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Introduction

Kinetics of chlorination stage have been studied extensively. Most of the workers have expressed the consumption of chlorine and removal of lignin as a function of time. Carmody¹, Giertz² and Borruso³ dealt with sulphite pulp. White⁴, Sprout⁵ Duncan⁶ and Chapenerkar⁷ studied kraft pulps. Generally the data were expressed by a reaction mechanism second order in chlorine concentration. Chapnerkar⁷ did not evaluate a second order reaction but assumed two first order reactions occuring simultaneously. Kinetic data and reaction mechanism of the fast reaction between pulp and chlorine water which occurs within, the first few minutes of their contact have not been reported in any detail. However, recently Russell⁸ has studied the kinetics of the initial fast reaction of, chlorination stage and found that the reaction mechanism followed a second order kinetics in chlorine concentration. States to Distance The studies of kinetics and mechanism of chlorination stage

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Kinetics Of Chlorination Stage Of Bleaching Bamboo Kraft Pulp

Kinetics of chlorination stage of bleaching for bamboo kraft pulp have been discussed. The reaction of chlorine with pulp is marked by an initial rapid reaction followed by a slow process. This behaviour is rationalised by assuming two types of reactions occuring at different velocities. The rate of consumption of chlorine in initial phase of the reaction (3-4 min) followed a first order kinetics in chlorine concentration and a second order kinetics was observed in slow process of oxidation. The kinetics of entire course of reaction followed the rate law $-\frac{d [Cl]}{dt} = k_1 [Cl] + k_2 [Cl]^2$

The delignification increases with an increase in the amount of chlorine. After a sharp initial drop in viscosity, there is only a slight further decrease in the value. The rate of delignification and pulp degradation increases with increasing temperature. It was found that the efficiency of chlorine consumption during chlorination stage of bleaching is independent of temperature.

of bleaching have been so far limited to wood pulps. No work is reported on pulps from other sources such as bamboo which is extensively used in pulp and paper industry in India. It is well understood that residual lignin of unbleached pulp is the principal carrier of the brown colour of the pulp. The lignins of soft woods, hardwoods and other lignocellulosic materials such as bamboo, bagasse, straw differ from each other in their structural features and chemical reactivity. The pulping process also changes the character of lignin left in the pulp. Thus it is obvious that the rate of chlorination and mechanism of the process would differ, depending on the species and mode of pulping. The studies made so far of bleaching of bamboo pulps using chlorination as one of the stages of bleaching sequence, do not deal with the rate law and mechanism of reaction⁹. It is also observed that very little data on the first initial rapid reaction phase of chlorination stage of bleaching are available even with wood pulps. These facts led us to investigate in detail the kinetics of chlorination stage of bleaching bamboo pulp and the effects of Chlorination on pulp' properties like kappa number and viscosity.

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Results and Discussions:

Bamboo kraft pulp (Kappa number 29.6) prepared from *Dendro*calamus strictus species was used in all the experiments. The initiation of the chlorination was carried out by mixing chlorine water and pulp slurry, both kept in separate black-coated jena flasks immersed in an electrically regulated thermostat. The consistency was kept constant at 3% in all the experiments. The progress of reaction was followed by estimating residual chlorine iodometrically¹⁰.

The reaction of chlorine water with pulp was marked by an initial rapid reaction followed by a slow process. This behaviour is rationalised by assuming two types of reactions occuring at different velocities.

Order of Reaction and Rate law: The order of reaction and rate law have been determined by studying the rate of consumption of chlorine at varying initial concentrations of chlorine charge. The results are recorded in Table I. The rate of consumption of chlorine with time elapsed is represented in Figure 1, which indicates that there is an initial rapid consumption of chlorine followed by a slow process.

The analysis of the order of reaction in initial rapid reaction phase (3-4 min) was done employing Vant Hoff's differential method as described below: The rate of decrease of chlorine concentration is given by—



 $-\frac{d [Cl]}{dt} = k [Cl]^n \dots (1)$

where k is velocity constant and n is the order of reaction on taking logarithm the equation (1) becomes $\log\left(-\frac{d\left[C\right]}{dt}\right) =$ $\log k +$ n $\log [C_i]$(2) From the equation (2) it is seen that if the rate of decrease of chlorine concentration (-d[Cl]/dt) is determined at various initial values of chlorine concentrations, a plot of logarithm of velocity against the logarithm of the concentration may give a straight line, the slope of which will give the order of reaction, n, and the _ <u>d [Cl]</u>) intercept on log dt. axis, the value log k. Thus, concentration-time curves were plotted from the runs made at various concentrations of chlorine (Fig.1A) and tangents were drawn at the beginning of each reaction. The slope of each of

these were determined which represents the initial rate corresponding to a particular inital concentration. The values of slopes are recorded in Table II. The logarithms of these rates or slopes were plotted against the logarithms of correponding initial' concentration. The slope of the straight line thus obtained (Fig.2) gave n=1; indicating that the rate of consumption of chlorine in initial rapid reaction which occurs within 3-4 min. from the start of the reaction follows a first order kinetics in chlorine concentration. Thus the rate for initial rapid reaction can be written as

$$-\frac{d[Cl]}{dt} = k_1[Cl]$$

The analysis of the order of reaction during later slow part of the reaction was carried out by plotting reciprocals or residual chlorine concentrations against time. The straight lines thus obtained (Fig.3)

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Effect of chlorine concentration and temperature on rate of consumption of chlorine and velocity constant of later part of slow reaction.

	Time of reaction, Min.				Second order velocity constant			
	0	3	5	10	20	35	60	graphically k ₂ , M ⁻¹ min ⁻¹
(Cl) x 10-5 M	2113	695	300	150	70	4	0	73.20
20°C	2746	970	530	395	315	24 4	175	6.57
	3170	1130	690	526	480	408	342	2.04
	3803	1440	910	800	760	726	66 7	0.50
(Cl) x 10-5M	2113	560	160	2	0	_	_	·
30°C	2746	810	380	253	171	115	24	19.0
	3170	1005	542	416	380	250	150	6. 38
	3803	1335	760	660	583	510	417	1.54
(Cl) x 10.5M	2746	675	240	132	75	46	0	56.0
40°C	3170	845	393	262	178	117	0	19 0
	3808	1190	620	537	433	330	217	4.68
(Cl) x 10 ⁵ M 50°C	3803	1080	` 49 0	360	283	150	60	14 35

*Pulp 9 g (oven-dry basis), Consistency 3%, pH 2.

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indicate a second order kinetics in chlorine concentration. The rate law for this slow later part of the reaction is governed by the equation $-\frac{d [Cl]}{dt} = k_2 [Cl]^2$. The value

of k₂ obtained at various temperatures are recorded in Table I.

From these results it is evident that the initial phase of rapid reaction (3-4 min.) follows a first order kinetics and later slow part of the reaction a second order kinetics in chtorine concentration. These findings suggest that the total process of chlorinationstage of bleaching is governed by a rate law equation-

$$-\frac{d [Cl]}{dt} = k_1 [Cl] + k_2 [Cl]^2$$

Dependence of Rate Constant on chlorine Concentration

Table I and Fig. 4 show the effect of chlorine concentration on rate constant of the later slow part of reaction. From these it is seen that the rate of reaction decreases with an increase in initial chlorine concentration and the effect is more pronounced in lower concentration range. This is in agreement with the fact that at lower initial concentrations of chlorine the reaction is very fast and almost entire chlorine is consumed instantaneously leaving remote quantity of HOCl for the slow oxidation reaction.

Dependence of Rate Constant on Temperature

The data on effect of temperature on rate constant of later part of the reaction are summarised in Table 1 and represented in Fig. 5.





Initial concentration chlorine (Cl) x 10 ⁵ , M	Slope of the tangents $\frac{d(Cl)}{dt} \times 10^{5}$	Concentration of chlorine at the point of slope, deter- mination (Cl) x 10 ⁵ , M	$\frac{d(Ci)}{(Ci)}$	
2113	675	2000	3.375	-
2746	875	2560	3.41	
3170	1000	2940	3.610	
2803	1200	3510	3.41	

Order of reaction of initial reaction is Univty in Chlorine concentration as determined by the slope of the line in Figure. 3 pulp 9 g (oven-dry basis), Consistency 3%, pH 2.

Table-III

Energy parameters of the later part of slow reaction, rate constants and temperature coefficient.

Temp •C	$\frac{\mathrm{K_{2}}\times10^{3}}{\mathrm{IM}^{1}\mathrm{Sec^{-1}}}$	Temperature coefficient	^E Kcal M-¹	∆F [±] Kcal M-¹	∆S [±] E.U.	A Sec ⁻¹
20	8.3	3.08	10.82	19.94	1.83	4.16
30	2 5.6	3.04	20.92	19.95	1.67	3 97
40	78.0	3.06	22.44	19.94	1.57	3.91
50	239.2		22.06	19.88	1.63	4.16
Pulp 9 g	(oven-drv) ha	sis. Consistence	, 20/ mI	I O		

Fulp 9 g (oven-dry) basis, Consistency 3%, pH 2

A. perusal of the data indicates the rate constant increased that nearly three times per every 10°C rise of temperature.

Energy Parameters of the Reaction The energy of activation was determined employing Arrhenius equation $k \Sigma A e^{-\Delta E/RT}$ where $\triangle E$ is the energy of activation, A is frequency factor, R is gas constant, T is temperature of Kelvion Scale and K is rate constant at temperature T. A plot of log k versus 1/T was made and the energy of activation was determined with the slope of the straight line in Fig.6. The free energy of activation and entropy of activation were determined employing standard thermodynamic equations

respectively, where $\triangle \overset{\pm}{S}$ is entropy of activation. $\triangle \overset{\pm}{F}$ is free energy of activation, K is Boltzmann constant, and h is planck constant. The values of these energy parameters are recorded in Table III.

Kappa Number and Viscosity Variation of pulps + During Chlorination:

The above findings of the order of reactions and rate laws governing the chlorination stage of bleaching would have been of no real consequence unless a quantitative relationship between chlorine consumption and one or

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more of the empirical parameters used to indicate bleaching progress could be established. There fore, relationships between kappa number and viscosity variations in pulps bleached for different intervals of time at different temperatures, and initial chlorine concentrations were investigated. The kappa number and cuprammonium viscosity of pulp were determined according Tappi standard methods¹⁴. The results are recorded in Table IV and represented in Figures 7-13.

From the figure 7 it is observed that at the beginning of chlorination lignin is removed rapidly after which the removal subsides quickly to a very slow rate, as chlorine is consumed rapidly in the initial stage 3-4 min and then by a slow process at later stage. Similar is the case with drop in viscosity (Fig. 8) i e. after a sharp initial drop in is very slight viscosity there further decrease indicating that there is no serious degradation of fibres in later part of chlorination reaction at lower temperatures. However at higher temperatures the degradation of carbohydrate fraction is more pronounced.

Figure 9 and 10 show that removal of lignin and degradation of carbohydrates depend upon the amount of chlorine used and increases with the amount. Figure 11 and 12 show that Kappa number of pulp chlorinated to a constant degree at different

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Table-IV Kappa number and viscosity values at different times and temperatures of reaction

Temp.	Time	Chlorine	Kappa number	Viscosity
<u>°C</u>	Min.	consumed x 10 ⁵ , M	(K)	(V), Cp
20	0	0	29.7	86.0
	5	2216	14.4	72.0
	10	2351	13 3	71.4
	20	2431	12.5	70.8
	35	2502	11.8	68.2
	60	2571	10.9	60.0
20	θ	0	29.7	86.0
	5	2366	14.0	51 7
	10	2493	12.7	47.7
	20	2575	11.6	44.9
	35	2631	11.2	43.8
	60	2722	10.7	42.0
40	0	0	29.7	86.0
	5	2506	13.1	44 0
	10	2614	12.0	42.0
	20	2671	11.0	38.6
	35	2700	10.8	351
	60	2746	10.5	32.0
50	0	0	29.7	86.0
	5	2656	12.0	40.0
	10	2735	10.6	38.0
1	20	2744	10.1	35.0
r -	35	2746	9.9	32.0
	60	2746	9.8	27.0

temperatures do not change whereas viscosity of the pulps decreases appreciably with every 10°C temperature rise. Fig. 13 shows the variation in kappa number with amount of chlorine consumed at different times at different temperatures indicating that kappa numbers are linearly related to chlorine consumed in the chlorination stage of bleaching. Thus the efficiency of chlorine consumption is independent of temperature. From these data on kappa number and viscosity of pulps chlorinated to different degree at temperature with varying initial chlorine concentration appropriate conditions could easily be chosen for the chlorination stage of bleaching desired in conjunction with the desired sequence.

As a result of this investigation the following conclusions are drawn:

- 1. The reaction of pulp with chlorine water is characterised by an initial rapid reaction followed by a slow reaction.
- 2. The initial rapid reaction follows a first order kinetics in chlorine concentration.
- 3. The later slow part of reaction follows a second order kinetics in chlorine concentration.

4. At low chlorine concentration, the whole of the chlorine is consumed in the fast reaction.

Pulp 9 g (oven-dry basis), Consistency 3%, pH 2; (Cl) 2746 x 10-5 M

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- of chlorine increases the rate of reaction degreases and delignification improves with greater degradation of carbohydrates.
- 5. The rate constant increases nearly three times for every 10°C rise of temperature in case of oxidation process.
- 7. The efficiency of chlorine consumption is independent of temperature.
- 8. At constant reaction time, the delignification improves with an increase in the temperature to a certain degree and a very severe degradation of the carbohydrate takes places.
- 9. At constant chlorine consumption the delignification decreases with the rise in temperature and the damage to the carbohydrate fraction shows a lesser dependence on temperature, than in the case, with a constant time of reaction.

5. As the initial concentration, 10. The influence of temperature on pulp degradation depends on the amount of chlorine added at low concentration the effect is weak.

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