 80% reduction in the effluent colour.

Figs. 5 and 6 indicate that the addition of calcium hypochlorite to the effluent after alkali extraction causes reduction in the effluent colour which is very similar to that obtained by the addition of hypochlorite during extraction stage. It is observed that the addition of hypochlorite at higher temperature slightly expedites the colour reduction process. For both bamboo and mixed hardwood pulps the addition of higher amounts of hypochlorite (more than 0.6% on pulp) has no significant effect on the effluent colour.

From Figs. 4 & 7, it is observed that by mixing the effluents of chlorination and extraction stages in the ratio 3.5: 2 the total colour load is reduced. In the case of bamboo the colour load of chlorination and extraction (EHO) stages is 6.3 and 122.5 kg. Pt/tonne of pulp respectively. When these are mixed the resulting colour load is observed to be only 60 instead of 128.8 kg. Pt/tonne of pulp. Thus about 53% reduction in the effluent colour at this level is obtained by just mixing the effluents of chlorination and extraction stages. In the case of mixed hardwoods, by mixing the above effluents the colour load is reduced by 27%. Thus by mixing the effluents of chlorination and extraction stages the colour load of the resultant effluent will be lower. It is observed that by mixing the effluents of the two stages, the pH of the resultant effluent remains low-around 2.9 for

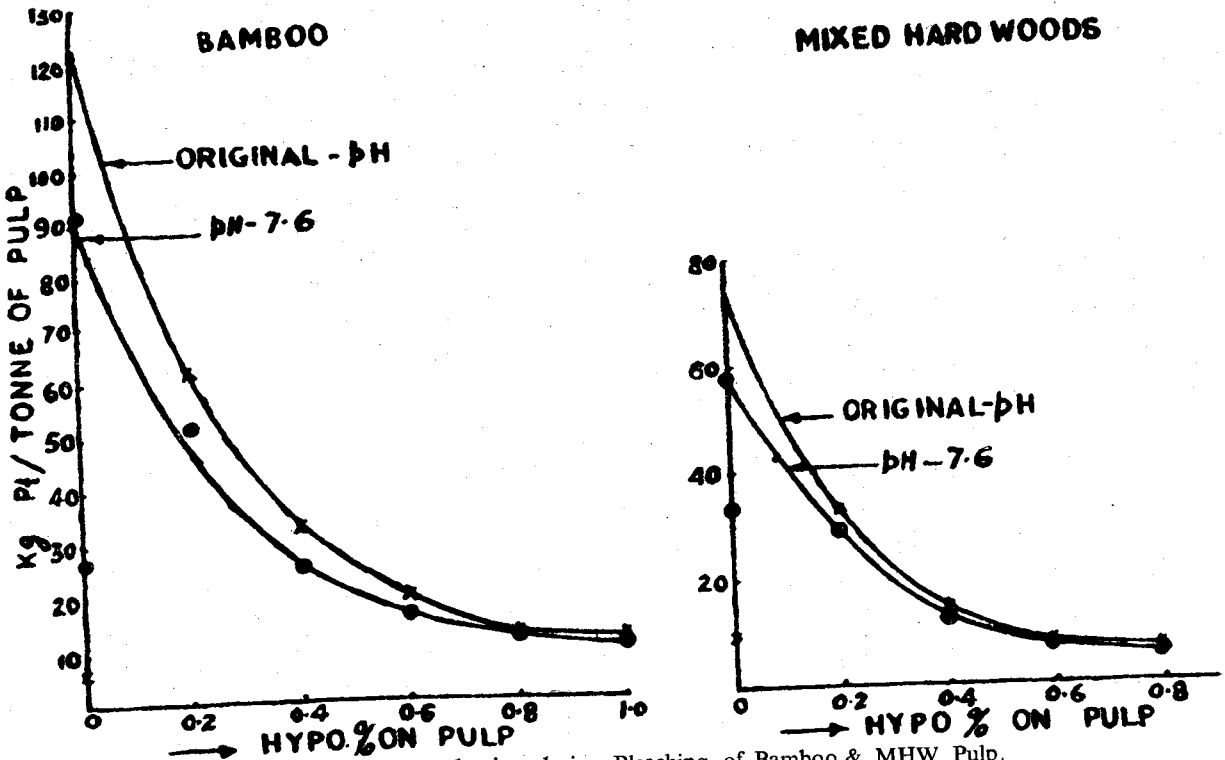

Fig. 3. Colour Reduction during Bleaching of Bamboo & MHW Pulp.

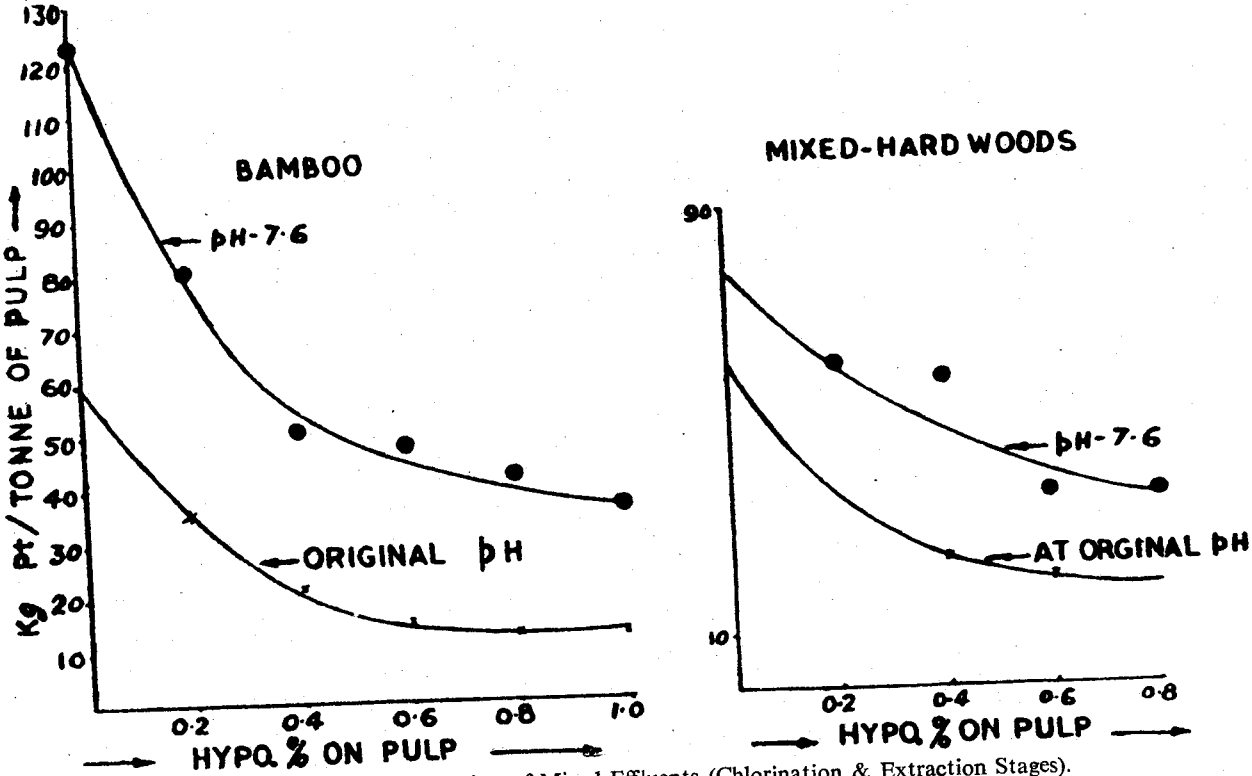

Fig. 4. Colour Reduction of Mixed Effluents (Chlorination & Extraction Stages).

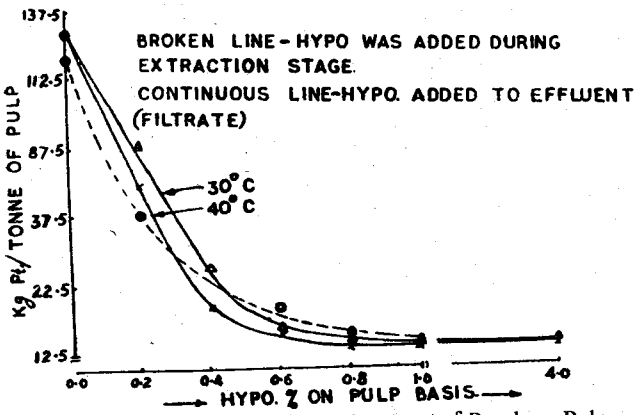

Fig. 5. Colour reduction of Alkali Extract of Bomboo Pulp on Addition of Hypo. (0.2 to 1.0% on Pulp Basis).

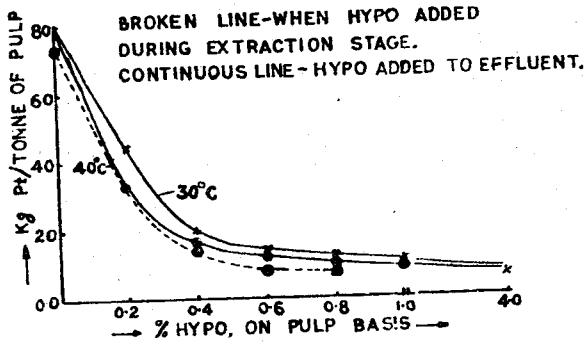

Fig. 6. Colour Reduction of Alkali Extract of MHW Pulp on Addition of Hypo (0.2% to 1.0% on Pulp Basis).

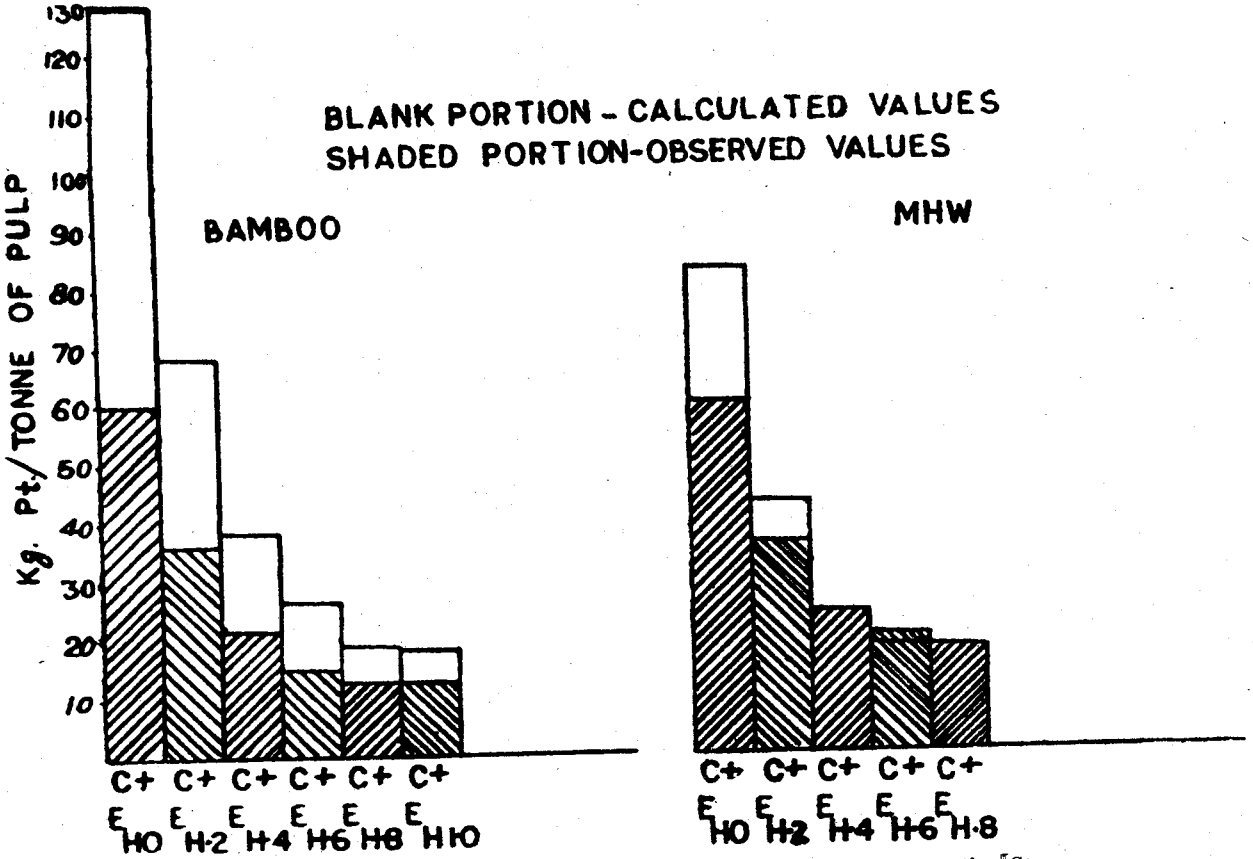

Fig. 7. Calculated & Observed Colour load of Mixed Effluents of Chlorination & Extraction Stage.

mixed hardwoods and 2.3 for bamboo. When colour measurements are carried out by adjusting the pH of the effluent to 7.6, in some cases, the colour load per tone of pulp of the mixed effluent is slightly increased.

PHENOLIC COMPOUNDS

From Figs. 8 and 9, it is seen that in case of bamboo, addition of 0.1, 0.2 and 0.4% hypochlorite brought down the phenolic hydroxyl content by 22, 35 and 52% of the original amount, whereas colour was reduced by 18, 32 and 67%. This indicates that the presence of phenolic hydroxyl groups in effluents contributes substantially towards the colour. Same trend was observed in case of mixed hardwoods except the initial concentration of phenolics was lesser and the colour reduction was faster as 0.2% hypochlorite reduced the phenolic by 17% whereas colour value dropped by 45%. Fig. 9 shows that 0.4% addition

of hypo in mixed hardwood effluent eliminated most of the phenolic hydroxyl groups as the shape of Delta-Epsilon curve altogether changed and was found to be similar to that of pure calcium hypochlorite.

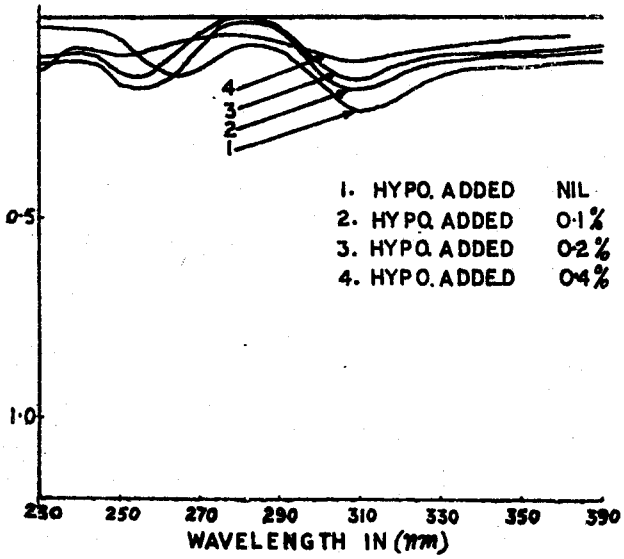

Fig. 8. $\Delta \varepsilon$ Curves of Alkali Extraction Effluent of Bamboo.

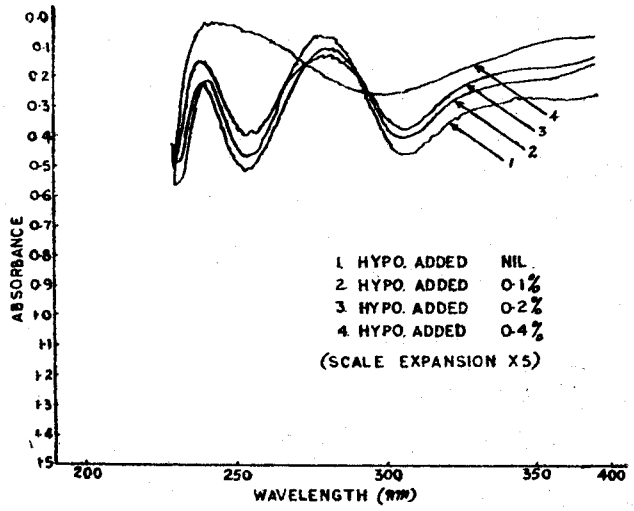

Fig. 9. $\Delta \varepsilon$ Curves of Alkali Extraction Effluent of Mixed Hardwoods.

RATE OF COLOUR REDUCTION

Fig. 10 shows that in the case of both bamboo and mixed hardwoods, in the beginning there is a very sharp decrease in the effluent colour. Maximum reduction in the colour is, attained within first four minutes of the hypochlorite addition, after this period, the effluent colour remains unchanged. The decolouration rate experiments could not be conducetd by using higher amounts of hypochrorite (more than 0.2% on o.d. pulp) as a precipitate was formed when calcium hypochlorite was added to the effluent. Before measuring the effluent colour, it was essential to remove the precipitate, which took considerable time.

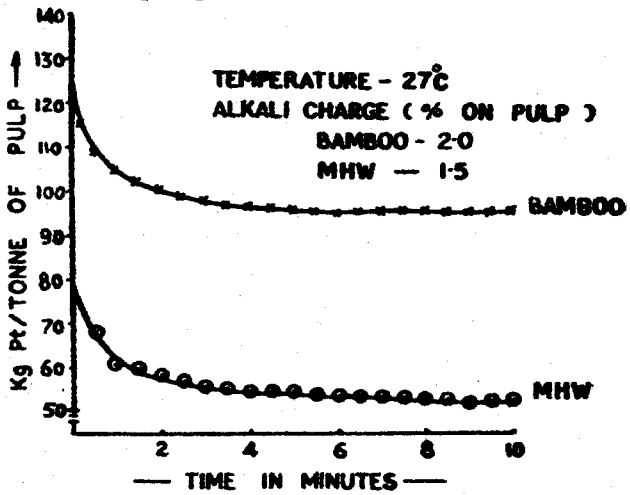

Fig. 10. Rate of Colour Reduction of Alkali Extracts on Addition of Hypo (0.2% on Pulp)

CHEMICAL OXYGEN DEMAND

From the results shown graphically in Fig. 11, it is observed that by the addition of hypochlorite in alkali extraction stage, there is considerable reduction in chemical oxygen demand, for both bamboo and mixed hardwood pulps. In case of bamboo pulp 0.6% hypochlorite addition affects 80% reduction in COD while in case of mixed hardwood pulp there is about 60% reduction in COD by applying same amount of hypochlorite. Further increasing hypochlorite concentration has very little effect.

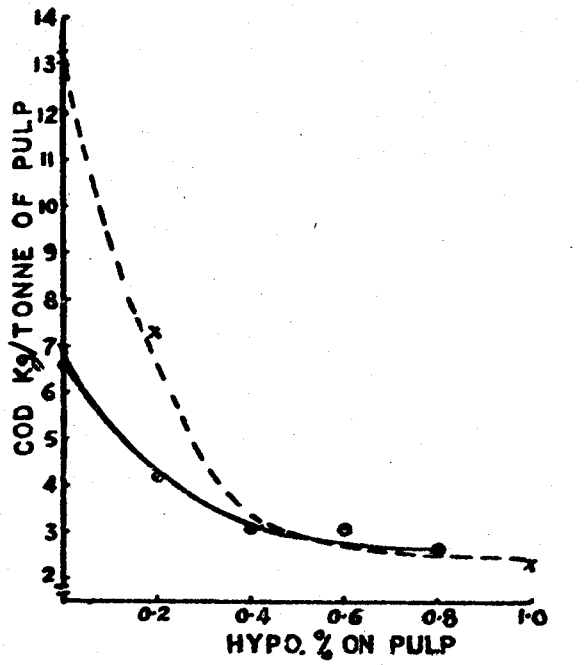

Fig. 11. Reduction in COD of – Alkali Extracts on Addition of Hypo during Extraction Stage.

TABLE—I. COLOUR OF ALKALI STAGE EFFLUENT AND PROPERTIES OF C-E-H-H AND C-E-(H)-H-H BLEACHED MIXED HARDWOOD AND BAMBOO PULPS.

	100% Mixed hardwood pulp		100% Bamboo pulp		70% Bamboo pulp + 30% Mixed hardwood pulp	
	CEHH	CE(H)HH	CEHH	CE(H)HH	CEHH	CE(H)HH
1. Hypochlorite in E, stage as available chlorine, %	—	0.2	—	0.6	—	0.6
2. Effluent colour in E. stage (Chloroplatinate units)	10180	1130	8180	3820	10580	4360
3. Yield loss during bleaching, %	13.0	11.0	6.3	5.5	7.3	6.7
4. Brightness of pulp, %	78.7	78.0	77.1	78.2	77.1	77.8
5. Viscosity, CED, cm^3/g	469	477	507	500	520	568
6. Total sodium hydroxide consumption, %	2.80	2.80	2.95	2.95	3.0	3.0

In another set of expriments ([12]), Mixed hardwoods, bamboo and mixture of bamboo and mixed hardwood pulps were bleached by C-E-H-H and C-E-(H)-H sequences. From Table-I, it is observed that addition of small amounts of hypochlorite during extraction stage i.e. using C-E-(H)-H-H sequence, there was a considerable reduction in the colour of the alkali extraction stage effluent. The overall alkali consumption, the final pulp brightness and viscosity ramained virtually the same, when compared to C-E-H-H sequence. Jauhari and Maheshwari also obtained similar results ([1]).

CONCLUSIONS

From this investigations it was found that the colour of the bleach effluent could be measured very quickly and accurately by spectrophotometric method. It was observed that the colour load of extraction stage effluents could be reduced to the extent of 80% by adding during extraction stage 0.4% calcium hypochlorite on o.d. pulp in case of mixed hardwoods and 0.6% in case of bamboo. Similar results were obtained when calcium hypochorite was added to the effluent obtained after alkali extraction of the pulps. It was found that addition of more than 0.6% calcium hypochlorite did not further produce any significant change in the colour of the effluents investigated. The total colour load of the effluents could also be reduced by mixing the effluents of chlorination and extraction stages. Delta-Epsilon studies of the effluents indicated that the presence of phenolic hydroxyl groups contributes substantially towards their colour and the amounts of phenolics were found to be reduced by the addition of calcium hypochlorite to the extraction stage effluents. Chemical oxygen demand (COD), measurements showed that the addition of small amounts of calcium hypochlorite during alkali extraction stage of bleaching, considerably reduced the COD load of the effluent.

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