PERSULPHATE PREBLEACHING OF CHEMICAL PULPS AND THEIR ENVIRONMENTAL IMPACT

A THESIS

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ROORKEE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled ***PERSULPHATE PREBLEACHING OF CHEMICAL PULPS AND THEIR ENVIRONMENTAL IMPACTS*** in partial fulfillment of the requirements for the award of the Degree of **Doctor of Philosophy** and submitted in the **Department of Paper Technology** of the Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out during a period from **July, 2002** to **November, 2006**, under the supervision of **Dr. N.J. Rao,** Formerly Professor, Indian Institute of Technology Roorkee, Roorkee and **Dr. Satish Kumar,** Professor, Indian Institute of Technology Roorkee, Roorkee.

The matter presented in the thesis has not been submitted by me for the award of any other degree of this or any other Institute.

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ABSTRACT

Environment concerns about the use of chlorine and chlorine containing reagents for pulp bleaching have led to implementation of a number of modified pulping and bleaching practices. Pretreatment of pulp so as to reduce incoming kappa number is one of such option which is expected to reduce bleach chemical demand and pollution loads.

Persulphate (Px) and persulphate-peroxide (PxP) as a predelignifying stage has been tried with conventional (CEH) and an ECF (DED) bleaching sequences. The studies have been performed on three different pulps, wheat straw soda, bagasse kraft and mixed hardwood kraft pulp. The pulp properties and environmental parameters for the bleaching process are evaluated and results are compared with oxygen as a prebleaching agent.

The conditions are optimized for persulphate (Px), persulphate-peroxide (PxP) and oxygen stages and the pretreated pulps are characterized for residual lignin content (kappa number) and pulp viscosity (CED). The bleaching charge is optimized in the three raw materials to arrive at 80% ISO brightness in wheat straw and mixed hardwood kraft pulps while 85% ISO brightness in bagasse pulp through different bleaching routes. The bleached pulp was characterized for brightness, viscosity and mechanical strength properties. The combined effluent from different sequences is characterized for COD, BOD, color and AOX. Pattern of chlorophenolics generated was studied on wheat straw soda pulp.

A comparison of the result of the different bleaching sequences viz CEH, OCEH, (Px)CEH, (PxP)CEH show that the active chlorine consumption follows the order CEH > (Px)CEH > (PxP)CEH ≈ OCEH in both, wheat straw and bagasse pulp. In mixed hardwood pulp, total active chlorine consumption followed the order CEH > (Px)CEH > (PxP)CEH > OCEH.

The strength values are observed to be lowest for CEH followed by (Px)CEH in all the raw materials while the OCEH and (PxP)CEH bleached pulps have comparable strength properties. The (PxP) pretreated pulps in all the raw materials are observed to show a higher tensile index values.

The various environmental parameters for the combined CEH effluent follows the same order in all the three raw materials for different bleaching sequences CEH > (Px)CEH > (PxP)CEH > OCEH. The BOD/COD ratio remains nearly at same level.

In ECF bleaching sequence for wheat straw and bagasse pulps, the active chlorine consumption follows the order DED > (Px)DED > (PxP)DED ≈ ODED. In mixed hardwood pulp, the pattern of chlorine consumption follows the pattern DED > PxDED > (PxP)DED > ODED.

Highest reduction in strength were observed in (Px)DED bleached pulps followed by DED bleached pulps. While the strength properties of ODED and (PxP)DED bleached pulps are nearly same, with only slight changes.

The COD, BOD, color and AOX of the combined DED effluent follows the order DED > (Px)DED > (PxP)DED > ODED for all the three pulps. The BOD/COD ratio remains nearly at same level.

The mills opting to meet environmental standards for AOX and close the bleach cycle necessarily will have to look at either oxygen or (PxP) as prebleaching stage irrespective of their cost limitations. Sustainable source of sodium persulphate onsite production will be sodium sesquisulphate which will reduce the cost of persulphate to one third of its commercial cost. Oxygen plants will be cost intensive and (PxP) bleach sequences are likely to be marginally higher in operating costs. Hence for environmental compliance, choice is to take the (PxP)CEH or (PxP)DED routes where oxygen plant installation is not feasible.

The concentration of chlorophenolic compounds was highest in combined effluent of CEH sequence in comparison to (PxP)CEH and OCEH bleaching effluent. The (PxP) prebleaching stage is found to reduce the generation of chlorophenolics by 36%. The formation of chlorophenolics is reduced by 86% via oxygen prebleaching. The highly toxic compounds like dichlorocatechol, tetrachlorocatechol, and pentachlorophenol are found in large quantities in CEH effluent, while the effluent toxicity reduces drastically in sequences following (PxP) or oxygen pretreatment stage. (PxP) pretreatment stage reduces toxicity of effluent but quantities of chloroguaiacols and chlorosyringaldehydes is found to increase.

In ECF bleaching sequences, DED, (PxP)DED and ODED the highly chlorinated and toxic compounds are not formed. The overall reduction in chlorophenols generation by (PxP) pretreatment is 46% in bleaching sequence (PxP)DED. In ODED, the chlorophenols are reduced drastically, the reduction being 78%.

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LIST OF TABLES

Table No.	Title	Page No.
2.1	Standard test methods followed for analysis	22
2.2	Variables studied in optimization of (Px), (PxP) and oxygen pretreatments	26
2.3	Bleach chemical (as aCl) charged to achieve target brightness	30
2.4	Absorbance of standard color solutions	31
2.5	GC conditions for the separation of chlorophenolics	36
2.6	Retention time, Extraction efficiency and Response factors of various chlorophenolics	38
3.311	Effect of persulphate dose in (Px) prebleaching	45
3.312	Effect of NaOH dose in (Px) prebleaching	47
3.313	Sulfamic acid as pulp protector in (Px) prebleaching	49
3.314	Effect of persulphate dose (without NaOH) in (Px) prebleaching	50
3.315	Effect of persulphate dose at 2% NaOH dose in (Px) prebleaching	52
3.316	Effect of NaOH and EDTA dose on kappa number in (Px) prebleaching	54
3.317	Effect of NaOH and EDTA dose on viscosity in (Px) prebleaching	55
3.318	Effect of temperature in (Px) prebleaching of different pulps	56
3.319	Effect of retention time in (Px) prebleaching of different pulps	58
3.320	Optimum parameters for (Px) pretreatment	59

3.321	Effect of peroxide and persulphate dose in (PxP) prebleaching	61
3.322	Comparison of optimized (Px), (PxP) at same dose & (PxP) at optimized dose	62
3.323	Effect of temperature in (PxP) prebleaching of different pulps	63
3.324	Effect of time in (PxP) prebleaching of different pulps	65
3.325	Optimized parameters for (PxP) pretreatment	66
3.326	Optimization of alkali charge during oxygen delignification on wheat straw pulp	67
3.327	Optimization of alkali charge during oxygen delignification on mixed hardwood pulp	68
3.328	Optimization of alkali charge during oxygen delignification on bagasse pulp	69
4.221	Bleaching conditions used to make 80% ISO brightness wheat straw pulp by different pretreatments (CEH)	81
4.222	Bleaching conditions used to make 80% ISO brightness mixed hardwood pulp by different pretreatments (CEH)	87
4.223	Bleaching conditions used to make 85% ISO brightness bagasse pulp by different pretreatments (CEH)	91
4.224	Bleaching conditions used to make 80% ISO brightness wheat straw pulp by different pretreatments (DED)	95
4.225	Bleaching conditions used to make 80% ISO brightness mixed hardwood pulp by different pretreatments (DED)	99
4.226	Bleaching conditions used to make 85% ISO brightness bagasse pulp by different pretreatments (DED)	103
4.227	Costs of various bleaching chemicals in India in 2006	106
4.228	Bleach chemical costs analysis of wheat straw soda pulp at sodium persulphate cost of Rs.22/kg	107
4.229	Bleach chemical costs analysis of mixed hardwood kraft pulp at sodium persulphate cost of Rs.22/kg	107

4.230	Bleach chemical costs analysis of bagasse kraft pulp at sodium persulphate cost of Rs.22/kg	108
4.231	Bleach plant effluent recycle/closure possibilities	109
5	Chlorophenolics detected in CEH combined effluent	113
5.1	Chlorophenolics detected in CEH combined effluent of (PxP)CEH sequence	116
5.2	Chlorophenolics detected in OCEH combined effluent	120
5.3	$^{96}LC_{50}$ values for various chlorophenolic compounds	122
5.4	Chlorophenolics detected in DED combined effluent	123
5.5	Chlorophenolics detected in DED combined effluent of (PxP)DED sequence	124
5.6	Chlorophenolics formed in ODED combined effluent	126

LIST OF FIGURES

Figure No.	Title	Page No.
2.1	Calibration curve used for color measurement	32
2.2	Separation of phenolic compounds from effluents	35
3.311	Effect of persulphate dose on (Px) prebleaching of wheat straw pulp	45
3.312	Effect of persulphate dose on (Px) prebleaching of mixed hardwood pulp	45
3.313	Effect of persulphate dose on (Px) prebleaching of bagasse pulp	46
3.314	Effect of NaOH dose on (Px) prebleaching of wheat straw pulp	47
3.315	Effect of NaOH dose on (Px) prebleaching of mixed hardwood pulp	47
3.316	Effect of NaOH dose on (Px) prebleaching of bagasse pulp	48
3.317	Effect of sulfamic acid on (Px) prebleaching of wheat straw pulp	49
3.318	Effect of sulfamic acid on (Px) prebleaching of mixed hardwood pulp	49
3.319	Effect of sulfamic acid on (Px) prebleaching of bagasse pulp	49
3.320	Effect of persulphate dose on (Px) prebleaching of wheat straw pulp	51

3.321	Effect of persulphate dose on (Px) prebleaching of mixed hardwood pulp	51
3.322	Effect of persulphate dose on (Px) prebleaching of bagasse pulp	51
3.323	Effect of persulphate dose on (Px) prebleaching of wheat straw pulp (with NaOH)	53
3.324	Effect of persulphate dose on (Px) prebleaching of mixed hardwood pulp (with NaOH)	53
3.325	Effect of persulphate dose on (Px) prebleaching of bagasse pulp (with NaOH)	53
3.326	Effect of varying NaOH dose on kappa number during (Px) prebleaching	55
3.327	Effect of varying NaOH dose on viscosity during (Px) prebleaching	55
3.328	Effect of temperature on (Px) prebleaching of wheat straw pulp	57
3.329	Effect of temperature on (Px) prebleaching of mixed hardwood pulp	57
3.330	Effect of temperature on (Px) prebleaching of bagasse pulp	57
3.331	Effect of retention time on (Px) prebleaching of wheat straw pulp	58
3.332	Effect of retention time on (Px) prebleaching of mixed hardwood pulp	58
3.333	Effect of retention time on (Px) prebleaching of bagasse pulp	58

3.334 Effect of $Na_2S_2O_8$ and H_2O_2 dose in (PxP) pretreatment of wheat straw pulp 61
3.335 Effect of $Na_2S_2O_8$ and H_2O_2 dose in (PxP) pretreatment of mixed hardwood pulp 61
3.336 Effect of $Na_2S_2O_8$ and H_2O_2 dose in (PxP) pretreatment of bagasse pulp 62
3.337 Effect of temperature in (PxP) prebleaching of wheat straw pulp 64
3.338 Effect of temperature in (PxP) prebleaching of mixed hardwood pulp 64
3.339 Effect of temperature in (PxP) prebleaching of bagasse pulp 64
3.340 Effect of R.T on (PxP) prebleaching of wheat straw pulp 65
3.341 Effect of R.T on (PxP) prebleaching of mixed hardwood pulp 65
3.342 Effect of R.T on (PxP) prebleaching of bagasse pulp 65
3.343 Effect of alkali charge during oxygen delignification of wheat straw pulp 67
3.344 Effect of alkali charge during oxygen delignification of mixed hardwood pulp 68
3.345 Effect of alkali charge during oxygen delignification of bagasse pulp 69
3.346 Effect of pretreatments on tear strength of wheat straw pulp 72
3.347 Effect of pretreatments on burst strength of wheat straw pulp 72

3.348 Effect of pretreatments on tensile strength of wheat straw pulp 72

3.349 Effect of pretreatments on double folds property of wheat straw pulp 72

3.350 Effect of different pretreatments on tear strength of mixed hardwood pulp 73

3.351 Effect of different pretreatments on burst strength of mixed hardwood pulp 73

3.352 Effect of different pretreatments on tensile strength of mixed hardwood pulp 73

3.353 Effect of different pretreatments on double folds property of mixed hardwood pulp 73

3.354 Effect of different pretreatments on tear strength of bagasse pulp 74

3.355 Effect of different pretreatments on burst strength of bagasse pulp 74

3.356 Effect of different pretreatments on tensile strength of bagasse pulp 74

3.357 Effect of different pretreatments on double folds property of bagasse pulp 74

4.221 Chemical savings in CEH bleaching from different pretreatments in wheat straw pulp 80

4.222 Effect of different bleaching sequences on tear strength of wheat straw pulp 83

4.223 Effect of different bleaching sequences on burst strength of wheat straw pulp 83

4.224	Effect of different bleaching sequences on tensile strength of wheat straw pulp	83
4.225	Effect of different bleaching sequences on double folds of wheat straw pulp	83
4.226	Combined effluent parameters from bleaching of wheat straw pulp	84
4.227	Combined effluent parameters from bleaching of wheat straw pulp	84
4.228	Chemical savings in CEH bleaching from different pretreatments in mixed hardwood pulp	86
4.229	Effect of different bleaching sequences on tear strength of mixed hardwood pulp	88
4.230	Effect of different bleaching sequences on burst strength of mixed hardwood pulp	88
4.231	Effect of different bleaching sequences on tensile strength of mixed hardwood pulp	88
4.232	Effect of different bleaching sequences on double folds of mixed hardwood pulp	88
4.233	Combined effluent characteristics from CEH bleaching of mixed hardwood pulp	89
4.234	Combined effluent characteristics from CEH bleaching of mixed hardwood pulp	89
4.235	Chemical savings in CEH bleaching followed by different pretreatments of bagasse pulp	90
4.236	Effect of different bleaching sequences on tear strength of bagasse pulp	92

4.237 Effect of different bleaching sequences on burst strength of bagasse pulp 92

4.238 Effect of different bleaching sequences on tensile strength of bagasse pulp 92

4.239 Effect of different bleaching sequences on double folds of bagasse pulp 92

4.240 Combined effluent characteristics from CEH bleaching of bagasse pulp 93

4.241 Combined effluent characteristics from CEH bleaching of bagasse pulp 93

4.242 Chemical savings in DED bleaching from different pretreatments in wheat straw pulp 94

4.243 Effect of different bleaching sequences on tear strength of wheat straw pulp 96

4.244 Effect of different bleaching sequences on burst strength of wheat straw pulp 96

4.245 Effect of different bleaching sequences on tensile strength of wheat straw pulp 96

4.246 Effect of different bleaching sequences on double folds of wheat straw pulp 96

4.247 Combined effluent characteristics from DED bleaching of wheat straw pulp 97

4.248 Combined effluent parameters from DED bleaching of wheat straw pulp 97

4.249 Chemical savings from DED bleaching from different pretreatments in mixed hardwood pulp 98

4.250 Effect of different bleaching sequences on tear strength of mixed hardwood pulp 100

4.251 Effect of different bleaching sequences on burst strength of mixed hardwood pulp 100

4.252 Effect of different bleaching sequences on tensile strength of mixed hardwood pulp 100

4.253 Effect of different bleaching sequences on double folds of mixed hardwood pulp 100

4.254 Combined effluent parameters from DED bleaching of mixed hardwood pulp 101

4.255 Combined effluent parameters from DED bleaching of mixed hardwood pulp 101

4.256 Chemical savings in DED bleaching from different pretreatments in bagasse pulp 102

4.257 Effect of different bleaching sequences on tear strength of bagasse pulp 104

4.258 Effect of different bleaching sequences on burst strength of bagasse pulp 104

4.259 Effect of different bleaching sequences on tensile strength of bagasse pulp 104

4.260 Effect of different bleaching sequences on double folds of bagasse pulp 104

4.261 Combined effluent parameters from DED bleaching of bagasse pulp 105

4.262 Combined effluent parameters from DED bleaching of bagasse pulp 105

5.0 Proportions of various categories of chlorophenolics in CEH combined effluent 114
5.1 Proportions of various categories of chlorophenolics in CEH combined effluent of (PxP)CEH sequence 117
5.2 Reduction of chlorophenolics in CEH effluents by different pretreatments 117
5.3 Proportion of various categories of chlorophenolics in CEH combined effluent of OCEH sequence 119
5.4 Proportion of various chlorophenolics detected in DED combined effluent 123
5.5 Proportions of various chlorophenolics detected in DED combined effluent of (PxP)DED sequence 125
5.6 Reduction of chlorophenolics in DED effluent by different pretreatments 126
5.7 Proportions of various chlorophenolics detected in DED combined effluent of ODED sequence 127

CONTENTS

Page no.

CANDIDATE'S DECLARATION i

ABSTRACT ii-iv

ACKNOWLEDGEMENTS v-vii

LIST OF TABLES viii-x

LIST OF FIGURES xi-xviii

CHAPTER1

INTRODUCTION 1-20

1.1 STATUS OF PAPER INDUSTRY IN INDIA 1

1.2 BLEACH PLANT EFFLUENT CHARACTERISTICS 3

1.3 TOXICITY OF BLEACH PLANT EFFLUENT 6

1.4 ORIGIN AND IDENTIFICATION OF CHLOROORGANICS 8

1.5 ABATEMENT OF BLEACH PLANT POLLUTION 8

1.5.1 Process Modifications 9

1.5.1.1Maximum lignin removal before bleaching 9

1.5.1.2 Improved brown stock washing and screening 11

1.5.1.3 Improvement in bleaching sequence 12

1.5.2 Control of outside contaminations 14

1.5.3 End of Pipe treatment methods 15

1.6 APPLICATIONS OF PERSULPHATE 17

1.7 STATEMENT OF THE PROBLEM 18

CHAPTER 2

MATERIALS & METHODS 21-38

2.1 REAGENTS & MATERIALS 21

2.1.1 Chemicals 21
2.1.2 Materials 21
2.2 TEST METHODS 21
2.3 TEST PROCEDURES 22
2.3.1 Analysis of bleach liquor 22
2.3.2 Analysis of residual chlorine 23
2.3.3 Analysis of hydrogen peroxide solution 23
2.3.4 Analysis of sodium persulphate 23
2.3.5 Disintegration of pulps 24
2.3.6 Preparation of sheets for brightness and kappa number 24
2.3.7 Oxygen delignification 25
2.3.8 Persulphate and Persulphate-Peroxide pretreatments 25
2.3.9 Bleaching of Pulp 26
2.3.9.1 Chlorination stage 27
2.3.9.2 Alkaline extraction stage 27
2.3.9.3 Hypochlorite stage 28
2.3.9.4 Chlorine dioxide stage 28
2.3.9.5 Persulphate prebleaching 28
2.3.9.6 Persulphate-peroxide prebleaching 29
2.4 CHARACTERIZATION OF BLEACHING EFFLUENTS 30
2.4.1 Color measurement 30
2.4.1.1 Preparation of standard color solution 30
2.4.1.2 Color measurement 31
2.4.2 Analysis of chlorophenolics 32
2.4.2.1 GC conditions 33
2.4.2.2 Derivatization procedure 33
2.4.2.3 Retention time determination 34
2.4.2.4 Separation of chlorophenolics from effluent 34
2.4.2.5 Quantitative analysis of various pollutants 36

2.5 STRENGTH PROPERTIES 37

CHAPTER 3
PERSULPHATE-PEROXIDE PREBLEACHING OF WHEAT STRAW SODA, MIXED HARDWOOD KRAFT AND BAGASSE KRAFT PULPS 39-74
3.1 INTRODUCTION 39
3.2 MECHANISM OF PREBLEACHING 40
    3.2.1 Oxidation of lignin in prebleaching 40
    3.2.2 Persulphate as an oxidizing agent 41
    3.2.3 Oxidation chemistry 41
    3.2.4 Free radical chemistry 42
    3.2.5 Sodium persulphate synthesis 43
3.3 RESULTS AND DISCUSSION 44
    3.3.1 Persulphate pretreatment optimization 44
        3.3.1.1 Effect of persulphate dose 44
        3.3.1.2 Effect of NaOH dose 46
        3.3.1.3 Effect of sulfamic acid 48
        3.3.1.4 Effect of sodium persulphate dose at 40°C
            a). Without NaOH 50
            b). With NaOH 51
        3.3.1.5 Effect of NaOH and EDTA dose 53
        3.3.1.6 Effect of temperature 55
        3.3.1.7 Effect of time 57
    3.3.2 Persulphate-peroxide pretreatment 59
        3.3.2.1 Effect of persulphate and peroxide 60
        3.3.2.2 Effect of temperature 62
        3.3.2.3 Effect of time 64
    3.3.3 Oxygen delignification 66
        3.3.3.1 Optimization of alkali charge during oxygen pretreatment 67

3.3.4 Strength properties of pulp treated by different pretreatments 71
3.3.4.1 Wheat straw pulp 71
3.3.4.2 Mixed hardwood pulp 72
3.3.4.3 Bagasse pulp 73

CHAPTER 4
BLEACHING OF PERSULPHATE, PERSULPHATE-PEROXIDE AND OXYGEN PRETREATED PULPS 75-110
4.1 INTRODUCTION 75
4.1.1 Process modifications 77
4.1.1.1 Oxygen &/or Extended delignification 77
4.1.1.2 Increased chlorine dioxide substitution 78
4.1.1.3 Persulphate prebleaching 79
4.2 RESULTS & DISCUSSION 80
4.2.1 CEH bleaching of wheat straw pulp 80
4.2.2 CEH bleaching of mixed hardwood pulp 85
4.2.3 CEH bleaching of bagasse pulp 89
4.2.4 DED bleaching of wheat straw pulp 94
4.2.5 DED bleaching of mixed hardwood pulp 98
4.2.6 DED bleaching of bagasse pulp 102
4.2.7 Economic analysis 105

CHAPTER 5
GAS CHROMATOGRAPHIC ANALYSIS OF CHLOROPHENOLICS 111-129
5.1 INTRODUCTION 111
5.2 RESULTS AND DISCUSSION 112
5.2.1 CEH bleaching sequence 112
5.2.2. (PxP)CEH bleaching sequence 115

5.2.3 OCEH bleaching sequence 119
5.3 GENERATION OF CHLOROPHENOLICS IN ECF SEQUENCE 122
5.3.1 DED bleaching sequence 122
5.3.2 (PxP)DED bleaching sequence 124
5.3.3 ODED bleaching sequence 126
5.3.4 Comparison of CEH and DED bleaching effluent 128

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS 130-133
6.1 CONCLUSIONS 130
6.2 RECOMMENDATIONS 132
6.3 FUTURE WORK 133

REFERENCES 134-151

CHAPTER 1

Chapter 1

INTRODUCTION

1.1 STATUS OF PAPER INDUSTRY IN INDIA

For almost 2000 years, paper has had a central and growing importance in the development of human society world over. It has been one of the drivers of world development, providing the means for people to record and communicate ideas, news and works of art. Even with the advent of modern world of plastic bags, electronic communication, computers and paperless office, paper remains essential ingredient of homes, factories, offices, schools and in dominant vehicle of modern communication and administration. Today the paper industry accounts for almost 2.5% of world's production and 2% of world trade (104).

"Paperless office" was something that was much talked about in the 80's, but we haven't seen this till date. In fact it was thought at one time that, people may not need or use paper once computers find extensive usage, but today as we see, more the computer usage more seems to be the need of paper (173).

In recent past, the Indian paper sector has maintained a growth rate of around 6%, which is way above the world average of about 2.8% (69). With such growth prospects, the Indian paper industry has a vital role to play in the socio-economic development of the country. As on date there are more than 600 pulp and paper mills producing nearly 5.5 million tons of paper and paper board and 0.68 tons of newsprint against the present installed capacity of 7.5 million tons of paper and paperboard and about 1.30 million tons of newsprint. The projected demand for paper, paperboard and newsprint is expected to touch 8.3 million tons by the year 2010. The per capita consumption of paper, which is the benchmark of modernization of any country, stands at 5.5 kg for India, which is a poor comparison to global average of about 50 kg. The turnover of industry is around Rs.1.6 billion employing 0.3 million persons directly and around 1 million persons indirectly (69).

The Indian paper industry is primarily dependent on three major raw materials viz. forest, agricultural residues and secondary fibers (174). Pulp and paper industry uses 39% of forest based fiber, 31% agro residue based fiber and 30% fiber is derived from waste paper (82). Wood continues to dominate as the main raw material for papermaking. Indian paper industry produces mostly two types of virgin pulps from fiber sources i.e. chemical pulps through either Soda process or Kraft process and chemi-mechanical pulps (82)

Indian paper industry is a typical mix of small, medium and large mills in terms of capacity with agricultural residues, wood, bamboo and recycled fibre as a raw material (150). Paper mills in India are broadly categorized into three groups i.e. Large (>100TPD), Medium (30-100 TPD) and Small (<30 TPD) (158). Large size paper mills based on wood and bamboo as raw materials are well equipped with chemical recovery. The small paper mills based on agro raw materials, producing writing and printing paper without chemical recovery are highly polluting (150). In large paper mills waste waters are generally segregated into two streams namely colored streams (due to lignin of pulp washing, caustic extraction and chemicals recovery section) and colorless/ less colored stream (chipper house, chlorination, hypochlorite and paper machines). A third stream of uncontaminated wastewaters is usually segregated and reused. The segregation is not practiced in small mills due to batch operation and discontinuous usage (132). The combined pollution load of small scale mills, in terms of lignin is about 4 times higher polluting than that of large paper mills (139).

Paper industry in India is on constant watch by the Ministry of Environment and Forest since it is an environment sensitive sector and falls under Red Category of industries (126). The pulp and paper industry is categorized under 17 highly polluting industries in India (81) and the quality and the quantity of effluents generated depends on the various units processes, size of unit, waste recycling capability etc. (170)

Water in nature is a free resource. Most countries require, however that pulp and paper mills get a permit to use this resource. Water use varies widely among the mills. Older mills tend to use more water than new mills (110). Pulp and paper industry is a very water intensive industry and ranks third in the world, after the primary metals and chemical industries, in terms of freshwater withdrawal (2). The fresh water consumption in large mills is 100-150m^3/t of paper, whereas in agro mills the water requirement is 170-230m^3/t (116).

1.2 BLEACH PLANT EFFLUENT CHARACTERISTICS

Pulp industry uses a chain of technological processes in order to transform raw wood into usable fiber (79). The fibrous raw materials essentially consist of cellulose, lignin and other extraneous substances. During pulping process mostly 80% of the lignin and other extraneous substances are dissolved in the cooking liquor (as black liquor). The aim of pulping process is to remove maximum lignin selectively without affecting the cellulose. A cooking to zero lignin content is not practically feasible as lignin condensation reactions and degradation reactions of hemicelluloses and celluloses occur simultaneously along with lignin removal at these stages (54). Thus the chemical pulping leaves behind small amounts of modified lignins, which are removed subsequently by various bleaching processes.

The amount of bleach chemical required for effective bleaching depends on the type of lignocellulosic material used to obtain fibre (pulp) and residual lignin content of pulp (measured by Kappa number). All the colored material cannot be eliminated by any single chemical in any single step, so bleaching is a multi-step procedure. The two types of bleaching chemicals are used: (55)

1. Oxidants are used to degrade and decolorize lignin.
2. Alkali is used to degrade lignin by hydrolysis and to aid in its dissolution.

In India, in few mills, chlorine gas (C) is mostly used during prebleaching to chlorinate lignin. For subsequent extraction (E) mills use NaOH. The remaining lignin is oxidized by either hypochlorite (H) or chlorine dioxide (D) because of their greater selectivity.

Large volumes of experimental data of bleaching of bagasse pulps with CEH sequence are available. (157, 54, 135)

The bleaching of pulp with chlorine and chlorine based chemicals generate various chlorinated compounds (28, 72) which include chlorinated phenolics, chlorinated resin and fatty acids, dioxins and furans which are found to have high toxic effects on receiving environment. Hence, bleach plants are considered to be the major source of polluting discharges accounting for 60-70% of BOD and 80-90% color load of the entire mill (with chemical recovery) (132). BOD and acute toxicity are caused by biodegradable, low molecular weight compounds. High molecular weight compounds are the primary cause of COD, color and chronic toxicity (188). It is estimated that production of 1 tonne of pulp is reported to contribute about 100 kg of color imparting substances and 2- 4 kg of organochlorines to bleach plant effluents (108). The Adsorbable Organic Halide (AOX), Extractable Organic Halide (EOX) and Purgeable Organic Halide (POX) are used normally to indicate the level of organochlorine compounds present in bleaching plant effluents.

During the last two decades the pulping and bleaching technologies have undergone extensive changes in order to reduce the discharge of chlorinated compounds to the environment (160). Major changes have been the replacement of elemental chlorine with chlorine dioxide in bleaching process giving elemental chlorine free bleaching (ECF) sequence, (24) without elemental chlorine or chlorine containing chemicals, termed as totally chlorine free (TCF) bleaching process. Modern bleaching sequences of both ECF and TCF types can meet the tough environmental demands of Best Available Technology (BAT) set up by European Commission (127). In India, the introduction of Charter on Corporate Responsibility for Environmental Protection (CREP) in the year 2003, by Central Pollution Control Board has brought out a time bound implementation schedule to address major environment issues particularly in bleaching (144).

1.3 TOXICITY OF BLEACH PLANT EFFLUENT

The toxicity of whole mill effluent of a given mill will directly depend upon the total organically bound chlorine, the extractive content of raw material being used and to what extent these extractives are removed during pulping and other processes (133). Most of the researchers separate the high molecular weight fraction (HMW>1000 Dalton) from the low molecular weight fraction (LMW<1000 Da) where molecular weight is operationally defined by ultra filtration (UF) process (33). Compounds from HMW fraction (forming ~ 80% of total) (105) are probably biologically inactive, because they cannot penetrate the cell membranes of living organisms, while compounds from LMW fraction (accounting nearly 20%) are more problematic (105, 79). Out of 20%, of low molecular weight AOX, nearly 19% are hydrophilic and can be metabolized while remaining 1% is extractable only by non polar solvents, is referred as Extractable Organic Halide (EOX). Compounds of this fraction are potentially toxic and bioaccumulable (105).

Lethal concentration [LC] is usually used to express effluent toxicity $^{96}LC_{50}$. Sublethal effects of bleach plant effluents are more important for environment than lethal effects, because they show long term effects from the accumulation of toxic substances in the organism (37). A small increase in concentration of chlorinated phenolic compounds will change the lethal effects from zero to 100% (178).

Dioxins is a family of 210 polychlorinated dibenzo-p-dioxin and dibenzo-p-furans (PCDD & PCDF). The most toxic member of this family is 2378 TCDD, about 100,000 times more toxic than the least potent in them (83). Pulp chlorination results in the production of PCDD's and PCDF's (64). 2378 TCDD has been shown to be highly toxic, bioaccumulative, mutagenic and carcinogenic (119).

The compounds responsible for the toxicity of C stage effluent are mainly chlorophenols, which contributes 80% of the toxicity at a charge equivalent to 50% of chlorine demand (176). This effluent is partly responsible for contributing effluent color, acute / chronic toxicity, mutagenicity and carcinogenicity (115). The E stage effluent contributes to 90% of acute toxicity, with major species being 3,4,5-trichloroguaiacol, tetrachloroguaiacol (115) and several fatty acids (e.g. mono & dichlorohydroabietic acid and epoxystearic acid) (88). The hypochlorite bleaching is the major contributor of chloroform and carbon tetrachloride which are classified as carcinogen (115).

Chlorinated phenols are generally biologically degradable. The biodegradation rate decreases as the level of chlorine substitution (i.e. the number of chlorine atoms which have been added to the basic phenolic structure) increases (88). Chlorophenolic compounds released from bleach plants can be methylated by bacteria, present in the sediment, into chlorinated anisoles and veratroles (109) and these group of compounds are even more toxic and potentially more bioaccumulating (7).

2,4-dichlorophenol, 2,4,5-trichlorophenol, pentachlorophenol, chlorinated dioxin, dibenzofurans and chloroform are carcinogenic, where as chlorocatechols are strongly mutagenic (146). Similarly mill effluents were found to have an inhibitory effect on growth of plants and animals, which may be caused due to inhibition of photosynthesis (37). It has been found that physical parameters such as pH, temperature etc. in the aquatic environment may strongly influence the toxicity of pollutants (37).

1.4 ORIGIN AND IDENTIFICATION OF CHLOROORGANICS

Native lignin is a polymer comprised of p-coumaryl, coniferyl and sinapyl alcohols. Softwood lignin is guaiacyl lignin derived mainly from coniferyl alcohol while hardwood lignin is guaiacyl – syringyl lignin formed by copolymerization of coniferyl and sinapyl alcohols. 1-5% of p-coumaryl alcohol also participates in the formation of both softwood and hardwood lignin. Grass lignin appears to be like hardwood lignin but some grass lignin is thought to contain p-coumaryl units as well (186). Chlorophenolic compounds such as chlorophenols, guaiacols and catechols are produced as degradation products of lignin during pulp bleaching using chlorination processes (88,186).

New developments in field of analytical chemistry, applying computer assisted Gas Chromatography – Mass Spectrophotometer & Capillary column of Gas Chromatography have led to successful estimation of the presence of chloroorganics in the bleach effluent. Lindstrom and Nordin were the first to categorize chloroorganics present in spent bleach liquor (93). Most of the studies on the identification of chlorophenolic compounds have been performed on softwoods (80,17). Nature and quantities of various chlorophenolic compounds present in bleach plant effluents formed from Indian varieties of hardwoods and agro-residues has been reported by Sharma, *et.al.,*1996 & Sharma *et.al.,*1996 (151, 152).

1.5 ABATEMENT OF BLEACH PLANT POLLUTION

With ever increasing awareness towards pollution abatement and with the implementation of stricter environmental regulations, the pulp and paper industry is forced to look for alternatives (74). In connection with innovation in the paper industry, it is at pulp bleaching plants that the greatest changes have taken place, since this is the section of pulp and paper manufacturing process generating the greatest degree of pollution (117). Some of the major approaches for detoxification of bleach plant effluent have been in combination of the following one or more measures:

1.5.1 Process modifications

1.5.2 Control of outside contaminations

1.5.3 External control measures (end of pipe treatment)

1.5.1 **Process modifications:** Pulp and paper industry is committed to implement changes in the bleach plant to reduce the discharge of undesirable byproducts into the receiving water environment (18)

1.5.1.1 Delignification of pulp as much as possible, to decrease residual lignin in pulp before bleaching.

1.5.1.2 Improved brown stock washing and screening to reduce carry over of dissolved organics and particles to bleach plants.

1.5.1.3 Improvement in bleaching sequence to reduce or eliminate use of elemental chlorine/ chlorine compounds.

1.5.1.1 Maximum lignin removal before bleaching: The quantity of chlorine necessary to bleach pulp is a function of kappa number (or K number) of pulp, a lower kappa number before the bleaching stage means lower bleach chemical usage (91).

Extended delignification based on the system design modification in batch digester are – Superbatch, Rapid displacement heating (RDH), Enerbatch (134).

Extended delignification in continuous digester based on system design modification are Extended modified continuous cooking, Isothermal cooking (123). MCC^{TM}, EMCC^{TM}, & ITC^{TM} methods are based on the principle that the alkali profile should be leveled out throughout the cook, so that the hydrogen sulfide concentration should be high in initial phase and at the beginning of bulk phase and temperature should be as low as possible, especially at beginning of cook (73). Compact cooking and Kobudo cooking method, improves selectivity by maintaining the concentration of hydroxide and hydrogen sulfide ions, in both initial and bulk phases leading to increased pulp yield (3). Organocell process using Methanol and NaOH in Methanol/water have been found to be most potential and organosolv mill can have much smaller size than the kraft mill (32). In Lo-Solids method, both the amount and concentration of dissolved wood solids in the bulk and residual phases are kept minimal while maintaining a uniform radial distribution of temperature and pulping chemicals (96). The use of chemical additive, anthraquinone and polysulphide, has been reported as low capital investment option for decreasing the kappa number and minimizing the impact on recovery boiler with higher bleached pulp yield (70,124). Another option is the Prenox process which is an acidic pretreatment prior to oxygen delignification. The active compound is NO_2 (57).

The concerns regarding the discharge of mill effluents and recycling of process streams have driven the pulp and paper industry to place more emphasis on chlorine free processes making oxygen delignification an attractive part of modern bleaching sequence (5, 125). Numerous benefits accrued from oxygen delignification are significant reduction in pollutant loads (COD, BOD & AOX) (59), power (20), water consumption and wastewater generation (34). Tangible benefits include savings through reduced chemicals for pulping and bleaching (21) higher pulp yield and wastewater treatment costs. Other significant benefit is partial closure of fiberline by recycle of effluent to chemical recovery system (66). Laboratory studies on conventional CEH bleaching of oxygen prebleached pulps of bagasse, bamboo & eucalyptus, it is evident that the pulps could be bleached to around 80% target brightness with drastic reduction in bleaching chemical requirements, pollution loads and pulp quality improvement (59). Presently a trend towards investments in two reactor oxygen delignification technologies is sweeping the world (128).

1.5.1.2 ***Improved Brown stock washing and screening:*** The purpose of pulp washing is to remove soluble components from pulp suspension using a small amount of wash filtrate as possible (140). Improved brown stock (BS) washing results in reduction of bleach liquor carry over with the pulp, thus decreasing the amount of chlorine and chlorinated chemicals for bleaching (64). The crux of washing operations is to wash pulp to highest cleanliness with least dilution (132). Removing extractable material from unbleached pulp in the laboratory with ethanol washing resulted in significantly lower concentration of TCDD/TCDF upon bleaching (64). Presence of knots, shives and rejects also serve as a precursor for AOX, so with improved screening and washing operation, reduction in AOX has been achieved.

1.5.1.3 Improvement in bleaching sequence to reduce or eliminate use of elemental chlorine:

a) **Modifying Chlorination Stage :**

i). *Slow and multipoint addition of chlorine* – Adding chlorine water continuously throughout various lengths of time at either 3.5 or 10% pulp consistency, increases pulp viscosity and decreases the formation of AOX compounds in the effluent (91). Split addition of chlorine in two or three stages rather than in single step and increasing pH of chlorination stage have been found effective in reducing dioxin, furan and AOX in the C stage effluent (64).

ii). *High or total substitution of first chlorination stage with ClO_2* – Chlorine dioxide reacts exclusively with free phenolic groups in lignin and residual lignin could be totally removed by ClO_2 (89). At 90-100% ClO_2 substitution BOD decreased by 20-30% and color by 50-80% (67). Pryke and Singh also reported that effluent toxicity decreases with increasing ClO_2 substitution (121, 154). ClO_2 substitution in C stage results in optimum pulp quality also (7). 100% ClO_2 substitution in C stage decreases AOX in the effluent by 70-80% and chlorinated phenolic compounds by 95% as confirmed in the mill trial (121).

b) **Use of oxygen and H_2O_2 in extraction stage** – Another approach for reduction of elemental chlorine application involves distribution of the delignification load over both the C and E stages instead of just C stage. This can be achieved by converting E stage into an oxidative stage by addition of hydrogen peroxide (E_P), oxygen (Eo) alone or both (E_{OP}) (120). Oxidative extraction reduces chlorine consumption, enhances delignification and reduces bleach chemical consumption in the next bleaching stage and generates wastewater with reduced pollution loads particularly AOX and color. A mill study of an agrobased mill confirms that oxidative extraction reduces BOD, COD & color by 10-20% in bleach plant effluent (153).

c) **Biobleaching** – The use of biological treatments for bleaching kraft pulps provide an alternative means of bleaching kraft pulps that could potentially yield distinct operating benefits (148). Xylanase (141, 84, 13, 14, 97*)* & *cellulase (39)* are two bio-based commercial products that are currently employed for the production of paper. The treatment with xylanases involves hydrolysis of bonds in xylan and/or of xylan lignin complexes, rendering lignin easily accessible for the conventional chemical pretreatment in subsequent bleaching stages (13). But white rot fungi produce oxidative enzymes which attack the lignin directly. Major oxidative enzymes found to affect lignin are laccases, lignin peroxidase (LiP) and Mn dependent peroxidases (MnP) (40). Laccases in the presence of 2,2'-azinobis(3-ethylbenzothiazoline-6-sulphonate) (ABTS), a mediator, could delignify both hardwood and softwood kraft pulp with high selectivity (22). As per a study, pulp bleached with the laccase / N-hydroxybenzotriazole system exhibited favorable bleachability properties (149). Laccase mediator system (LMS) treatment can be effectively employed on high-lignin content kraft pulps, followed by reinforced oxidative extraction stage (26). Sequential treatment of wheat straw chemical pulp with xylanase and laccase followed by alkaline extraction lowered the kappa number by about 60% (63).

d) **Totally chlorine free bleaching (TCF)** – Total chlorine free bleaching processes employ chlorine free compounds like molecular oxygen, hydrogen peroxide, ozone and peracetic acid. One of the advantages of TCF bleaching compared to ECF process is that chlorate, a byproduct of ClO_2 bleaching is not formed (78). Ozone is a very efficient oxidant capable of oxidizing all types of lignin structures (56). In order to ensure an efficient use of ozone as well as a good selectivity, medium consistency ozone bleaching seems to be primary choice (127). Another bleaching concept is use of ClO_2 and ozone in combination in the same bleaching stage resulting in effective delignification, AOX formation is reduced and pulp viscosity is mostly maintained because of low ozone charge (87). Peracetic acid could be used in ECF and TCF bleaching (138). Peracetic acid was applied with oxygen and hydrogen peroxide to produce high quality TCF pulps while maintaining pulp viscosity (42). Hydrogen peroxide is used extensively to brighten mechanical pulps and its successful application depends on chelating step to remove metal ions which promote rapid decomposition of active perhydroxyl ions (16).

1.5.2. Control of outside contaminations – Brown stock defoamers and washing aids have undergone an evolution after dioxin precursors were found to be present. Use of polychlorinated phenolics based preservatives have been suspected to be source of chlorinated dioxins. Oil based defoamers are also responsible for increased level of dioxins and furans in pulp mill effluent, as certain oil based defoamer contains relatively high level of unchlorinated dibenzodioxin and dibenzofuran (156). Folke argued that black liquor spills can also contribute to toxicity of effluent (43). Thus preventive action should be taken to avoid spillage and leakage of fibre and liquor by providing sumps around various processes and reprocessing the connections.

1.5.3. End of Pipe Treatment methods – Although toxicity of bleach plant effluent can be reduced appreciably by various internal control measures and process modifications, however, unless the fully closed mill is achieved, external methods for treatment will be always essential in order to meet the regulatory standards for chlorinated organic matter including AOX (94). Santos found that dissolved organic matter from pulp mill effluents exhibit higher content of aromatic carbons and lignin derived structural moieties than dissolved organic matter from non polluted waters. Therefore discharge of pulp mill effluents changes the bulk properties of dissolved organic matter from receiving water (142, 143).

The Indian pulp and paper mills essentially treat effluents by primary treatment followed by secondary treatment. Primary treatment comprises removal of suspended solids. The two principle methods employed in pulp and paper industry are gravity sedimentation and clariflocculation.

Most common secondary or biological treatment used in pulp and paper industry include oxidation lagoon, aerated stabilization basin (ASB), activated sludge process (ASP), anaerobic process, biological filter process such as trickling filter, rotating disc etc. Despite their effectiveness at enhancing the quality of effluents, these processes cannot eliminate the hardly biodegradable recalcitrant organic matter (ROM) and sometimes bioaccumulative compounds present in this wastewater (181). Biological treatment has reduced the COD load by 40-90% and BOD load by over 90% (145). Laboratory studies indicate that anaerobic-aerobic process for treatment of pulping spent liquor generated from agroresidues, is effective in reducing pollution loads i.e. BOD, COD and SS by 95%, 67% and 95%

respectively (114). Both aerobic and anaerobic degradation have been widely used for treating bleaching effluents containing chlorinated organic compounds. Chlorinated organics in bleaching effluents were poorly removed by biological wastewater treatment and about 30-60% of non biodegradable substrates of influent were left over (25). Advanced oxidation processes (AOPs) involve promoting strong oxidants (O_3 or H_2O_2) with UV radiation or hydroxide ion to produce hydroxyl radical (OH^o), a powerful oxidizing agent that attacks different compounds non selectively. The ability of hydroxyl radicals in breaking down the molecular structure of chemical compounds is advantageous for partial oxidation of non biodegradable HMW organics in dechlorination of Persistent Organic Matter (POM) (19). Integrated AOPs & biological treatment provides a viable alternative and could help remove ROM from the effluent economically and effectively. Effluent streams containing toxic & inhibitory compounds (eg. alkaline stage effluent) can be pretreated by AOPs to produce biodegradable intermediates which are then readily treated biologically (19). *Pseudomonas sp.* strain CA10 (recently classified into *Pseudomonas resinovorans* strain CA10) (65) a carbazole-utilizing bacterium has also been employed as dioxin degrader in contaminated soil (60). Some studies reveal the successful performance of UASB reactor in the treatment of pulp & paper mill effluent (112, 129).

The tertiary treatment techniques (physico-chemical treatments) have been developed to control the discharge of deleterious substances from pulp bleaching section. Tertiary treatment is employed for removal of effluent color, COD and toxicity. The major tertiary treatment techniques include adsorption and ion exchange, flocculation and chemical precipitation methods and membrane methods (47, 177). Lime treatment for color removal has been found to be technically and economically feasible, achieving over 90% color removal and 20 -

40% reduction in BOD (32). Recently, a study showed that Tetra Amide Macrocyclic Ligand (TAML)/H_2O_2 iron catalysts is able to substantially reduce color (50-90%) in effluent streams from bleach plant of chlorine dioxide mills (51). *Aspergillus fumigatus* is an efficient strain for decolorization of agroresidues based mill effluent (139). With *Rhizopus oryzae*, reduction in color load, COD, lignin, AOX & EOX was 95, 50, 70, 72 & 37% respectively in 24 h. Removal of 4-chlorophenol, 4,5-dichloroguaiacol, 3,4,6-trichloroguaiacol, 2-chlorosyringaldehyde, tetrachloroguaiacol were to a level of 94, 53, 95, 51 & 58% respectively, after treatment with *Rhizopus oryzae* (14).

Traditionally Indian paper mills use the End of Pipe treatment to reduce pollution loads and are combination of primary and secondary treatment plants to reduce BOD and suspended solids significantly, with a small reduction of color, AOX and COD. Though tertiary treatment techniques are quite efficient for removal of AOX and color loads, yet being expensive it is not viable for Indian paper mills under the present operating conditions.

Considering all above aspects, it can be safely concluded that to minimize formation and discharge of toxic substances, the best way is to adopt Inplant measures and process modifications.

1.6 APPLICATIONS OF PERSULPHATE

Sodium persulphate is a strong oxidizing agent and finds extensive applications in many industrial processes including paper industry. The following examples further illustrate the chemical versatility of persulphates (185)

- **Polymerization** - Persulfates are used as initiators for emulsion polymerization reactions in the preparation of acrylics, polyvinyl chlorides, polystyrenes and neoprene, initiators in polymeric concrete formulations and polymeric coating of graphite filaments.

- **Oxidation** - Persulfates are important oxidants in plating and coating processes, cleaning and microetching printed circuit boards, in preparation of aldehydes, ketones, carboxylic acids, quinones and a variety of other compounds. The cosmetic industry has developed formulations which use persulfates to boost hair bleaching performance.
- **Other applications** - Persulfates are used in the preparation of dispersants for ink jetting and toner formulations. FMC Corporation developed a process using ammonium and sodium persulfates to prepare peroxymonosulfate solutions. This patented process allows fast, efficient, on-site production of an alternative to Caro's acid and potassium caroate. Persulfates are used in many photographic applications, including bleaching solutions, solution regeneration, equipment cleaning and wastewater treatment. In textile industry, ammonium and sodium persulfates are used in the desizing and bleaching of textiles and the development of dyestuff.
- **In pulp and paper industry** - Persulfates are used in the sizing of paper, preparation of binders and coatings and production of special papers. An activated alkali metal persulfates effectively repulps neutral/alkaline wet strength broke and decolorizes dyes and optical brightener.

1.7 STATEMENT OF THE PROBLEM

Bleach plant effluent contains high levels of chloroorganics making the effluent toxic and perhaps bioaccumulating. These effluents also have high AOX, Color, BOD and COD loads. Today the pulp and paper industry is undergoing pressures from authorities, consumers and environment groups to reduce the effluent loads from the mills (97). The large integrated pulp and paper mills in India are using forest based materials for papermaking where as small and medium based are dependent on non-wood or agro residue raw materials for their pulp manufacturing. But in all these sectors, still conventional pulping and bleaching technologies are employed, as modern technologies developed in Western countries are prohibitively expensive for Indian mills, particularly because the production technologies applied in these mills are mostly old and poorly maintained (162).

The bleaching process used by Indian Paper mills is chlorination, followed by alkali extraction and calcium hypochlorite. The bleaching sequences include CEH, CEHH, CE_PHH, CE_OHH. The oxygen delignification as a prebleaching stage is attempted by some mills. Use of chlorine dioxide, hydrogen peroxide and oxygen reinforced alkali extraction is limited to a few large mills which are producing rayon grade pulp and high brightness quality pulp. An estimate shows that approximately 2.5 million tonnes of chemical pulp are produced in India. 60% of this is high brightness bleach pulp, mostly bleached by chlorine and chlorine based chemicals (113).

Oxygen prebleaching is known to reduce the residual lignin content to about 45 - 50% hence, reduces the bleach chemical consumption, COD, Color, BOD and AOX. But the equipment needed is expensive. Small scale mills without chemical recovery are more polluting than large mills and cannot make huge investments. So oxygen delignification is impediment for small mills. Hence for small mills alternatives have to be tried which can reduce AOX levels to CREP stipulations. Also in large scale mills where one or two oxygen stage or enzymatic prebleaching is used, the possibility of persulphate step as an alternative needs to be explored. A preliminary study reported by Wong (182) shows that persulphate can be used as prebleaching agent. In this study persulphate made by a electrochemical process was tried as prebleaching agent on a softwood kraft pulp. It is planned to explore the possibility of using sodium persulphate as prebleaching agent in conventional CEH and ECF bleaching sequences. Three different chemical pulps, (wheat straw soda, mixed hardwood kraft pulp and bagasse kraft pulp) have been chosen for this study. The objectives formulated for the study are:

1. To optimize conditions of persulphate (Px) and persulphate-peroxide (PxP) prebleaching. The optimization has been done based on drop in residual lignin (kappa number) and pulp viscosity (CED).
2. To compare the performance of persulphate (Px), persulphate-peroxide (PxP) and oxygen pretreatments followed by CEH and DED sequences with regard to:
    - Bleach chemical consumption
    - Pollution load generation
    - Mechanical strength properties of paper produced
    - Bleaching chemical costs
3. To study & compare the generation of chlorophenolic compounds during persulphate (Px), persulphate-peroxide (PxP) and oxygen pretreatments followed by CEH and DED bleaching sequences. This study has been performed with wheat straw pulp.

CHAPTER 2

Chapter 2

MATERIALS AND METHODS

2.1 REAGENTS AND MATERIALS

2.1.1 Chemicals

- Sodium persulphate analytical grade (SD Fine Chemicals, India)
- GC Standards Various isomers of chlorophenols (Aldrich, USA), chloroguaiacols, chlorocatechols, chlorovanillins, chlorosyringaldehydes (all from Helix, Canada) were used as reference compounds.
- Solvents n-hexane and acetone (HPLC grade) and di-ethylether (LR grade) were used.
- Analytical grade acetic anhydride was used after redistillation.
- Other reagents used were of Laboratory grade.

2.1.2 Materials

2.1.2.1 Pulps

Unbleached Wheat Straw soda pulp (*Triticum aestivium*), Mixed Hardwood kraft pulp and Bagasse kraft pulp were procured from paper mills in India. Unbleached pulps were washed and screened in the laboratory, air dried and stored in air tight polythene bags for study.

2.2 TEST METHODS

Different standard test procedures used for the analysis of pulp and handsheets are given in Table 2.1.

- TECHNIBRITE ERIC 950 from Technibrite Corporation, USA was used for brightness measurement (166)

- BOD was estimated by Respirometric method using BOD bottles, manufactured by WTW, Germany (183)
- COD was estimated by closed reflux titrimetric method using THERMOREACTOR CR 2010 (168, 184)

Table 2.1: Standard test methods followed for analysis

Test No.	Description
SCAN C 18: 65	Disintegration of chemical pulps for testing
SCAN C 24:67	Beating of pulp in a PFI mill
SCAN C 26 :76	Forming handsheets for physical testing of pulp
T- 227 om-99	Determination of CSF, ml
T 410 om-98	Grammage of paper and paperboard (weight per unit area)
SCAN C 15: 62	Viscosity of cellulose in cupriethylenediamine solution (CED)
SCAN C16:6	Preparation of cupriethylenediamine(CED) solution
T230 om-94	Viscosity of pulp (capillary viscometer method)
T-236	Kappa number of pulp
T-403	Bursting strength of paper
T-404	Tensile breaking length & elongation of paper and paperboard (Using Pendulum Type Tester)
T-414om-98	Internal tearing resistance of paper (Elmendorf type method)
ISO Standard 2469	Brightness of pulp
T 610 om-87	Preparation of indicators and standard solutions

2.3 TEST PROCEDURES

2.3.1 Analysis of Bleach Liquor

2.3.1.1 Hypochlorite - In 10 ml of diluted bleach liquor, 10 ml of 10% Potassium iodide and 10 ml of 10% of acetic acid were added. This solution was titrated with standard 0.1N sodium thiosulphate solution with 0.5% starch as indicator. The end point was blue to colorless.

The active chlorine (gpl) was calculated = Normality of bleaching liquor X 35.5

2.3.1.2 Sodium chlorite - 20 gpl solution of sodium chlorite was made and this solution was titrated by same procedure as used for analysis for calcium hypochlorite solution.

2.3.2 Analysis of Residual Chlorine

Same procedure as described earlier was used except volume of spent bleach liquor was increased to 100 ml and titrated with standard 0.1 N sodium thiosulphate solution (85)

2.3.3 Analysis of H_2O_2 Solution

10 ml of H_2O_2 solution was diluted and was made upto 250 ml in a volumetric flask. Now 5 ml of this diluted solution was taken. 10 ml of 10% KI, 10 ml 4N H_2SO_4 and 1 ml of 1% ammonium molybdate were added. This solution was titrated with standard 0.1N $Na_2S_2O_3$ solution with 0.5% starch as an indicator (175). The end point was blue to colorless.

The concentration of H_2O_2 solution = Normality of H_2O_2 solution X 34

2.3.4 Analysis of Sodium Persulphate

Ferrous ammonium sulphate (25ml) was standardized with standard 0.02M $KMnO_4$ solution in acidic media. ($KMnO_4$ was standardized with sodium oxalate method). To 25ml of 0.1M Ferrous ammonium sulphate was added 25ml of 0.5M H_2SO_4 and the resulting solution was titrated with 0.02M $KMnO_4$ solution till the appearance of faint pink color which marks the endpoint. To 3ml of 100gpl sodium persulphate solution, add 47ml distilled water, 5ml phosphoric acid followed by 10ml of 2.5M H_2SO_4 and 50ml of 0.1M Ferrous ammonium sulphate. After 5 minutes solution is titrated with standardized 0.02M $KMnO_4$ till the appearance of faint pink color at the end point (175).

Strength of sodium persulphate = Normality of sodium persulphate X 118.95

2.3.5 Disintegration of Pulps

Before bleaching and oxygen delignification the air-dried pulp was disintegrated to break the fiber bundles and lumps. Air dried pulp was soaked in water overnight and then disintegrated in a laboratory disintegrator (maximum 25g OD pulp was disintegrated in one run) for 2 minutes. Then the water was drained on a screen and the pulp was squeezed and kept in refrigerator in plastic bags for not more than 7 days. This wet pulp was used for further bleaching experiments.

2.3.6 Preparation of Sheets for Brightness and Kappa Number Determination

The consistency of the disintegrated pulp was adjusted to 1%. The pulp suspension was then transferred into a Swedish hand sheet former. Water was then drained from the hand sheet former, so as to give sheet of about 5g OD weight. The pulp was picked with the help of two blotting papers and then pressed with a metallic plate and air-dried. The sheets were protected against dirt and dust. The brightness was measured within 24 hours after drying. For kappa number determination the sheets were stored in polythene bags.

2.3.7 Oxygen Delignification

Oxygen delignification was performed in autoclaves (which could hold about 100g of wet pulp) revolving in hot oil bath. NaOH (40 gpl) at various doses and $MgSO_4$ (0.2g/100g OD pulp) were mixed with the disintegrated wet pulp and pulp consistency after mixing was adjusted to 10%. These pulps were then transferred into autoclaves mounted on stands. After expelling air, autoclaves were filled with oxygen to a pressure of $6kg/cm^2$ which was fed into the autoclaves through the top valve. The autoclaves were checked for leakage and then placed in glycol bath preheated at 100°C for a period of 75 minutes (85).

The autoclaves were taken out and cooled to room temperature. Pulp was then taken out and washed on a screen, excess water was drained out by squeezing. The pulp was stored in polythene bags for further bleaching experiments. The oxygen delignification optimization was targeted at a kappa number drop between 40-50% without sacrificing much on pulp yield and viscosity. The oxygen and non-oxygen pulps were characterized for kappa number, viscosity and brightness. The ranges of variables studied are given in the Table 2.2.

2.3.8 Persulphate and Persulphate-Peroxide Pretreatments

Two pretreatment methods were tried namely, sodium persulphate designated as (Px) and sodium persulphate with hydrogen peroxide designated as (PxP). Optimization was tried by changing one process parameter at a time and keeping the other parameters constant and reduction in the amount of residual lignin (Kappa number) and viscosity (CED) were used as indicators of process selectivity. Parameters studied were chemical dose, temperature, time, pH and pulp protectors in both the processes. The impact of one parameter was studied maintaining the other parameter constant. Thus, for all the three raw materials set of optimized conditions were formulated, which were carried throughout all pretreatment studies. Variables studied are given in Table 2.2.

Table 2.2: Variables studied in optimization of (Px), (PxP) and oxygen pretreatments.

Optimization	Variables studied	Pulps		
		Wheat straw	Mixed hardwood	Bagasse
Oxygen	Alkali charge (kg/t)	30-60	10-30	4-20
Persulphate (Px)	Persulphate dose (kg/t)	20-160	20-160	20-160
	NaOH charge (kg/t)	20-100	20-100	20-100
	EDTA charge (kg/t)	2-5	2-5	2-5
	Temperature (°C)	40-70	40-70	40-70
	Time (hours)	1 - 4	1 - 4	1 - 4
Persulphate-peroxide (PxP)	Persulphate dose (kg/t)	25-50	25-50	25-50
	Peroxide charge (kg/t)	5-8	5-8	5-8
	Temperature (°C)	40-70	40-70	40-70
	Time (hours)	1 - 4	1 - 4	1 - 4

2.3.9 Bleaching of Pulps

All the bleaching steps were performed in polythene bags, in temperature controlled water bath except chlorination that was performed in plastic bottle at ambient temperature. The pulp and the chemicals were well kneaded at desired pulp consistency by hand mixing or shaking the bottle from time to time during bleaching. Unbleached pulp equivalent to 25g OD was taken and all bleaching experiments were conducted in duplicates. The chlorine demand was calculated from the following formula:

Chlorine demand (%) = 0.25 X Kappa no.

Of the total bleach chemical dose, 70% was charged in C stage and remaining 30% was charged in H stage. Alkali was charged according to given formula:

Alkali charge (%) = ½ C stage charge (%) + 0.3

Similarly in D_1 stage 70% bleach chemical was charged and in D_2 30% whereas alkali charge was also on similar lines.

2.3.9.1 Chlorination (C) Stage Bleaching

The disintegrated pulp suspension was diluted and the pH of the suspension was reduced to pH 2 with calculated amount of dilute H_2SO_4 so that the pH remains around 2 and pulp consistency 3% even after adding bleach liquor to the pulp suspension. The bleach liquor was transferred to pulp suspension in bottle through a funnel. Funnel was joined to a rubber tube which reached the bottom of bottle, to prevent any leakage of chlorine gas. Then the bottle was capped tightly and contents were well shaken. The chlorination was carried out at ambient temperature. After 45minutes of pulp chlorination, the pulp was washed and the effluent collected for residual chlorine and environmental parameters analysis.

2.3.9.2 Alkaline Extraction (E)

The required amount of alkali (NaOH) and water were mixed with the pulp suspension to give a pulp consistency of 10% in a polythene bag. The bag was placed in a waterbath maintained at 70°C.The pulp was kneaded from time to time for proper mixing. The end pH was recorded. After alkali extraction the pulp was washed and the effluent was collected for further analysis.

2.3.9.3 Hypochlorite (H) Stage Bleaching

The washed alkali extracted pulp was mixed with requisite amount of bleach liquor and water so as to give 10% pulp consistency. The initial pH was adjusted between 10 -11. After each half an hour, pH of the pulp was checked and adjusted to pH 10.5 by dilute NaOH so as to give a final end pH 10 -10.5. The contents were transferred to plastic bag that was placed in a water bath at 40°C. After 3.5h the bag was removed, the pulp washed and the effluent analyzed for residual chlorine and environmental parameters.

2.3.9.4 Chlorine Dioxide (D) Stage Bleaching

Calculated amount of $NaClO_2$ solution and water was mixed with disintegrated pulp so that the starting pH was around 5 and the pulp consistency was 10% at which the bleaching was performed for 1.5 h in plastic bags kept in water bath at 70°C. In D_2 stage, all the other parameters were same, only retention time was increased to 3 h. The pulp was mixed from time to time. The plastic bag was removed and the pulp was washed. The residual chlorine dioxide, end pH and the environmental parameters were measured after the bleaching.

2.3.9.5 Persulphate (Px) Bleaching

The required amount of sodium persulphate was charged in disintegrated pulp sample along with NaOH and EDTA, water was mixed to make consistency 10%. The plastic bags were kept in water bath at 40°C. At the completion of 4h plastic bags were removed, pulp was washed and effluent was collected for residual chemical analysis, end pH and environmental parameters.

2.3.9.6 Persulphate-Peroxide (PxP) Bleaching

Calculated amount of sodium persulphate was mixed along with hydrogen peroxide, EDTA, $MgSO_4$ and NaOH were added to disintegrated pulp, water was added to make consistency 10%. The plastic bags containing pulp were kept in water bath at temperature 40°C and pulp was shaken several times. After completion of 4h pulp sample was taken out of water bath and the pulp was washed. Effluent was collected for analysis of COD, BOD and residual chemical.

The untreated, oxygen pretreated, (Px) and (PxP) pretreated pulps (wheat straw and mixed hardwood) were bleached to 80% ISO brightness and bagasse pulp to 85% ISO brightness using different sequences like CEH and DED.

All the bleaching experiments were performed in duplicates and the brightness measured as % ISO.

Various active chlorine doses given to achieve the target brightness levels (80% ISO for wheat straw and mixed hardwood pulps and 85% ISO for bagasse pulp) are given in Table 2.3.

Table 2.3: Bleach chemical (as aCl) charged to achieve target brightness

Pulp type	Bleaching sequence	Bleach chemical charge (as aCl kg/t)		
		Wheat straw	Mixed hardwood	Bagasse
Untreated	CEH	59.3 – 65	35 – 42.2	20 – 40
	DED	90 -100	40 – 80	60– 80
O_2 pretreated	CEH	25 - 31	20 - 25	9 – 15
	DED	40 – 75	20 - 27	30 – 40
(Px) pretreated	CEH	46.7 – 52	28 – 36.2	12 - 30
	DED	60 – 80	35 - 50	40 – 60
(PxP) pretreated	CEH	25 - 40	20 – 35	8 -15
	DED	50 – 75	23– 27	35 – 40

2.4 CHARACTERIZATION OF BLEACHING EFFLUENTS

Bleach plant effluents collected after each stage of bleaching were transferred to 2 liters volumetric flask, mixed, volume made to 2 liters and were analyzed for BOD, COD, color and chlorophenols in the laboratory. 100ml of combined effluent was adjusted to pH below 2 by HNO_3 and then stored in 100ml bottles in refrigerator for AOX analysis. The AOX was got analyzed from an outside agency.

2.4.1 Color measurement

2.4.1.1 Preparation of standard color solution of 2500 Pt-Co units.

250 mg of platinum (purity 99.99%) was dissolved in hot aqua-regia. This solution was heated to dryness to remove nitric acid (as oxides of nitrogen) by repeated evaporation and addition of fresh quantity of concentrated HCl. The

residue was dissolved in distilled water and thereafter, 500 mg of $CoCl_2.6H_2O$ (equivalent to 125 mg Co) was added along with 5 ml of concentrated HCl. The total volume of the solution was made up to 100 ml with distilled water to yield a standard solution of 2500 Pt-Co color units (29).

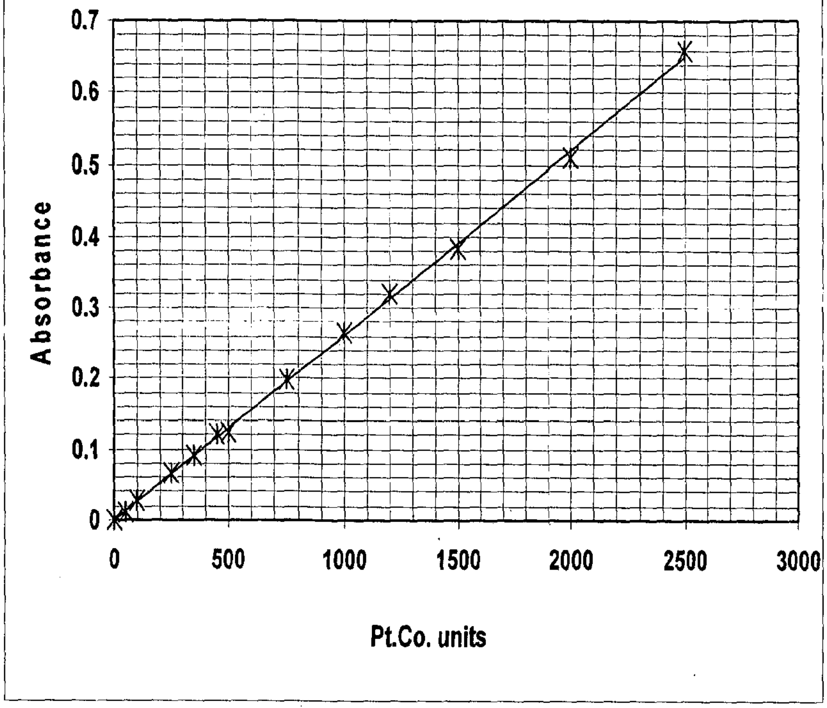
2.4.1.2 Color measurement

Standard solutions of 50, 250, 350, 500, 1000, 1500, 2000 Pt-Co units were prepared by diluting 0.5, 2.5, 3.5, 5, 10, 15 and 20 ml of standard stock solution to 25ml in a volumetric flask. Absorbance of different standard solutions (Table 2.4) was determined at 465nm on Systronics spectrophotometer model UV Visible 118 (163) and calibration curve was plotted as shown in Figure 2.4 This curve was used to determine the color of the effluent. The pH of effluent was adjusted to 7.6 and then the suspended particles were removed by centrifuging the effluent for 5 minutes at 1500rpm. The absorbance of the solution was determined at 465nm and color was calculated from the calibration curve.

Table 2.4: Absorbance of standard color solutions

Pt-Co units	Absorbance
50	0.012
100	0.027
250	0.066
350	0.09
450	0.122
500	0.125
750	0.198
1000	0.264
1200	0.319
1500	0.382
2000	0.51
2500	0.66

Figure 2.1 Calibration curve used for color measurement



2.4.2 Analysis of Various Chlorophenols

Modern analytical methods such as, High Performance Liquid Chromatography and Gas Chromatography alone or in combination with Mass Spectrometry have been used for determining chlorophenolic compounds in the pulp and paper effluents. Of these methods, GC or GC-MS are the more commonly used techniques. In GC, detection of the chlorophenols has been done using Flame Ionization Detector (FID).

In principle, solvent extraction should provide a simpler and faster method for isolation of chlorophenols from waste water sample. Mainly, two extraction procedures are used today for chlorophenols analysis in pulp and paper mill effluent. One proposed by BCRC (British Columbia Research Canada) and another by Lindstrom *et.al.* (93). For present study, extraction of various chlorophenolic compounds has been done, as per procedure suggested by Lindstrom *et.al.* using diethyl ether (93).

The chlorophenols are converted to readily volatilized acetyl derivatives prior to GC analysis. Different procedures for derivatising phenols directly in the water sample have been suggested including extractive alkylation with pentafluorobenzyl bromide and acylation with tri-chloroacetic anhydride, heptafluorobutyl anhydride or acetic anhydride. For the present study, acetylation was done with acetic anhydride based on procedure suggested by Abrahamsson and Xie (1, 151)

2.4.2.1 GC Conditions

Shimadzu Gas chromatograph model GC-9A was used to analyze various chlorophenolics like chlorophenols, chloroguaiacols, chlorocatechols, chlorovanillins, chlorosyringols and chlorosyringaldehydes. The separation of the acetyl derivative was achieved on Ulbon HR-1 glass capillary column (30m× 0.32mm ID). The injection was splitless for two minutes. The GC conditions used are given in the Table 2.5

2.4.2.2 Derivatization procedure

4.5ml of the sample of standard chlorophenolics was taken in a PTFE lined screw capped glass tube and 0.5ml of buffer solution of 0.5M Na_2HPO_4 was added. 1ml of n-hexane and 0.05ml of acetic anhydride were added to derivatize and extract the chlorophenolics. The mixture was shaken for 3 minutes and 1μl of acetyl derivative taken from the hexane layer through a syringe, was injected into the GC column (151).

2.4.2.3 Retention time Determination

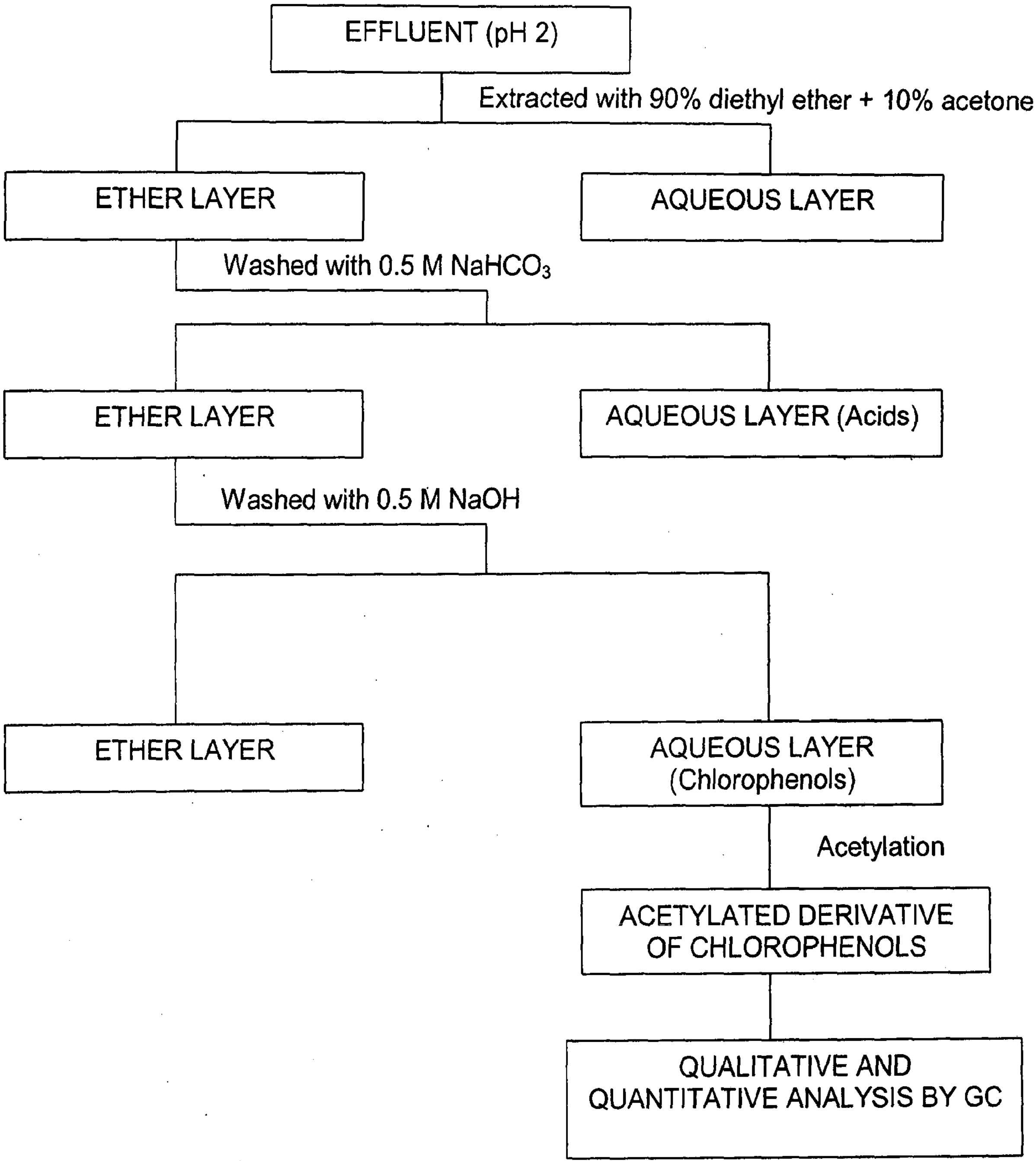
Standard solutions of various chlorophenolic compounds (20-30 mg/l) were prepared in 10% acetone water. 1ml of the sample was derivatized and 1µl of the hexane extract was injected into the column. The retention time was recorded.

2.4.2.4 Separation of Chlorophenols from the Effluent

The procedure suggested by Lindstrom *et.al.* (93) was followed to achieve the separation of chlorophenolics from the effluents. A schematic presentation of the method followed is depicted in the flow chart (Figure 2.2). Two liters of C-stage, two liters of E-stage and two liters of H-stage effluent were mixed and then 1.8 liters of combined effluent was taken. The pH of the effluent was adjusted to 2 with dilute H_2SO_4. Similar volumes were considered for effluent from DED sequence. Then the effluent was transferred to a screw capped conical flask and extracted for 48 h with 400ml of 90% ethyl ether and 10% acetone mixture per liter of effluent. The emulsion formed in ether layer was broken by using a heat gun. Then the whole ethereal extract of the effluents was transferred into another separating funnel and shaken with 5ml of 0.5M $NaHCO_3$ solution to remove acidic impurities. Thereafter, the ether layer was shaken with 5ml of 0.5M NaOH to extract the chlorophenolics.

Figure 2.2

Separation of phenolic compounds from effluents



The emulsion formed in ether layer was broken by using a heat gun. Then the whole ethereal extract of the effluents was transferred into another separating funnel and shaken with 5ml of 0.5M $NaHCO_3$ solution to remove acidic impurities.

Thereafter, the ether layer was shaken with 5ml of 0.5M NaOH to extract the chlorophenolics. Aqueous NaOH layer, which contained chlorophenolics from bleaching effluent, was separated and washed with 10ml of fresh diethyl ether to remove the neutrals. The extracted chlorophenolics were derivatized as under: 4ml of the extracted sample was diluted to 4.5ml with water and was acetylated using 0.1ml of the acetic anhydride. The remaining process was same as per 2.4.2.2 procedure. 0.5μl of the derivatized sample was injected into column for identification and quantitative analysis of chlorophenolics.

Table 2.5: GC conditions for the separation of chlorophenols

Parameters	
Detector	FID
Detector range	10°
Carrier gas (N_2) flow rate	20ml/min.
Injection and Detector temperature	275°C
Column temperature	80°C for 3 min.
	80°C-160° at 2°C/min.
	160°C for 5 min.
	160°C - 260°C at 10°C/min.
	260°C for 15 min.
Injection (splitless)	2 min.
Sample size	0.5 μl
Chart speed	2 cm/min

2.4.2.5 Quantitative Analysis of Various Pollutants

The Response Factor and Extraction Efficiency of various chlorophenols were determined for quantitative analysis of the chlorophenolics.

- **Response factor**

1ml of the standard solution of chlorophenol was deriavatized as per procedure described under 2.4.2.2. 1μl of the n-hexane layer was injected into the column. The area of the peak was recorded and the Response Factor (RF) was calculated as under:

$$RF = \frac{\text{Area of the peak}}{\text{Wt. of the sample injected}}$$

- **Extraction Efficiency**

For the extraction of various standard chlorophenolics, 1ml of standard solution of various chlorophenols was diluted to 1liter with distilled water. The pH of the solution was adjusted to 2. The solution was then extracted with 400ml of 90% ethyl ether and 10% acetone mixture for 48 hours and derivatized as acetyl derivative as described under 2.4.2.2 for chlorophenolics. 1µl of the derivatized sample was injected into the column and the peak area was recorded. From the area of peak the quantity of chlorophenolics present in the extracted sample was determined. The percentage extraction efficiency was calculated as under:

$$\text{Extraction Efficiency (\%)} = \frac{\text{Quantity in the extracted sample}}{\text{Quantity in the sample before extraction}} \times 100$$

The values of retention time, response factors and extraction efficiency values of various chlorophenolics determined are given in Table 2.6. These values are the average of minimum three values. The retention value indicates that most of the chlorophenolics studied can be resolved on capillary column of HR-1. The various chlorophenols are identified by matching time (±0.1min) of a component with that of pure standard.

2.5 STRENGTH PROPERTIES

The unbleached, (Px) pretreated, (PxP) pretreated pulps and oxygen pretreated and bleached pulps were beaten in a PFI mill to a CSF of 300±20. Handsheets (60±2gsm) were made in Swedish hand sheet former. Air-dried sheets were used to determine the various strength (Tensile, tear, burst and double fold) properties as per test procedures given in Table 2.1.

Table 2.6: Retention time, Extraction efficiency and Response factors of various chlorophenolics compounds

S. No.	Chlorophenolics	Retention time (minutes)	Extraction efficiency (%)	Response factor (pg)
1	2,4-Dichlorophenol	7.26	34	1.67
2	2,5-Dichlorophenol	7.43	73	1.48
3	2,3-Dichlorophenol	7.64	98	2.33
4	3-Chloroguaiacol	8.12	59	1.96
5	2,6-Dichlorophenol	8.52	35	1.96
6	4-Chlorophenol	8.87	95	0.44
7	3-Chlorophenol	8.97	42	1.05
8	4-Chloroguaiacol	11.53	93	3.50
9	5-Chloroguaiacol	12.15	102	1.52
10	6-Chloroguaiacol	13.44	98	0.88
11	2-Chlorophenol	14.29	14	2.26
12	2,3,5-Trichlorophenol	14.58	89	3.28
13	2,4,6-Trichlorophenol	15.17	31	1.73
14	2,4,5-Trichlorophenol	15.68	63	1.28
15	3,5-Dichloroguaiacol	15.70	50	2.44
16	2,3,4-Trichlorophenol	16.02	85	1.68
17	2,3,6-Trichlorophenol	16.79	72	3.40
18	3,6-Dichloroguaiacol	17.17	105	2.57
19	3,4-Dichloroguaiacol	17.22	103	1.97
20	3,4-Dichlorocatechol	19.40	76	1.12
21	3,4-Dichlorophenol	20.12	106	1.35
22	4,5-Dichloroguaiacol	22.04	98	2.58
23	4,6-Dichloroguaiacol	22.27	52	2.10
24	5-Chlorovanillin	23.54	47	0.31
25	5,6-Dichloroguaiacol	24.34	57	1.69
26	4-Chlorocatechol	24.94	87	0.24
27	3,5-Dichlorocatechol	25.52	08	0.53
28	2,3,5,6-Tetrechlorophenol	25.65	53	2.91
29	2,3,4,5-Tetrachlorophenol	25.98	51	3.45
30	2,3,4,6-Tetrachlorophenol	26.08	76	1.48
31	3,5,6-Trichloroguaiacol	26.80	68	2.18
32	3,4,6-Trichloroguaiacol	27.15	81	1.71
33	3,5-Dichlorosyringol	27.45	57	2.63
34	3,4,5-Trichloroguaiacol	27.71	31	2.54
35	3-Chlorocatechol	28.20	103	0.30
36	6-Chlorovanillin	28.48	38	1.23
37	3,6-Dichlorocatechol	30.61	81	0.42
38	4,5,6-Trichloroguaiacol	34.16	99	1.12
39	2-Chlorosyringaldehyde	35.10	34	1.16
40	4,5-Dichlorocatechol	35.57	33	1.63
41	Pentachlorophenol	36.63	100	0.27
42	3,4,5-Trichlorocatechol	37.15	75	0.84
43	Tetrachloroguaiacol	38.21	49	0.87
44	Trichlorosyringol	39.29	17	1.14
45	3,4,6-Trichlorocatechol	40.62	76	0.48
46	2,6-Dichlorosyringaldehyde	40.74	100	0.38
47	5,6-Dichlorovanillin	41.80	100	0.44
48	Tetrachlorocatechol	43.11	31	0.54

CHAPTER 3

Chapter 3

PERSULPHATE-PEROXIDE PREBLEACHING OF WHEAT STRAW SODA, MIXED HARDWOOD KRAFT AND BAGASSE KRAFT PULPS

3.1 INTRODUCTION

In the developed economies pulp and paper industries has been continually investing in the cleaner manufacturing technologies since early 80's. New technologies have emerged in the areas of oxygen delignification, ECF and TCF bleaching sequences, recovery of solids and almost zero discharge concept (58). Delignification achieved during early stages of bleaching is a continuation of pulping reactions employing lignin specific chemicals to preserve the yield and strength attributes of unbleached pulp (68). Aim of all these developments has been to reduce pollutant loads of suspended solids, BOD, COD, organic chlorine compounds (AOX) and wastewater discharge (58).

To reduce the use of chlorine and chlorine containing compounds which are most polluting, industries/researches have developed alternative bleaching methods which are oxygen, ozone, peroxide etc. but these are quite expensive to adopt, since they require lots of changes in equipment hence are only viable to large paper mills (97).

The major objective of prebleaching of pulps has been directed towards reducing the incoming kappa number of the pulp, so as to reduce the bleach chemical demand in bleaching process thereby reducing the adsorbable organic halides (AOX) content of the effluent and making the effluent amenable to biological treatment.

Sodium persulphate was chosen as prebleaching agent for bleaching of hardwood pulp and agro residue pulps. Two types of pretreatment was performed namely persulphate prebleaching, designated as (Px) in which only sodium persulphate was used, while in the other pretreatment, sodium persulphate and hydrogen peroxide were used together as a prebleaching agent and this stage was designated as (PxP).

The impact of the various operating parameters has been studied to optimize the pretreatment conditions. Two parameters i.e. pulp kappa number and pulp viscosity were used for optimization studies i.e. maximum drop in kappa number at minimum or acceptable drop in pulp viscosity.

3.2 MECHANISM OF PREBLEACHING

3.2.1 Oxidation of Lignin in Prebleaching

Lignin as such is a complex chemical formed by polymerization of 5 types of monomers. Main functional groups of lignin to name a few are phenolic hydroxyl group, methoxyl group and unsaturated propionic group in aromatic ring (139). After kraft pulping, the content of phenolic hydroxyl group in residual lignin has increased to ~ 30 phenolic hydroxyl groups per 100 phenyl propane units (48). From reactivity point of view, the most important functional group in kraft lignin is free phenolic group. In most chemical reactions on lignin, phenolic phenyl propane units are preferentially attacked. In addition, the phenolic group is able to ionize under alkaline conditions improving the aqueous solubility of lignin (137). The phenolic group is the only type of functional group, except for a small number of carboxylic acid groups, conferring water solubility on unbleached kraft lignin (167).

The predominant mode of lignin removal in bleaching is the oxidation of lignin. Acidic and carbonyl groups are formed which increase the water solubility of lignin polymer and induce cleavage of carbon-carbon and carbon-oxygen bonds. Muconic acids are formed when aromatic rings are degraded and aliphatic acids produced when carbonyl groups in the side chains are oxidized (167). The dissolved lignin from bleaching stages always contained a higher amount of carboxyl groups than did residual lignin in the pulp (155).

3.2.2 Persulphate as an Oxidizing Agent

Sodium persulphate or sodium peroxydisulphate ($Na_2S_2O_8$) is a stable, highly soluble, monoclinic crystalline white solid with no odor, which on activation generates the persulphate radical. Its crystal density (g/cc) is 2.59 with loose bulk density being 1.12g/cc and active oxygen content 6.68%. The oral LD_{50} of sodium persulphate in rats is 895 mg/kg (76). Persulphates are oxidizing chemicals that require careful attention to all aspects of handling and use.

3.2.3 Oxidation Chemistry

The persulphate anion is the most powerful oxidant of the peroxygen family of compounds. The electromotive force data listed below compares three commonly used peroxygens.

$S_2O_8^{2-} + 2H^+ + 2e^- \rightarrow 2HSO_4^-$ $E = 2.12V$

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $E = 1.77V$

$HSO_5^- + 2H^+ + 2e^- \rightarrow HSO_4^- + H_2O$ $E = 1.44V$

Many metals are oxidized by persulphate to form soluble metal sulphates, for example, copper:

$Cu + S_2O_8^{2-} \rightarrow CuSO_4 + SO_4^{2-}$

Under certain circumstances, hydrolysis of the persulphate anion will yield the bisulphate anion and hydrogen peroxide, a kinetically faster oxidant than persulphate:

$$S_2O_8^{2-} + 2H_2O \xrightarrow{H^+} 2HSO_4^{2-} + H_2O_2$$

Another reaction of importance is the acid–catalyzed hydrolysis of persulphate to form peroxymonosulphate anion. Fast, high-temperature, acid hydrolysis followed by thermal quenching will yield solutions of peroxymonosulfate:

$$S_2O_8^{2-} + H_2O \xrightarrow{H^+} HSO_4^- + HSO_5^-$$

The resulting solution is a useful replacement for Caro's acid, H_2SO_5 and potassium caroate, $KHSO_5$.

Reactions at different pH:

Neutral (pH 3 to 7)

$$S_2O_8^{2-} + H_2O \rightarrow 2HSO_4^- + \frac{1}{2}O_2$$

Dilute acid (pH>0.3; [H$^+$] <0.5M)

$$S_2O_8^{2-} + 2H_2O \rightarrow 2HSO_4^- + H_2O_2$$

Strong acid ([H$^+$]>0.5M)

$$S_2O_8^{2-} + H_2O \xrightarrow{H^+} HSO_4^- + HSO_5^-$$

Alkaline (pH>13)

$$S_2O_8^{2-} + OH^- \rightarrow HSO_4^- + SO_4^{2-} + \frac{1}{2} O_2$$

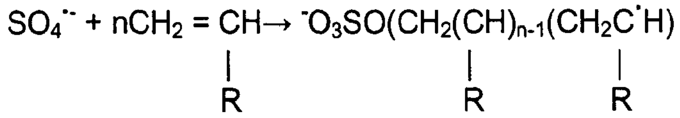
3.2.4 Free Radical Chemistry

Persulphates produce free radicals in many diverse reaction situations.

When solutions of the persulphates are heated, free radicals are formed:

$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{\cdot -}$$

In the presence of suitable monomers, the radical anions act as polymerization initiators to produce polymer molecules:



$$SO_4^{\cdot -} + nCH_2 = \underset{\substack{|\\ R}}{CH} \rightarrow {}^{-}O_3SO(CH_2\underset{\substack{|\\ R}}{(CH)}_{n-1}(CH_2\underset{\substack{|\\ R}}{C^{\cdot}}H)$$

Free radicals suitable as polymerization initiators are also generated in the presence of reducing agents, for example, the bisulphite anion:

$$S_2O_8^{2-} + HSO_3^{-} + ½O_2 \rightarrow HSO_4^{-} + 2SO_4^{\cdot -}$$

Free radicals can also be generated in the presence of transition metals:

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\cdot -}$$

and mercaptans:

$$S_2O_8^{2-} + 2RSH \rightarrow 2HSO_4^{-} + 2RS^{\cdot}$$

3.2.5 Sodium Persulphate Synthesis

- Addition of SO_3 to H_2O_2 generates the formulae of other oxoacids as follows: (147)

$$H_2O_2 \xrightarrow{SO_3} \underset{\text{Peroxomono-sulphuric}}{H_2SO_5} \xrightarrow{SO_3} \underset{\text{peroxodisulphuric}}{H_2S_2O_8}$$

- Wong (182) has developed an economical method for the manufacture of persulphate using the surplus sulphate/ sesquisulphate, generated as waste in the manufacture of chlorine dioxide, as feedstock. This study showed that persulphate can function as prebleaching agent during the bleaching of softwood kraft pulp.

$$2SO_4^{-} + 2H_2O \rightarrow S_2O_8^{-} + 2OH^{-} + H_2$$

3.3 RESULTS AND DISCUSSION

3.3.1 Persulphate (Px) Pretreatment Optimization

The impact of various pretreatment parameters has been studied by changing one parameter and maintaining the other parameters constant.

3.3.1.1 Effect of Persulphate Dose

The initial trials were made using varying dose of sodium persulphate at 70°C for 2hours. NaOH dose was kept constant i.e. 5% and pulp consistency was maintained 10%. It is seen that as persulphate dose is increased, kappa number reduces while large viscosity drop is also observed simultaneously. In wheat straw pulp as the charge is increased from 2% to 16%, kappa number is reduced from 20.9 to 13.8 respectively while viscosity is reduced from 24.3cP to 13.6cP respectively (Table 3.311). In mixed hardwood pulp, kappa number is reduced from 14.9 to 10.1 while viscosity is reduced from13.2cP to 7.4cP (Table 3.311). In bagasse pulp kappa number is reduced from 7.9 to 4.2 while viscosity is reduced from 17.9cP to 9.9cP (Table 3.311). The percentage drop in kappa number and viscosity as a function of persulphate dose for the three pulps are shown in Figures 3.311 - 3.313 and it can be stated that the drop follows the order:

Bagasse > Wheat straw > Mixed hardwood

A high dose of sodium persulphate (12%) was selected for further studies so as to optimize conditions wherein nearly 40-45% reduction in kappa number is achieved with acceptable viscosity drop so that process can be compared to oxygen delignification.

Table - 3.311: Effect of persulphate dose in (Px) prebleaching

$Na_2S_2O_8$ dose (%)	Kappa number			Viscosity (cP)		
	Wheat straw	*Mixed hardwood*	*Bagasse*	*Wheat straw*	*Mixed hardwood*	*Bagasse*
0	23.7	16.9	9.2	27.7	14.6	20.6
2	20.9	14.9	7.9	24.3	13.2	17.9
4	18.9	13.5	7.3	23.3	12.3	17.1
6	18.3	13.2	6.9	22.1	11.8	16.1
8	17.9	12.8	6.4	20.8	11.0	15.1
10	16.7	12.1	5.7	19.4	10.3	13.9
12	15.9	11.3	5.4	18.1	9.6	12.7
14	14.8	10.7	4.8	16.1	8.5	11.4
16	13.8	10.1	4.2	13.6	7.4	9.9

NaOH 5%, Temperature 70°C, RT 2h, Cy 10%

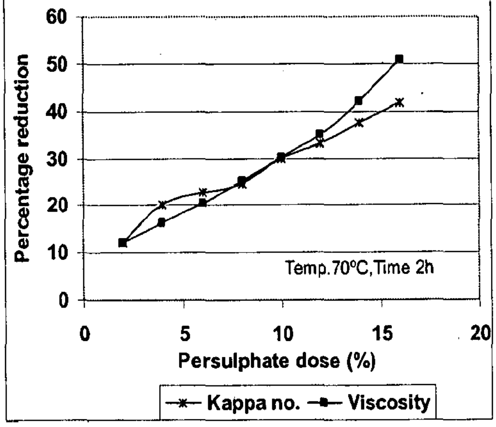


Fig.3.311 Effect of Persulphate dose on (Px) prebleaching of wheat straw pulp

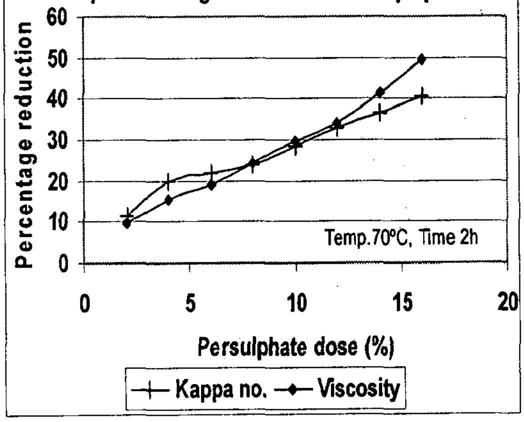


Fig. 3.312 Effect of Persulphate dose on (Px) prebleaching of mixed hardwood pulp

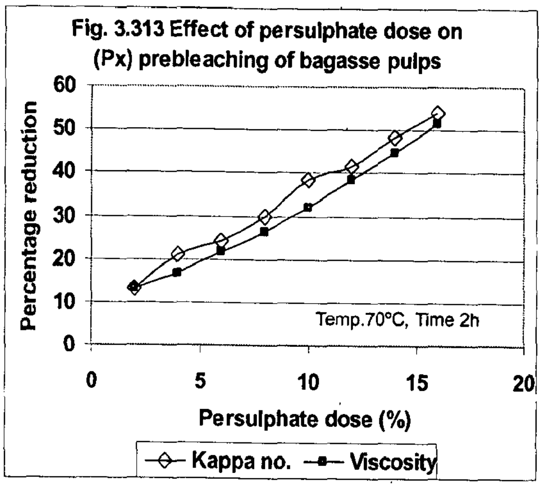


Fig. 3.313 Effect of persulphate dose on (Px) prebleaching of bagasse pulps

3.3.1.2 Effect of NaOH Dose

Higher lignin reduction is achieved at higher doses of persulphate with concurrently large drop in CED viscosity. So a high dose of persulphate was selected i.e. 12% and different doses of NaOH were charged on pulp at 10% consistency, so as to minimize viscosity drop. The results as given in the Table 3.312 indicate that as NaOH dose is increased residual lignin associated with pulp reduces and pulp viscosity is dropped progressively. The trend observed for percentage kappa number reduction is

Bagasse > Wheat straw > Mixed hardwood

Similar trend is also followed for viscosity drop (Figures 3.314 to 3.316). The results are in agreement with the reported results by Liebergott *et.al.* which show that increasing alkali concentration by increasing alkali charge at constant consistency substantially accelerates both delignification and cellulose degradation (92). Thus we can conclude that increasing persulphate dose and alkali dose increases pulp delignification and pulp degradation. 5% NaOH dose was selected as drop in kappa number is 35-40% with similar decrease in viscosity.

Table - 3.312: Effect of NaOH dose in (Px) prebleaching

NaOH dose (%)	Kappa number			Viscosity (cP)		
	Wheat straw	*Mixed hardwood*	*Bagasse*	*Wheat straw*	*Mixed hardwood*	*Bagasse*
0	23.7	16.9	9.2	27.7	14.6	20.6
2	16.8	12.0	6.5	20.2	10.8	14.7
4	16.4	11.9	6.1	18.8	10.0	13.7
5	15.9	11.3	5.4	18.1	9.6	12.7
6	15.3	11.0	4.8	15.6	8.4	11.3
8	14.8	10.7	4.6	12.8	7.0	9.3
10	13.7	10.2	3.9	11.9	6.3	8.7

$Na_2S_2O_8$ 12%, Temperature 70°C, RT 2h, Cy 10%

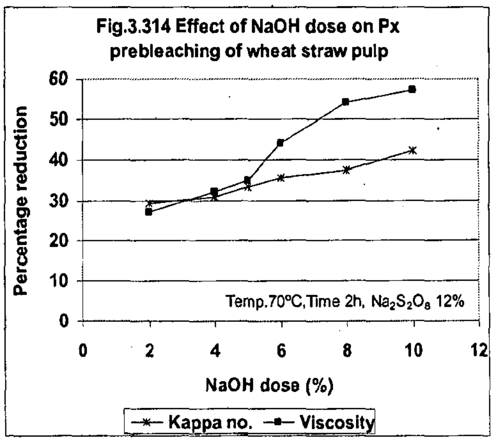


Fig.3.314 Effect of NaOH dose on Px prebleaching of wheat straw pulp

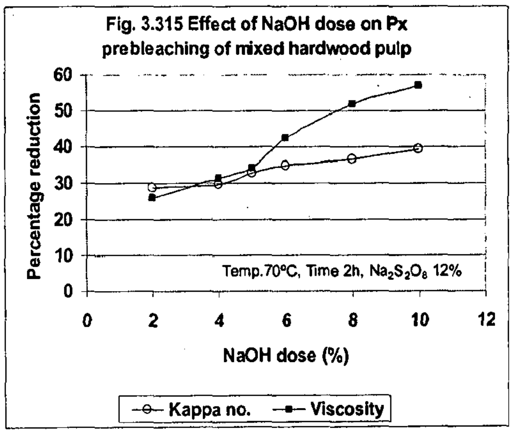


Fig. 3.315 Effect of NaOH dose on Px prebleaching of mixed hardwood pulp

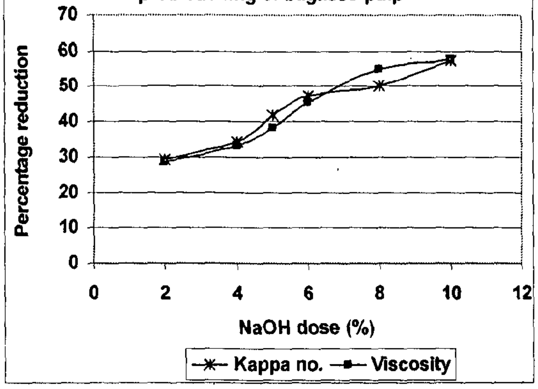


Fig. 3.316 Effect of NaOH dose on Px prebleaching of bagasse pulp

3.3.1.3 Effect of Sulfamic Acid

Sodium persulphate along with NaOH has been able to reduce the pulp kappa number by 30-50%. Simultaneously, there is a considerable reduction in pulp viscosity indicating high cellulose degradation. The rate of degradation is dependent upon temperature, so lower temperature of 40°C was attempted, with increase in the reaction time to 4 hours. The effect of sulfamic acid as a pulp protector was studied by varying its doses from 0.2-1.0% with 12% $Na_2S_2O_8$ dose and 5% NaOH dose at 10% pulp consistency. Results are given in Table 3.313 and illustrated in Figures 3.317 to 3.319. In wheat straw pulp kappa number is reduced from 16.2 to 15.1 with small increase in viscosity 18.9cP to 20.1cP while in mixed hardwood pulp, kappa number is reduced from 11.5 to 11.0 and viscosity increases from 10cP to 10.9cP and in bagasse pulp kappa number is dropped from 5.7 to 4.8 and viscosity increases from 14.2cP to 16.1cP. The Figures 3.317 to 3.319 indicate that percentage kappa number reduction follows the trend: Bagasse > Wheat straw > Mixed hardwood

While percentage viscosity drop follows the order:

Wheat straw > Mixed hardwood > Bagasse.

Hence, the results indicate that sulfamic acid is not very effective as a pulp protector at lower doses (0.2-1%) as viscosity drop is still high (20 - 27%).

Table - 3.313: Sulfamic acid as pulp protector in (Px) prebleaching

Sulfamic acid (%)	Kappa number			Viscosity (cP)		
	Wheat straw	*Mixed hardwood*	*Bagasse*	*Wheat straw*	*Mixed hardwood*	*Bagasse*
0	23.7	16.9	9.2	27.7	14.6	20.6
0.2	16.2	11.5	5.7	18.9	10.0	14.2
0.5	15.9	11.4	5.4	19.3	10.3	14.9
0.7	15.5	11.3	4.9	19.5	10.5	15.6
1.0	15.1	11.0	4.8	20.1	10.9	16.1

NaOH 5%, $Na_2S_2O_8$ 12%, Temperature 40°C, RT 4h, Cy 10%

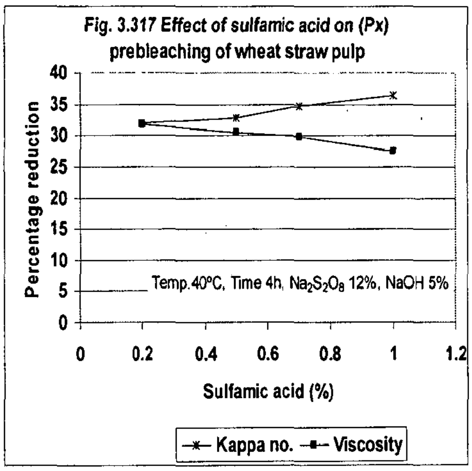


Fig. 3.317 Effect of sulfamic acid on (Px) prebleaching of wheat straw pulp

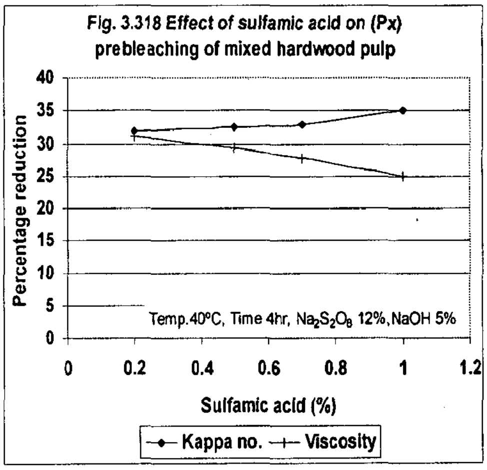


Fig. 3.318 Effect of sulfamic acid on (Px) prebleaching of mixed hardwood pulp

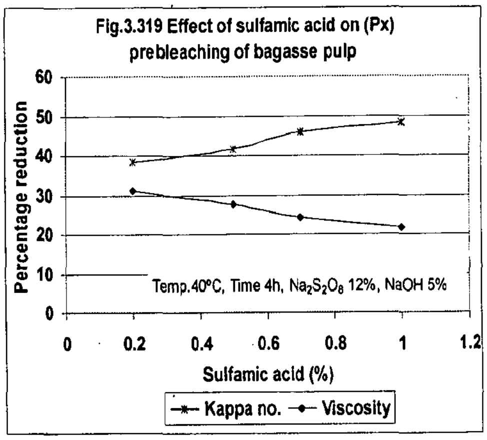


Fig.3.319 Effect of sulfamic acid on (Px) prebleaching of bagasse pulp

3.3.1.4 Effect of Sodium Persulphate Dose at 40°C

A) Without NaOH – The effect of persulphate dose without alkali addition was studied at lower temperature of 40°C. Persulphate dose is increased from 2-12% with 10% pulp consistency. The results given in the Table 3.314 show that increasing persulphate dose in absence of alkali enhances the decrease in pulp kappa number and pulp viscosity. In wheat straw pulp kappa number is reduced from 23.4 to 18.1 and pulp viscosity is decreased from 27cP to 22.3cP, in mixed hardwood pulp, kappa number is reduced from 16.7 to 13.1 with viscosity drop from 14.2cP to 11.8cP while in bagasse pulp kappa number reduction is from 8.9 to 6.8 and viscosity drop from 20cP to 16.3cP (Table 3.314). Results illustrated in the Figures 3.320 – 3.322 shows that the trend followed for percentage kappa no. reduction and viscosity is bagasse > wheat straw > mixed hardwood. Thus, it can be concluded that without NaOH, lignin reduction is not efficient.

Table- 3.314 Effect of persulphate dose (without NaOH) in (Px) prebleaching

$Na_2S_2O_8$ dose (%)	Kappa number			Viscosity (cP)		
	Wheat straw	*Mixed hardwood*	*Bagasse*	*Wheat straw*	*Mixed hardwood*	*Bagasse*
0	23.7	16.9	9.2	27.7	14.6	20.6
2.0	23.4	16.7	8.9	27.0	14.2	20.0
5.0	22.1	15.8	8.4	26.1	13.7	19.3
8.0	20.1	14.4	7.7	24.6	12.9	18.2
10.0	19.1	13.8	7.3	23.3	12.3	17.1
12.0	18.1	13.1	6.8	22.3	11.8	16.3

Temp. 40°C, RT 4 h, Cy 10%

Fig.3.320 Effect of Persulphate dose on (Px) prebleaching of wheat straw pulp

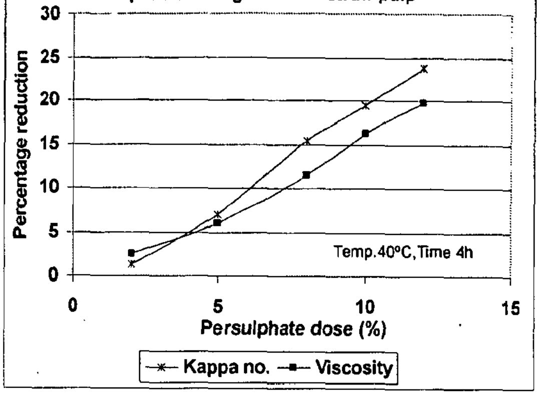


Fig. 3.321 Effect of persulphate dose on (Px) prebleaching of mixed hardwood pulp

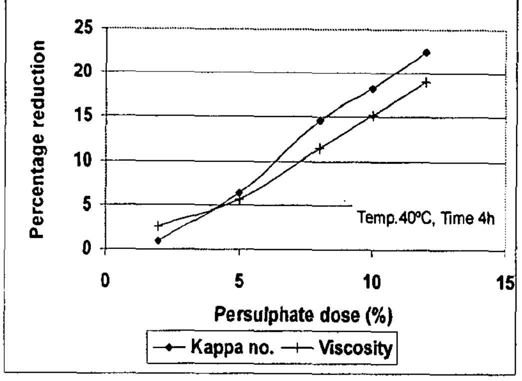
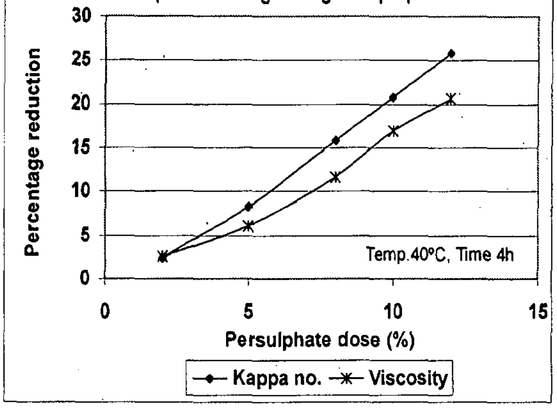


Fig. 3.322 Effect of persulphate dose on (Px) prebleaching of bagasse pulp



B) With NaOH Dose - From the initial trials it is observed that sodium persulphate shows oxidizing nature in alkaline medium so in this study 2% NaOH dose was tried with varying persulphate dose1-12% at 10% pulp consistency. The results shown in the Table 3.315 indicate that the drop in pulp kappa number and drop in pulp viscosity increases as the persulphate dose increases. The results illustrated in the Figures 3.323 – 3.325 further shows that maximum percentage drop in kappa number occurs in bagasse pulp and then in wheat straw pulp and lowest occurs in mixed hardwood pulp. Same trend is seen in viscosity reduction (Figures 3.323 – 3.325). Further reduction in pulp kappa number and viscosity is higher in the presence of alkali than in absence of alkali. (Table 3.314). The results are in agreement to that reported by Wong *et.al.* (182), stating that alkaline condition is necessary for (PxP) pretreatment and hence it can be stated that for optimum performance of (Px) stage also, alkaline condition is necessary. At 5% $Na_2S_2O_8$ charge and 2% alkali charge, in wheat straw pulp, kappa number is 20.6 while pulp viscosity is 12.2cP, in mixed pulp kappa number is 14.8 while viscosity is 12.9cP and in bagasse pulp, kappa number is 7.8 and viscosity is 17.7cP. Thus at 5% $Na_2S_2O_8$ dose kappa number reduction is in the range of 12-15% while viscosity drop is of the order of 11-14%, so 5% $Na_2S_2O_8$ is taken as the optimum dose for pretreatment.

Table - 3.315: Effect of persulphate dose at 2% NaOH dose in (Px) prebleaching

$Na_2S_2O_8$ dose (%)	**Kappa number**			**Viscosity (cP)**		
	Wheat straw	***Mixed hardwood***	***Bagasse***	***Wheat straw***	***Mixed hardwood***	***Bagasse***
0	23.7	16.9	9.2	27.7	14.6	20.6
1.0	23.1	16.5	8.7	26.3	13.8	19.4
3.0	22.2	15.9	8.3	24.9	13.2	18.4
5.0	20.6	15.0	7.8	24.3	12.9	17.7
7.0	19.9	14.3	7.4	23.3	12.2	16.9
8.0	19.2	13.8	7.1	21.2	11.4	15.6
10.0	18.1	12.9	6.7	19.9	10.8	14.6
12.0	16.5	12.1	5.9	19.0	10.1	13.5

NaOH 2%, Temp. 40°C, RT 4 h, Cy 10%

Fig. 3.323 Effect of persulphate dose on (Px) prebleaching of wheat straw pulp

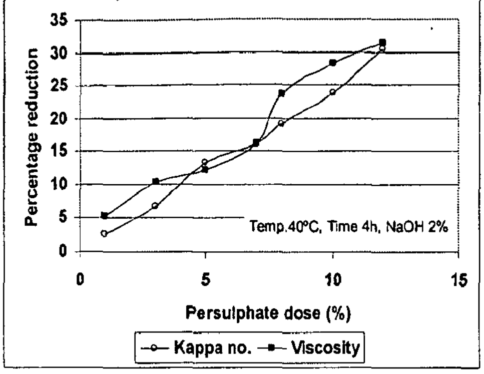


Fig. 3.324 Effect of persulphate dose on (Px) prebleaching of mixed hardwood pulp

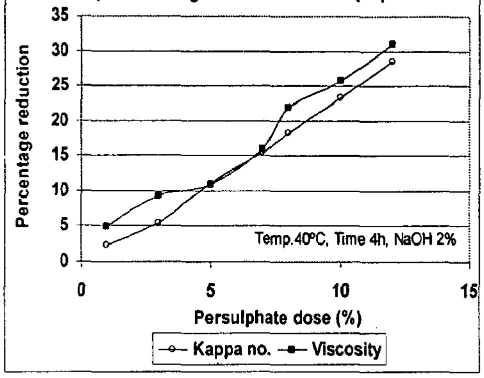
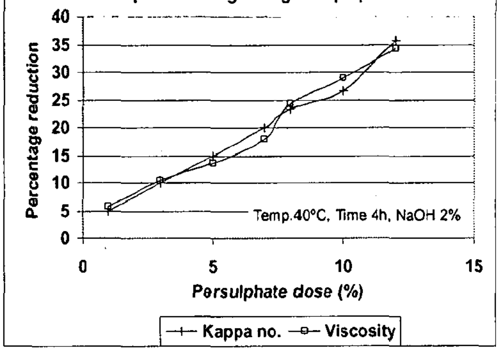


Fig. 3.325 Effect of persulphate dose on (Px) prebleaching of bagasse pulp



3.3.1.5 Effect of NaOH and EDTA Dose

EDTA was added in (Ep) stage to stabilize the peroxide to avoid decomposition by metal ions (135). Hence, the role of metal ions on the persulphate bleaching was studied by using two doses of EDTA 0.2% and 0.5% at different doses of NaOH from 0.5 -2.0%, maintaining persulphate dose at 5%. Results are shown in the Tables 3.316 – 3.317 and Figures 3.326 - 3.327. The results indicate that addition of EDTA at constant persulphate dose (5%) and constant NaOH dose (2%) improves both the drop in kappa number and pulp viscosity. A pulp kappa number of 20.6, 20.3 and 19.6 is observed with wheat straw pulp at 0, 0.2 and 0.5% EDTA. The corresponding values of pulp viscosity are 24.3, 22.8 and 22.3cP. Similar behaviour is also observed with mixed hardwood and bagasse pulps as reflected by their pulp kappa number and viscosity values. The results shown in Figures 3.326 – 3.327 indicate that drop in kappa number and viscosity increases with increasing alkali dose at constant EDTA charge (0.2%). Likewise the drop in kappa number and viscosity also increases with increasing EDTA dose to 0.5% at constant alkali charge of 2%. Addition of EDTA enhances the action of persulphate by reducing the concentration of transition metal ions by converting them to metal EDTA complexes. In all the three raw materials, maximum kappa number reduction is achieved at 2% NaOH and 0.5% EDTA while pulp viscosity drop is also lower. Kappa number drop is in the range of 14 -19% while viscosity drop is in the range of 18 - 20% for the three pulps studied. Thus, EDTA enhances both delignification and bleaching in all the three pulps. The results are similar to those reported by Lachenal *et.al.* (86) for hydrogen peroxide delignification where EDTA improves both delignification and bleaching. So, 2% NaOH and 0.5% EDTA dose is selected for persulphate pretreatment.

Table - 3.316: Effect of NaOH and EDTA dose on Kappa number in (Px) prebleaching

NaOH (%)	**EDTA dose (%)**	**Kappa number**			**% Kappa number drop**		
		Wheat straw	***Mixed hardwood***	***Bagasse***	***Wheat straw***	***Mixed hardwood***	***Bagasse***
0	0	23.7	16.9	9.2	-	-	-
0.5	0.2	21.7	15.9	8.4	8.4	5.9	8.7
1.0	0.2	21.4	15.6	8.2	9.7	7.7	10.9
1.5	0.2	21.2	15.4	8.1	10.5	8.9	11.9
2.0	0.2	20.3	14.8	7.6	14.3	12.4	17.4
1.5	0.5	20.7	15.2	7.9	12.7	10.1	14.1
2.0	0.5	19.6	14.5	7.4	17.3	14.2	19.6

$Na_2S_2O_8$ 5%, Temp. 40°C, RT 4 h, Cy 10%

Fig. 3.326 Effect of varying NaOH dose on kappa number during (Px) prebleaching

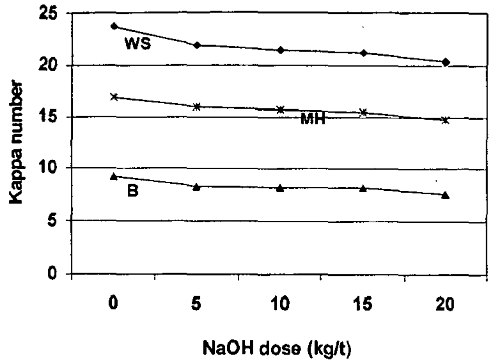
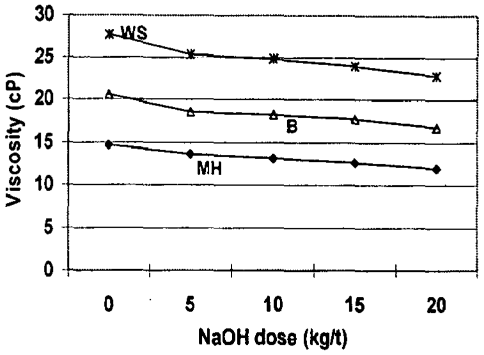


Fig. 3.327 Effect of varying NaOH dose on viscosity during (Px) prebleaching



WS- wheat straw, MH- mixed hardwood, B- bagasse

Table - 3.317: Effect of NaOH and EDTA dose on viscosity in (Px) prebleaching

NaOH (%)	EDTA dose (%)	Viscosity (cP)			% Viscosity drop		
		Wheat straw	*Mixed hardwood*	*Bagasse*	*Wheat straw*	*Mixed hardwood*	*Bagasse*
0	0	27.7	14.6	20.6	-	-	-
0.5	0.2	25.4	13.5	18.5	8.3	7.5	10.2
1.0	0.2	24.9	13.1	18.2	10.1	10.3	11.7
1.5	0.2	24.0	12.7	17.7	13.4	13.1	14.1
2.0	0.2	22.8	12.0	16.8	17.7	17.8	18.4
1.5	0.5	23.5	12.4	17.4	15.2	15.1	15.5
2.0	0.5	22.3	11.9	16.4	19.5	18.5	20.4

$Na_2S_2O_8$ 5%, Temp. 40°C, RT 4 h, Cy 10%

3.3.1.6 Effect of Temperature

Temperature is an important parameter in optimization of bleaching conditions. As initial trials were made at 70°C and later trials were made at 40°C so a study was done, to observe the effect of different temperatures on prebleaching efficiency. In this experiment, persulphate dose was 5%, NaOH dose was 2%, EDTA 0.5% and pulp consistency was 10%, 4 hours retention time. As observed by the results given in the Table 3.318 and Illustrations 3.328 – 3.330, it is noticed that increasing temperature decreases pulp kappa number and pulp viscosity. Percentage kappa number reduction is highest in bagasse pulp, then in wheat straw pulp and lowest drop in mixed hardwood pulp. This may be due to lower lignin content of bagasse pulp. The chemical charges are the same and the lignin content is lower in bagasse pulp, so lignin is more extensively attacked giving higher percent reduction with bagasse pulp. Similar pattern is seen in viscosity drop also. Increase of temperature enhances the attack of persulphate on lignin as well as cellulose giving a pulp of lower kappa number and viscosity. Similar results are reported by Süss *et.al.* (161) stating that temperature increase results in significantly lower pulp viscosities. Pulp viscosity is highest at 40°C so this temperature is chosen as optimum temperature for persulphate treatment.

Table - 3.318: Effect of temperature in (Px) prebleaching of different pulps

Temp. (°C)	Kappa number			Viscosity (cP)		
	Wheat straw	***Mixed hardwood***	***Bagasse***	***Wheat straw***	***Mixed hardwood***	***Bagasse***
Initial	23.7	16.9	9.2	27.7	14.6	20.6
40	19.6	14.5	7.4	22.3	11.9	16.4
50	19.0	13.7	7.2	21.5	11.3	15.8
60	18.7	13.4	7.1	20.3	10.8	14.9
70	18.4	13.2	6.9	19.4	10.3	14.2

$Na_2S_2O_8$ 5%, NaOH 2%, EDTA 0.5%, RT 40°C, Cy 10%

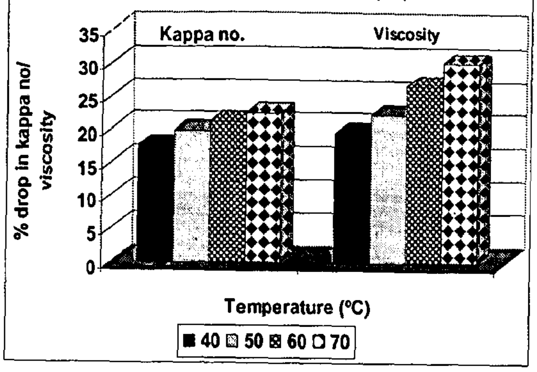


Fig. 3.328 Effect of temperature on (Px) prebleaching of wheat straw pulp

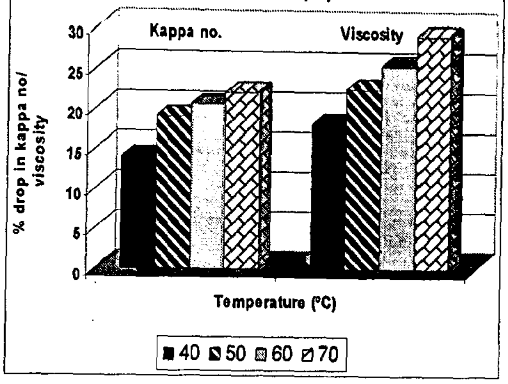


Fig.3.329 Effect of temperature on (Px) prebleaching of mixed hardwood pulp

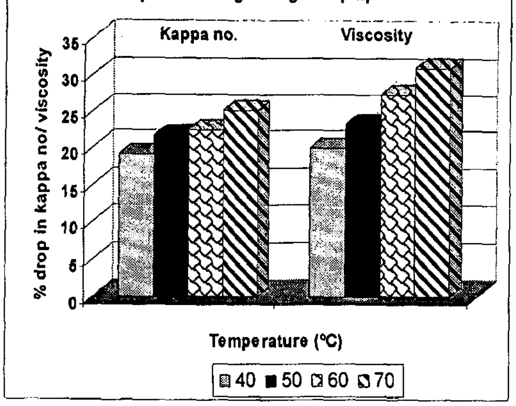


Fig. 3.330 Effect of temperature on (Px) prebleaching of bagasse pulp

3.3.1.7 Effect of Time

Effect of time was studied at optimized dose of persulphate, NaOH and EDTA at 10% pulp consistency at 40°C. As shown in Figures 3.331 – 3.333 and in Table 3.319 that pulp kappa number and pulp viscosity reduces with increasing reaction time in all the three pulps (Table 3.319). The percent drop in pulp kappa number and pulp viscosity also increases with reaction time (Figures 3.331- 3.333). Kappa number drop is in range of 14-19% and viscosity drop is in the range of 18-20%. Thus, 4 hours is selected as the optimum time for persulphate pretreatment process. An optimum time of 4 hours was also selected by Wong *et.al.* (182) for persulphate prebleaching of softwood kraft pulp.

Table - 3.319 Effect of retention time in (Px) prebleaching of different pulps

Time (h)	Kappa number			Viscosity (cP)		
	Wheat straw	*Mixed hardwood*	*Bagasse*	*Wheat straw*	*Mixed hardwood*	*Bagasse*
Initial	23.7	16.9	9.2	27.7	14.6	20.6
1	21.5	15.4	8.3	25.3	13.4	18.1
2	20.9	15.1	8.1	24.0	12.9	17.4
3	20.2	14.8	7.7	23.4	12.3	16.9
4	19.6	14.5	7.4	22.3	11.9	16.4

$Na_2S_2O_8$ 5%, NaOH 2%, EDTA 0.5%, Cy 10%

Fig. 3.331 Effect of R.T on (Px) prebleaching of wheat straw pulp

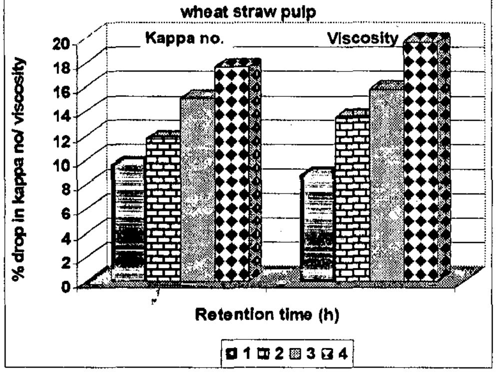


Fig.3.332 Effect of R.T on (Px) prebleaching of mixed hardwood pulp

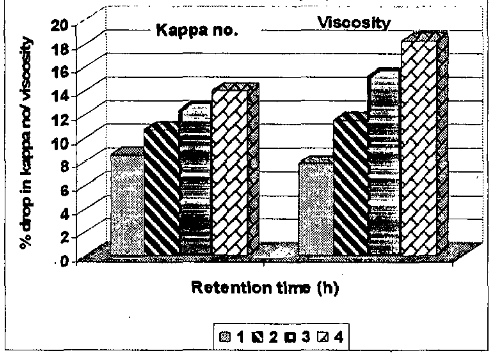
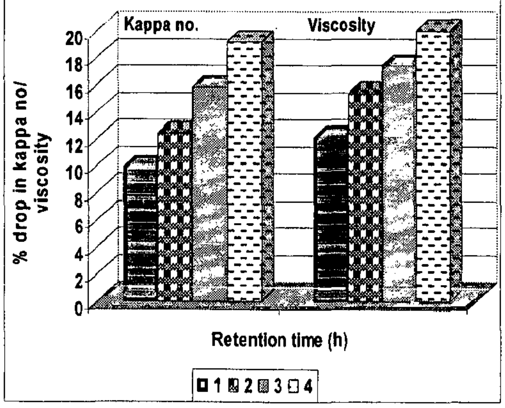


Fig. 3.333 Effect of R.T on (Px) prebleaching of bagasse pulp



Based on the results of persulphate prebleaching of all the three pulps, the optimum operating conditions selected for further bleaching studies chosen are given in Table 3.320. Under these conditions a drop in 14-19% pulp kappa number is obtained which is far lower than 40-50% obtained with oxygen delignification. The viscosity drop is also higher 18-20% for persulphate prebleaching stage.

Table – 3.320: Optimum parameters for (Px) pretreatment

Parameter	Value
Persulphate (%)	5.0
NaOH (%)	2.0
EDTA (%)	0.5
Consistency (%)	10.0
End pH	10.8-12.0
Retention time (h)	4
Temperature (°C)	40

3.3.2 Persulphate-Peroxide (PxP) Pretreatment

Peroxide shows bleaching action at a temperature around 70°C and delignification above 90°C. A temperature of 90°C is usually required to produce a substantial decrease in kappa number (171). When hydrogen peroxide is added to conventional oxygen prebleaching process, delignification is extended, even for low peroxide additions, 0.2-0.5% (77). Hence, studies were made to know whether using a small dose of peroxide at a lower temperature of 40°C reinforces the delignification action of persulphate. Studies were performed at two doses of peroxide 0.5 and 0.8% and at two doses of persulphate 2.5 and 5%. $MgSO_4$ (0.2%) was also tried as pulp protector. Persulphate-peroxide pretreatment has been optimized by using following process parameters.

3.3.2.1 Effect of Persulphate and Peroxide

In this study, pulps were bleached at two doses of sodium persulphate (2.5 and 5%) and two doses of peroxide (0.5 and 0.8%). The other parameters maintained were the same as maintained in (Px) stage (i.e. NaOH 2%, EDTA 0.5%, Cy 10%, RT 4 h and Temp. 40°C). $MgSO_4$ as a pulp protector at 0.2% was used. The results are given in Table 3.321 and Figures 3.334 – 3.336. In all the three pulps, as the persulphate and peroxide dose increases kappa number is reduced. Similar trend is observed with pulp viscosity. The trend is similar to that obtained by Lachenal, *et.al.* where plots showed that kappa number reduction is maximum at the highest applications of sodium hydroxide and peroxide (86). Mg^{2+} ion on OD pulp, is believed to function by precipitating as magnesium hydroxide, which adsorbs metal ions, making them unavailable for catalysis of peroxide decomposition (136) or by forming complexes with them (31). The addition of magnesium sulphate does not seem to improve delignification either; its effect on cellulose degradation is favorable (172). The results indicate that at a 2.5% persulphate and 0.5% peroxide dose, the drop in pulp viscosity is minimal 11-12% and drop in pulp kappa number is reasonably good 28-32%. Doubling the dose of persulphate from 2.5 to 5% (Table 3.322) or increasing dose of peroxide from 0.5 – 0.8% increases the drop in kappa number by merely 5 - 10% and also reduces pulp viscosity by another 7 - 15%. So increasing chemical charge of persulphate and peroxide increases the chemical cost without much reduction in kappa number and also yields a more degraded pulp. So, a lower chemical dose of 2.5% persulphate and 0.5% peroxide was taken as optimum dose for (PxP) pretreatment. At this chemical charge the viscosity of (PxP) pretreated pulps are better than (Px) pretreated pulps (Table 3.322). A drop of 30-35% in kappa number is also reported by Van Lierop *et.al.* (172) in E_{OP} stage at 0.5% peroxide charge which is similar to that observed by us in (PxP) prebleaching.

Table 3.321: Effect of peroxide and persulphate dose in (PxP) prebleaching

$Na_2S_2O_8$ (%)	H_2O_2 (%)	Kappa number			Viscosity (cP)		
		Wheat straw	*Mixed hardwood*	*Bagasse*	*Wheat straw*	*Mixed hardwood*	*Bagasse*
0	0	23.7	16.9	9.2	27.7	14.6	20.6
2.5	0.5	16.6	12.2	6.2	24.3	12.9	18.3
2.5	0.8	16.0	11.5	6.1	22.4	11.9	16.0
5	0.5	14.9	10.7	5.6	20.4	10.8	15.4
5	0.8	13.7	9.8	5.2	18.7	9.6	14.6

NaOH 2%, EDTA 0.5%, $MgSO_4$ 0.2%, Temp. 40°C, RT 4h, Cy 10%

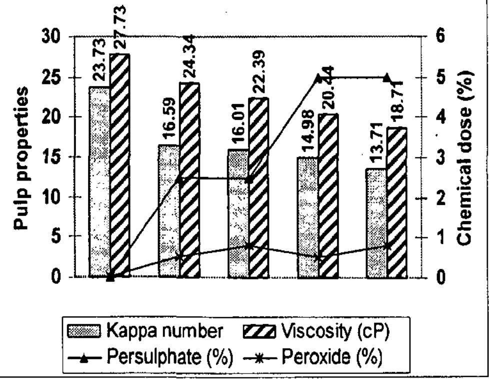


Fig.3.334 Effect of $Na_2S_2O_8$ and H_2O_2 dose in (PxP) pretreatment of wheat straw pulp

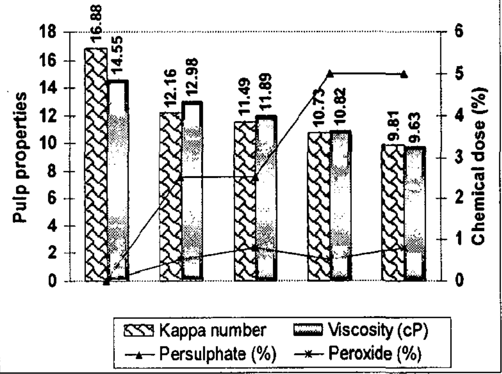


Fig.3.335 Effect of $Na_2S_2O_8$ and H_2O_2 dose in (PxP) pretreatment of mixed hardwood pulp

Fig. 3.336 Effect of $Na_2S_2O_8$ and H_2O_2 dose in (PxP) pretreatment of bagasse pulp

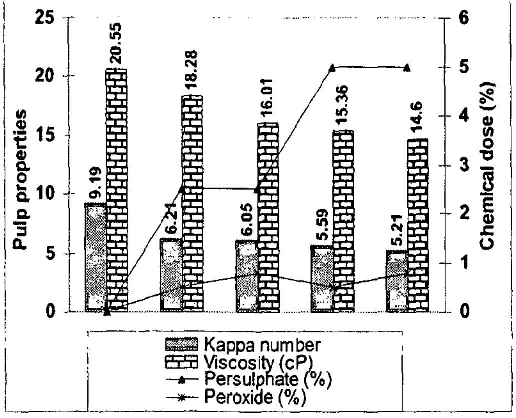


Table 3.322: Comparison of optimized (Px), (PxP) at same dose & (PxP) at optimized dose

S.No.	Condition	Kappa number			Viscosity		
		Wheat straw	Mixed hardwood	Bagasse	Wheat straw	Mixed hardwood	Bagasse
1	Optimized (Px) stage	19.6	14.5	7.4	22.3	11.9	16.4
2	(PxP) stage	14.9	10.7	5.6	20.4	10.8	15.4
3	Optimized (PxP) stage	16.6	12.2	6.2	24.3	12.9	18.3

1. *$Na_2S_2O_8$ 5%, NaOH 2%, EDTA 0.5%, Temp. 40°C, RT 4h, Cy 10%*
2. *$Na_2S_2O_8$ 5% ,H_2O_2 0.5%, NaOH 2%, EDTA 0.5%, $MgSO_4$ 0.2%, Temp. 40°C, RT 4h, Cy 10%*
3. *$Na_2S_2O_8$ 2.5%, H_2O_2 0.5%, NaOH 2%, EDTA 0.5%, $MgSO_4$ 0.2%, Temp. 40°C, RT 4h, Cy 10%*

3.3.2.2 Effect of Temperature

After optimizing the dose of $Na_2S_2O_8$, NaOH and peroxide, the optimization of PxP treatment was made for temperature as it is an important factor, governing delignification rates. Experiments were performed at optimized dose of persulphate 2.5%, NaOH 2%, EDTA 0.5% and $MgSO_4$ 0.2%. The pulp consistency was 10% and retention time of 4 hours. The temperature was varied from 40-70°C. Results are shown in Table 3.323 and percentage reduction in kappa number and viscosity is illustrated in Figures 3.337 – 3.339. In all the three raw materials as the temperature increases, kappa number reduction increases with large drop in viscosity. As reported for each 10°C increase in temperature, the delignification rate doubles (31). At 40°C an appreciable drop in kappa number is achieved in the range of 27-32% with viscosity drop ranging from 10-12% (Figures 3.337 – 3.339). At higher temperatures viscosity drop increases largely. Thus 40°C was chosen as the optimum temperature. In this process, with 10°C increase in temperature the delignification increases but not doubles.

Table – 3.323: Effect of temperature in (PxP) prebleaching on different pulps

Temp. (°C)	**Kappa number**			**Viscosity (cP)**		
	Wheat straw	***Mixed hardwood***	***Bagasse***	***Wheat straw***	***Mixed hardwood***	***Bagasse***
40	16.6	12.2	6.2	24.3	12.9	18.3
50	15.9	11.8	6.1	21.6	11.6	16.0
60	14.9	11.1	5.6	21.2	11.4	15.4
70	14.3	10.5	5.2	20.2	10.7	14.6

$Na_2S_2O_8$ 2.5%, Peroxide 0.5%, NaOH 2%, EDTA 0.5%, $MgSO_4$ 0.2%, RT4h, Cy 10%

Fig. 3.337 Effect of temperature in (PxP) prebleaching of wheat straw pulp

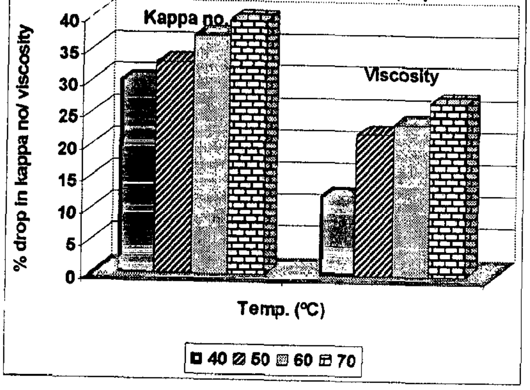


Fig.3.338 Effect of temperature in (PxP) prebleaching of mixed hardwood pulp

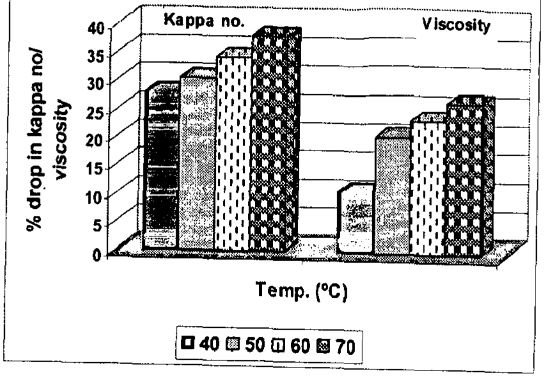
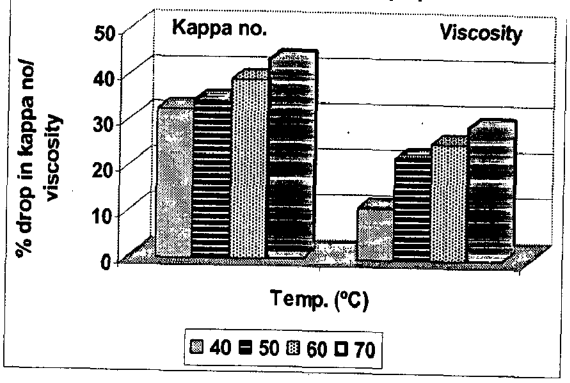


Fig.3.339 Effect of temperature on (PxP) prebleaching of bagasse pulp



3.3.2.3 Effect of Time

Keeping all the other parameters constant, time was varied to check its effect on the pretreatment efficiency. Results are shown in Table 3.324 and Figures 3.340 - 3.342. Results show that as the retention time is increased the drop in kappa number and viscosity also increases. As shown in the Figures 3.340 – 3.342, the trend followed for percent reduction in kappa number is: Bagasse > Wheat straw > Mixed hardwood. While percent reduction in viscosity follows the trend: Wheat straw > Bagasse ≥ Mixed hardwood.

At the completion of one hour kappa number drop is from 17-19% while viscosity drop is from 5 -7.5%. While at 4 hours retention time kappa number reduction has increased to 28-32% and drop in viscosity is 11 - 12% which is acceptable. So a reaction time of 4 hours has been chosen for further studies.

Table - 3.324: Effect of time in (PxP) prebleaching of different pulps

Time	Kappa number			Viscosity (cP)		
(h)	*Wheat straw*	*Mixed hardwood*	*Bagasse*	*Wheat straw*	*Mixed hardwood*	*Bagasse*
Initial	23.7	16.9	9.2	27.7	14.6	20.6
1	19.2	13.9	7.1	25.6	13.7	19.0
2	18.2	13.4	6.9	25.1	13.5	18.7
3	17.4	12.7	6.6	24.7	13.2	18.4
4	16.6	12.2	6.2	24.3	12.9	18.3

$Na_2S_2O_8$ 5%, Peroxide 0.5%, NaOH 2%, EDTA 0.5%, $MgSO_4$ 0.2%, Temp. 40°C, Cy 10%

Fig. 3.340 Effect of R.T on (PxP) prebleaching of wheat straw pulp

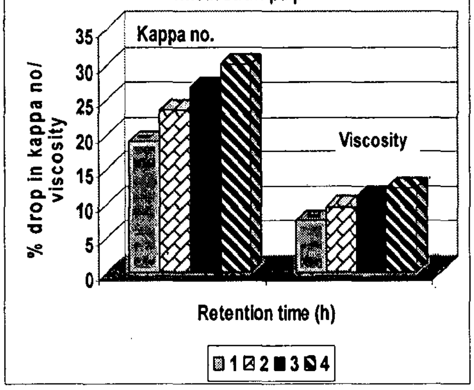


Fig.3.341 Effect of R.T on (PxP) prebleaching of mixed hardwood pulp

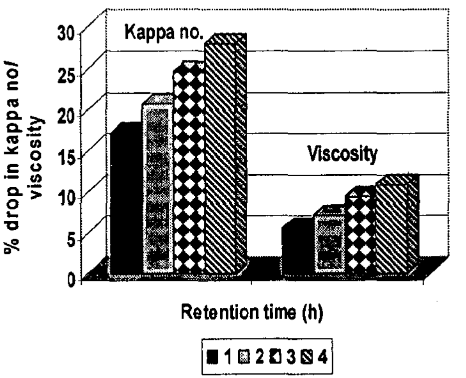
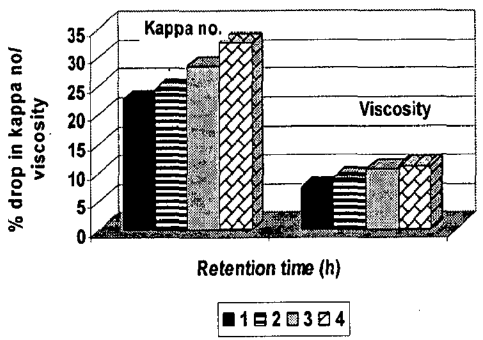


Fig.3.342 Effect of R.T on (PxP) prebleaching of bagasse pulp



By looking at the results it can be concluded that in all the raw materials nearly same response of kappa number drop and viscosity drop is observed, under the optimized parameters for (PxP) process. The optimized parameters are given in Table 3.325.

Table - 3.325: Optimized parameters for (PxP) pretreatment

Parameter	Value
Persulphate (%)	2.5
Hydrogen Peroxide (%)	0.5
NaOH (%)	2.0
EDTA (%)	0.5
$MgSO_4$ (%)	0.2
Consistency (%)	10.0
pH	10.8- 12.0
Retention time (h)	4
Temperature (°C)	40

Replacing sodium persulphate by 0.5% peroxide in (PxP) pretreatment doubles the drop in pulp kappa number from 14-19% to 28-32% and lowers the drop in pulp viscosity by 40% from 18-20% to 11-12%. So (PxP) pretreatment proves to be better as given in Table 3.322.

3.3.3 Oxygen Delignification

Oxygen delignification is capable of removing upto 50% of residual lignin in the unbleached pulp as pulp strength may drop, beyond this point (5). Thus, reduction in kappa number results in reduction of bleach chemical demand and hence pollution load of bleaching sequence is reduced drastically. The optimization of alkali charge was carried out by performing oxygen stage under optimum conditions of oxygen pressure at 6kg/cm^2, pulp consistency of 10%, retention time of 75 minutes, temperature of 100°C and magnesium sulfate charge of 2kg/t.

3.3.3.1 Optimization of Alkali Charge During Oxygen Pretreatment

The objective of oxygen delignification was to target around 40-45% reduction in kappa number maintaining minimum drop in pulp viscosity. Results are shown in Tables 3.326 - 3.328 and effect of NaOH dose on kappa number, brightness and viscosity are illustrated in Figures 3.343 – 3.345.

Table – 3.326: Optimization of alkali charge during oxygen delignification on wheat straw pulp

Parameter	Untreated	Set 1	Set 2	Set 3	Set 4
Alkali charge (as NaOH) (kg/t)	-	30	35	40	60
Kappa no.	23.7	17.0	15.7	12.3	10.5
Viscosity (cP)	27.7	27.0	26.4	25.6	24.9
Brightness (% ISO)	30.8	39.5	43.6	45.7	48.4
(σ)	*(0.15)*	*(0.22)*	*(0.21)*	*(0.18)*	*(0.26)*
Oxygen pressure (kg/cm^2)	-	6	6	6	6
Consistency (%)	-	10	10	10	10
Retention time (mins.)	-	75	75	75	75
Temperature (°C)	-	100	100	100	100
MgSO$_4$(kg/t)	-	2	2	2	2

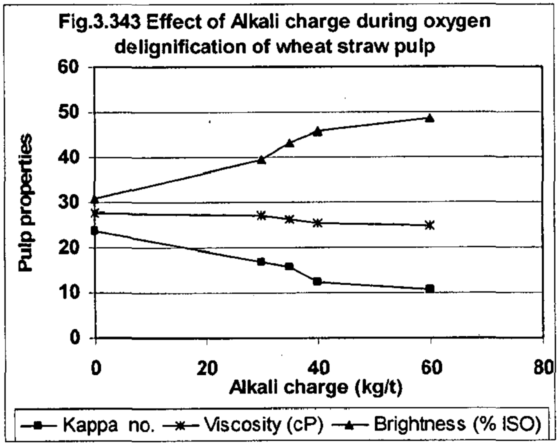


Fig.3.343 Effect of Alkali charge during oxygen delignification of wheat straw pulp

Table – 3.327: Optimization of alkali charge during oxygen delignification on mixed hardwood pulp

Parameter	Untreated	Set 1	Set 2	Set 3
Alkali charge (as NaOH) (kg/t)	-	10	20	30
Kappa no.	16.9	10.7	9.6	8.5
Viscosity (cP)	14.6	13.1	12.9	11.9
Brightness (% ISO) *(σ)*	27.6 *(0.15)*	38.4 *(0.23)*	41.0 *(0.12)*	47.6 *(0.19)*
Oxygen pressure (kg/cm^2)	-	6	6	6
Consistency (%)	-	10	10	10
Retention time (mins.)	-	75	75	75
Temperature (°C)	-	100	100	100
MgSO$_4$(kg/t)	-	2	2	2

Fig.3.344 Effect of Alkali charge during oxygen delignification of mixed hardwood pulp

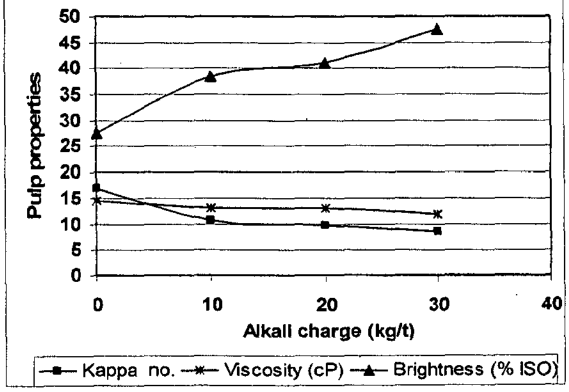


Table – 3.328: Optimization of alkali charge during oxygen delignification on bagasse pulp

Parameter	Untreated	Set 1	Set 2	Set 3	Set 4
Alkali charge (as NaOH) (kg/t)	-	4	8	10	20
Kappa no.	9.2	4.9	4.5	4.2	3.9
Viscosity (cP)	20.6	18.6	18.3	17.3	16.7
Brightness (% ISO) *(σ)*	47.8 *(0.21)*	59.2 *(0.26)*	63.3 *(0.34)*	66.5 *(0.4)*	69.3 *(0.24)*
Oxygen pressure(kg/cm^2)	-	6	6	6	6
Consistency (%)	-	10	10	10	10
Retention time (mins.)	-	75	75	75	75
Temperature (°C)	-	100	100	100	100
MgSO$_4$(kg/t)	-	2	2	2	2

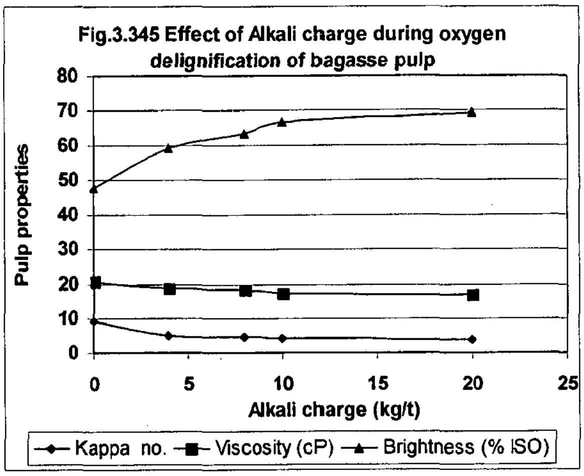


Fig.3.345 Effect of Alkali charge during oxygen delignification of bagasse pulp

In all the three raw materials it is evident that as alkali charge is increased there is decrease in pulp viscosity with reduction in kappa number. Similar trend is reported by Dathathreya, *et.al.* (30) that as caustic soda charge is increased, viscosity of resulting pulp drops. Hence, it is necessary that alkali charge is not excessive. In case of wheat straw pulp as given in Table 3.326 and Figure 3.343, at alkali charge of 30 kg/t and 35 kg/t kappa number drops to 17 and 15.7 respectively, from the initial value of 23.7 giving a percent drop of 28.3% and 33.8% which is below the target reduction by 40-50%. So higher doses of 40 kg/t and 60 kg/t are tried. At 40 kg/t alkali charge, kappa number drops to 12.3 and viscosity to 25.6cP. So it is selected as optimum dose as almost 48% kappa number drop is achieved with 7.6% viscosity drop. In mixed hardwood pulp, as illustrated in Figure 3.344 and in Table 3.327 it can be deduced that an alkali dose of 20 kg/t gives a kappa number reduction of 43% and viscosity drop by 12%. At higher alkali dose of 30 kg/t the viscosity drops by 18% and at lower alkali dose of 10 kg/t, kappa number drop by 37% so an alkali dose of 20 kg/t is selected for oxygen delignification of mixed hardwood pulp. In bagasse pulp at highest alkali dose of 20 kg/t the percentage reduction is 57 and 19 for kappa number and viscosity drop respectively. At 10 kg/t alkali charge, kappa number is 4.2 and viscosity is 17.3cP giving a percentage drop of 54 and 16 respectively which was higher than 45-50% kappa number reduction so lesser alkali dose was tried so as to give kappa number drop in the range of 45-50% and reduce drop in viscosity. So from Table 3.328 and Figure 3.345, it is observed that at 4 kg/t alkali charge, kappa number reduction is 47% and viscosity drop is 9.7% and at alkali charge of 8 kg/t kappa number reduction is 51% and viscosity drop is 11%. Hence 4kg/t is selected as optimum alkali charge for oxygen delignification of bagasse pulp. At lower doses of NaOH highest reduction in kappa number is obtained in bagasse pulp with highest brightness. The bagasse pulp responds much better than the other two pulps studied. As reported, bagasse by nature produces a low kappa pulp by normal kraft process itself. Thus, extending the same with an oxygen delignification step results in an ultra low kappa number (130).

3.3.4 Strength Properties of Pulps Treated by Different Pretreatments

Pulp viscosity is indicative of the strength properties but cannot be taken as direct measure of the mechanical properties of the paper sheet. So, the pulps treated with different pretreatments were beaten to similar levels in a PFI mill to target CSF values and mechanical strength properties were evaluated from air dried sheets.

3.3.4.1 ***Wheat straw pulp*** **-** The mechanical properties of wheat straw pulp with different pretreatments are given in Figures 3.346 – 3.349. The wheat straw pulp is beaten in a PFI mill at 1000 revolutions to give a pulp of nearly 300 CSF(± 20). Both (PxP) and oxygen pretreated pulps has been found to show comparable strength properties. Tear index, burst index and double fold for oxygen-delignified pulps are observed to be nearly similar to (PxP) pretreated pulp while tensile index is slightly higher for (PxP) pretreated pulp. The (Px) pretreatment has not been found to be suitable, as it gives high drop in strength properties.

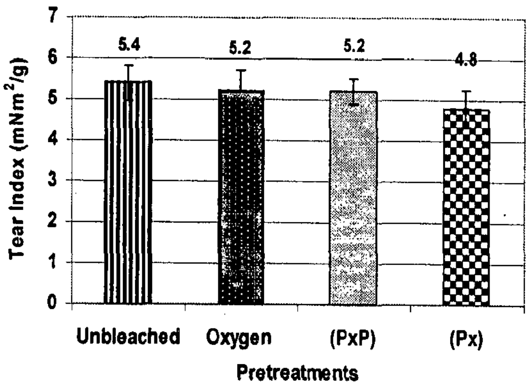


Fig. 3.346 Effect of pretreatments on tear strength of wheat straw pulp

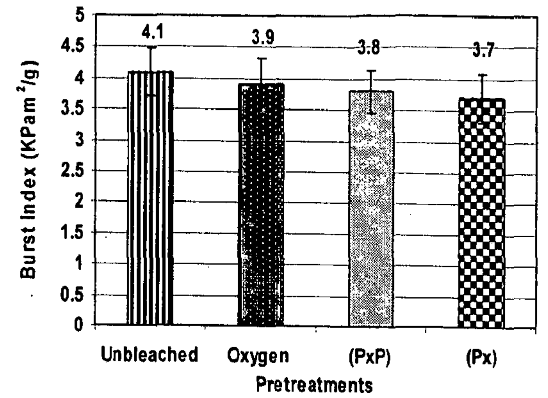


Figure 3.347 Effect of pretreaments on burst strength of wheat straw pulp

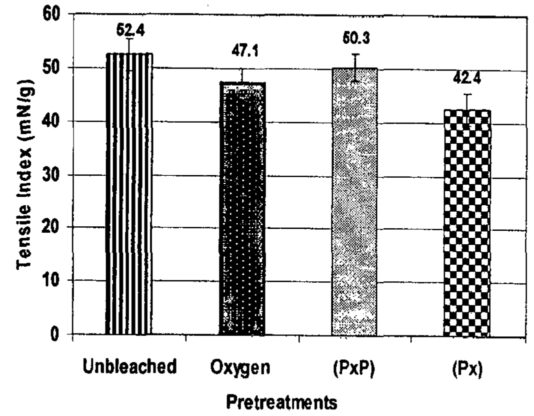


Fig.3.348 Effect of pretreaments on tensile strength of wheat straw pulp

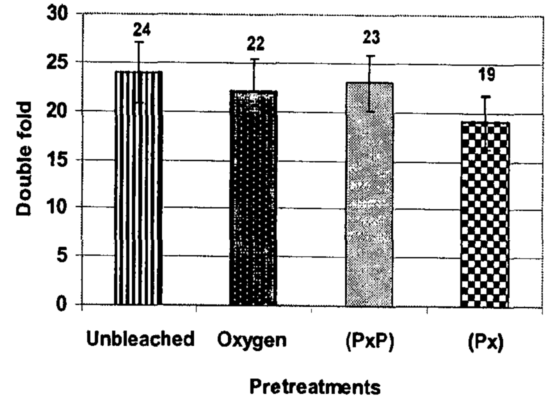


Fig. 3.349 Effect of pretreaments on double folds property in wheat straw pulp

I Represents Standard deviation (σ) from mean

The plotted values are mean of 10 readings

3.3.4.2 Mixed hardwood pulp - Pulp strength properties of untreated, (Px), (PxP) and oxygen pretreated are depicted in Figures 3.350 – 3.353. Both treated and untreated pulp is beaten in PFI mill at 10500 revolutions to attain CSF of 300ml(±20). As evident from the Figures 3.350 – 3.353 and comparing the three pretreatments, (Px) pretreatment has not been found to be suitable as maximum drop in strength properties occurs. In oxygen pretreated pulps, tear index and double folds are slightly higher than (PxP) pretreated but tensile index is observed to be highest for (PxP). Burst index is found to be nearly similar for oxygen and (PxP) pretreated pulps. Thus, the strength properties of oxygen and (PxP) pretreated pulps are nearly similar.

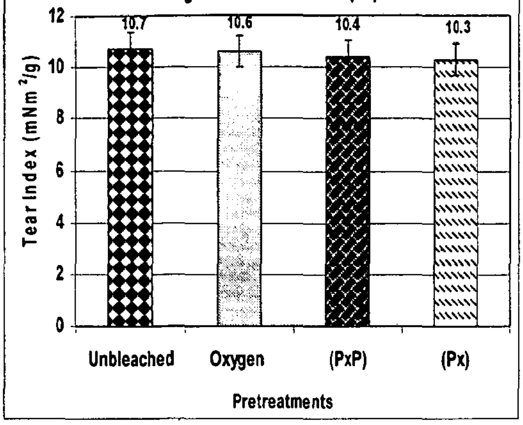


Fig.3.350 Effect of different pretreatments on tear strength of mixed hardwood pulp

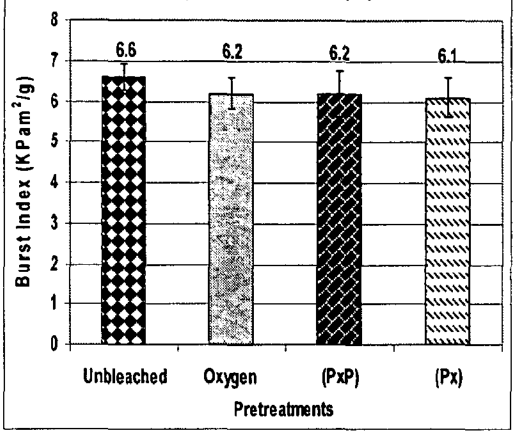


Fig.3.351 Effect of different pretreatments on burst strength of mixed hardwood pulp

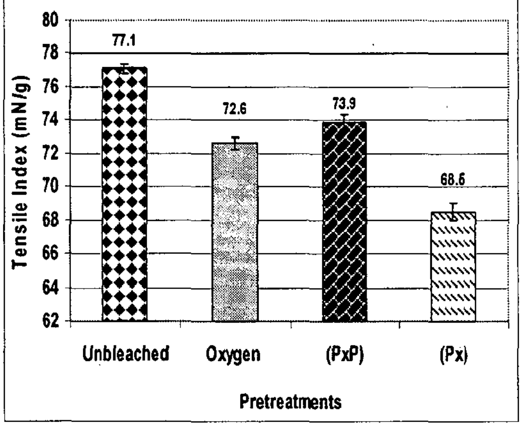


Fig. 3.352 Effect of different pretreatments on tensile strength of mixed hardwood pulp

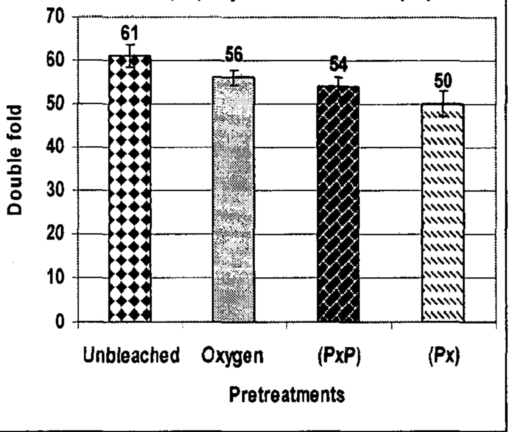


Fig.3.353 Effect of different pretreatments on double fold property in mixed hardwood pulp

] Represents Standard deviation (σ) from mean

The plotted values are mean of 10 readings

3.3.4.3 Bagasse pulp - A low kappa bagasse pulp is collected from a pulp mill and is washed and air-dried in laboratory. Hand sheets of bagasse untreated, (Px) pretreated, oxygen delignified and (PxP) pretreated pulp were prepared by beating pulp to 2000 revolutions in a PFI mill to attain 300(±20) ml CSF and mechanical strength properties of air dried hand sheets were evaluated. The results of mechanical strength properties of unbleached, (Px) pretreated, oxygen delignified and (PxP) pretreated pulp shown in Figures 3.354 – 3.357 concludes that (Px) pretreatment reduces strength properties to large extent. Comparing (PxP) and oxygen pretreated pulps, it is observed that tear index, double fold and burst index are higher for oxygen pretreated pulps and tensile index is highest for (PxP) pretreated pulp. Hence by observing the results of all the pulps, it can be stated that strength properties of oxygen and (PxP) pretreated pulps is nearly similar and tensile index is higher for (PxP) treated pulp in the three raw materials.

Fig. 3.354 Effect of different pretreatments on tear strength of bagasse pulp

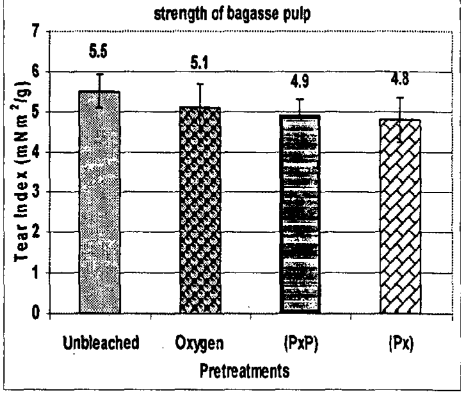


Fig. 3.355 Effect of different pretreatments on burst strength of bagasse pulp

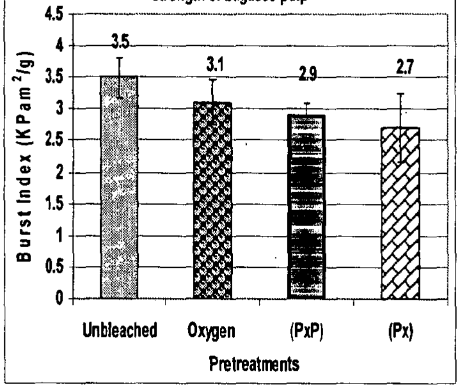


Fig. 3.356 Effect of different pretreatments on tensile strength of bagasse pulp

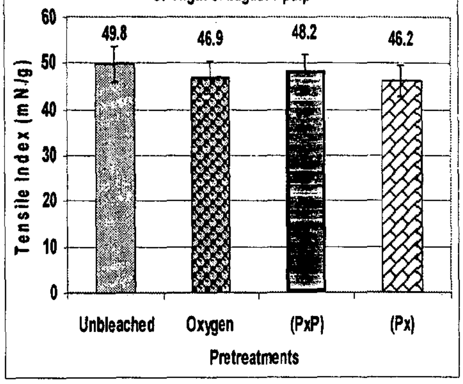
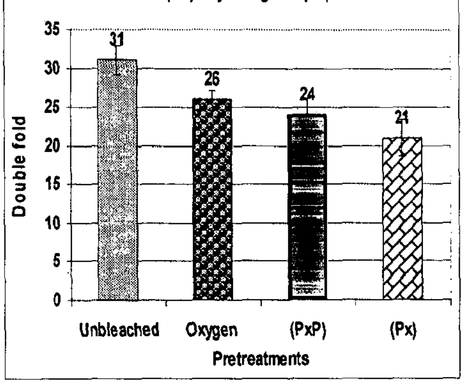


Fig. 3.357 Effect of different pretreatments on double fold property in bagasse pulp



[Represents Standard deviation (σ) from mean

The plotted values are mean of 10 readings

CHAPTER 4

Chapter 4

BLEACHING OF PERSULPHATE (Px), PERSULPHATE- PEROXIDE (PxP) AND OXYGEN (O_2) PRETREATED PULPS

4.1 INTRODUCTION

In Indian context, the awareness and concern about AOX and its control has grown in the last decade. While by switching over to new fibre line (involving modern technologies in pulping, bleaching, pulp washing etc), the mills in developed countries have reduced the AOX below toxicity level and it is now no longer a major issue, the mills in India producing bleached variety of paper have continued to use elemental chlorine for bleaching (in most cases) due to techno-economic reasons (115). Thus, the need of the hour is to implement suitable strategies (internal or external measures) so as to make ecofriendly products for national and international markets.

The Central Pollution Control Board of India under Charter on Corporate Responsibility for Environmental Protection (CREP) has proposed AOX norm at 1.5kg/t of paper produced which is to be brought down to 1kg/t for next 2 years (144). Thus having recognized the main agents responsible for AOX formation, one of the two approaches or combination of both can be implemented to reduce the discharge of AOX:

1. Internal measures – modification in pulping and bleaching unit operations so that AOX formation is reduced.
2. End of Pipeline methods - external treatment involving treatment of effluent to meet discharge standards. It involves huge investments and has high operating costs.

Ever increasing demand for paper and shortage of conventional raw materials has necessitated the industry to search for alternative raw materials (107).

Bagasse and wheat straw have been found to be the most potential non-conventional raw materials particularly in context of their huge availability (131). Wheat straw is one of the raw materials used in Northern India and can be used for manufacturing writing and printing paper (52) In view of economically available and technologically acceptable source of fibre for pulp and paper making, bagasse (residue after sugarcane crushing in sugar mills) is being identified as techno-economically appealing, perennially replenishable source of fibre (187).

The nonwood plants fibers are morphologically different from those of wood fibers. The pulps derived from these plants have the problems of poor drainability, poor retention and poor wet web strength and so on (189, 179). Mixed pulping of nonwoods with bamboo and other conventional wood species may minimize the above problems (53). Thus, most of the industries use mixed pulp, by pulping a hardwood, agroresidue or a nonwood together. So, a mixed hardwood pulp was also used as a raw material for the study as it is a common raw material of Indian paper mills.

4.1.1 Process Modifications

4.1.1.1 Oxygen &/or Extended Delignification

Oxygen delignification can be defined as the use of oxygen and alkali to remove a substantial fraction of lignin in unbleached pulp. The process is conducted under pressure and oxygen delignification is normally in the range of 35-50% (31). Oxygen delignification is a prebleaching stage that decreases the kappa number prior to chlorination and effluent loading (BOD, COD, Color, AOX, chlorinated phenolics and toxicity to fish) emanating from bleach plant. (91).

The trend today is to implement two-stage oxygen delignification. By an appropriate choice of operating conditions in first oxygen and second oxygen it is possible to minimize cellulose degradation. 60% delignification seems to represent a practical limit even after two steps (89). Activation and catalysis of oxygen is another pathway aimed at improving efficiency of oxygen delignification (4). The addition of catalysts and activators such as polyoxometalates (41), metalloporphyrins (118) and other mostly transition-metal-based catalysts improve lignin removal and/or selectivity of oxygen delignification process (61).

Oxygen stage will allow most of bleached kraft mills to reduce BOD discharges by approximately 50%, color by 60% and organochlorine compounds by 35-50% (100). In addition, the liquor from oxygen delignification is recirculated to evaporation and incineration which means that oxygen delignification is also more beneficial for the environmental performance of a mill than an extensive bleaching (180, 71). Of the chief disadvantages, capital cost is the most apparent (6). A further drawback is the possibility of overloading systems in the chemical recovery area of the mill.

4.1.1.2 Increased Chlorine Dioxide Substitution

Chlorine dioxide is an electrophile which attacks predominantly aromatic rings, with free phenolic hydroxyl groups through oxidation. Such structures are abundant in residual lignin after kraft pulping (27).

An increase in the percentage of chlorine dioxide leads to substantial reduction in the AOX concentration in total bleaching effluents. Chlorine dioxide produces organically bound chlorine but only one-fifth of the same amount of the elemental chlorine when compared on chlorine basis (50, 8). AOX decreases as the chlorine dioxide substitution increases and varies linearly with the elemental chlorine used in the first stage (8). Liebergott also found a linear decrease in effluent AOX accompanying increased chlorine dioxide substitution (90). An increase from 15% to 75% chlorine dioxide gives a 45% AOX reduction (49). At very high levels of substitution, AOX was lower than anticipated based on linear relationship observed at lower substitution levels (7).

BOD decreased by 20-30% and color by 50-80% at 90-100% chlorine dioxide substitution (67). Other studies have shown that COD and color can be reduced by increasing chlorine dioxide substitution (122, 154). Pryke & Singh also reported that effluent toxicity decreases with increasing chlorine dioxide substitution (122, 154).

The greatest consideration in the use of chlorine dioxide delignification is the chemical cost. In many studies lowest cost is obtained in the range of 30-50% substitution with the cost being relatively insensitive over this range (7). As 100% substitution is approached the chemical cost increases sharply (31). The change to 100% substitution with chlorine dioxide is a response to environment and market pressures (101).

4.1.1.3 Persulphate Prebleaching

Persulphate is a strong oxidizing agent which can be used as a prebleaching agent for cellulosic materials. (PxP) treatment has been tried by Wong *et.al*, (1995) in the laboratory by bleaching a (PxP) treated pulp with an ECF bleaching sequence (182).

By (PxP) pretreatment a satisfactory reduction in kappa number is achieved with an acceptable decrease in viscosity. A reduction in bleach chemicals in the range of 15% has been reported (182). As the incoming kappa number is reduced so the bleach chemical demand is also reduced, resulting in the reduction of AOX, COD, BOD and color of the effluent.

The (PxP) effluent may be recycled to either the mill's chemical recovery system or its effluent treatment system. Retrofitting an existing pulp mill with oxygen bleaching to reduce AOX, COD, BOD and color is an option but it is expensive, persulphate bleaching can be an economical alternative to achieve a similar degree of lignin removal. Sodium persulphate made electrochemically from surplus sodium sesquisulphate from R_8 chlorine dioxide plant has been tried by Wong *et.al,* using (PxP) pretreatment and is further used for ECF bleaching, to produce bleached softwood pulp (182).

New bleaching technologies, which do not use chlorine-based chemicals, continue to be developed in the pulp and paper industry worldwide to meet strict environmental regulations. Research work on bleaching agents that use oxygen, ozone, peroxide and peroxy acid has been proceeding in the laboratory, pilot facilities and commercial installations for many years. The experiments as outlined below were planned to try persulphate as prebleaching agent for some agroresidue and hardwood pulps. Wheat straw soda, bagasse kraft and mixed hardwood kraft pulps were chosen for the study.

1. To perform Persulphate (Px), Persulphate-peroxide (PxP) and oxygen pretreatments (O_2) followed by conventional and ECF bleaching sequences to obtain medium and high brightness bleached pulps. The comparisons of the different pretreatments is to be done based on the following:
   - Bleach chemical dosage
   - Strength properties of paper sheets
   - Effluent characteristics
2. Bleaching costs comparisons of different pretreatments

4.2 RESULTS AND DISCUSSION

4.2.1 CEH Bleaching (80% ISO) of Wheat Straw Pulp

Though CEH bleaching is not so appealing to the advanced countries because of its impact of pollution, it is considered to be the most dependable and popular bleaching process in Asian countries (54). Wheat straw untreated, (Px), (PxP) and oxygen pretreated pulps has been bleached by conventional CEH sequence to 80% ISO brightness.

Bleach Chemical Demand

The conditions of CEH bleaching, chemical doses with different pretreatments are given in Table 4.221. The savings in chemical dose to obtain 80% ISO bleached pulp is given in the Figure 4.221.

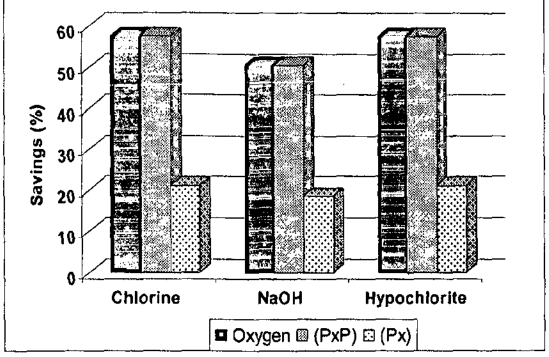


Fig. 4.221 Chemical savings in CEH bleaching from different pretreatments in wheat straw pulp

The bleach chemical requirements are a function of pulp kappa number, chemical requirement increases with increase in pulp kappa number. The kappa number of the different pulps follows the order, unbleached > (Px) pretreated > (PxP) pretreated > oxygen pretreated. So the order of bleach chemical charge is expected to be unbleached > (Px) pretreated > (PxP) pretreated > oxygen pretreated.

Table – 4.221: Bleaching conditions used to make 80% ISO brightness wheat straw pulp by different pretreatments

Conditions	**Sequences**											
	CEH			*OCEH*			*(Px)CEH*			*(PxP)CEH*		
	C	E	H	C	E	H	C	E	H	C	E	H
Temp. (°C)	Amb.	70	40	Amb.	70	40	Amb.	70	40	Amb.	70	40
Cy (%)	3.0	10.0	7.0	3.0	10.0	7.0	3.0	10.0	7.0	3.0	10.0	7.0
RT (mins.)	45	60	210	45	60	210	45	60	210	45	60	210
End pH	1.9	11.5	10.9	2.15	11.4	10.8	2.2	11.7	10.9	2.0	11.0	10.6
aCl (%)	4.15	_	1.78	1.75	_	0.75	3.27	_	1.40	1.75	_	0.75
NaOH (%)	_	2.38	_	_	1.18	_	_	1.94	_	_	1.18	_
Residual aCl (%)	0.6	_	1.7	0.5	_	1.5	0.4	_	1.6	0.3	_	1.5
Brightness (%ISO) σ	-	-	80.2 *0.19*	-	-	80.6 *0.11*	-	-	80.4 *0.15*	-	-	80.5 *0.16*
Viscosity (cP)	-	-	18.6	-	-	19.5	-	-	15.7	-	-	18.9
Total aCl (%)	5.9			2.5			4.7			2.5		

The results given in Table 4.221 show that (PxP) and oxygen pretreated CEH bleached pulps require the same bleach chemical dose (25kg/t) but the (Px) pretreated pulp requires comparatively higher chemical dose (47kg/t). Thus as shown in the Figure 4.221 the chemical savings obtained by both (PxP) and oxygen pretreatment are the same (58%), although the kappa number of (PxP) pretreated pulp is 26% higher. Results given in Table 4.221 also indicate that, viscosity of oxygen pretreated pulp is slightly higher than the (PxP) pretreated pulp expecting slight increase in pulp degradation with (PxP) pretreatment than oxygen. Results are similar to that reported by Gupta, *et.al.* (59).

Mechanical properties

Although, the viscosity results obtained in conventional CEH and ECF bleaching with persulphate and oxygen were apparently good, but pulp viscosity is indicative of the strength properties so it cannot be taken as direct measure of the mechanical properties of the paper sheet. Therefore, to determine impact of these chemical treatments, mechanical properties of the handsheets of different pretreated bleached pulps were evaluated by beating wheat straw bleached pulp in PFI mill at 1000 revolutions to reach a CSF value of 300ml (±20). The results are indicated in Plots 4.222 – 4.225. The results show a stronger (PxP) pretreated pulp than oxygen pretreated pulp. Lowest strength properties were observed in CEH sequence followed by (Px)CEH.

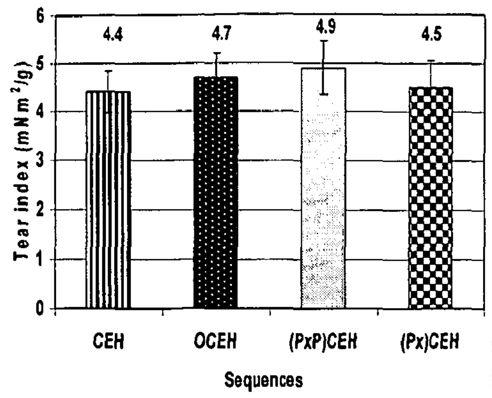


Fig.4.222 Effect of different bleaching sequences on tear strength of wheat straw pulp

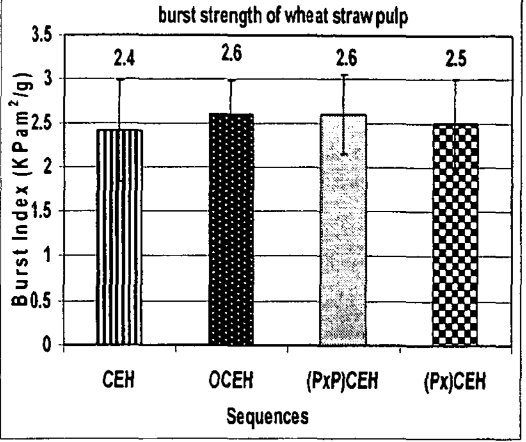


Fig. 4.223 Effect of different bleaching sequences on burst strength of wheat straw pulp

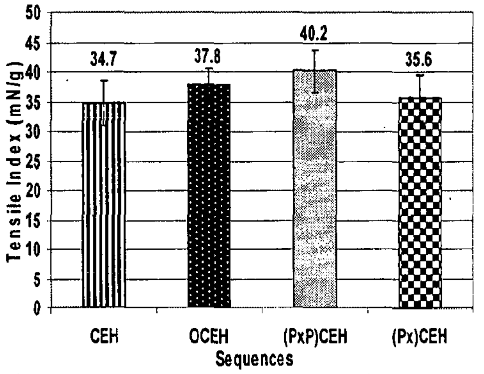


Fig. 4.224 Effect of different bleaching sequences on tensile strength of wheat straw pulp

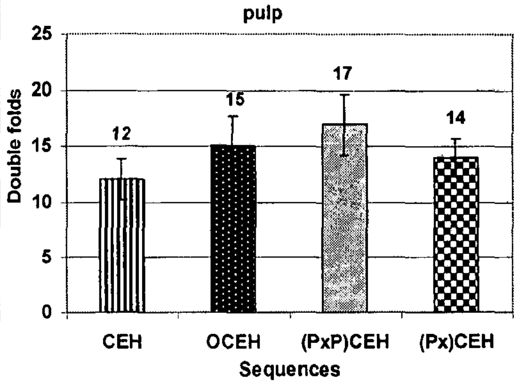


Fig. 4.225 Effect of different bleaching sequences on double folds of wheat straw pulp

I Represents Standard deviation (σ) from mean

The plotted values are mean of 10 readings

Thus, as depicted in the Figures 4.222 – 4.225, it can be stated that in wheat straw pulp, all the strength properties are higher for (PxP) pretreated pulps than oxygen pretreated pulps, other than burst index, which is found to be nearly similar for both. The changes in the values are consistent but are small and lie between the experimental limits of variation.

Effluent characteristics

The combined effluent was analyzed for COD, BOD, color and AOX from different bleaching sequences CEH, OCEH, (Px)CEH and (PxP)CEH. Results are given in Figures 4.226 – 4.227. The combined effluent refers to effluent from CEH portion of the bleaching sequence.

The environmental parameter to a large extent depends upon the bleach chemical consumption, higher the chemical consumption higher will be the values of BOD, COD, color and AOX. Pollution load values were highest for CEH sequence. As the pulp kappa number is higher so the bleach chemical charge required in CEH sequence to attain 80% target brightness is also high, giving higher COD, BOD, AOX and color values in comparison to other sequences.

Fig. 4.226 Combined effluent parameters from bleaching of wheat straw pulp

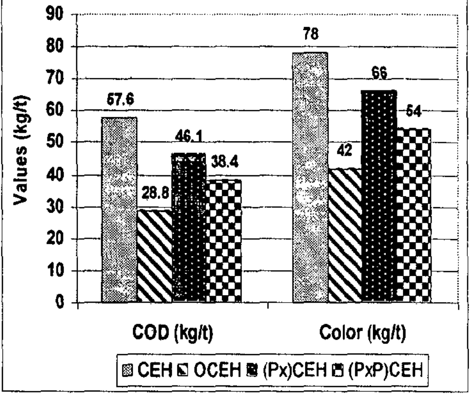
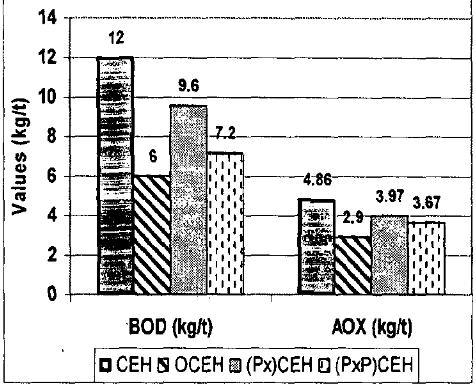


Fig. 4.227 Combined effluent parameters from bleaching of wheat straw pulp



BOD, color and COD values are mean of 3 readings

In the sequence (Px)CEH, COD is reduced by 20%, BOD is reduced by 20% and color reduction is 15%. The calculated AOX values for this sequence is 3.97 kg/t about 18% less than the conventional CEH sequence. In the sequence (PxP)CEH COD reduction is 33%, BOD reduction is 40%, color reduction is 31% and AOX is estimated to be 3.67 kg/t which is higher than the calculated AOX value. In OCEH sequence, as bleach chemical consumption is reduced by 53%, so effluent parameters are reduced to a great extent. COD value is 48% less while BOD is reduced by 50%. The percentage reduction in color is 46 and AOX is 40. Although the total bleach chemical demand is similar for both OCEH and (PxP)CEH at same target brightness but the BOD, COD and AOX is higher in (PxP)CEH.

Results are similar to that reported by Kringstad *et.al.* (80) stating that the formation of AOX and TOCl is linearly proportional to the consumption of elemental chlorine which depends on incoming kappa no. of unbleached pulp.

Thus it can be deduced that (PxP) pretreatment reduces the color forming compounds in pulps so the total bleach chemical dose is reduced but environmental parameters are not reduced to that extent in comparison to oxygen because incoming kappa number is 26% higher by (PxP) process.

4.2.2 CEH Bleaching (80% ISO) of Mixed Hardwood Pulp

The mixed hardwood pulp is bleached by conventional CEH sequence in untreated, oxygen delignified, (Px) pretreated and (PxP) pretreated pulps to target brightness of 80%ISO and a comparison is made regarding the bleach chemical demand, effluent characteristics and strength properties.

Bleach Chemical Demand

The CEH bleaching conditions, chemical dosages and properties is indicated in Table 4.222. While the chemical savings obtained in CEH bleaching followed by different pretreatments to obtain 80% ISO brightness pulp is given in Figure 4.228.

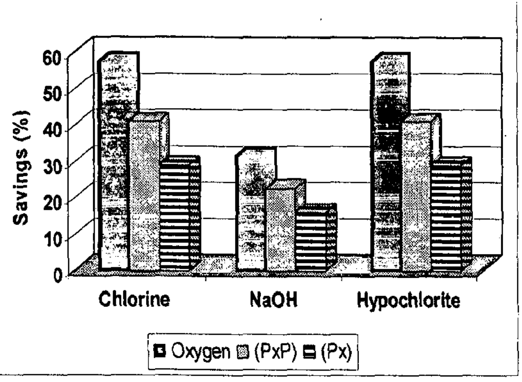


Fig.4.228 Chemical savings in CEH bleaching from different pretreatments in mixed hardwood pulp

The results given in the Table 4.222 show that the trend followed for active chlorine consumption for the bleaching sequences is:

CEH > (Px)CEH > (PxP)CEH > OCEH i.e. 42.2kg/t, 30kg/t, 25kg/t and 18kg/t. The savings obtained by different pretreatments shown in Figure 4.228 indicate that oxygen pretreatment reduces active chlorine consumption by 57.4% and alkali consumption by 31.5% as nearly 43% reduction in kappa number occurs by this route. While, percentage reduction of kappa number by (PxP) pretreatment is 28, giving savings in active chlorine consumption by 40.7% and alkali consumption by 22.4%.

The (Px) pretreatment is not quite effective as it reduces kappa number by 14% and gives reduction in total active chlorine consumption by 28.9% and alkali consumption by 15.8%. Also, highest viscosity reduction is observed for CEH sequence, followed by (Px)CEH sequence. While viscosity for OCEH and (PxP)CEH bleaching sequences is found to be nearly similar (Table 4.222).

Table – 4.222: Bleaching conditions used to make 80% ISO brightness mixed hardwood pulp by different pretreatments

Conditions	Sequences											
	CEH			*OCEH*			*PxCEH*			*PxPCEH*		
	C	E	H	C	E	H	C	E	H	C	E	H
Temp.(°C)	Amb.	70	40	Amb.	70	40	Amb.	70	40	Amb.	70	40
Cy (%)	3.0	10.0	7.0	3.0	10.0	7.0	3.0	10.0	7.0	3.0	10.0	7.0
RT (mins.)	45	60	210	45	60	210	45	60	210	45	60	210
End pH	2.1	12.3	11.0	1.9	11.8	10.9	2.0	12.4	11.2	1.9	11.9	10.7
aCl (%)	2.95	_	1.27	1.26	_	0.54	2.1	_	0.9	1.75	_	0.75
NaOH (%)	_	0.67	_	_	0.46	_	_	0.56	_	_	0.52	_
Residual aCl (%)	0.3	_	1.9	0.5	_	2.5	0.3	_	2.0	0.4	_	1.8
Brightness (% ISO) σ	_	_	80.4 *0.18*	-	-	80.5 *0.16*	-	-	80.3 *0.11*	-	-	80.3 *0.19*
Viscosity (cP)	-	-	9.41	-	-	10.28	-	-	9.7	-	-	10.4
Total aCl (%)	4.22			1.8			3.0			2.5		

Mechanical properties

The hand sheets of bleached mixed hardwood kraft pulp were analyzed by beating to 10500 revolutions in a PFI mill to attain a CSF value of 300 ml (±20). As shown in Figures 4.229 - 4.232 maximum reduction in pulp strength is observed in CEH sequence followed by (Px)CEH. All the strength properties of OCEH and (PxP)CEH sequences is found to be nearly similar, while tensile index is found to increase after (PxP) pretreatment. Hence, the strength properties of OCEH and (PxP)CEH sequences are comparable. It can also be observed from

Table 4.222 that viscosity values of OCEH and (PxP)CEH bleached pulps are similar. Results are in accordance to that reported by Suman *et.al.* stating that increasing pulp viscosity increases burst factor, tear factor, double fold and breaking length significantly (159).

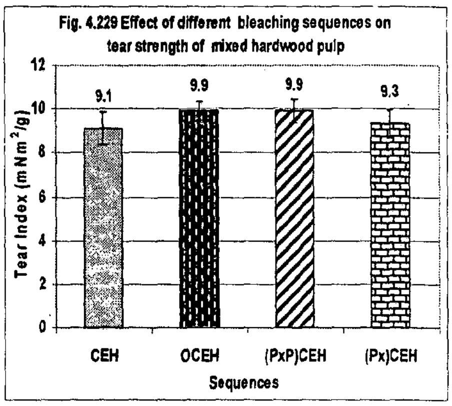


Fig. 4.229 Effect of different bleaching sequences on tear strength of mixed hardwood pulp

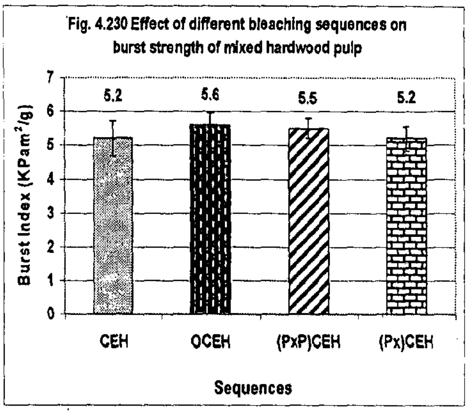


Fig. 4.230 Effect of different bleaching sequences on burst strength of mixed hardwood pulp

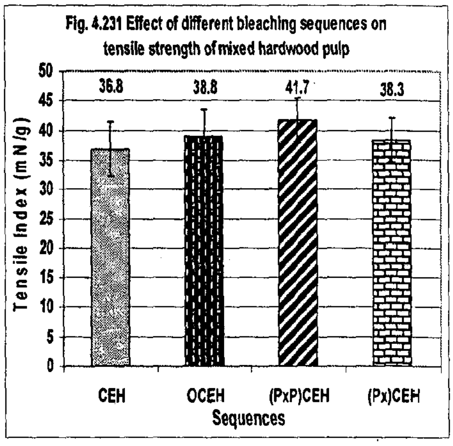


Fig. 4.231 Effect of different bleaching sequences on tensile strength of mixed hardwood pulp

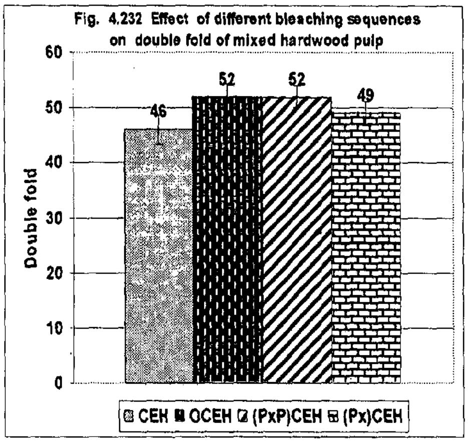


Fig. 4.232 Effect of different bleaching sequences on double fold of mixed hardwood pulp

[Represents Standard deviation (σ) from mean

The plotted values are mean of 10 readings

Effluent characteristics

The combined effluent of CEH, OCEH, PxCEH and (PxP)CEH sequences is characterized for COD, BOD, and color. The AOX is calculated by Germgard equation for these sequences according to the bleach chemical dose (49). The results are shown in Figures 4.233 – 4.234.

Fig. 4.233 Combined effluent characteristics from CEH bleaching of mixed hardwood pulp

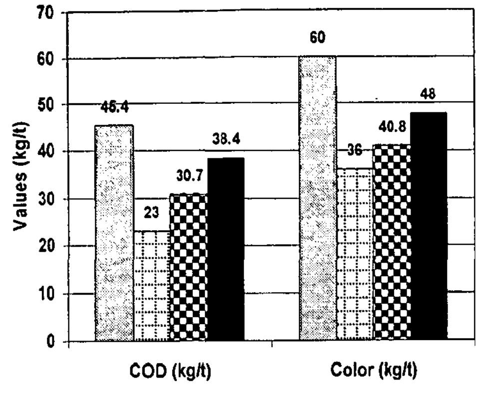
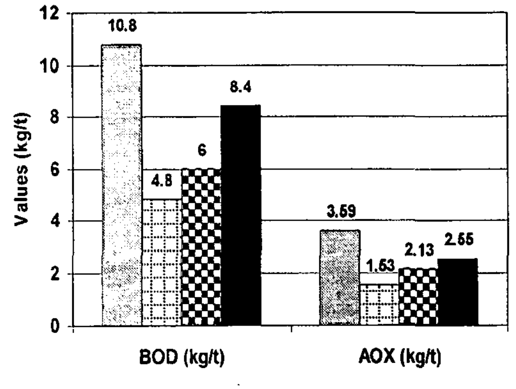


Fig. 4.234 Combined effluent characteristics from CEH bleaching of mixed hardwood pulp



BOD, color and COD values are mean of 3 readings

The COD, BOD, color and AOX are found to be higher for CEH sequence followed by (Px)CEH. However, in (Px)CEH sequence COD is reduced by 16%, BOD is decreased by 22% , color reduction is 36% and AOX is about 29% lesser than CEH. In OCEH sequence COD reduction is 50%, BOD reduction is 56%, color reduction is 40% and AOX reduction is 57%. The pollution load is reduced because oxygen delignification reduces the pulp kappa number by 45%. While in (PxP)CEH sequence COD is reduced by 31%, BOD by 44%, color reduction is in the range of 32% and AOX is decreased by 41%. Results are similar to that reported by Liebergott, *et.al.* stating that delignification before chlorination stage reduces AOX formation (90).

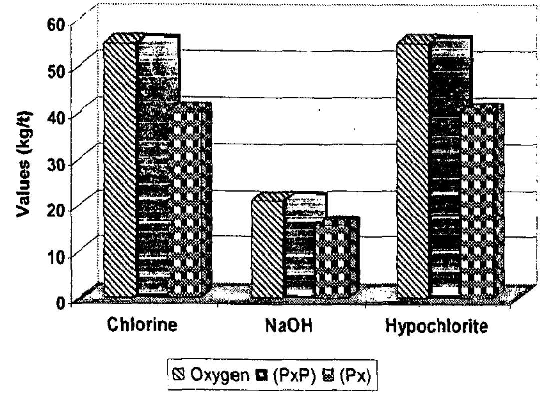
4.2.3 CEH Bleaching (85% ISO) of Bagasse Pulp

The untreated, (PxP) pretreated, oxygen pretreated and (Px) pretreated pulps are bleached by conventional CEH sequence and a comparative evaluation is made regarding the bleach chemical dosage, environmental parameters and strength properties. The bagasse pulp is low kappa pulp so the target brightness is kept 85% ISO.

Bleach Chemical Demand

The CEH bleaching conditions, chemical dosages and strength properties are given in Table 4.223. The chemical savings obtained in CEH bleaching followed by different pretreatments is illustrated in Figure 4.235.

Fig. 4.235 Chemical savings in CEH bleaching followed by different pretreatments of bagasse pulp



As the chemical dosage will depend on the initial kappa number of pulp to attain target brightness so the trend followed for total chemical consumption in bleaching sequences is: CEH > (Px)CEH > OCEH ≈ (PxP)CEH i.e. 20kg/t, 12kg/t and 9kg/t. The results are similar to that observed in wheat straw pulp. Although, the kappa number of (PxP) pretreated pulp is 19.8% higher than oxygen pretreated pulp, but the total active chlorine consumption for the two pulps to attain target brightness is similar.

Table – 4.223: Bleaching conditions used to make 85% ISO brightness bagasse pulp by different pretreatments

Conditions	Sequences											
	CEH			*OCEH*			*(Px)CEH*			*(PxP)CEH*		
	C	E	H	C	E	H	C	E	H	C	E	H
Temp.(°C)	Amb	70	40	Amb	70	40	Amb	70	40	Amb	70	40
Cy (%)	3.0	10.0	7.0	3.0	10.0	7.0	3.0	10.0	7.0	3.0	10.0	7.0
RT (mins.)	45	60	210	45	60	210	45	60	210	45	60	210
End pH	2.0	12.3	11.2	1.9	11.9	10.7	1.9	12.0	10.8	2.1	12.0	10.7
aCl (%)	1.40	_	0.60	0.63	_	0.27	0.84	_	0.36	0.63	_	0.27
NaOH (%)	_	0.48	_	_	0.38	_	_	0.405	_	_	0.38	_
Residual aCl (%)	0.4	_	2.3	0.3	_	2.3	0.5	_	2.3	0.6	_	2.5
Brightness (% ISO)	_	_	85.2	-	-	85.3	-	-	85.4	-	-	85.4
σ			*0.15*			*0.24*			*0.15*			*0.18*
Viscosity (cP)	-	-	13.4	-	-	14.6	-	-	13.9	-	-	14.8
Total aCl (%)	2.0			0.9			1.2			0.9		

Thus as shown in Figure 4.235 the chemical savings obtained by (PxP) and oxygen pretreatment is highest, with 55 and 21 percent reduction in active chlorine consumption and alkali consumption respectively. The (Px) pretreatment does not reduce kappa number as effectively as other two methods, so active chlorine consumption reduces by 40% while alkali consumption reduces by 16%. The strength indicated by CED viscosity follows the trend:

(PxP)CEH > OCEH > (Px)CEH > CEH

By comparing the Figures 4.221, 4.228 and 4.235 it can be observed that bleaching response of bagasse pulp is the best, as higher chemical savings are obtained in bagásse pulp with high target brightness. Hence, results are similar to that reported by Mantri *et.al.* stating that bagasse pulps are easier to bleach by usage of CEH sequence (95).

Mechanical properties

The bagasse pulp bleached by CEH, OCEH, (Px)CEH and (PxP)CEH sequences were beaten to similar degree in a PFI mill so that pulp attains CSF of 300 ml(±20). The results are given in Figures 4.236 – 4.239. By observing the Figures 4.236 – 4.239, it can be stated that strength properties of (PxP) and oxygen pretreated pulp is comparable. The burst index and tear index is slightly higher in oxygen treated pulp while tensile index is highest in (PxP) pretreated pulp and double fold is similar in both. Highest drop in strength is observed in (Px) pretreated pulp, as observed in the other two raw materials.

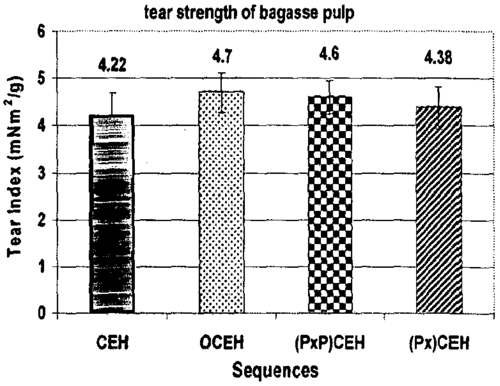


Fig. 4.236 Effect of different bleaching sequences on tear strength of bagasse pulp

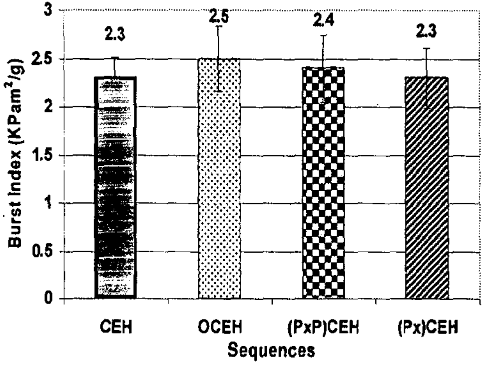


Fig. 4.237 Effect of different bleaching sequences on burst index of bagasse pulp

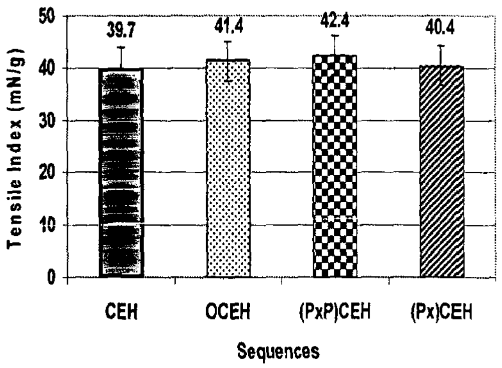


Fig. 4.238 Effect of different bleaching sequences on tensile strength of bagasse pulp

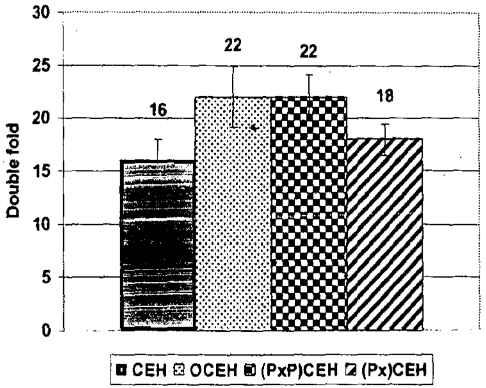


Fig. 4.239 Effect of different bleaching sequences on double fold of bagasse pulp

Ι Represents Standard deviation (σ) from mean
The plotted values are mean of 10 readings

Effluent Characteristics

The combined effluent from conventional CEH, OCEH, (Px)CEH and (PxP)CEH were analyzed for COD, BOD and color. AOX was quantified by Germgard equation according to the bleach chemical dose (49). The results are illustrated in Plots 4.240 – 4.241.

Fig. 4.240 Combined effluent parameters from CEH bleaching of Bagasse pulp

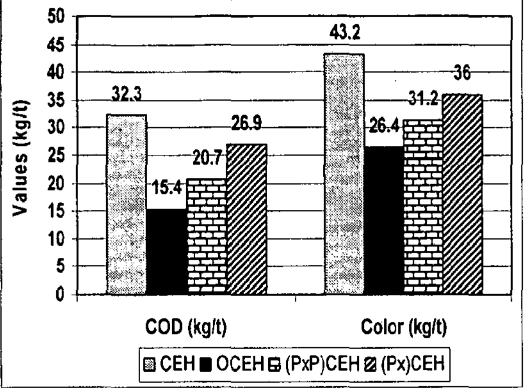
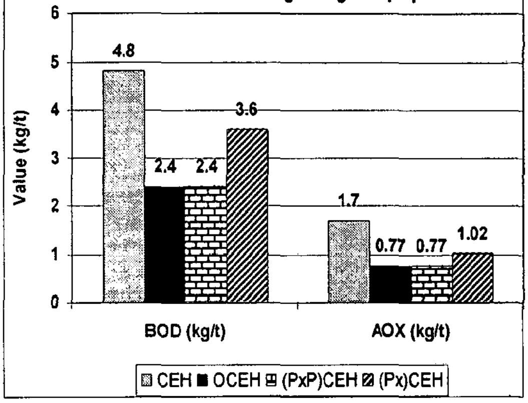


Fig. 4.241 Combined effluent characteristics from CEH bleaching of bagasse pulp



BOD, color and COD values are mean of 3 readings

In CEH, COD is 32kg/t, BOD is 4.8kg/t, color is 48kg/t and AOX 1.7kg/t. In comparison to the other pulps, in bagasse pulp the quantities of pollutants is less, as the incoming kappa number of the pulp is low. In (Px)CEH sequence, COD is reduced by 17%, BOD reduction is 25%, color reduction 17% and AOX reduction is 40%. However, in OCEH and (PxP)CEH, the COD and color is higher for (PxP)CEH as shown in Figure 4.240, although the chemical charges are same for the both (Table 4.223). In OCEH, COD reduction is 52%, BOD reduction is 50%, color reduction is 39% and AOX reduction is 55%. In (PxP)CEH sequence, COD is reduced by 36%, BOD reduced by 50%, color reduction is 28% and AOX reduction similar to that of OCEH, that is 55%.

ECF BLEACHING

ECF bleaching is a specific sequence but can be any bleaching sequence avoiding the use of elemental chlorine and can include the use of chlorine dioxide (128). Chlorine is an effective and selective chemical for removing lignin, but it forms maximum amounts of chlorinated organics. While both chlorine and chlorine dioxide contribute to AOX formation, the molecular chlorine does so to a much greater extent (15).

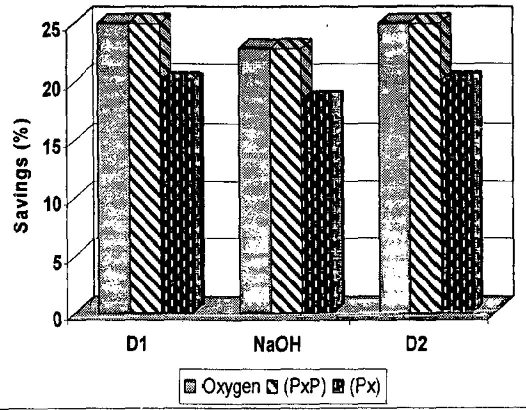
4.2.4 DED Bleaching (80%ISO) of Wheat Straw Pulp

The untreated, (Px) pretreated, oxygen delignified and (PxP) pretreated pulps were bleached by DED sequence to 80% ISO brightness and comparison was made in all the four sequences regarding the bleach chemical demand, environmental parameters and strength properties.

Bleach Chemical Demand

The bleaching parameters, chemical dosages and viscosity for DED bleaching following different sequences are reported in Table 4.224. The chemical savings by (PxP), oxygen and (Px) pretreatment sequences is shown in Figure 4.242.

Fig. 4.242 Chemical savings in DED bleaching from different pretreatments in wheat straw pulp



The total active chlorine consumption follows the order:

DED > (Px)DED > ODED ≈ (PxP)DED. Thus, the chemical savings obtained after oxygen and (PxP) pretreatment are the same although kappa number (Figure 4.242) after (PxP) is 26% higher than oxygen delignified pulp. The viscosity trend observed in the sequences is:

ODED > (PxP)DED > DED > (Px)DED (Table 4.224). The (Px) pretreatment is not found to be very effective as the chemical consumption is higher with high drop in viscosity in comparison to (PxP) and oxygen pretreatments.

Table – 4.224: Bleaching conditions used to make 80% ISO brightness wheat straw pulp by different pretreatments

Conditions	**Sequences**											
	DED			***ODED***			***(Px)DED***			***(PxP)DED***		
	D	**E**	**D**	**D**	**E**	**D**	**D**	**E**	**D**	**D**	**E**	**D**
Temp.(°C)	70	70	70	70	70	70	70	70	70	70	70	70
Cy (%)	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
RT (mins.)	90	60	180	90	60	180	90	60	180	90	60	180
End pH	4.8	11.2	4.3	4.5	10.9	4.2	4.9	11.5	4.53	5.0	10.9	4.5
aCl (%)	7.0	–	3.0	5.25	–	2.25	5.6	–	2.4	5.25	–	2.25
NaOH (%)	–	3.8	–	–	2.93	–	–	3.1	–	–	2.93	–
Residual chemical (%)	0.8	–	1.4	0.9	–	1.2	0.9	–	1.2	0.9	–	1.3
Brightness (% ISO) *σ*	–	–	80.5 *0.15*	-	-	80.4 *0.18*	-	-	80.5 *0.25*	-	-	80.6 *0.19*
Viscosity (cP)	-	-	21.6	-	-	23.8	-	-	21.1	-	-	22.7
Total aCl (%)	10.0			7.5			8.0			7.5		

Mechanical Properties

The mechanical properties of air dried hand sheets of different pretreated bleached pulps were evaluated by beating bleached pulp in PFI mill at 1000 revolutions to arrive at 300 ± 20 CSF values. The results are illustrated in Figures 4.243 – 4.246.

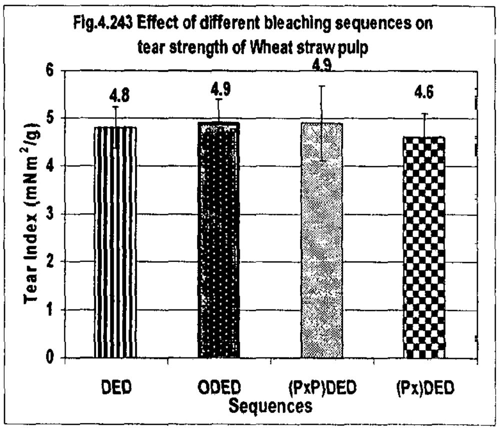


Fig.4.243 Effect of different bleaching sequences on tear strength of Wheat straw pulp

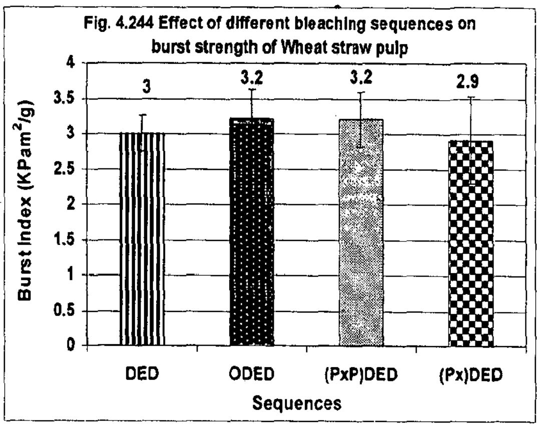


Fig. 4.244 Effect of different bleaching sequences on burst strength of Wheat straw pulp

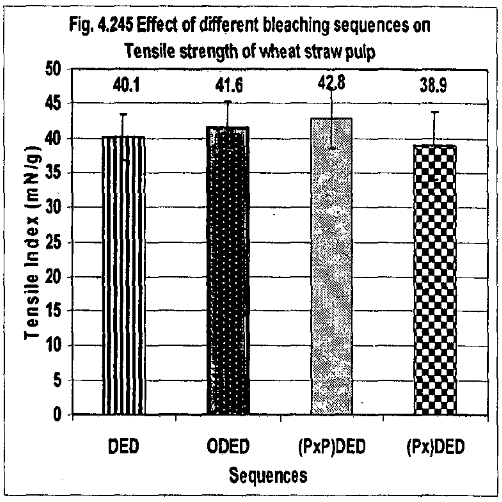


Fig. 4.245 Effect of different bleaching sequences on Tensile strength of wheat straw pulp

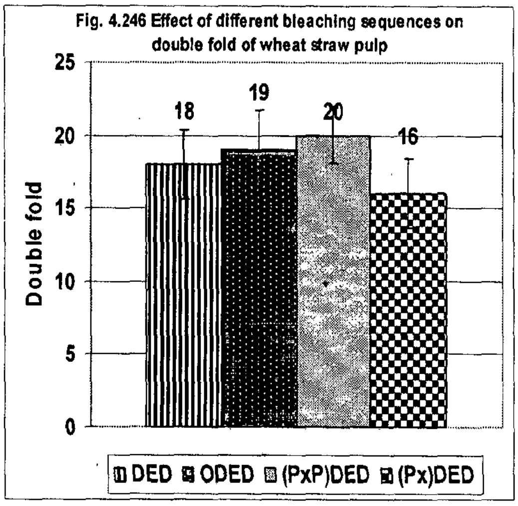


Fig. 4.246 Effect of different bleaching sequences on double fold of wheat straw pulp

[Represents Standard deviation (σ) from mean

The plotted values are mean of 10 readings

It can be deduced from the following Figures 4.243 – 4.246 that (PxP) pretreated pulp strength properties are similar or better than oxygen pretreated pulps. Tear index, burst index and double fold is observed to be similar in

(PxP)DED and ODED bleached pulps while tensile index is slightly higher in (PxP)DED bleached pulp. Maximum drop in strength is observed in (Px)DED bleached pulp, hence (Px) stage is not very effective.

Effluent Characteristics

The combined effluent collected after bleaching was characterized for COD, BOD, AOX and color for different bleaching sequences DED, (Px)DED, (PxP)DED and ODED. Estimated AOX values were found to be slightly higher than the calculated values. For (Px)DED sequence, AOX could not be measured. The results are illustrated in Plots 4.247 – 4.248.

Fig. 4.247 Combined effluent characteristics from DED bleaching of wheat straw pulp

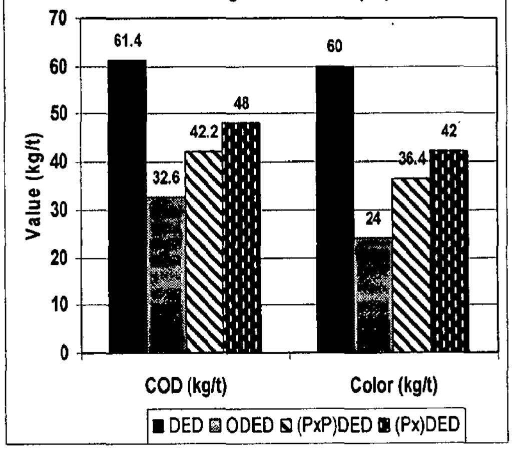
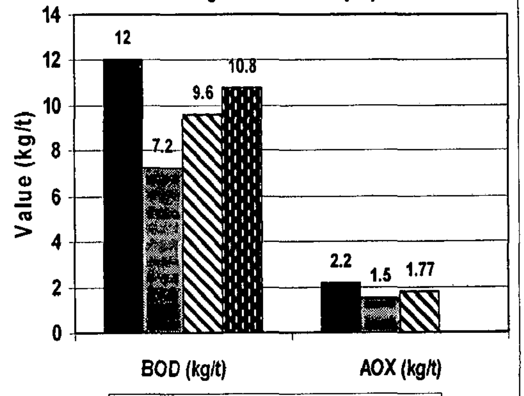


Fig. 4.248 Combined effluent parameters from DED bleaching of wheat straw pulp



BOD, color and COD values are mean of 3 readings

In DED as the total active chlorine consumption was higher so the COD, BOD, AOX and color was higher. COD was 61.44kg/t, BOD was 12kg/t, color was 60kg/t while AOX was 2.2kg/t. In (Px)DED sequence COD reduction was 22%, BOD reduction 10% and color reduction was 30%. In (PxP)DED sequence, COD is decreased by 31%, BOD reduced by 20%, 36% color reduction is achieved and AOX reduction is 20%. However, in ODED sequence, COD decreased by 47%, BOD reduction 40%, color reduction is 60% and AOX reduction is 32%. In ODED sequence, AOX is 1.5kg/t, thus results are similar to that reported by Mc Cubbin *et.al.* (100) stating that oxygen stage followed by 100% chlorine dioxide bleaching stage will reduce AOX to 1.5kg/t. Although, same chemical charge is applied in ODED and (PxP)DED but still AOX of (PxP)DED sequence could not be lowered to similar levels as ODED bleaching sequence.

4.2.5 Mixed hardwood pulp

The hardwood pulp is bleached by DED, (Px)DED, (PxP)DED and ODED sequences to target brightness of 80% ISO. The impact of bleaching sequences was considered on bleach chemical dose, environmental parameters and mechanical strength properties.

Bleach Chemical Demand

The bleach chemical charge, bleaching conditions and viscosity of DED sequence following different pretreatments is tabulated in Table 4.225 and the chemical savings achieved is illustrated in Figure 4.249.

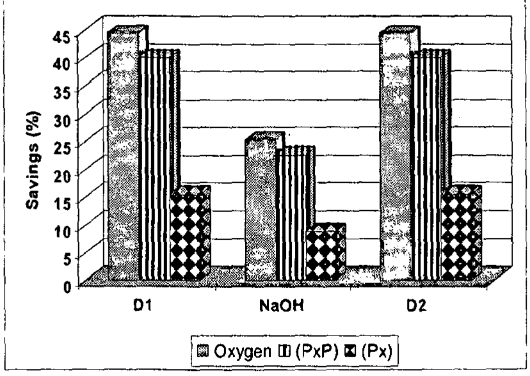


Fig. 4.249 Chemical savings from DED bleaching from different pretreatments in mixed hardwood pulp

The total active chlorine consumption follows the trend according to the initial kappa number of pulp, which is:

DED > (Px)DED > (PxP)DED > ODED

The chemical savings obtained by oxygen delignification is 44% for active chlorine consumption while 40% by (PxP) route and 16% by (Px) pretreatment (Figure 4.249). The alkali savings by oxygen pretreatment is 25%, by (PxP) alkali reduction is 23% and by (Px) alkali savings are 9%. The viscosity follows the trend ODED > (PxP)DED > DED > (Px)DED, similar to that observed in wheat straw pulp. (Tables 4.225 and 4.224).

Table – 4.225: Bleaching conditions used to make 80% ISO brightness mixed hardwood pulp by different pretreatments

Conditions	**Sequences**											
	DED			***ODED***			***PxDED***			***(PxP)DED***		
	D	**E**	**D**	**D**	**E**	**D**	**D**	**E**	**D**	**D**	**E**	**D**
Temp.(°C)	70	70	70	70	70	70	70	70	70	70	70	70
Cy (%)	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
RT (mins.)	90	60	180	90	60	180	90	60	180	90	60	180
End pH	4.6	11.1	4.3	4.8	10.9	4.4	5.0	10.8	4.60	4.7	11.1	4.4
aCl (%)	3.15	_	1.35	1.75	_	0.75	2.66	_	1.14	1.89	_	0.81
NaOH (%)	_	0.69	_	_	0.52	_	_	0.63	_	_	0.54	_
Residual chemical (%)	0.43	_	1.1	0.43	_	1.13	0.46	_	1.18	0.48	_	1.05
Brightness (% ISO)	–	–	80.2	-	-	80.6	-	-	80.3	-	-	80.5
σ			*0.16*			*0.07*			*0.11*			*0.14*
Viscosity (cP)	-	-	11.3	-	-	12.2	-	-	10.9	-	-	11.9
Total aCl (%)	4.5			2.5			3.8			2.7		

Mechanical strength properties

The handsheets of bleached ECF pulp by various sequences were beaten to similar revolutions in a PFI mill so that pulp attains 300ml (±20)CSF. The results are illustrated in Figures 4.250 – 4.253. The maximum reduction in pulp strength is observed in (Px)DED sequence followed by DED. In ODED, tear index, burst index and double fold are slightly higher than the (PxP)DED sequence, while tensile index is highest for (PxP)DED bleached pulp. Hence (Px) pretreatment forms a weaker pulp than other pretreated pulps, while strength properties of ODED and (PxP)DED are nearly similar.

Fig. 4.250 Effect of different bleaching sequences on tear strength of mixed hardwood pulp

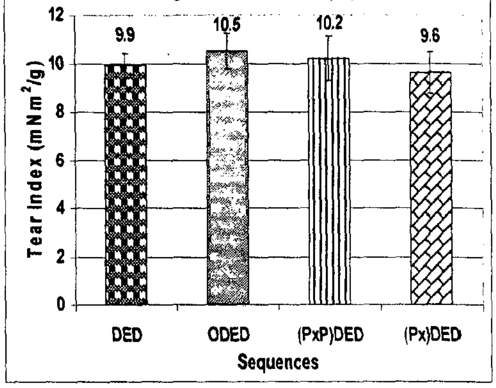


Fig. 4.251 Effect of different bleaching sequences on burst strength of mixed hardwood pulp

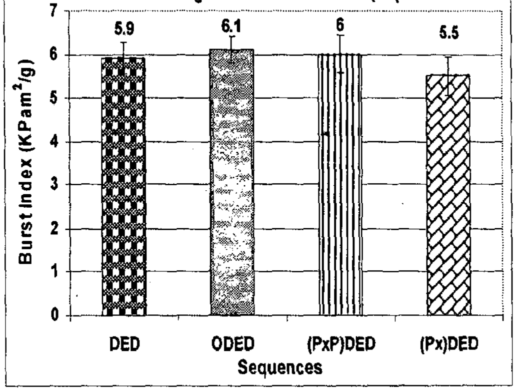


Fig. 4.252 Effect of different bleaching sequences on tensile strength of mixed hardwood pulp

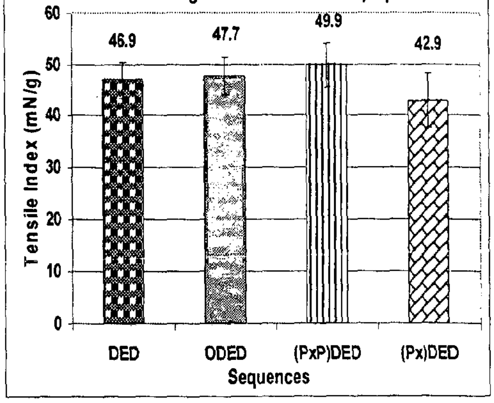
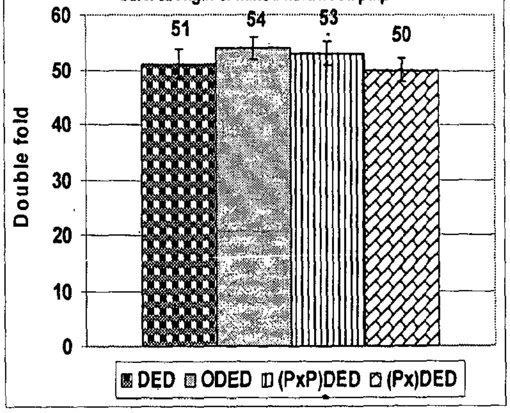


Fig. 4.253 Effect of different bleaching sequences on burst strength of mixed hardwood pulp



I Represents Standard deviation (σ) from mean

The plotted values are mean of 10 readings

Pollution Load Generation

The combined effluent from ECF sequences was analyzed for COD, BOD, color and AOX. The AOX values are calculated by Germgard equation from the bleach chemical charged (49). The results are represented in Figures 4.254 and 4.255. In DED sequence, COD is 46.1kg/t, BOD 9.6kg/t, color 33.6kg/t and AOX is 0.9kg/t. However in (Px)DED sequence, COD reduces by 8.3%, BOD reduction is 25%, color reduction 21.4% and AOX reduction is 15.6%. In (PxP)DED sequence percentage reduction in COD, BOD, color and AOX is 25, 50, 28.6 and 40 respectively. While highest reduction is observed by sequence following oxygen delignification. Here, COD reduces by 41.7%, BOD decreases by 62.5%, color reduces by 50% and AOX reduces by 44.4%. Therefore by all of these sequences, AOX has been brought down to meet the requirement of CREP.

Fig. 4.254 Combined effluent parameters from DED bleaching of mixed hardwood pulp

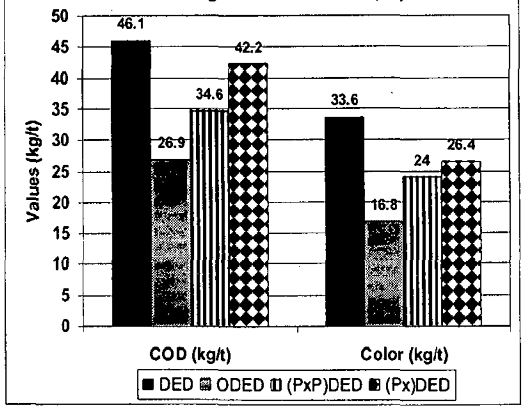
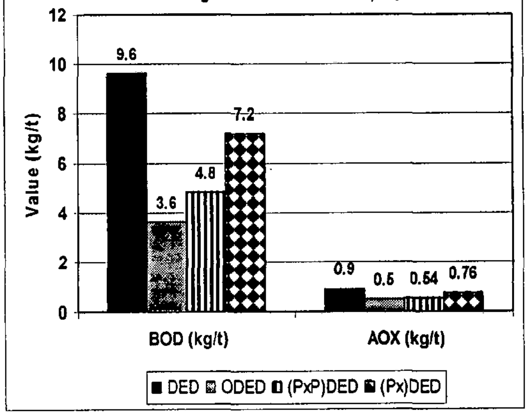


Fig. 4.255 Combined effluent parameters from DED bleaching of mixed hardwood pulp



BOD, color and COD values are mean of 3 readings

4.2.6 Bagasse Pulp (85% ISO)

The bagasse pulp is bleached by short ECF sequence followed by (Px), (PxP) and oxygen pretreatments to target brightness of 85% ISO. The bleached pulp was characterized for viscosity, brightness and mechanical properties and comparison was made regarding the active chlorine consumption, strength and pollution load generated.

Bleach Chemical Charge

The total chemical dosage, pulp properties and bleaching conditions are tabulated in Table 4.226 for DED, (Px)DED, (PxP)DED and ODED sequences and chemical savings obtained are given in Figure 4.256. The total active chlorine consumption follows the trend: DED > (Px)DED > ODED ≈ (PxP)DED. While the kappa number of (PxP) pretreated pulp is 19.8% higher than oxygen pretreated pulp, but the total active chlorine consumption for the two pulps to attain target brightness is similar. The viscosity follows the trend similar to wheat straw and mixed hardwood pulps. The oxygen and (PxP) pretreatment reduces chemical consumption by 38.5% and alkali consumption by 25.2%, while percentage reduction by (Px) process is 30.8 and 20.1 for active chlorine consumption and alkali consumption respectively.

Fig. 4.256 Chemical savings in DED bleaching from different pretreatments in bagasse pulp

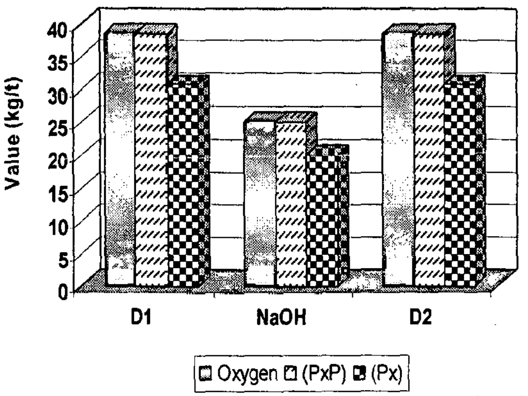


Table – 4.226: Bleaching conditions used to make 85% ISO brightness bagasse pulp by different pretreatments

Conditions	Sequences											
	DED			*ODED*			*PxDED*			*(PxP)DED*		
	D	E	D	D	E	D	D	E	D	D	E	D
Temp.(°C)	70	70	70	70	70	70	70	70	70	70	70	70
Cy (%)	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
RT (mins.)	90	60	180	90	60	180	90	60	180	90	60	180
End pH	4.7	11.7	4.3	4.9	11.1	4.4	4.6	11.5	4.2	4.76	11.4	4.20
aCl (%)	4.55	_	1.95	2.8	_	1.2	3.15	_	1.35	2.8	_	1.2
NaOH (%)	_	0.87	_	_	0.65	_	_	0.69	_	_	0.65	_
Residual chemical (%)	0.45	_	1.15	0.49	_	1.21	0.42	_	1.11	0.79	_	1.03
Brightness (% ISO) σ	_	_	85.3 *0.16*	-	-	85.2 *0.16*	-	-	85.4 *0.15*	-	-	85.3 *0.22*
Viscosity (cP)	-	-	15.9	-	-	18.4	-	-	14.3	-	-	16.4
Total aCl (%)	6.5			4.0			4.5			4.0		

Strength properties

The trend of strength properties in ODED, DED, (Px)DED and (PxP)DED sequences are depicted in Figures 4.257 – 4.260. The bleached pulp by above stated sequences was beaten to similar levels so as to have a pulp of nearly same CSF (300±20ml). The lowest strength is observed in (Px)DED sequence. Tear index, burst index and double fold are slightly higher for ODED sequence while tensile index has higher values in (PxP)DED bleached pulps.

Fig. 4.257 Effect of different bleaching sequences on Tear strength of bagasse pulp

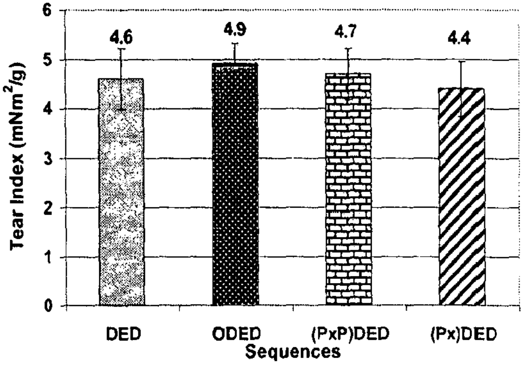


Fig. 4.258 Effect of different bleaching sequences on burst strength of bagasse pulp

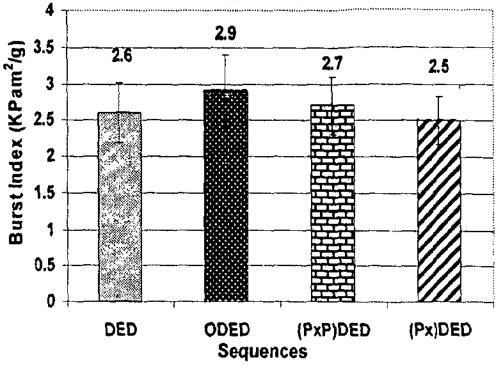


Fig. 4.259 Effect of different bleaching sequences on tensile strength of bagasse pulp

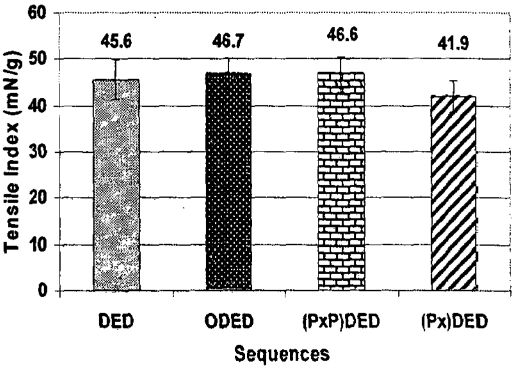
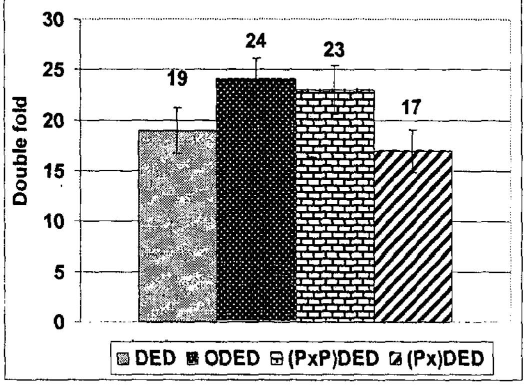


Fig. 4.260 Effect of different bleaching sequences on double foldof bagasse pulp



[Represents Standard deviation (σ) from mean

The plotted values are mean of 10 readings

Effluent characteristics

The combined effluent from DED, ODED, (Px)DED and (PxP)DED sequences is analyzed for COD, BOD, color and AOX which is calculated according to the bleach chemical charge by Germgard equation (49). The results are given in Figures 4.261 and 4.262. In DED sequence, the COD is 47.6kg/t, BOD 6kg/t, color 26.4kg/t and AOX 1.3kg/t. The BOD/COD ratio is almost similar in all the sequences. In (Px)DED sequence, COD reduction is 8%, BOD reduction 20%, color reduction is 36% and AOX reduction is 31%. However, in (PxP)DED sequence the percentage reductions in COD, BOD, color and AOX are in the range of 19%, 40%, 46% and 39% respectively. In ODED, percentage reductions are higher, about 40% reduction in COD and reduction in color is 55% while BOD and AOX reduction are similar to that in (PxP)DED sequence. Hence, pollution load seems to increase with increasing chemical dose. Results are similar to that reported by Ray *et.al.* (135) stating that COD load of effluent from DED sequence seems to increase with increasing active chlorine dose.

Fig.4.261 Combined effluent parameters from DED bleaching of bagasse pulp

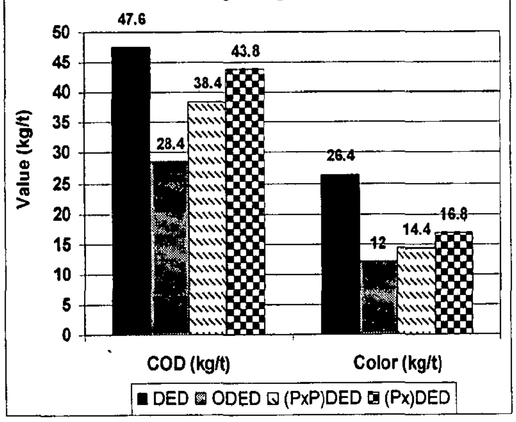
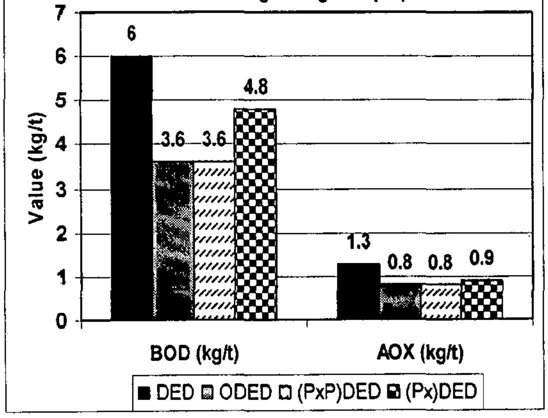


Fig. 4.262 Combined effluent parameters from DED bleaching of bagasse pulp



BOD, color and COD values are mean of 3 readings

4.2.7 Economic Analysis

Economic evaluation of any process modification is essentially made by evaluating the measurable economic impacts in terms of either additional input costs (operating costs) or gain in output costs (value addition).

However, when the variables offer intangible benefits it becomes difficult to assign an economic value of such a benefit. In case of improved environmental performance one can see the viability of a process from its meeting the set regulatory standards. Non-compliance usually results in closure of an operation. In such situations one can consider the increase input costs for making a system operational as investment cost and cost of closure for non compliance as a measurable economic benefit of such an investment. In the present economic analysis the following costs have been considered towards input:

a) Costs of oxygen, (Px) and (PxP) pretreatments.

b) Change in the input bleach chemical costs for a given pulp during bleaching compared to such costs for conventional pulp bleaching sequences.

c) The cost of reduction of AOX through end of pipeline treatment technologies like – adsorption and ion exchange has been taken as an additional cost of operation to meet the set regulatory standards (as per present price index).

d) The intangible benefits of keeping operations sustainable due to environmental compliance with modified bleaching sequence involving (PxP) pretreatment, which would otherwise have been closed for non compliance is non included in the current cost estimates.

e) The Central Pollution Control Board of India under Charter for Corporate Responsibility (CREP) has proposed norm of AOX at 1.5kg/t of paper produced which is to be reduced to 1kg/t for next two years (144).

The prices in India in 2006 of different bleaching chemicals used for bleaching are given in Table 4.227 which was obtained from nearby paper mill and chemical manufacturers. The estimated bleaching costs are shown in Tables 4.228 – 4.230.

4.227: Costs of various bleaching chemicals in India in 2006

Chemical	Cost (Rs./kg)
Chlorine	8.5
Sodium hydroxide	15
Calcium hypochlorite	22
Hydrogen peroxide	46
Chlorine dioxide (as such)	59.8
Oxygen (manufactured onsite)	2.9
Magnesium sulphate	28
Sodium persulphate	70
EDTA	22.5

4.228: **Bleach Chemical Costs Analysis of wheat straw soda pulp at sodium persulphate cost of Rs.22/kg**

Sequence	Bleaching cost (Rs/t) of pulp			AOX (kg/t)			Bleaching cost including cost of AOX reduction (Rs/t)
	Cost of Pretreatment Stage (Rs./t)	Bleach Chemical (Rs./t)	Total Cost (Rs./t)	Values	Reduction		
					Kg/t	Rs/t (@190/kg)	
CEH	-	1099	1099	4.86	-	-	-
OCEH	735	491	1226	2.9	1.96	372	854
(Px)CEH	1515	877	2392	3.97(*)	0.89	169	2223
(PxP)CEH	1215	491	1706	3.67	1.19	226	1480
DED	-	2843	2843	2.2	-	-	-
ODED	735	2141	2876	1.5	0.7	133	2743
(Px)DED	1515	2284	3799	1.5(*)	0.7	133	3666
(PxP)DED	1215	2141	3355	1.77	0.43	82	3273

** represents calculated value of AOX (kg/t)*

4.229: **Bleach Chemical Costs Analysis of mixed hardwood kraft pulp at sodium persulphate cost of Rs.22/kg**

Sequence	Bleaching cost (Rs/t) of pulp			AOX (kg/t) *			Bleaching cost including cost of AOX reduction (Rs/t)
	Cost of Pretreatment Stage (Rs./t)	Bleach Chemical (Rs./t)	Total Cost (Rs./t)	Value (kg/t)	Reduction		
					Kg/t	Rs/t (@190/kg)	
CEH	-	631	631	3.59	-	-	-
OCEH	407	295	702	1.53	2.06	391	311
(Px)CEH	1515	461	1976	2.55	1.04	198	1778
(PxP)CEH	1215	392	1607	2.13	1.46	277	1330
DED	-	1127	1127	0.9	-	-	-
ODED	407	647	1054	0.5	0.4	76	978
(Px)DED	1515	959	2474	0.76	0.14	27	2447
(PxP)DED	1215	695	1910	0.54	0.36	68.4	1842

** represents calculated value of AOX (kg/t)*

4.230: Bleach Chemical Costs Analysis of bagasse kraft pulp at sodium persulphate cost of Rs.22/kg

Sequence	Bleaching cost (Rs/t) of pulp			AOX (kg/t) *			Bleaching cost including cost of AOX reduction (Rs/t)
	Cost of Pretreatment Stage (Rs/t)	Bleach Chemical (Rs/t)	Total Cost (Rs/t)	Values (kg/t)	Reduction		
					kg/t	Rs/t (@190/kg)	
CEH	-	323	323	1.7	-	-	-
OCEH	146	170	316	0.77	0.93	177	139
(Px)CEH	1515	212	1727	1.02	0.68	129	1598
(PxP)CEH	1215	170	1385	0.77	0.93	177	1208
DED	-	1609	1609	1.3	-	-	-
ODED	146	1008	1154	0.8	0.5	95	1059
(Px)DED	1515	1127	2642	0.9	0.4	76	2566
(PxP)DED	1215	1008	2223	0.8	0.5	95	2128

** represents calculated value of AOX (kg/t)*

The results indicate that total bleaching costs is higher with (PxP) and (Px) based sequences. In Table 4.227 the cost of persulphate is given as Rs.70/kg but in a commercial plant, a sustainable source for persulphate manufacture will be sodium sesquisulphate (byproduct) from the chlorine dioxide plant. The manufacturing process for persulphate from sesquisulphate is based on process suggested by Wong *et.al.* (182) is essentially by electrochemical cell. The cells using sesquisulphate have higher current efficiency (60%) and lower energy requirements.

The manufacture of persulphate in a commercial scale from sesquisulphate will drastically reduce the cost of persulphate on one hand and on the other hand will reduce the problems related operation of multiple effect evaporator (MEE) of recovery plants with respect to scaling and corrosion. If sesquisulphate is not recovered in mill then huge losses will be incurred, as release of this byproduct into sewer is not feasible and it requires neutralization before discharge to mill's effluent treatment plant.

The raw material price being absent (use of waste from chlorine dioxide manufacture) the cost of persulphate will be negligible; however an intermediate price at one third of the current market persulphate price is used in the present calculation. The cost of sodium persulphate by this manufacturing process onsite is likely to be between Rs.22-23/kg. The cost of persulphate will be much cheaper for onsite manufacture in plants having captive power plants as the power costs are much lower than purchased power from the grid.

The CREP norms suggest several initiatives to reduce environmental impacts of pulp mills. These include among other things a chemical recovery unit to be installed with chemical pulping. All such mills with chemical pulping can process the effluents generated from (Px) and (PxP) prebleaching and close the bleaching cycle. The possibilities of recycling bleach plant effluents and closing bleach filtrate cycle for different stages is shown in Table 4.231.

Table 4.231: Bleach plant effluent recycle/ closure possibilities

Stage	**Bleach effluent recycle possibilities (Yes/ No)**
Oxygen (O)	Yes
Chlorination (C)	No
Extraction (E)	No
Hypochlorite (H)	No
Chlorine dioxide (D)	No
Persulphate (Px)	Yes
Persulphate-peroxide (PxP)	Yes

As given in Tables 4.228-4.230 and Table 4.231 the mills opting to meet environmental standards for AOX and close the bleach cycle necessarily will have to look at either oxygen delignification or (PxP) as a prebleaching stage irrespective of their cost limitations. One of the main reasons for not adopting oxygen delignification processes in small mills particularly those using nonwoods is the high installation costs of oxygen delignification process. Such mills will find the (PxP) route attractive, either with or without chlorine dioxide. This is because persulphate manufacturing unit is much less capital intensive and easily adaptable compared to oxygen plant.

The conventional CEH bleaching sequence in wheat straw, mixed hardwood and bagasse pulp with regard to AOX are high and cannot be adopted in view of changing AOX norms. Mills which will not be able to install oxygen delignification stage can meet desired environmental standards for liquid effluents particularly with respect to AOX by the two routes namely (PxP)CEH in bagasse kraft pulp and (PxP)DED in mixed hardwood kraft and bagasse kraft pulps. The (PxP)CEH is cheaper for operation but the possibilities of getting AOX values much below 1.5kg/t is doubtful in case of wheat straw and mixed hardwood pulp (Tables 4.228-4.230). The suggested cost effective and environmentally sound options from results given in Tables 4.228-4.230, based on capital costs for oxygen plants will be ODED and (PxP)DED for wheat straw soda pulp, OCEH, DED, ODED and (PxP)DED in mixed hardwood kraft pulp and OCEH, (PxP)CEH, DED, ODED and (PxP)DED in bagasse kraft pulp. The (Px) pretreatment is not found to economically as well as environmentally viable.

CHAPTER 5

Chapter 5

GAS CHROMATOGRAPHIC ANALYSIS OF CHLOROPHENOLICS

5.1 INTRODUCTION

More than 500 low molecular weight organic compounds are now identified in bleaching effluents (45, 46). Most of compounds identified in bleaching effluents are degradation products of lignin (103) or are derived from wood components such as extractives or carbohydrates. Lignin degradation products are also commonly considered as major precursors of chlorinated compounds (103).

The quantities of various chlorophenolic compounds formed will depend upon nature of lignin, raw material used and pulping process, the bleaching chemical and bleaching conditions (186, 35,113). As reported, six categories of chlorophenolic compounds are present in various bleaching effluents. These are phenols, catechols, guaiacols, vanillins, syringaldehydes and syringols (151, 152). Recently, three monochlorinated compounds derived from glucuronoxylan were identified as major components of ethyl acetate extract of chlorine dioxide bleaching filtrates (45).

Chlorophenols are toxic and hardly biodegradable. They make upon a particular group of priority toxic pollutants listed by the US EPA in Clean Water Act (75, 62, 38) and by European Decision 2455/2001/EC (36). Their persistence in environment is due to their chlorinated nature (164).

Studies on impact of pulp mill effluents have been reported for instance, stimulated growth and enzymatic induction (98) and decrease in levels of sex hormones and in reproductive capacity (165, 169). Pulp chlorination results in the formation of dioxins. Dioxins include polychlorinated dibenzo-p-dioxin (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar polychlorinated biphenyls (CoPCBs) are highly thermally stable, highly lipophilic and water insoluble (111). Some dioxins are highly toxic, carcinogenic or have endocrine disrupting characteristics (106). They produce large reproductive and immunological effects on mammals and aquatic organisms and are persistent in an aquatic environment (111). The presence of large amounts of chlorophenolics in non-wood pulp bleaching effluents, as reported by Xie (186), indicate that grass lignins contain more p-hydroxyphenyl units. The presence of potential hazardous organic substances in wheat straw pulp mill effluent has also been detected by Folke (44). Results on the identification and determination of various pollutants formed during chlorination and caustic extraction of bleaching of Indian varieties of hardwoods or agroresidues has been reported by Sharma & Sharma (151, 152).

The quantitative and qualitative analysis have been carried out for various chlorophenolic compounds present in laboratory generated wastewater from various bleaching sequences in wheat straw pulp. The analysis of chlorophenolics is performed only in wheat straw pulp to know how the formation of chlorophenolics is affected by different prebleaching agents.

5.2 RESULTS AND DISCUSSION

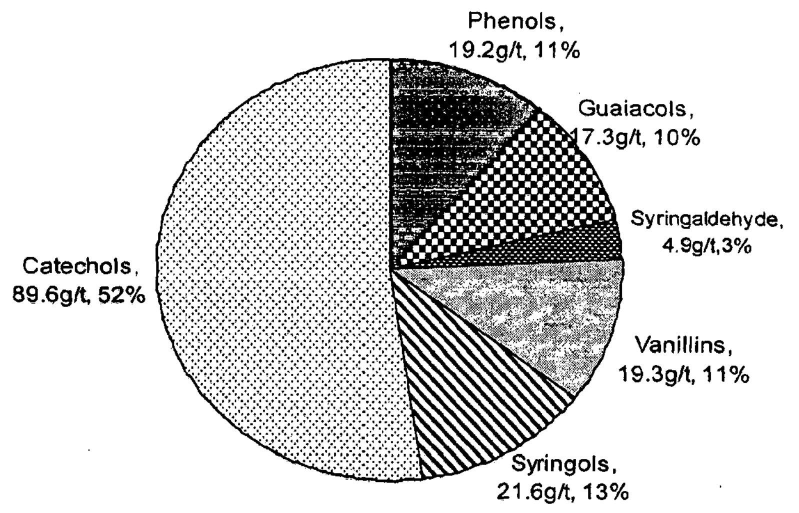
5.2.1 *CEH Bleaching Sequence* - In combined effluent of CEH sequence total 26 compounds are detected with 2,3,4,6-tetrachlorophenol, 5-chloroguaiacol, 5-chlorovanillin, tetrachlorocatechol and trichlorosyringol forming a major share. Results are given in Table 5. Of the total chlorophenolics formation, chlorocatechols are found to be highest followed by chlorosyringols and chlorophenols.

Table- 5: Chlorophenolics detected in CEH combined effluent

S.No.	Chlorophenolic compounds	g/t
1	2,5-Dichlorophenol	0.3
2	2,3-Dichlorophenol	0.6
3	3-Chloroguaiacol	0.1
4	2,6-Dichlorophenol	5.8
5	4-Chloroguaiacol	0.1
6	5-Chloroguaiacol	7.1
7	6-Chloroguaiacol	2.3
8	2,3,6-Trichlorophenol	0.1
9	3,4-Dichloroguaiacol	5.1
10	5-Chlorovanillin	15.0
11	4-Chlorocatechol	2.1
12	3,5-Dichlorocatechol	17.8
13	2,3,4,6-Tetrachlorophenol	9.9
14	3-Chlorocatechol	4.2
15	6-Chlorovanillin	3.2
16	4,5,6-Trichloroguaiacol	1.5
17	2-Chlorosyringaldehyde	1.7
18	4,5-Dichlorocatechol	2.0
19	Pentachlorophenol	2.5
20	3,4,5-Trichlorocatechol	0.2
21	Tetrachloroguaiacol	1.1
22	Trichlorosyringol	21.6
23	3,4,6-Trichlorocatechol	2.4
24	2,6-Dichlorosyringaldehyde	3.2
25	5,6-Dichlorovanillin	1.1
26	Tetrachlorocatechol	60.9
Total		**171.9**

Thus, the category wise formation of chlorophenolics follows the order: Chlorocatechols » Chlorosyringols > Chlorophenols ≥ Chlorovanillins > Chloroguaiacols » Chlorosyringaldehydes, as shown in the π Chart 5. Results are similar to that reported by different authors (93, 102) that chlorocatechols, guaiacols and syringols are byproducts of pulp bleaching with chlorine.

Fig. 5 Proportions of various categories of chlorophenolics in CEH combined effluent



Total chlorophenolics formed in CEH effluent is 171.9g/t of pulp, about 52% share is of chlorocatechols with major proportion of tetrachlorocatechol (60.9g/t), followed by 3,5-dichlorocatechol, the value being 17.8g/t, as shown in Table 5. Chlorosyringols contribute 13% share to the total chlorophenolic formation, the contribution coming from only one compound trichlorosyringol (21.6g/t). Of the di, tri, tetra and pentachlorophenol, 2,3,4,6-tetrachlorophenol is found to have highest value 9.9g/t followed by 2,6-dichlorophenol (5.8g/t). Total share of chlorovanillins present in combined CEH effluent is 19.3g/t with 5-chlorovanillin contributing 78% share to total chlorovanillin formation value being 15g/t as observed by Table 5. Chloroguaiacols form 10% of total chlorophenols as shown in the π Chart 5.0 with 5-chloroguaiacol having maximum share of about 41% of total chloroguaiacols followed by 3,4-dichloroguaiacol (29%). Chlorosyringaldehydes are lowest in quantity in CEH combined effluent forming 3% of total chlorophenolic compounds with major contributor being 2,6-dichlorosyringaldehyde (3.2g/t).

Effluent toxicity depends upon concentration of individual compounds. The $^{96}LC_{50}$ values given in Table 5.3 indicate that pentachlorophenol, catechols, tri and tetrachloroguaiacol and 2,4,6-trichlorophenol are relatively more toxic than 2,4dichlorophenol and dichloroguaiacol. As shown in Table 5, the concentration of pentachlorophenol (0.2mg/l), tetrachlorocatechol (5.1mg/l), dichlorocatechol (1.7mg/l) exceeds the higher limits of $^{96}LC_{50.}$ The concentration of 3,4,5-trichlorocatechol (0.02mg/l), dichloroguaiacol (0.4mg/l) and tetrachloroguaiacol (0.09mg/l) are lower than the lower limits of $^{96}LC_{50}$ values. Quantity of trichloroguaiacol (0.13mg/l) is much lower than the lower limits of $^{96}LC_{50}$ value. The $^{96}LC_{50}$ values describe the toxicity of a particular compound when present alone. However when a number of toxic compounds are present, interfering effects may be observed. The threshold concentration for various sublethal parameters is reported to be approximately between 0.05 and 0.1 of the $^{96}LC_{50}$ value. At the concentration of pulp mill effluents in or below this range no sublethal stress has been observed. However, the concentration of some of the chlorophenolics identified exceeds their threshold concentrations. Hence, the untreated effluent generated from CEH bleaching sequence of wheat straw pulp can be considered toxic in nature.

5.2.2 (PxP)CEH Bleaching Sequence- In combined CEH effluent of (PxP)CEH sequence, 24 chlorophenolic compounds are detected with total quantity being 109.9g/t. Thus, (PxP) route reduces chlorophenolics formation by 36%. Results are given in Table 5.1 and illustrated in π Chart 5.1.

Table - 5.1: Chlorophenolics detected in CEH combined effluent of (PxP)CEH sequence

S.No.	Chlorophenolic compounds	g/t
1	2,3-Dichlorophenol	0.3
2	3-Chloroguaiacol	2.8
3	4-Chloroguaiacol	0.1
4	5-Chloroguaiacol	0.2
5	6-Chloroguaiacol	7.4
6	2,3,5-Trichlorophenol	2.8
7	3,6-Dichloroguaiacol	5.8
8	3,4-Dichlorocatechol	1.0
9	3,4-Dichlorophenol	0.8
10	4,6-Dichloroguaiacol	0.9
11	5-Chlorovanillin	4.7
12	2,3,4,6-Tetrachlorophenol	9.6
13	3,4,6-Trichloroguaiacol	0.8
14	3,4,5-Trichloroguaiacol	0.6
15	3-Chlorocatechol	7.9
16	6-Chlorovanillin	4.2
17	4,5,6-Trichloroguaiacol	4.1
18	2-Chlorosyringaldehyde	7.9
19	4,5-Dichlorocatechol	5.3
20	Pentachlorophenol	4.5
21	3,4,5-Trichlorocatechol	0.3
22	Tetrachloroguaiacol	1.4
23	Trichlorosyringol	18.1
24	2,6-Dichlorosyringaldehyde	18.4
	Total	**109.9**

Although there is overall reduction in the total chlorophenolics generation yet quantities of some of the compounds is found to increase as shown in the Figure 5.2. The trend of chlorophenolics in combined effluent is: Chlorosyringaldehydes > Chloroguaiacols > Chlorosyringols ≥ Chlorophenols > Chlorocatechols > Chlorovanillins. The quantity of the total chlorophenolics is found to be higher in CEH effluent than (PxP)CEH effluent (Tables 5 and 5.1). In CEH effluent chlorosyringaldehydes are found to be lowest but in (PxP)CEH sequence chlorosyringaldehydes (25% of the total) form a major proportion, the value of 2,6-dichlorosyringaldehydes being highest (18.4g/t) as observed in π Charts 5 and 5.1.

Fig. 5.1 Proportions of various categories of chlorophenolics in CEH combined effluent of (PxP)CEH sequence

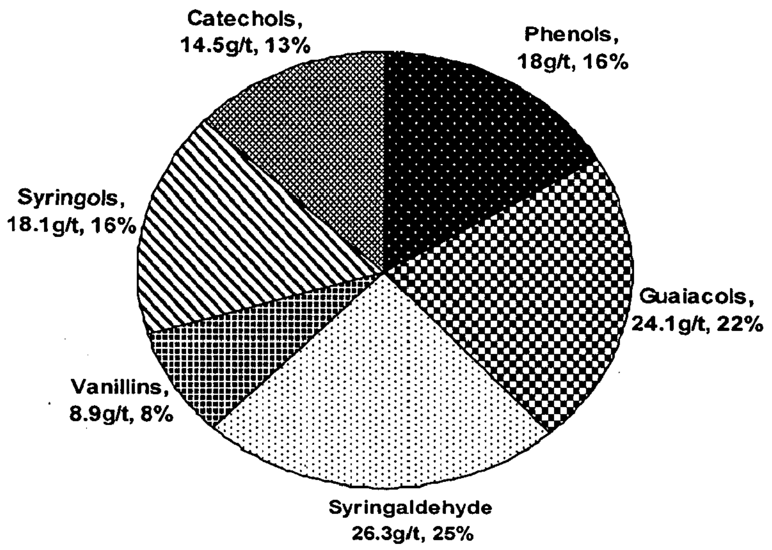
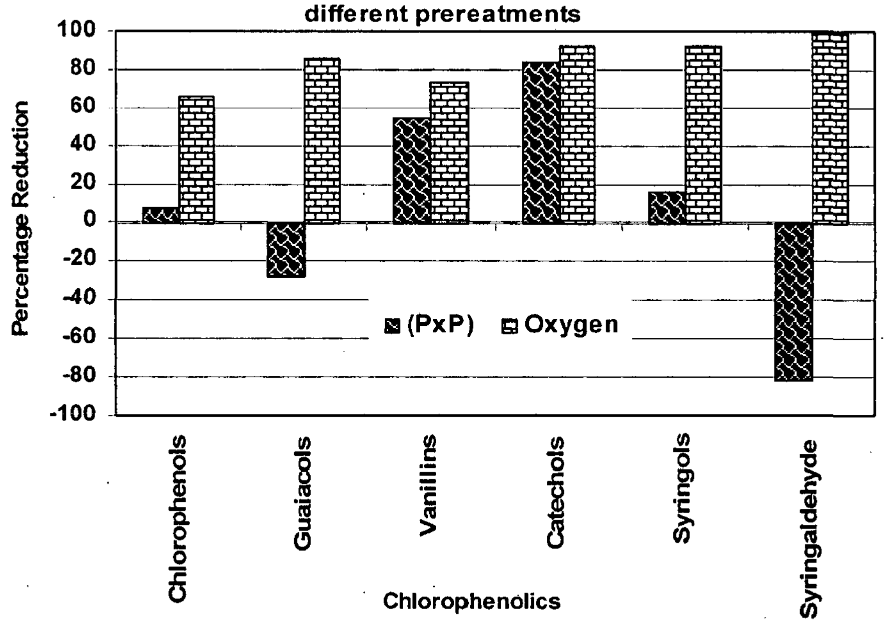


Fig.5.2 Reduction of chlorophenolics in CEH effluent by different prereatments



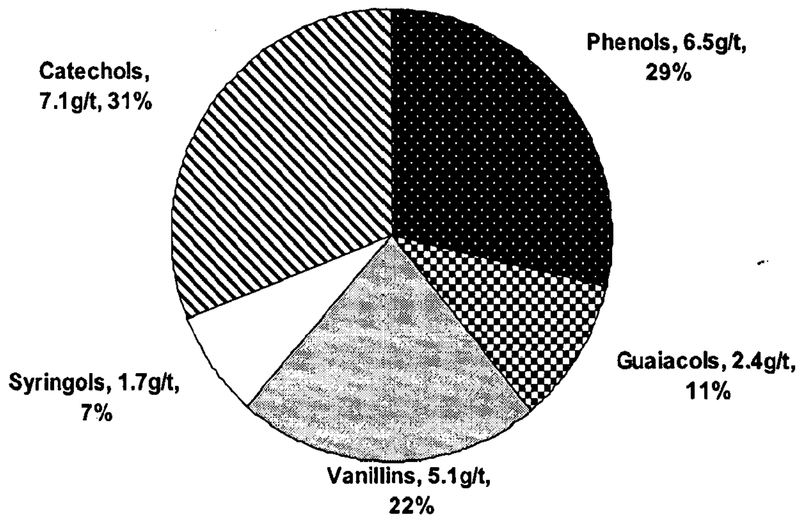
Thus, the quantity of chlorosyringaldehydes is increased from 4.9g/t in CEH effluent to 26.3g/t in (PxP)CEH. In (PxP)CEH the overall quantity of chlorophenols (Di, tri, tetra and pentachlorophenol) is reduced from 19.4g/t to 17.9g/t but the quantity of pentachlorophenol has increased from 2.5g/t in CEH to

4.5g/t in (PxP)CEH. 2,3,4,6-tetrachlorophenol remains unchanged and 2,3-dichlorophenol is reduced from 0.6g/t to 0.3g/t. The quantity of chloroguaiacols is found to increase from 17.3g/t in CEH effluent to 23.9g/t in (PxP)CEH effluent. 3,6-dichloroguaiacol, 4,6-dichloroguaiacol, 3,4,6-trichloroguaiacol, 3,4,5-trichloroguaiacol are present in (PxP)CEH effluent but not in CEH effluent. The quantity of 3-chloroguaiacol, 6-chloroguaiacol, 4,5,6-trichloroguaiacol and tetrachloroguaiacol is increased and values are 2.8g/t, 7.4g/t, 4.1g/t and 1.4g/t respectively but the quantities of 4-chloroguaiacol and 5-chloroguaiacol are reduced to 0.1g/t and 0.2g/t respectively. Chlorovanillins are reduced from 19.3g/t in CEH to 8.9g/t in (PxP)CEH with 5-chlorovanillin quantity being reduced from 15g/t to 4.7g/t but 6-chlorovanillin is increased to 4.2g/t. Chlorocatechols are reduced substantially by (PxP) pretreatment to 14.7g/t in comparison to CEH where it is 89.7g/t as shown in the Figure 5.2. Major component of chlorocatechols in CEH were tetrachlorocatechol and 3,5-dichlorocatechol which are not formed in (PxP)CEH sequence. The quantities of three other chlorocatechols, 3-chlorocatechol, 4,5-dichlorocatechol and 3,4,5-trichlorocatechol are increased to 7.9g/t, 5.3g/t and 0.3g/t respectively. Trichlorosyringol is reduced in (PxP)CEH sequence from 21.6g/t to 18.1g/t. The concentration of pentachlorophenol (0.4mg/l) exceeds the higher limits of $^{96}LC_{50}$ values (Table 5.3) while tetrachlorocatechol (5.08mg/l) formed in large quantities in CEH bleaching effluent is not detected in (PxP)CEH effluent. The concentration of dichlorocatechol (0.53mg/l) is near to lower limits of $^{96}LC_{50}$ value. The concentration of 3,4,5-trichlorocatechol (0.03mg/l), trichloroguaiacol

(0.45mg/l), dichloroguaiacol (0.56) and tetrachloroguaiacol (0.1mg/l) is found to be quite lower than the lower limits of $^{96}LC_{50}$ value. Hence (PxP) pretreatment reduces the toxicity of the effluent in comparison to CEH bleaching effluent.

5.2.3 *OCEH Bleaching Sequence-* In combined CEH effluent of OCEH bleaching sequence the chlorophenolics formation is reduced drastically in comparison to CEH and (PxP)CEH sequence, the total quantity being 22.8g/t. Hence giving a reduction of 86% by oxygen pretreatment in comparison to 36% in (PxP)CEH over CEH sequence. The results are given in Table 5.2 and illustrated in π Chart 5.3. The trend of chlorophenolics in combined effluent is: Chlorocatechols > Chlorophenols > Chlorovanillins > Chloroguaiacols > Chlorosyringols as shown in π Chart 5.3. Chlorophenols (Di, tri and tetrachlorophenols) have been reduced substantially in OCEH combined effluent in comparison to CEH effluent as shown in Figure 5.2, while quantity of only 2,3-dichlorophenol is increased (0.8g/t) as given in Table 5.2.

Fig. 5.3 Proportion of various categories of chlorophenolics in CEH combined effluent of OCEH sequence



Also, 2,4-dichlorophenol is formed only in OCEH effluent, value being 0.4g/t. In OCEH sequence, chloroguaiacols are reduced substantially, from 17.3g/t in CEH to 2.4g/t as given in Tables 5 and 5.2. Chlorovanillins are reduced from 19.3g/t to 5.2g/t and chlorosyringols from 21.6g/t to 1.7g/t. Results are similar to that reported by Voss *et.al.* (176) that the generation of chlorovanillins and chloroguaiacols in bleaching are directly related to chlorine dosages.

Table - 5.2: Chlorophenolics detected in OCEH combined effluent

S.No.	Chlorophenolic compounds	g/t
1	2,4-Dichlorophenol	0.4
2	2,5-Dichlorophenol	0.3
3	2,3-Dichlorophenol	0.8
4	2,6-Dichlorophenol	0.4
5	4-Chloroguaiacol	0.1
6	5-Chloroguaiacol	1.6
7	2,3,6-Trichlorophenol	0.1
8	3,4-Dichloroguaiacol	0.7
9	5-Chlorovanillin	3.9
10	2,3,4,6-Tetrachlorophenol	4.5
11	3-Chlorocatechol	1.8
12	6-Chlorovanillin	1.2
13	3,6-Dichlorocatechol	5.3
14	Trichlorosyringol	1.7
	Total	22.8

In combined CEH effluent of OCEH sequence, 14 chlorophenolic compounds are detected while in CEH effluent of (PxP)CEH, 24 chlorophenolic compounds are analyzed (Tables 5.1 and 5.2). By (PxP) pretreatment quantity of chlorophenols (di, tri, tetra and pentachlorophenol) in CEH effluent is reduced from 17.9g/t to 6.6g/t in oxygen pretreatment as observed in Tables 5.1 and 5.2. No formation of pentachlorophenol occurs by oxygen pretreatment.

Chloroguaiacols are formed in much lower quantities by oxygen pretreatment than (PxP) pretreatment, the values being is 23.9g/t in (PxP) to 2.4g/t in oxygen. Chlorovanillins, chlorocatechols and chlorosyringols formation is also reduced substantially by oxygen pretreatment than (PxP) pretreatment as shown in Figure 5.2. But the quantity of 4-chloroguaiacol and 5-chloroguaiacol is higher in oxygen than (PxP).

The formation of chlorophenolics in the bleaching effluents depends upon chlorine charge. The lower amount of chlorine is used in the (PxP)CEH and OCEH sequences over CEH sequence, thereby forming lesser quantity of the total chlorophenolics in the present study which is in agreement with the results of many authors (11, 176, 151*)*. However same quantity of chlorine is charged in (PxP)CEH and OCEH but the quantity of chlorophenolics generated in OCEH is lower than (PxP)CEH. The quantity of chlorine is also a function of pulp kappa number before CEH sequence. Oxygen pretreatment gives a pulp of lower kappa number (12.3) than (PxP) pretreated pulp (16.6). The chlorophenolic content is reduced substantially by oxygen delignification stage and highly toxic compounds like pentachlorophenol, tetrachlorocatechol, 3,4,5-trichloroguaiacol and tetrachloroguaiacol are not detected in OCEH effluent, thus the effluent toxicity decreases. The concentration of dichlorocatechol (0.44mg/l) and dichloroguaiacol is lower than the lower limits of reported $^{96}LC_{50}$ values. 2,4-dichlorophenol is not detected in CEH or (PxP)CEH bleaching effluent but occurs in OCEH effluent, though its quantity (0.03mg/l) is much lower than the reported $^{96}LC_{50}$ value.

Table 5.3: $^{96}LC_{50}$ values for various chlorophenolic compounds

S.No.	Compounds	$^{96}LC_{50}$ (mg/l)
1	Dichlorocatechol	0.5-1.0
2	Dichloroguaiacol	2.3
3	2,4-dichlorophenol	2.8
4	Pentachlorophenol	0.047-0.106
5	2,4,6-trichlorophenol	0.45-2.6
6	Tetrachlorocatechol	0.25-1.5
7	3,4,5-trichlorocatechol	0.89-1.5
8	Trichloroguaiacol	0.7-1.0
9	Tetrachloroguaiacol	0.2-1.7

5.3 GENERATION OF CHLOROPHENOLICS IN ECF SEQUENCE

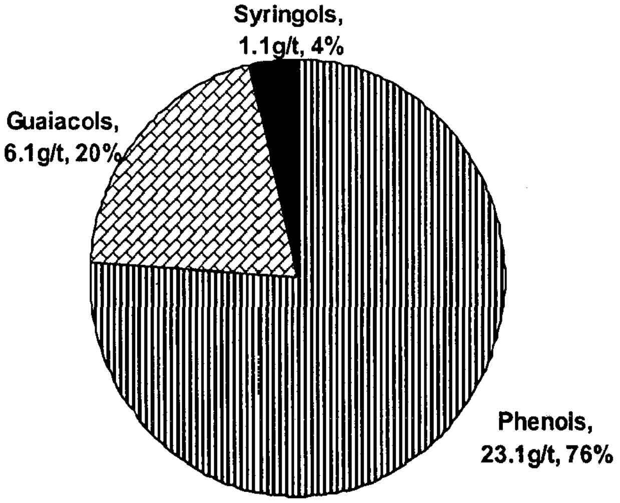
Axegård (10) showed that at high levels of ClO_2 substitution, the formation of highly halogenated phenolic compounds decreases. The total amount of chlorinated compounds in bleaching effluents resulting from ECF bleaching process is only 10-20% of that found in chlorine based bleaching effluents (23). Therefore, the impact of different pretreatments followed by an ECF bleaching on chlorophenolics generation was studied on wheat straw pulp.

5.3.1 ***DED Bleaching Sequence-*** In combined effluent of DED sequence eight chlorophenolic compounds are formed with major compounds being 4-chlorophenol, 5-chloroguaiacol, 2,6-dichlorophenol and 2,4-dichlorophenol. The results are reported in Table 5.4 and π Chart 5.4.

Table - 5.4: Chlorophenolics detected in DED combined effluent

S.No.	Chlorophenolic compounds	g/t
1	2,4-Dichlorophenol	2.6
2	2,3-Dichlorophenol	1.4
3	2,6-Dichlorophenol	4.1
4	4-Chlorophenol	15.0
5	5-Chloroguaiacol	4.5
6	6-Chloroguaiacol	1.0
7	3,6-Dichloroguaiacol	0.6
8	3,5-Dichlorosyringol	1.1
	Total	30.3

Fig. 5.4 Proportions of various chlorophenolics detected in DED combined effluent



The total quantity of chlorophenolics generated in DED sequence is 30.3g/t which is 82% lower than that of CEH effluent, which is in agreement with above stated literature. The quantity of different categories of chlorophenolics detected follows the order: Chlorophenols > Chloroguaiacols > Chlorosyringols. The results show that chlorophenols constitute 76% of the total chlorophenolics (π Chart 5.4).

The share of monochlorophenols and dichlorophenols being 49.5% and 26.6% respectively (Table 5.4). Chloroguaiacols form 20% of the share, 5-chloroguaiacol (4.5g/t), 6-chloroguaiacol (1.0g/t) and 3,6-dichloroguaiacol (0.6g/t) being detected. 3,5-dichlorosyringol forms 4% share of the total chlorophenolics and its quantity detected is 1.1g/t. The concentration of 2,4-dichlorophenol (0.21mg/l) and dichloroguaiacol (0.05mg/l) is lower than the reported [96]LC_{50} values. Also, tetrachlorocatechol, 3,4,5-trichlorocatechol, and tetrachloroguaiacol are not detected in the DED bleaching effluent. The toxicity of effluent reduces substantially as tri, tetra and pentachlorophenols are not detected in DED bleaching effluent.

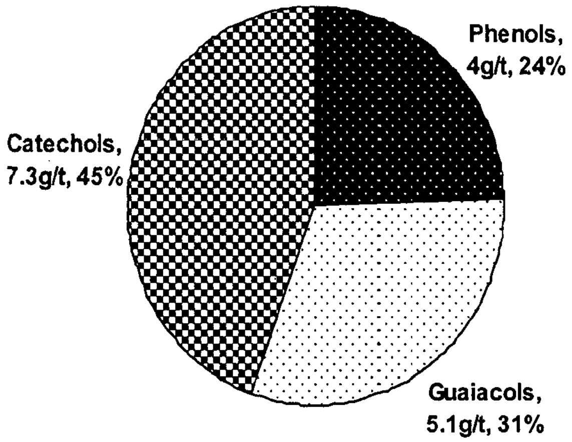
5.3.2 *(PxP)DED Bleaching Sequence-* In DED combined effluent of (PxP)DED sequence, five compounds are detected with total quantity being 16.4g/t. Results on (PxP) pretreatment are given in Table 5.5 and π Chart 5.5.

Table - 5.5: Chlorophenolics detected in DED combined effluent of (PxP)DED sequence

S.No.	Chlorophenolic compounds	g/t
1	2,3-Dichlorophenol	0.1
2	4-Chlorophenol	3.9
3	6-Chloroguaiacol	4.9
4	3,4,5-Trichloroguaiacol	0.2
5	3-Chlorocatechol	7.3
	Total	16.4

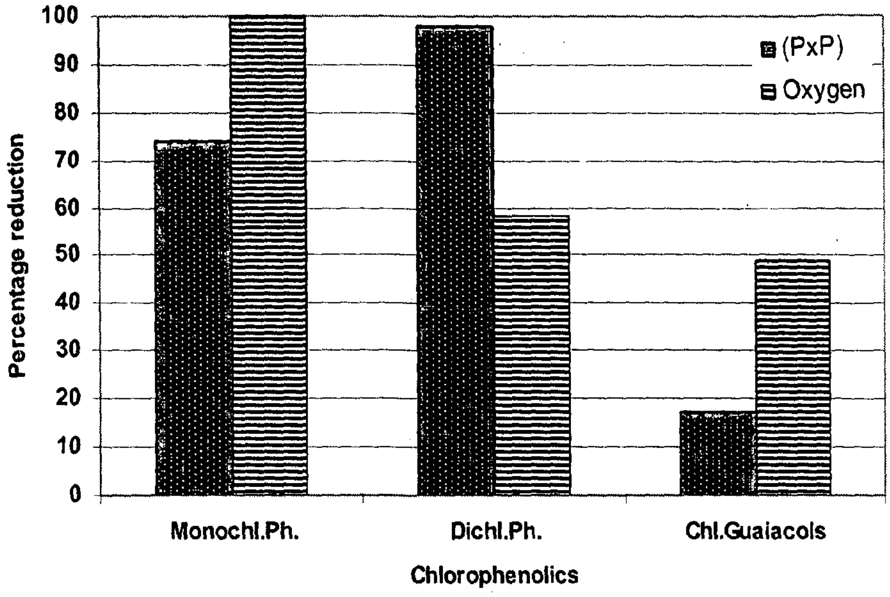
(PxP) pretreatment reduces the chlorophenolics generation by 46%. Major compounds detected in the effluent are 3-chlorocatechol, 6-chloroguaiacol and 4-chlorophenol. The order based on quantity is Chlorocatechols > Chloroguaiacols > Chlorophenols as shown in the π Chart 5.5.

Fig.5.5 Proportions of various chlorophenolics detected in DED combined effluent of (PxP)DED sequence



3-chlorocatechol forms 44% of the total chlorophenolics and is detected only in (PxP)DED effluent. However, the overall quantity of chloroguaiacols is lesser in (PxP)DED than DED but the quantity of 6-chloroguaiacol is increased substantially from 1.0g/t in DED to 4.9g/t in (PxP)DED (Tables 5.4 and 5.5). 6-chloroguaiacol constitutes 29.8% of the total chlorophenolics in (PxP)DED effluent. 4-chlorophenol is reduced by 74% by (PxP) treatment in comparison to DED sequence. Also, quantity of 2,3-dichlorophenol is reduced to 0.1g/t in (PxP)DED from 1.4g/t in DED, that is 93% lesser than DED. The concentration of trichloroguaiacol is much lower than the lower limit of $^{96}LC_{50}$ value. As shown in Figure 5.6, reduction of monochlorophenols, dichlorophenols and chloroguaiacols by (PxP) route is 74%, 98% and 17% respectively. Chlorosyringols, chlorovanillins and chlorosyringaldehydes are not detected in (PxP)DED combined effluent. Thus, (PxP) pretreatment followed by DED sequence lowers the effluent toxicity.

Fig. 5.6 Reduction of chlorophenolics in DED effluent by different pretreatments



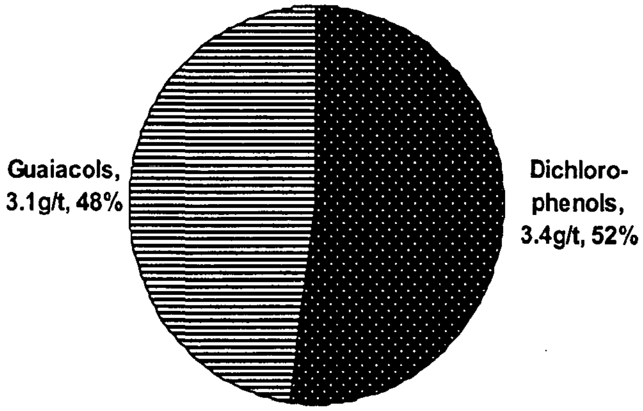
5.3.3 *ODED Bleaching Sequence*- Results of combined ODED effluent are given in Table 5.6 and π Chart 5.7.

Table - 5.6: Chlorophenolics formed in ODED combined effluent

S.No.	Chlorophenolics	g/t
1	2,3-Dichlorophenol	0.8
2	2,6-Dichlorophenol	2.6
3	5-Chloroguaiacol	3.1
Total		6.5

Results show that oxygen pretreatment is observed to reduce the chlorophenolics generation in DED drastically by 79% and only three compounds with total quantity 6.5g/t are detected. Chlorophenolics identified in ODED effluent are 2,3-dichlorophenol (0.8g/t), 2,6-dichlorophenol (2.6g/t) and 5-chloroguaiacol (3.1g/t). 5-chloroguaicol forms a major share (48%) as given in the Table 5.6 and is reduced by 31% in comparison to DED sequence (4.5g/t). In (PxP)DED effluent 5-chloroguaicol is not detected.

Fig.5.7 Proportions of various chlorophenolics detected in DED combined effluent of ODED sequence



As illustrated in Figure 5.6, chloroguaiacols are reduced by 17% by (PxP) pretreatment and 49% by oxygen pretreatment. The reduction of dichlorophenols is 58% by oxygen and 98% by (PxP) pretreatments. Monochlorophenols are not detected in ODED effluent whereas in (PxP)DED effluent, quantity is drastically reduced from 15g/t in DED to 3.9g/t. Concentration of 2,6-dichlorophenol is detected to be 2.6g/t in ODED and is reduced by 37% in comparison to DED effluent (4.1g/t). This compound is not detected in (PxP)DED combined effluent. Quantity of 2,3-dichlorophenol is reduced to 0.8g/t in ODED from 1.4g/t in DED and 0.1g/t in (PxP)DED. 4-chlorophenol, a major compound detected in DED and (PxP)DED is not formed in ODED sequence. Chlorosyringols, chlorovanillins, chlorosyringaldehydes and chlorocatechols are not detected in ODED sequence. As the concentration of the chlorophenolics is reduced substantially and polychlorinated compounds are not detected, so the effluent toxicity of ODED effluent will be comparatively less than DED effluent.

5.3.4 *Comparison of CEH and DED Bleaching Effluent*

It can be inferred from the results shown in Tables 5 and 5.4 that chlorophenolics are reduced substantially from 171.9g/t in CEH to 30.3g/t in DED. The concentration of 2,3-dichlorophenol is 0.6g/t in CEH while 1.4g/t is detected in DED. 2,4-dichlorophenol is detected only in DED effluent but not in CEH effluent. Also, 4-chlorophenol form a major proportion in DED is not detected in CEH effluent. Thus, total concentration of chlorinated phenols in DED is 23.1g/t while quantity detected in CEH is 19.2g/t. But, higher chlorinated phenols are not detected in DED. Results are in accordance to that reported by Axegard, *et.al.* (9) stating that with chlorine dioxide substitution formation of more lipophilic, higher chlorinated (tri, tetra and penta) phenolic compounds decreases. 5-chloroguaiacol is detected to be around 7.1g/t in CEH and is reduced to 4.5g/t in DED. The concentration of 6-chloroguaiacol is detected to be 2.3g/t in CEH and is reduced to 1g/t in DED. 3,6-dichloroguaiacol is not formed in CEH sequence but 0.6g/t is detected in DED effluent. Hence, total chloroguaiacol concentration in CEH effluent is 17.3g/t and is reduced to 6.1g/t in DED giving a percentage reduction of 65%. Results are similar to that reported by Berry, *et.al.* (18) stating that chlorovanillins and chloroguaiacols are formed less in D stage effluent. In CEH effluent, 3,5-dichlorosyringol is not detected while in DED 1.1g/t of this compound is detected. The total quantity of chlorosyringols in CEH is 21.6g/t and is reduced to 1.1g/t in DED, giving a reduction of 95%. Chlorovanillins, chlorosyringaldehydes and chlorocatechols are not detected in DED effluent. Hence, results are similar to that reported by Liebergott *et.al.* (91) stating that catechols and guaiacols generation reduces drastically with chlorine dioxide substitution. The highly chlorinated compounds like pentachlorophenol, tetrachlorocatechol and tetrachloroguaiacol are not detected in DED effluent and other chlorophenolics are detected in quite low quantities so the effluent toxicity of DED effluent will be quite lesser than CEH effluent. Hence results are on similar trends as reported that the ECF bleaching filtrates are known to have a much lower AOX and toxicity (10, 135) as a result of reduction of chlorinated compound discharges and also because of their lower degree of chlorination (44).

CHAPTER 6

Chapter 6

CONCLUSIONS & RECOMMENDATIONS

6.1 CONCLUSIONS

The present study concludes that:

1. The (Px) and (PxP) prebleaching is possible for wheat straw soda, mixed hardwood kraft and bagasse kraft pulp.
2. The optimized operating conditions and dosage for (Px) & (PxP) is similar for wheat straw soda, mixed hardwood kraft and bagasse soda pulp.
3. The optimized operating temperature is 40°C, consistency is 10%, time 4h and end pH is 10.8-12 for (Px) stage. The optimum dosage of $Na_2S_2O_8$ is 5%, NaOH 2% and EDTA is 0.5%.
4. In optimized (PxP) stage, the operating conditions are similar to that of (Px) stage. The optimum dosage of $Na_2S_2O_8$ is 2.5%, H_2O_2 0.5%, NaOH 2%, $MgSO_4$ 0.2% and EDTA is 0.5%.
5. The kappa number reduction by (Px) process is 14 -19% and viscosity drop is 18-20%. While (PxP) process gives a kappa number reduction in the range of 28-32% and viscosity drop in the range of 11-12%.
6. The (PxP) process is comparable to oxygen delignification step used in reducing the bleach chemical consumption and maintaining the mechanical strength properties.
7. The (Px) process is not found to be a viable option as substantial drop in strength properties is observed.

8. A target brightness of 80% ISO is achievable for both wheat straw soda and mixed hardwood kraft pulp using CEH, (Px)CEH, (PxP)CEH, OCEH, DED, (Px)DED, (PxP)DED and ODED sequences. In bagasse kraft pulp, target brightness of 85% ISO can be achieved by using above stated sequences.

9. In wheat straw pulp, the chemical savings obtained by both (PxP) and oxygen pretreatment (58%) are the same for CEH sequence, although the kappa number of (PxP) pretreated pulp is 26% higher.

10. Although the chemical consumption of (PxP) pretreatment is of the same level as observed with oxygen pretreatment, but (PxP) step is not able to reduce the COD, color and AOX to same levels.

11. The mechanical strength properties of pulps pretreated with oxygen and (PxP) process followed by CEH and DED sequences are nearly similar. Tensile index is found to be higher for (PxP) pretreated pulps in all the three raw materials.

12. Mills having chemical recovery can be benefited by (PxP) process in terms of reduction of AOX, COD, BOD, color and chloroorganics in the combined effluent from bleaching sequences.

13. The concentration of a large number of chlorophenolics identified exceeds their threshold concentrations in CEH effluent. Hence, the untreated effluent generated from CEH bleaching sequence of wheat straw pulp can be considered toxic in nature.

14. The (PxP) prebleaching stage is found to reduce the generation of chlorophenolics by 36% in (PxP)CEH sequence. The formation of chlorophenolics is reduced by 86% via oxygen prebleaching in OCEH bleaching effluent.

15. In ECF sequence (PxP) stage is able to reduce the AOX to the levels to fulfill the CREP stipulations.
16. The (PxP) stage reduces generation of chlorophenolics by 46% in (PxP)DED bleaching sequence, while substantial reduction of 78% is achieved by oxygen delignification.
17. The mills opting to meet environmental standards for AOX and close the bleach cycle necessarily will have to look at either oxygen or (PxP) as prebleaching stage irrespective of their cost limitations.
18. Onsite production of sodium persulphate from sodium sesquisulphate will reduce the cost of persulphate to one third of its market price.
19. In mills where oxygen plant installation is not possible, (PxP)CEH or (PxP)DED bleaching sequences need to be adopted for compliance with environmental standards.

The above study clearly indicates the effectiveness of (PxP) prebleaching not only for improving environmental performance of the bleach plants but also a means of significant decrease in bleach chemical consumption. This process can be applied to any traditional or modern bleach sequence without significant investment in the infrastructure.

6.2 RECOMMENDATIONS

1. Sodium persulphate is a recommended prebleaching agent for hardwood and agroresidue pulps.
2. Sodium persulphate can be economically produced from sodium sesquisulphate, a byproduct from R_8 chlorine dioxide generator.
3. (PxP) prebleached pulps is amenable to conventional and ECF bleaching sequences and hence can be introduced in both types of mills.

4. Mills which will not be able to install oxygen delignification stage can meet desired environmental standards for liquid effluents particularly with respect to AOX by the two routes namely (PxP)CEH in bagasse kraft pulp and (PxP)DED in mixed hardwood kraft and bagasse kraft pulps.
5. The adoption of (PxP) prebleaching as an essential step in treatment of pulps for bleaching must be taken up seriously to comply with environmental regulations.

6.3 FUTURE WORK

- Residual lignin from pulp before and after (PxP) treatment can be analyzed for changes in functional group composition. Analysis of reaction products should help in elucidating reaction mechanisms.
- Incorporation of (PxP) stage with oxygen delignification stage can be investigated under milder reaction conditions.
- (PxP) stage can also be developed as a brightening stage for ECF and TCF bleaching sequences.
- Size Exclusion Chromatography (SEC) studies to study the change in molecular weight profiles of lignin and carbohydrates in the pulp to confirm the attack of persulphate-peroxide on lignin carbohydrate complexes (LCC) in pulps are suggested.
- It is important to determine if the benefits observed in laboratory are achievable when process is performed on a large scale.

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