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POLLUTION REDUCTION FROM PULP BLEACHING EFFLUENTS BY PROCESS CHANGE

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Abstract :

The pulp bleaching following DEPD and ODED sequences has been studied for pollution load reduction in the effluents. The mixed hardwood kraft pulp is bleached to 87% ISO target brightness under optimum conditions in the laboratory. The effluents of individual pulp bleaching stages are characterized for comparision of pollution load generation. The optimum kappa number reduction of 45%, during oxygen delignification, was achieved at a NaOH dose of 20 kg/t of O.D. pulp with minimal viscosity drop (12%). KF value of 0.3 was found optimum for attaining the target brightness for both the sequences. The ODED sequence required lesser total active chlorine (aCl^-) as compared to DEPD sequence. The bleach chemical (aCl^-) saving by use of O2 delignification is 45% as compared to DEPD sequence. ODED sequence effluents were found to be having low pollution load as compared to DEPD sequence due to the reduction (45%) of initial kappa number of the pulp after O2 delignification stage.

Keywords: Bleaching, hardwood pulp, adsorbable organic halides, effluents

INTRODUCTION

The paper manufacture involves pulping of fibrous raw material and bleaching as major processes. The pulping degrades the lignin network, removes its soluble fractions from the plant tissue, and produce unbleached pulp which still contains residual lignin (2.5-4%). The residual lignin is accountable for the undesirable dark colour of the pulp [1]. The pulp bleaching is aimed to attain desired brightness and purify the pulp from unwanted impurities that may affect the quality of the final product. Wood preparation, pulping, bleaching, and coating operations are the major sources of pollution generation during paper manufacture.

The paper industry effluent is a complex mixture of various organic and inorganic pollutants i.e. chlorinated organics (phenols, resin and fatty acids, dioxins and furans etc.), heavy metals, dyes, starch, nutrients etc. The pulp bleaching effluent is responsible for most of the pollution load and toxicity [2, 3]. When chlorine (Cl2) or chlorine based chemicals are used for bleaching chlorinated organics are generated in the bleach plant effluent which are collectively estimated as adsorbable organic halides (AOX) [4, 5]. Chloroorganics are toxins, tend to persist in the environment, and can biomagnify through food chain [6]. The paper mill effluents have been reported to potentially induce aquatic toxicity, particularly at the reproductive stage [7].

The paper industry is now facing the challenge to meet out effluent discharge standards. The pollutants generation in the effluent can be reduced by adopting various internal process improvement measures and end-of- pipe effluent treatment. The reduction of pollutant generation at source is the best approach. The substitution of hazardous Cl2 based conventional pulp bleaching with elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching has resulted in reduction of AOX generation in the effluent. AOX generation can be decreased by reducing the amount of Cl2 used for the bleaching i.e. by pre-chlorination modifications e.g. extended delignification [8] and oxygen (O2) delignification [9], chlorination stage changes e.g. replacement of Cl2 by chlorine dioxide (ClO2) [1], and post chlorination modifications e.g. use of O2 and H2O2 in the first caustic extraction stage [10-12].

ECF bleaching is presently the dominant technology producing about 75% of the

world's bleached chemical pulp [13]. O2 delignification is an attractive pre-bleaching stage of current ECF and TCF bleaching processes [14]. It is a commonly used process before bleaching to further remove lignin and reduce the bleach chemical dose and cost [15]. The paper industry uses huge amount of fresh water i.e. 150-200 m3/ton of paper produced and 75% of which is released as effluent [16]. The recycling of the oxygen stage effluent reduces water consumption, volume, and colour of the effluent. ClO2 has been utilized as a promising delignifying reagent for pulp bleaching owing to its high selectivity, i.e. preferentially oxidizing lignin in the presence of carbohydrates thus preserving pulp quality, and significant decrease in generation of AOX [17].

The aim of the present investigation is to study reduction of effluent pollution load, i.e. BOD, COD, color, and AOX during mixed hardwood kraft pulp bleaching with ODED and DEPD sequences.

EXPERIMENTAL

Materials

NaClO2 solution was used for in-situ generation of chlorine dioxide (D stage). NaOH solution was used for the alkaline extraction (E stage). H2O2 (30%) (SQ grade) was used as oxidant in alkaline extraction (EP stage) of pulp. The pH of the pulp and the aqueous solutions was adjusted with 1M H2SO4 or NaOH solutions. The unbleached mixed hardwood (Eucalyptus: Poplar, 70: 30) kraft pulp was procured from a paper mill in India. The pulp was hand washed, screened, air dried, and stored in air tight polythene bags for further bleaching experiments in the laboratory.

Pulp Bleaching

Before oxygen delignification and bleaching the air dried pulp was soaked in water overnight and disintegrated at 3% consistency for 4-5 min using a laboratory pulp disintegrator. The disintegrated pulp was squeezed and placed in refrigerator below 4 °C in plastic bags which was used for further bleaching experiments within one week. The pulp was bleached to a target brightness of 87% ISO following OD1ED2 and D1EPD2 sequences under the controlled laboratory conditions (Table 1). O, D, E, and EP refer to O2 delignification, ClO2, alkaline extraction, and H2O2 reinforced alkaline extraction stages, respectively. O2 delignification was performed with 100 g O.D. pulp (one autoclave). NaOH and MgSO4.7H2O were added to the disintegrated pulp and desired consistency was set. The pulp was hand mixed and transferred into laboratory autoclaves which were then filled with O2 after expelling air. The autoclaves were then placed in ethylene glycol bath [18]. After completion of the reaction, autoclaves were taken out and cooled to room temperature. Pulp was taken out and washed with plenty of water on a screen. The excess water was drained off by squeezing and the pulp was stored in polythene bags for further bleaching experiments. The oxygen delignified pulp was characterized for kappa number, viscosity, and brightness. The chlorine demand on the pulp was calculated using the following formula:

$$\text{Chlorine demand } (\%aCl^{-}) = \text{Kappa no.} \times \text{Kappa factor} \quad \ldots\ldots (1)$$

Of the total chemical dose, 70% was given in the first (D1) stage and remaining 30% in last stage (D2). All the bleaching experiments were performed in polythene bags with 200 g O.D. pulp. The disintegrated pulp was adjusted

TABLE 1 Pulp bleaching conditions for different stages of DEPD and ODED sequences

Parameter	DE_PD			ODED			
	D_1	E_P	D_2	O	D_1	E	D_2
Kappa no.	15			15 (8.3 after O stage)			
Kappa factor	0.30			0.30			
Total aCl^- (% O.D. pulp)	4.5			2.49			
Bleach chemical (% aCl^-)	3.15	----	1.35	----	1.74	----	0.75
Residual aCl^- (%)	Nil	----	0.04	----	Nil	----	Nil
NaOH (% O.D. pulp)	----	0.7	----	2.0	----	0.7	----
H_2O_2 (% O.D. pulp)	----	0.3	----	----	----	----	----
Consistency (%)	10	10	10	10	10	10	10
End pH	3.5	10.5	3.3	----	3.5	11.4	3.2
Temperature (°C)	70	70	70	100	70	70	70
Time (min)	180	90	180	75	180	90	180
O_2 pressure (kg/cm^2)	----	----	----	6	----	----	----
$MgSO_4.7H_2O$ (%)	----	----	----	0.2	----	----	----
Brightness (% ISO)	87.3			86.9			

to desired consistency and pH, bleach chemicals were added, hand mixed, and placed in the water bath at desired temperature. The pulp was well kneaded by hand from time to time during bleaching. After bleaching, the pulp was filtered and filtrate was collected. The pulp was washed with distilled water in a Buchner funnel. The filtrate and washings were mixed and characterized. All the bleaching experiments were performed in duplicate and average values reported.

Analytical methods

The pulp brightness was measured with TECHNIBRITE ERIC 950 from Technibrite Corporation, USA (ISO standard 2469). The viscosity of the pulp was estimated by capillary viscometer method using 1 M cupriethylenediamine (CED) solution. TAPPI test method (T 230 om-99) was followed. Pulp kappa number was determined by TAPPI test method T 236 om – 99.

Bleach liquor and residual chlorine analysis

Strength of NaClO2 solution (40 g/L of NaClO2), as active chlorine (aCl^-), was determined by titrating against standard 0.1 N Na2S2O3 solution using starch (0.5%) as indicator. To 10 mL of NaClO2 solution, 10 mL KI (10%), and 10 mL acetic acid (10%) were added and the resulting solution was titrated against standard Na2S2O3 solution. End point was blue to colorless. Strength of the bleach liquor was calculated using the following formula:

Strength of bleachliquor (g/L)
= Normality of bleachliquor x 34.5 ..... (2)

Same procedure was followed for the determination of residual chlorine in the spent bleach liquor. Here, 100 mL of spent bleach liquor was titrated against standard 0.01 N Na2S2O3 solution [18].

Hydrogen peroxide analysis

10 mL of H2O2 solution was diluted to 250 mL in a volumetric flask. 10 mL KI (10%), 10 mL H2SO4 (4N), and 1 mL ammonium molybdate (1%) were added to 5 mL of this solution and the resulting solution was titrated against standard 0.1 N Na2S2O3 solution using starch (0.5%) as indicator [19]. The end point was blue to colorless. Strength of H2O2 solution was calculated using the following formula:

Strength of H_2O_2 (g/L)
= Normality of H_2O_2 solution x 34 ..... (3)

Effluent characterization

The pulp bleaching (individual stage) effluents were characterized for colour (Pt-Co method, measured at 465 nm using UV-VIS spectrophotometer, SPEKOL 2000, Analytic Jena), pH, BOD (by measuring dissolved oxygen before and after incubation at 20 °C for 5 days), COD (determined by closed reflux titrimetric method) [20], and AOX (analyzed on AOX analyzer, ECS 1200, using column method).

RESULTS AND DISCUSSION

O2 delignification was targeted for 40-50% reduction in pulp kappa number with minimum drop in the pulp viscosity. O2 is poorly selective at high degree of delignification and may lead to reduction in pulp quality and yield, if used extensively, by carbohydrate degradation [21]. The carbohydrate degradation is caused by active O2 species and chain type reactions initiated by HOO•, O2•−, and HO•, which are generated through the reduction of O2 species and the lignin reactions [22]. The optimization of the alkali charge (NaOH) during O2 stage was carried out by varying alkali dose (10-30 kg/t O.D. pulp) under optimum conditions (Table 1). Figure 1 depicts the effect of NaOH charge during O2 delignification on pulp kappa number, viscosity, and brightness. As NaOH charge is increased there is a decrease in the pulp kappa number but the pulp viscosity also drops. At a NaOH charge of 10 kg/t O.D. pulp, kappa number is reduced by 39% which is below the target reduction of 40-50%. At 20 kg/t O.D. pulp of NaOH charge, almost 45% kappa number reduction is achieved with 12% viscosity drop. At higher NaOH dose (30 kg/t O.D. pulp), the viscosity drops by 19% and kappa number by 51%. The target kappa no. reduction (40-50%) was achieved with 20 kg/t O.D. pulp of NaOH charge with minimal viscosity drop. Hence, a NaOH dose of 20 kg/t O.D. pulp was selected as optimum for generating oxygen delignified pulp. The pulp brightness increased as NaOH charge was increased. A brightness of 49% ISO was obtained at 20 kg/t O.D. pulp of NaOH charge.

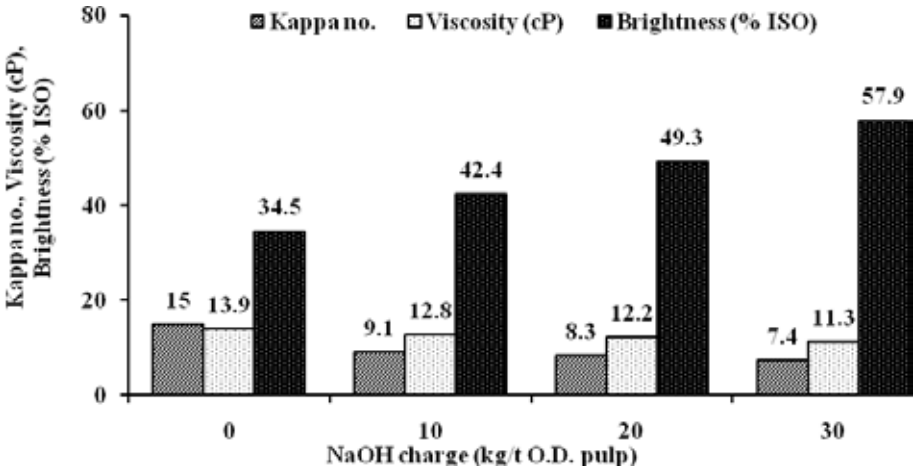

Figure 1 Effect of alkali charge during oxygen delignification on pulp kappa number, viscosity (cP), and brightness (% ISO).

The pulp was bleached to 87% ISO target brightness following DEPD and ODED sequences. The pulp bleaching conditions for different stages of DEPD and ODED sequences are mentioned in Table 1. The kappa factor (KF) was varied (0.28-0.35) for attaining 87% ISO target brightness. KF value of 0.3 was found optimum for attaining the same target brightness for both sequences. Figure 2 (a) and (b) illustrates the effect of KF on pulp brightness during DEPD and ODED bleaching sequences for achieving 87% ISO target brightness, respectively. Table 2 shows quantity of different chemicals charged for attaining 87% ISO target brightness during DEPD and ODED sequences. The total active chlorine consumption followed the order: DEPD > ODED. The bleach chemical (aCl^-) saving by use of O2 delignification is 45% as compared to DEPD sequence.

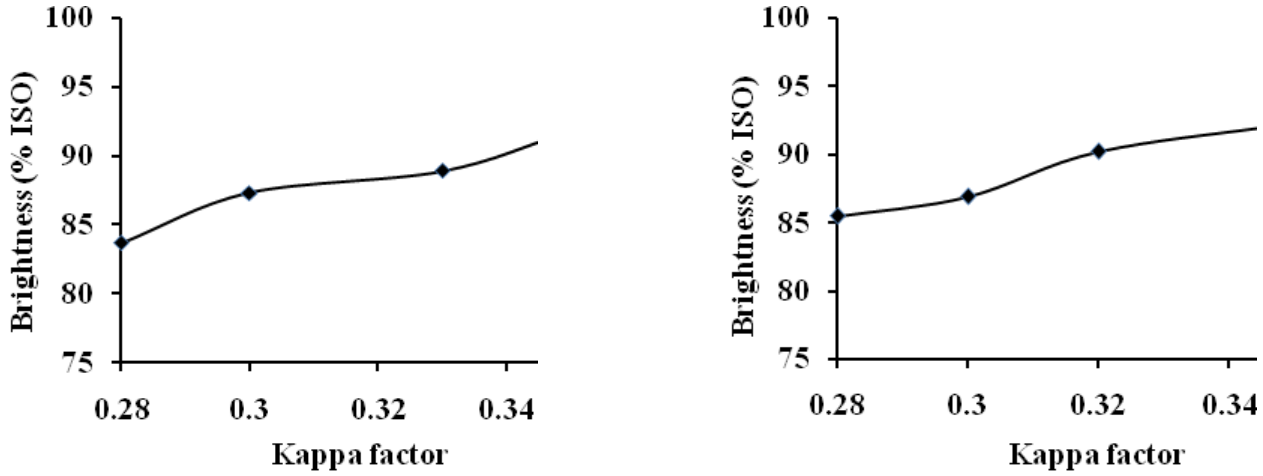

Figure 2 Effect of kappa factor on pulp brightness during (a) DEPD and (b) ODED sequence for 87% ISO target brightness

The average analytical effluent characteristics of different stages of DEPD and ODED pulp bleaching sequences are summarized in Table 3. ODED sequence effluents were found to be having low pollution load as compared to DEPD sequence. This is due to the reduction (45%) of initial kappa number of the pulp after O2 delignification stage, which in turn reduces the active chlorine multiple required for the next bleaching stages and environmental load [1]. The major pollution load came from first two bleaching (D1 and E or EP) stages for both the sequences. During kraft pulp bleaching, a significant amount of organic matter is dissolved in the first two bleaching stages i.e. chlorination and alkaline extraction [23].

TABLE 2 Chemical charge (kg/t O.D. pulp) required for different bleaching sequences for achieving 87% ISO target brightness

Stage	Chemical	Chemical charge (kg/t O.D. pulp)	
		DE_PD	**ODED**
O	O_2	------	20*
	NaOH	------	20
	$MgSO_4.7H_2O$	------	2
D_1	ClO_2	11.98	6.63
E or E_P	NaOH	7	7
	H_2O_2	3	------
D_2	ClO_2	5.13	2.84
Final brightness (% ISO)		87.3	86.9

TABLE 3 Generation (kg/t O.D. pulp) of BOD, COD, color, and AOX during different stages of DEPD and ODED sequences

Sequence	Stage	Quantity (kg/t O.D. pulp)			
		BOD	COD	Color	AOX
DE_PD	D_1	3.2	12.2	14.1	0.27
	E_P	2.5	10.1	16.7	0.23
	D_2	0.8	2.3	1.1	0.05
ODED	D_1	1.8	6.5	1.8	0.16
	E	1.5	5.1	2.0	0.14
	D_2	0.8	1.6	0.9	0.04

The higher color was generated in DEPD sequence as compared to ODED sequence. While E or EP stage effluents were characterized with high color as compared to D1 and D2 stages of both the bleaching sequences. The COD and color load of the effluents is also a function of the kappa number of the unbleached pulp and KF, the kappa number being the variable having the highest impact. The kappa number decrease of the unbleached pulp decreases the amount of COD, color, and AOX generation during pulp bleaching at high ClO2 substitution levels [23]. The higher amount of AOX was generated in DEPD sequence effluents as compared to ODED sequence. This is due to the requirement of higher chemical charge (45 kg C/t OD pulp) for achieving the same target brightness as compared to ODED sequence (24.9 kg aCl^-/t OD pulp). For ODED sequence lowest AOX was generated due to use of O2 stage. The effluent AOX loadings decrease with a decrease in initial kappa number [23, 24]. Both the bleaching sequences (DEPD and ODED) were effective in reducing AOX generation below the set regulatory standard (1 kg/t of product) [25].

O2 stage effluent can be recycled to the chemical recovery system which decreases the environmental impact of bleach plant [1]. Application of O2 delignification has been reported to offset the total bleaching costs by 20% on an average [26]. One of the main reasons for not adopting O2 delignification process (particularly in small mills) is the high capital costs of O2 delignification plant. But in order to meet AOX discharge standards and closing of the bleach cycle, the mills may look at O2 as a pre-bleaching stage. The mills which will not be able to install O2 pre-bleaching stage can meet up effluent discharge standards, particularly with regard to AOX, by using DEPD sequence. ODED and DEPD sequences can be adopted with regard to meeting AOX discharge standards.

CONCLUSIONS

ODED bleaching sequence produced lower pollution load in the effluent as compared to DEPD sequence. AOX generation in the effluents is reduced below the set regulatory standard (1 kg/t of product) by both the bleaching sequences. O2 pre-bleaching stage is found to be an attractive option for meeting AOX discharge standards as well as closing of the bleach cycle. O2 delignification required 45% less bleach chemical (aCl^-) as compared to DEPD sequence for achieving same target brightness. Hence, paper mills can meet effluent discharge standards, cleaner production, and water conservation using ODED sequence. While, DEPD bleaching sequence could be a potential option for smaller paper mills to achieve AOX discharge standard. The control of AOX in the effluent is one of the major environmental challenges before the pulp and paper industry. Hence, adoption of new cleaner bleaching technologies is the need of the hour.

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