FINAL REPORT

ON

FEASIBILITY STUDIES ON COLOR REMOVAL FROM MECHANICAL PULPING EFFLUENTS

Submitted to

Indian Newsprint Manufacturers Association (INMA)

By

Central Pulp & Paper Research Institute, Saharanpur

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Under the Technical Guidance of

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Director

Central Pulp & Paper Research Institute, Saharanpur

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Executive Summary

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1.0 BACKGROUND AND OBJECTIVE OF THE PROJECT

The project on **"Color removal of liquid effluents from Mechanical Pulping"** was sponsored by Indian Newsprint Manufacturer's Association (INMA). **The objective of the project is to prepare a feasibility report on color removal from mechanical pulping effluents after evaluating various state-of-art technologies commercially available for color removal and propose a techno economic viable process for treating the mechanical pulping effluents.**

The project team comprised of following scientists:

Dr. A. G. Kulkarni, Director	-	Advisor
Dr. R. M. Mathur, Scientist E – II	-	Project Leader
Mrs. Rita Tandon, Scientist E – I	-	Member
Ms. Manju Prajapati, Senior Scientific Assistant	-	Member

The removal of color from industrial waste has received an increasing amount of attention in recent years. This interest has been prompted by public demand for a cleaner environment as well as by efforts to comply with federal regulations regarding the color discharge which are expected to come into effect in the years to come. In India also the public perception and restrictive environmental discharge limits imposed by some of the state pollution control authorities have made the color removal a prominent issue for pulp & paper industry. Though the effluent color load varies from mill to mill depending upon the raw material used, process employed, type of end products and extent of closure of the system, however the problem of effluent color is more pronounced in newsprint mills than other mills producing cultural grades of paper.

The effluent color load in newsprint mills is mainly due to presence of extractives in woods. The newsprint mills in India which are using hardwood for mechanical pulp production employing CMP or CSRMP process are generating highly colored effluent as the extractives having strong chromophoric groups and present in high proportion are leached out during pre steaming and refining operation. The color in mechanical pulping liquors exist mainly in macromolecular colloidal and dissolved form and more than 50% color in mechanical pulping effluent is in dissolved form making it difficult to remove with conventional chemical precipitation method. The intensity of color in CMP effluent from hardwood is 3-4 times higher than color intensities in the normal lignin bearing compounds at the same concentrations. The average effluent color load in these mills is around 300-400 kg/t and requires heavy dosage of coagulant to remove the suspended color.

Keeping in view the problem of effluent color in newsprint mills, a need was felt that a systematic study should be carried out on various combinations of color removal techniques to achieve maximum color reduction. However prior to taking up the systematic study it was decided to carry out feasibility studies on various color reduction technologies which are available or emerging as promising technologies.

1.1 METHODOLOGY FOLLOWED

- To fulfill the objectives, extensive literature review was undertaken to assess the commercially available state–of–art technologies for color reduction of mechanical pulping effluents.
- Information has been collected through questionnaires on prevailing practices of color reduction technologies in Indian newsprint mills employing mechanical pulping process.
- Mill visits were undertaken to newsprint mills employing mechanical pulping process for collection of data and colored effluent samples to assess the

magnitude and intensity of color load generated during various unit operations of mechanical pulping process.

- Based on the reviews and assessment of newsprint mills with respect to magnitude of color loads and the practices being adopted by the mill for color reduction, preparation of feasibility report of commercially available technologies.

1.2 CONTENTS OF THE REPORT

The report is presented in a comprehensive form consisting of three parts.

PART I - **General Introduction**

It gives an overview of different sources and magnitude of effluent color in pulp & paper industry and the continued R&D efforts in development of different color reduction technologies till date. It also covers update of commercially available technology and new emerging technologies, which have a potential to be employed for pulp & paper industry.

PART II - This broadly covers a detailed assessment of current status of Indian newsprint mills with respect to magnitude of color loads in mechanical pulping effluent generated and prevailing practices for its control/reduction/removal. The status is based on first hand information collected during mill visit and also includes data on characterization of raw material and mill effluent carried out at CPPRI.

PART III - **Feasibility Studies**

Based on collected information and technical data on effluent characteristics evaluated at CPPRI, studies were conducted at CPPRI to evaluate the techno-economic viability of commercially available technologies for treating mechanical pulping effluents.

2.0 SUMMARY & CONCLUSIONS

2.1 INDIAN SCENARIO

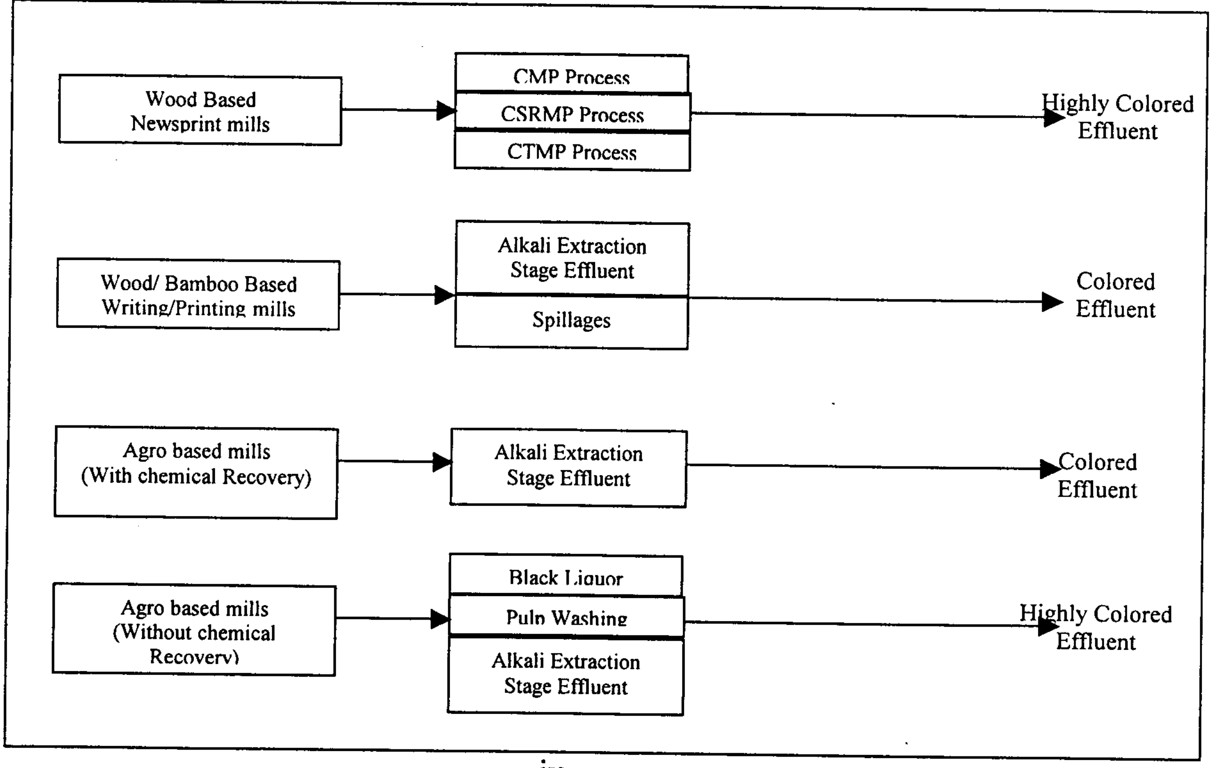
The Indian paper industry uses on an average 100 to 250 m^3 of fresh water/ton of paper and nearly 75% of which is discharged as effluent. In addition to high proportion of inorganics and organic pollutant the effluent from paper industry contains significant color loads. Although there is no stringent legislation for the discharge of color by Central Pollution Control Board (CPCB), some states however have imposed tolerance limits for discharge of color i.e. 100 PCU + color of the receiving stream, which is too low and difficult to achieve target for the mills generating effluents with high color loads.

In general color can broadly be categorized into two groups

(i) Color due to colloidal particles

(ii) Color due to relatively large colloidal macromolecules i.e. suspended color.

It is easy to remove the color due to larger colloidal macromolecules, but the dissolved color is very difficult to remove and is sensitive to ionic strength, electrical charges etc. Various sources generating colored effluent in pulp & paper industry are :



It is estimated that the quantity of lignin going through spent liquors varies from 300- 400 Kg / ton of pulp, generating a color load of about 1400-1500 Kg PCU (platinum-Cobalt Unit) per ton of pulp. It is estimated that 90% of the color is due to lignin.

In alkali extraction stage only about 50-60 Kg of lignin per ton of paper is going into effluents and the combined efl1uent will have color load of about 1500 PCU.

In newsprint mills where eucalyptus constitutes the main raw material for production of mechanical pulp component, very high color loads are noticed in the effluents. Eucalyptus contains about 3-6% extractives, mostly tannins that are leached out during presteaming and refilling stages. The washings of CMP pulp are highly colored and the color intensity is several times higher when compared to color due to lignin compounds.

The mills which are based on waste paper do not have effluent color problem, however on the contrary in wood based mills the effluent color problem has become a major environmental issue. The problem is further aggravated for the mills, which have mechanical pulping street for the production of newsprint based on Eucalyptus. **In mechanical pulping effluent the effluent color is mainly contributed by presence of extractives, which is the specific organic component present in hard woods known to be the compounds with chromophoric groups.** The mills, which are based on non-woody raw material particularly bamboo, problem of effluent color is relatively less and the major sources of colored effluent is from bleaching operation. The mills, which are based on agricultural residues, in absence of available chemical recovery system, are discharging the spent liquor directly to receiving stream and the color load of which is high due to presence of higher molecular weight lignin components.

2.2 GLOBAL SCENARIO

No official color standards is promulgated by EPA in USA for pulp and paper industry. Some states in USA such as Florida do not have color requirements but have transparency requirements. Other States in USA are now becoming more concerned about color issue. Some existing facilities have attempted the use of end-of-pipe technologies on wastewater treatment facilities to remove color.

In developed countries the concern for effluent color is mainly for bleach effluents and most mills have been able to demonstrate the color removal technologies as an unviable option due to higher cost of treatment. The industry is now inclined towards process changes like using extended delignification, ClO_2 substitution and more sophisticated spill collection and recovery systems.

2.3 OVERVIEW OF EFFLUENT COLOR REDUCTION TECHNOLOGIES

Following approaches can be adopted to reduce the problem of effluent color

(i) Inplant control measures
(ii) Process modification/technology innovation to control the generation of highly colored compounds.
(iii) End-of-Pipe treatment methods.

Extensive literature review has revealed that whatsoever R&D efforts have been done to control/reduce the effluent color loads were confined to chemical pulping street and bleach plants only. Not much attention was given to contain effluent color loads from mechanical pulping process. The reason is attributed mainly to worldwide trend of producing mechanical pulps using TMP process. In developed countries TMP being predominant pulping process and use of softwood species as raw material for mechanical pulp production, the effluent color is not a major issue. On the contrary, in India, out of three newsprint mills having mechanical pulping street, only one is based on TMP process based on bagasse and other two mills using E.hybrid are based on CMP process. The effluent generated from these mills has very high color loads. For these mills, adoption of APMP (Alkaline Peroxide Mechanical Pulping) is one alternative to contain effluent color loads, however economic feasibility needs to be worked out.

Various EOP treatment options which have been tried, are confined to bleach effluents only. These methods include physico-chemical treatment method physical separation method, UV Irradiation methods, biological methods etc. An overview showing the status of these technologies is summarized in **Table-1**.

TABLE-1

Status of Various EOP Treatment Technologies

TREATMENT TECHNOLOGY	STATUS
Chemical Precipitation Alum Lime Polymer addition followed by air flotation	**Full Scale application** On mill effluent On bleach & mill effluent On unbleached kraft mill effluent
Membrane Filtration	Mill scale application in E-stage effluent
Ozonation	Bench scale application with bleach effluents
UV Irradiation	Bench scale trials on bleach effluents
Electro-flocculation	Lab scale trials on bleach effluents
Biological Process Mycor Process Lacasse Treatment	 Bench Scale Development trial stage

From the above table it is clear that till date only chemical precipitation and ultra-filtration techniques have been demonstrated on mill scale for reducing color from bleach effluents. In the current study both these techniques have been tried using mechanical pulping effluents. Other emerging technologies, which have been identified and can be studied using mechanical pulping effluent are

- Ozonation
- Photo-oxidation/UV Irradiation
- Electro-flocculation Process.

2.4 CURRENT STATUS OF NEWSPRINT MILL IN INDIA

Among 62 newsprint mills in India, only three mills viz. M/s Hindustan Newsprint Ltd. (HNL), Kerala, M/s Mysore Paper Mills (MPM), Bhadravati and Tamil Nadu Newsprint Ltd. (TNPL), Tamil Nadu are producing mechanical pulp from wood/non wood employing mechanical pulping process for Newsprint production.

Mill I is presently using E. hybrid, E. grandis and Acacia as raw material for mechanical pulp production employing chemi-mechanical process. Presently the ratio is 60% E. grandis and 40% E. hybrid, which may gradually change towards more use of E. hybrid and Acacia as E. grandis, which is available through state Govt. may cease after 2004. Due to increase in the ratio of E. hybrid the mill is facing acute effluent color problem. In the colored stream, color variation ranges between 6000 to 8000 PCU and sometimes even more due to plant upsets. The mill has adopted cross recovery of CMP and CP liquor for partial control of color in effluent and also using alum as a coagulant for EOP treatment. The mill has separate treatment facility for colored effluent. Due to high effluent color the alum requirement is very high and the mill is incurring Rs. 1.4 crores annually on EOP treatment. Besides, due to poor settleability of alum flocs there is a carry over of sludge with clarifier overflow. The discharge color remains between 600-800 PCU after treatment.

Mill II is presently using Acacia as raw material employing cold soda refiner mechanical pulping process. The mill has made some internal modifications which has helped in controlling the effluent color to some extent. Since the mill is based on Acacia which is a light colored wood and due to which the color load in effluent is 50% lower than the mill based on E. hybrid. In the ETP, combined effluent is treated and no separate treatment is followed for colored stream. The discharge color in the final effluent is around 811 PCU.

Mill III is using Bagasse as a raw material employing TMP process. The effluent color load is significantly low compared to other two mills. The mill is using 1.2 g/l alum presently to treat the colored effluent (bagasse washing) and the final discharge color obtained is 200 PCU.

3.0 FEASIBILITY STUDIES UNDERTAKEN AT CPPRI

Studies conducted at CPPRI on impact of raw material species on effluent color generation has clearly revealed that the amount of alcohol soluble extractives, which represents a group of color bearing compounds like phlobanes, tannins and stilbens is higher for E. hybrid and Acacia compared to bagasse and E. grandis. The color intensity under alkaline conditions is also of the same order.

Extensive literature review has revealed that only alum precipitation and ultrafiltration techniques have been commercialized and have been practiced by mills in USA and Europe to treat bleach effluents. Studies conducted on mechanical pulping effluents using these two technologies have clearly indicated that both theses technologies when used alone are not ideally suited for mechanical pulping effluent having higher color loads. However a combination of both these technologies will be a more suitable option, by incorporating alum treatment to remove suspended color followed by ultrafiltration to remove true color. However this option will have higher economics.

For the effluents having low color loads ultrafiltration is suitable, though the technology is an expensive one.

Among emerging technologies, three technologies have been identified which have been tried for treating bleach colored effluents only. The same techniques can be studied in detail with mechanical pulping effluents. The technologies are:

(i) UV/Photo Irradiation Process

Irradiation of effluents in the presence of oxygen/or hydrogen peroxide has also been found promising for significant reduction in effluent color and total organically bound chlorine (TOCl) in bleach plant effluents.

The efficacy of enhanced photo-oxidation of bleached kraft mill effluent for color reduction has been demonstrated on bench scale. The effectiveness and versatility of photo oxidation method has given rise to the development of various process alternatives employing $UV/O_2/H_2O_2/O_3$ + H_2O_2/fentons reagents and various combination of these. Preliminary experimental results have demonstrated the potential of photo-assisted catalytic oxidation of organic contaminants and have shown promise of being developed into a viable process for commercial application.

(ii) Ozonation

Use of ozone for removal of color in liquid effluents have been found to be very effective. Ozone has been increasingly used for waste water treatment and tried on lab scale for treating paper mill effluent. The high cost of ozone generation and operation limits the commercial installation. However, this technology can be used as a combination technology for tertiary treatment only, and need to be studied in for generating data base for its application on mechanical pulping effluent.

(iii) Electroflocculation Process

This is the technology of new millennium. Extensively tried on small industrial plants for treating waste waters, the process is very promising in reducing the effluent color. Only lab studies have been conducted on bleach effluents. Some preliminary studies on lab scale have been conducted at CPPRI using mechanical pulping effluents and the findings are very encouraging. A detailed study would be required to establish the economic feasibility of the process.

4.0 RECOMMENDATIONS

1. With the growing public concern over the discharge of colored effluents to the river, the problem of effluent color has become a prominent issue for the Pulp & Paper Industry. The problem is more serious for newsprint mills based on wood. For newsprint mills effluent color reduction can be achieved either by a proper selection of the raw material or by adopting a suitable pretreatment process in order to extract out the extractives from the wood. A systematic study would be required.
2. In the existing system when the mills do not have an option to change its raw material, the mills should look into the possibility of adopting new pulping technology i.e. Alkaline Peroxide Mechanical Pulping Process (APMP) for mechanical pulp production to reduce effluent color load.
3. For EOP treatment technology it is essential that mill should have a separate street for treating the colored effluents and then combine it with other effluents for conventional treatment.
4. The EOP treatment facility should essentially have an equalization tank prior to treatment to absorb the shock loads due to variations in color loads. This will improve the overall performance of the treatment plant.
5. Feasibility studies conducted at CPPRI on Chemical precipitation method using alum have clearly indicated the alum precipitation is not a viable option for treating mechanical pulping effluents due to the following reasons:

   - Highly colored effluents require high alum dosage leading to higher costs.
   - Formation of very light flocs of precipitate having poor settleability, which leads to carryover of precipitated color with supernatant.

- The addition of acid to bring down Alum consumption may further increase the treatment cost, however some improvement in sludge settleability is obtained.
- The addition of polymers in combination of Alum to improve settleability will substantially increase the treatment cost.

6. Studies conducted employing ultra-filtration technology clearly indicates that the technique is viable only for effluents having low color loads. For high color load effluents, a combination of alum precipitation followed by ultrafiltration is more suitable option for higher efficiency, however the cost of treatment will be substantial.
7. From the literature review three emerging technologies have been identified which are
    - UV Irradiation Process
    - Ozonation
    - Electro-flocculation

    Of these three technologies, preliminary studies on lab scale have been conducted on electro-flocculation process using mechanical pulping effluents. A color reduction efficiency of 97% with 50% reduction in•COD and 70% reduction in organic components is achieved. The process is technically feasible and needs to be studied on pilot scale to establish the economic viability of the process.
8. Also there is need to take up detailed R&D activities to study ozonation and irradiation process for treating mechanical pulping effluent.
9. In view of this, CPPRI has already taken up a project as one of the plan schemes in which identified technologies will be studied on lab scale and pilot scale to evaluate the techno economic viability of the process for treating mechanical pulping effluents.

B

General Introduction

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PART– I : GENERAL INTRODUCTION

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PART –I

INTRODUCTION

1.0 BACKGROUND

The removal of color from industrial wastes has been receiving an increasing amount of attention in recent years. This interest has been prompted by public demands for a cleaner environment as well as by efforts to comply with federal regulations regarding the color output which are expected to come into effect in the years to come.

Pulp & paper industry is one of the highly polluting industries. In the process of converting wood chips to bleached pulp and paper, large amount of wastewater is generated and these wastes contain both organic and inorganic pollutants and also carry significant color loads due to the presence of very high proportion of colored organic pollutants. The color bodies in pulp & paper mill effluents have never been completely characterized but are generally believed to consist primarily of lignin fragments, lignin derivatives and tannins.

Characteristics of wastewater depend on the wood species, pulping and bleaching processes employed, dissolved wood components and other additives such as sizing agents, dyes and coating solutions. The volume of effluent discharged and the concentration of pollutants depend on the degree of system closure and type of accidental discharges and spillages in the pulping process. By definition color is caused by both suspended and colloidal solids. **"Apparent color"** refers to color from suspended matter while **"true color"** refers to color after removal of turbidity and it is the true color that leads to a persistent color problem.

Principal colloidal color bodies include tannins, humic acids and humates from the decomposition of lignins. These lignin derivatives are highly colored and quite resistant to biological attack resulting in their long persistence to the environment.

Color interferes with aquatic life by limiting light transmittance. Color also contributes to taste problems and increase stability of some bivalent metal ions by chelation. Color bodies present in the effluent may also serve as a potential bacterial nutrient. As a rule color bodies are resistant to removal by conventional methods of effluent treatments such as primary sedimentation clarifiers followed by biological methods (Aerated lagoons or activated sludge treatment) which are effective only in reducing biological oxygen demand (BOD) Chemical oxygen demand (COD), total organic carbon (TOC) and suspended solids (SS). For this reason process modification and/or end-of–pipe (EOP) treatment methods are becoming necessary to satisfy pollution discharge limits.

1.1 CHEMISTRY OF COLOR BEARING COMPOUNDS

In the pulp and paper industry, the concern is predominantly about the colors of organic compounds, the so-called "chromophores". These are the groups which generally absorb ultraviolet (UV) light through their functional groups having excess electrons such as C=C, C ≡ C, six carbon aromatic rings, nitro, sulfur and oxygen containing groups and heterocyclic compounds containing oxygen, nitrogen or sulfur as a member of cyclic ring. Those compounds which absorb light in a visible range also containing the same high electron density functional groups, but usually arranged in a long chain and the nature of the electron rich group dictates the shade of the color. Cleavage of one of these groups break the molecular chain and generally shifts the color from visible spectrum to either UV or IR range.

The soluble color-bearing portion of the pulp mill effluent is composed primarily of wood extractives and lignin degradation products, which are formed during pulping and bleaching. It is established that the condensation and oxidation reactions taking place during cooking, chlorination or extraction stage results in the formation of quinonoid structure, may be conjugated with carbonyl and ethylenic groups, which contribute for the color absorbance in the visible spectrum. Secondly the color bodies are polydisperse and a single effluent may contain species ranging in molecular weight from less than 400 upto 150,000 mass units with an average molecular weight of about 6000 mass units.

1.2 EFFLUENT COLOR ISSUES IN INDIA

The Indian paper industry uses on an average 100 to 250 m^3 of fresh water/ton of paper and nearly 75% of which is discharged as effluent. In addition to high proportion of inorganic and organic pollutants, the effluent from paper industry contains significant color loads. Although there is no stringent legislation for the discharge of color by Central Pollution Control Board (CPCB), some states however have imposed tolerance limits for discharge of the color i.e. 100 PCU + color of the receiving stream which is too low and difficult –to- achieve target for the mills generating effluents with high color loads. The color load varies from mill to mill depending upon the raw material used, process employed, type of end products, and extent of system closure in the mill. In newsprint industry, the major color load comes from extractives leached out during pre-steaming and refining operations. In paper mill producing cultural papers, the color load is attributed to discharge of alkaline extracts of bleaching operation. In small pulp and paper mills the origin of the color is from discharged spent pulping liquors.

The present practice of color and suspended solids removal is by chemical treatment methods. Although the chemical treatment methods are expensive but the industry has perforce adopted such systems to contain the tolerance limits for suspended solids and color.

In general color can broadly be categorized into two groups:

(i) Color due to colloidal particles.

(ii) Color due to relatively large colloidal macromolecules i.e. Suspended color.

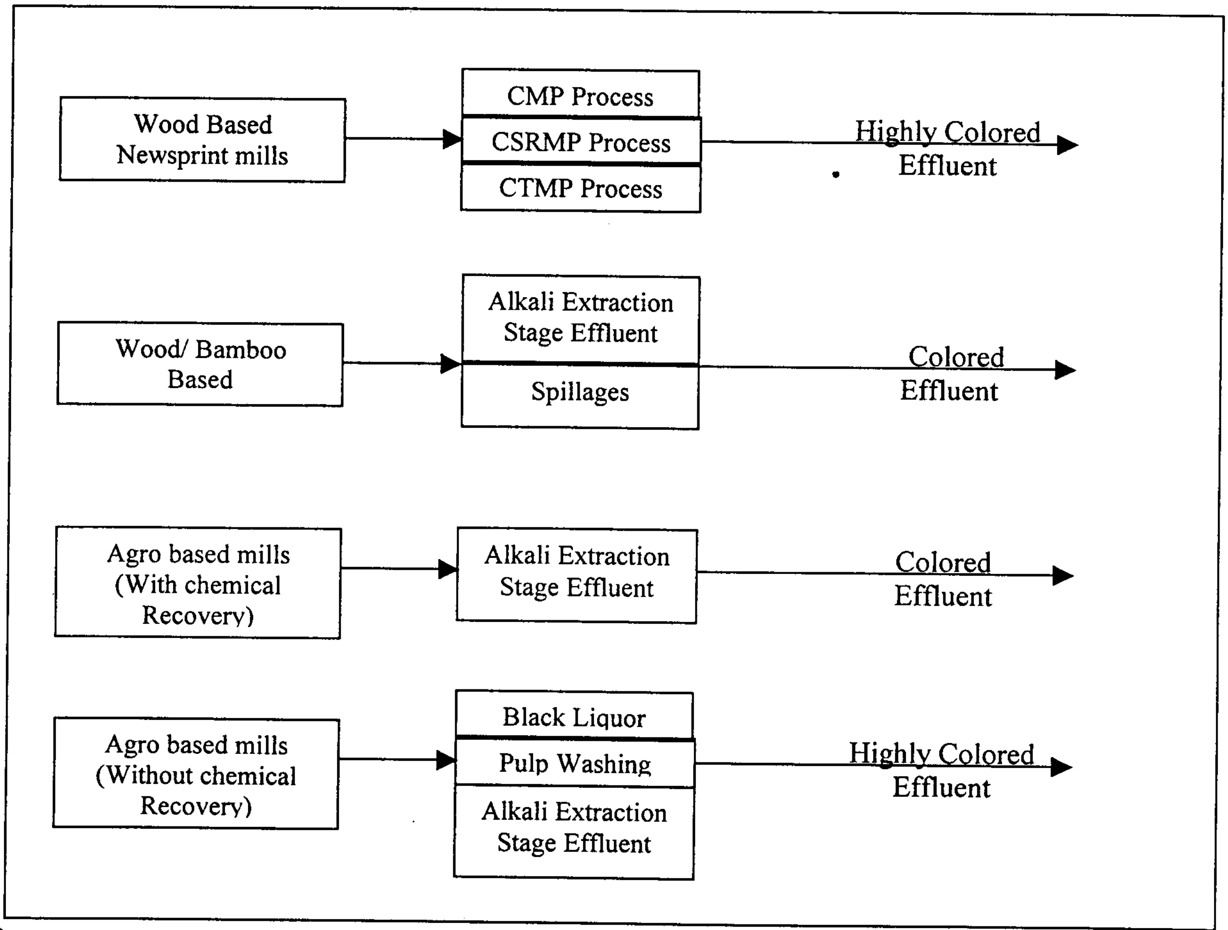
It is easy to remove the color due to larger colloidal macromolecules, but the dissolved color is very difficult to remove and is sensitive to ionic strength, electrical charge etc. For example, the extractives having particle size in the range of 10^{-1} microns are quite stable and require very high dosage of chemical coagulants for precipitation and subsequent flocculation, which is economically unviable.

1.2.1 Sources and Magnitude of Color in Pulp & Paper Mill Effluent

Color in pulp & paper mill effluent results from the following operations:

- The pulping process
- Pulp washing
- Bleaching
- Spills and leaks

The various sources for generation of colored effluent in pulp & paper industry are –



The principal source of color from pulp & paper making process is the lignin originally present in the wood, which is separated from the cellulose fibres into the process liquids. The amount of lignin separated and removed from the cellulose fibres is different for each pulp and paper making process and for each part of the process. The amount of color discharged from each source is further dependent upon process conditions such as temperature, pH, mechanical action and reaction with process chemicals.

Preliminary findings and review of sources of color indicates that approximately 30% to 50% of the color in the effluent may result from the pulp mill. Depending on the pulping process (kraft, neutral sulfite, semichemical, sulfate, mechanical, or thermomechanical) and the bleaching process being employed at the mill, the effluent color load can vary significantly. The effluent color load is directly proportional to the extent of lignin extraction during pulping. The pulping process contributes between approximately 50% and 70% of the color load in the effluent. The remaining color usually results from bleaching operations and spills.

The brown to black color imparted to effluents is mainly due to lignins, tannins, and other extractives bearing chromophoric groups. Lignin and extractives are highly polymerised substances and are difficult to biodegrade. **Table- 1** shows the major sources and magnitude of color loads in pulp & paper effluent streams.

TABLE- 1

Sources and Magnitude of Color in Effluent Streams

Sources	Color, Pt-Co Units at 1% Concentration
Spent liquor from Small Pulp mills	10,000 – 15,000
Effluent from Alkali Extraction stage	4,000 – 6,000
Washing of Chemi- Mechanical Pulp in Newsprint	20,000 – 30,000

It is estimated that the quantity of lignin going through spent liquors varies from 300- 400 Kg / ton of pulp, generating a color load of about 1400-1500 Kg PCU (Platinum-Cobalt Unit) per ton of pulp. It is estimated that 90% of the color is due to lignin.

In alkali extraction stage only about 50-60 Kg of lignin per ton of paper is going into effluents and the combined effluent will have color load of about 1500 PCU.

In newsprint mills where eucalyptus constitutes the raw material for production of mechanical pulp component, very high color loads are noticed in the effluents. Eucalyptus contains about 3-6% extractives, mostly tannins that are leached out during presteaming and refilling stages. The washings of CMP pulp are highly colored and the color intensity is several times more when compared to color due to lignin compounds.

Lignin and extractives exist as colloidal particles and they possess different molecular size and electrical charge. It is reported that extractives are much more colloidally stable and thus more difficult to remove compared to lignin macromolecules.

1.3 EFFLUENT COLOR ISSUES IN DEVELOPED COUNTRIES

Currently no official color standards are promulgated by EPA in USA for pulp and paper industry. Some states have implemented color requirements in individual permits for specific mills. These typically take the form of a maximum color increase in the river after discharge and after a zone of mixing. Requirements are based on river flow, the higher the flow, the higher the allowable color discharge. For most permit allowances, agencies carefully consider, low river flow conditions. The typical permit allows an incremental increase in color of the river, but usually the increase is difficult to measure visually.

Some states in USA such as Florida do not have color requirements but have transparency requirements. States with transparency requirements measure color by the amount of light that can be transmitted through water. The procedure is to place a reflective plate in the water at a certain depth and measure the amount of light that reaches the plate. The more material in the water, the more the light is absorbed and the lower the transparency. But suspended solids can also cause absorption of light, so that method of measurement is much more complicated in defining color.

States in USA are becoming more concerned about color issue. As companies attempt to site mills on smaller streams and in more sensitive areas, the pressure on regulatories agencies to control color emissions will be greater. Some existing facilities have attempted to require the use of end-of-pipe technologies on wastewater treatment facilities to remove color.

Color removal technologies are normally so expensive that most mills have been able to demonstrate that they are not practicable. Currently no good practicable color removal technology is available for reduction to very low levels. A 50% reduction with some technologies is possible but that is still a fairly heavy color load and at substantial cost.

The industry is inclined towards process changes to reduce color instead of end-of-pipe technology. Many mills have converted to oxygen delignification in the bleaching area. Co incidentally, the same technologies that reduce color also help to reduce total organic chlorine (TOCl). Mills are also using extended delignification, chlorine dioxide substitution and more sophisticated spill collection and recovery systems. There is a payback to those systems as mills not only reduce color and TOCl but also reduce BOD levels in their waste water, which often translates into less horsepower required to treat waste water.

2.0 ORIGIN OF CHROMOPHORES OR COLOR BEARING COMPOUNDS IN MILL EFFLUENT

As already mentioned the effluent color is mainly due to presence of organic components, which are released during pulping and bleaching operations from the raw materials used for papermaking. The pulping process employed has a profound influence on magnitude & intensity of color generated in liquid effluents, as summarized in **Table- 2**. It has also been observed that primarily the chemical composition of raw material used has more pronounced effect on generation of color in effluents.

TABLE- 2

Magnitudes of Color Load in Different Effluent Streams

Streams	Color in PCU (1% TS)	Chromophores
Combined Bleach Effluent (Bamboo, Chemical Pulping)	2771	Chlorolignins
Treated Effluent (Bamboo, Chemical Pulping)	2993	Degraded lignin products
Mechanical Pulping Effluent (Eucalyptus)	13,888	Extractives (Poly phenols & tannins)
Mechanical Pulping Effluent (Acacia)	8,488	Extractives (Poly phenols & tannins)
Mechanical Pulping Effluent (Bagasse)	893	Extractives (Poly phenols & tannins)
Effluent from Agro based Mill	14,808	Lignin & Its degraded products

Source – CPPRI Data

The Indian paper industry utilizes a wide variety of raw materials for papermaking including forest-based raw material viz. wood & bamboo, agricultural residues viz. wheat straw, rice straw, bagasse, jute, etc. grasses and recovered paper/waste paper.

The mill which are based on waste paper do not have effluent color problem however on the contrary in wood based mills the effluent color problem has become a major environmental issue. The problem is further aggravated for the mills, which have mechanical pulping street for the production of newsprint based on Eucalyptus. In mechanical pulping effluent the effluent color is contributed by presence of extractives, which is the specific organic component present in hard woods known to be the compounds with chromophoric groups. The mills, which are based on non-woody raw material particularly bamboo, problem of effluent color is relatively less and the major sources of colored effluent is from bleaching operation. The mills, based on agricultural residues in absence of a viable chemical recovery system, are discharging the spent liquor directly to receiving stream, the color load of which is high due to presence of higher molecular weight lignin components.

2.1 CHEMICAL COMPOSITION OF WOOD

The chemical components of wood can broadly be categorized into the following two main components.

(1) Macromolecular cell wall components like cellulose, hemi cellulose and lignin, which are present in all woods.

(2) Minor low molecular weight components (extractives and mineral substances), which are generally more related to special wood species.

A short introduction to the chemical wood components follows the general scheme as shown in **Fig.- 1**.

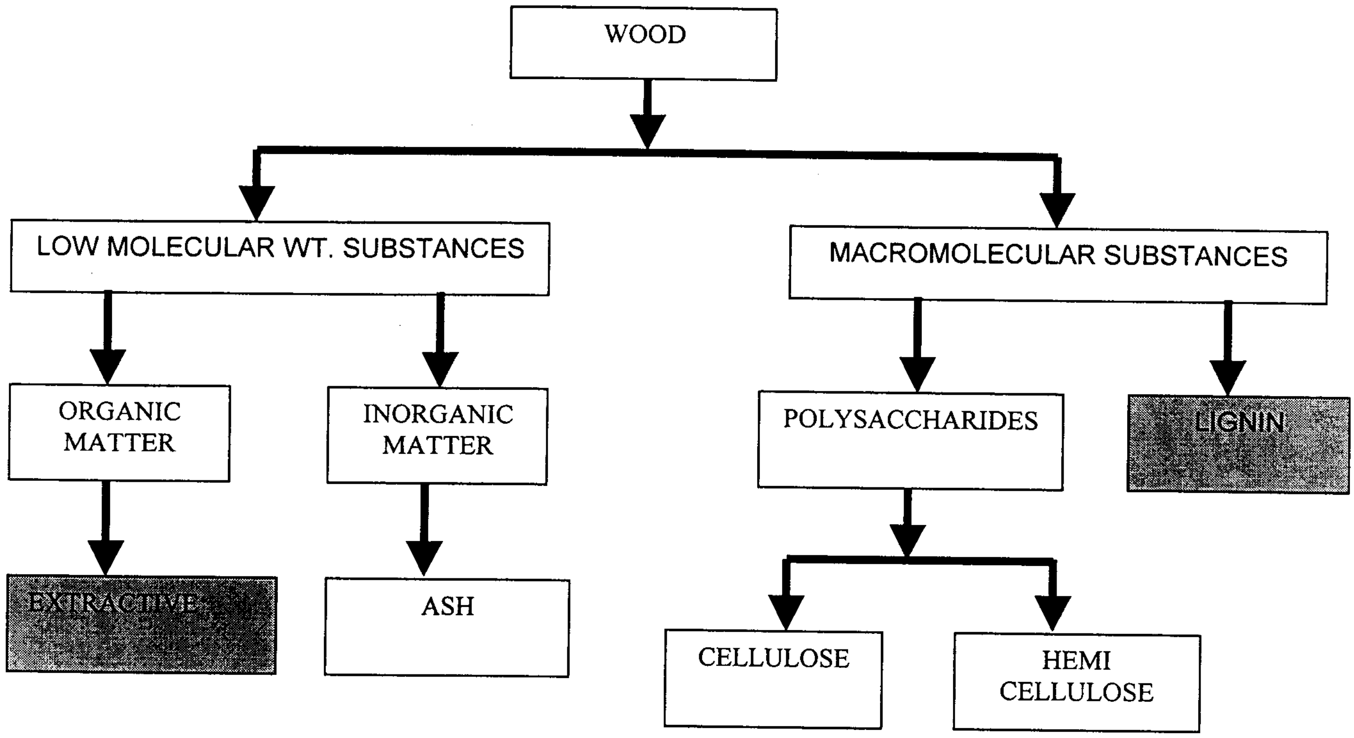


FIG. 1: General Scheme of the Chemical Wood Components

The major color bearing components of wood are:

- Lignin
- Extractives

(1) **Lignin**: It is the third macromolecular wood components consist of an aromatic system composed of phenyl propane units.

(2) **Extractives**: It belongs to low molecular weight substances. The most important substance of this group are the tannins compounds (aromatic phenolic compounds) which can be divided into hydrolysable tannins and condensed Phlobaphenes. Other phenolic substances are e.g. the stilbenes, lignins, flavanoids and their derivatives. Simple compounds deriving from the lignin metabolism also belong to this group.

The isolation of the extractives is carried out by extraction with neutral solvents mixture and/or with single solvents in succession **Fig.-2** gives an overview of the groups of extractives from an analytical standpoint, with examples of subgroups and individual components.

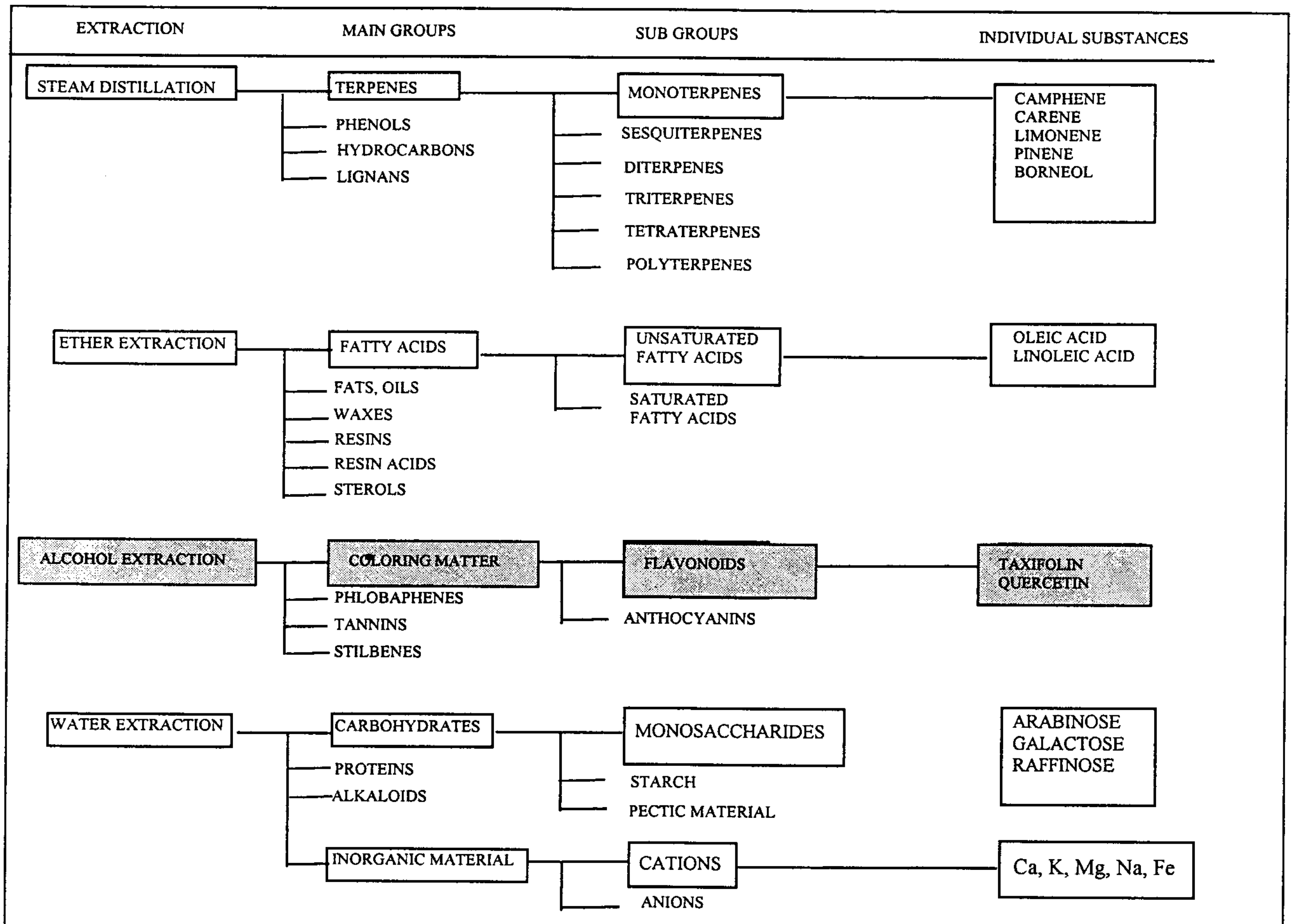


FIG. 2: Classification of the Extractives With Examples According to Analysis Groups

3.0 WOOD COMPONENTS AS A SOURCE OF COLOR

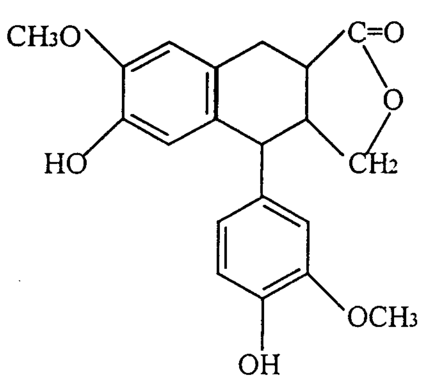
Pulp mills introduce a large number of pollutants to the receiving water through their effluents. These effluents are characterized not only on the basis of traditional pollutional parameters like BOD, COD, SS, TOCI etc. but also on the basis of their dark objectionable color. The primary source of all these pollutants lies in the dissolved organic fraction of the effluent, which generally comprises of the degradation products of various components like cellulose, lignin and some extraneous wood component like extractives. The color of the effluents is however mostly contributed by lignin derivatives and the polyphenolic extractives, which are known to carry the bulk of the light absorbing materials or the chromophores. Lignin and the extractives on reaction with various process chemicals produce chromogenic compounds like quinones, quinone methides and alkenes conjugated with aromatic rings or compounds like hexa- hydroxy diphenyle which darken on exposure to air. Compounds like O-benzoquinones are known chromophores and due to their highly chromophoric nature, even a small amount of the compounds makes significant contribution to effluent color.

3.1 EXTRACTIVES AS THE SOURCE OF COLOR

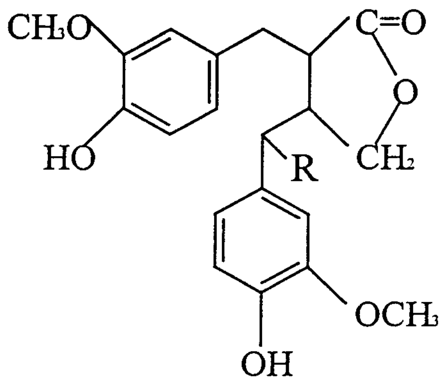
The extractives are known to be the major source of color contributing component for mechanical pulping effluents. The lignin component which is retained with the mechanical pulp makes an insignificant contribution to effluent color. The extractives which are the extracellular component of wood are generally divided into three sub groups which include the aliphatic compounds, terpenes, terpenoids and the polyphenolic compounds. In Eucalyptus wood, polyphenolic components constitutes the major proportion of extractives present in it.

The phenolic compounds however form a heterogenous class and consists of hydrolysable tannins (like Ellagitannin), the condensed tannins or proanthocyanadines, lignans, and stilbenes.

The **lignans (I-III)** are either colorless or pale yellow and would not be expected to cause color in effluent or pulp. Their lack of vicinal phenolic hydroxyl groups and their stable ring systems preclude colored oxidation by-products.

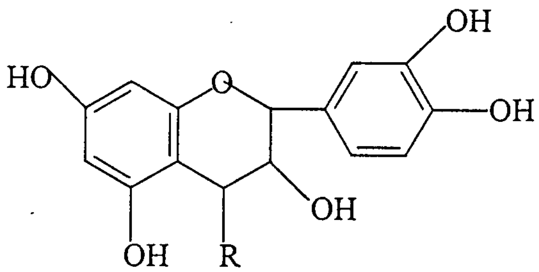


I α -conidendrin



II Hydroxymatairesinol (R=OH)
III Matairresinol (R=H)

On the other hand, **flavonoid-type phenolic extractives** such as **leucocyanidin (IV) and Catechin (V)** are known precursors of the highly colored tannins and polymeric phenolics.



IV Leucocyanidin (R=OH)
V Catechin (R=H)

Nathway and Seakins found that Catechin is a very reactive compound which would be susceptible to acid catalysed polymerization alkali-ring fission and auto –oxidation. From these studies catechin would be expected to form colored polymers by extended quinone formation as indicated in **Fig. 3**.

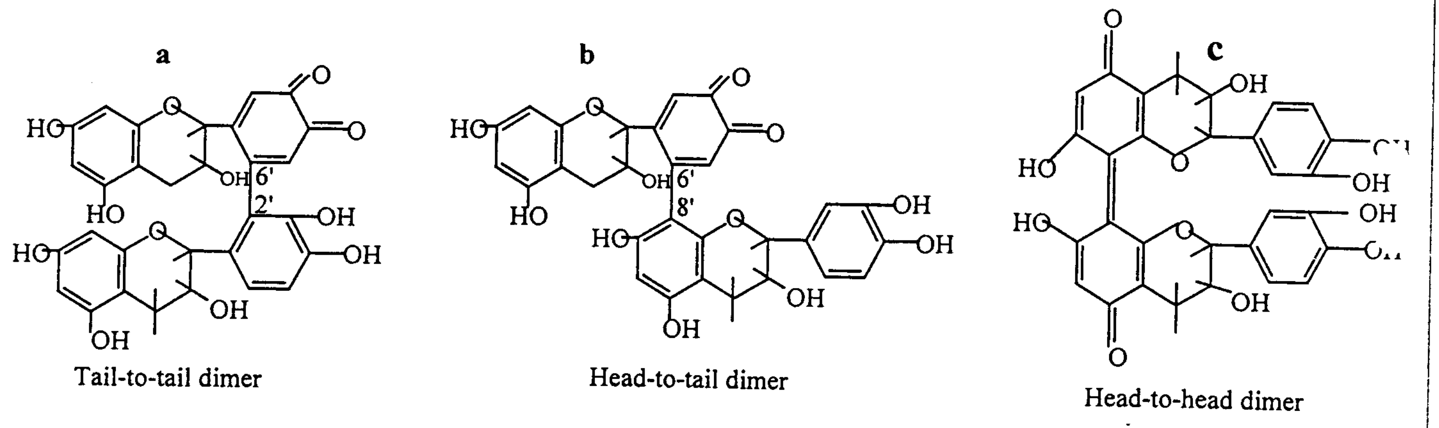
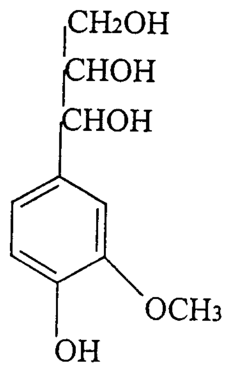


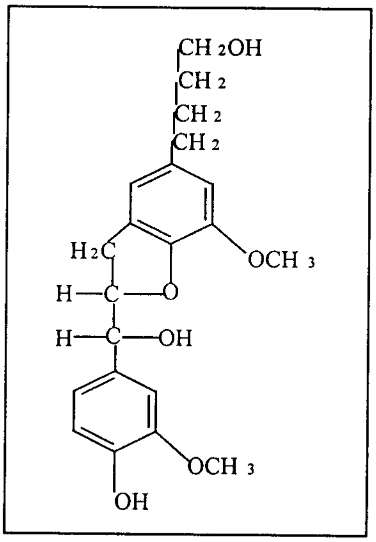
FIG. 3

Guiacyl glycerol (VI) is stable in neutral solution. In acid solution it forms carbonyl compound, which have been shown to be color precursors. In alkaline solutions, guaiacyl glycerol is stable and becomes colored.



VI Guaiacylglycerol

The **Coumaran (VII)** is also present as a glycoside in which sugar moity is attached through an alcoholic rather than a phenolic linkage. Compounds of this type are susceptible to further depolymerisation and could contribute to colored components.



VII 2 – (α-hydroxyguaiacyl) -5-(3-hydroxypropyl)- 7-methoxy-coumaran

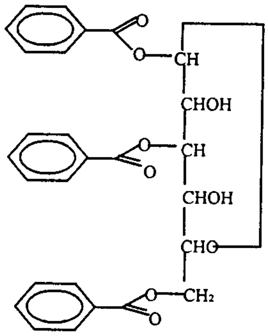
The polyphenols are present in all pulpwoods but their amount and composition and reaction to pulping conditions vary. **It is expected that the polyphenols that are more susceptible to hydrolysis are more likely to form a part of the effluent and contribute to its color. While the extractives that are resistant to hydrolysis contribute more to the pulp color. Ellagitannins that are resistant to alkaline hydrolysis would not hydrolyse rapidly under conditions of cold soda or alkaline ground wood and consequently they could contribute appreciably to color of pulp. However during Kraft, soda or NSSC pulping process the ellagitannins are probably rapidly hydrolyzed.**

The work carried out by W.E.Hillis have shown that some components of extractives have more pronounced effect on color than others. This is because different polyphenols give chromophoric groups of different color intensities. On treatment with pulping liquor, the greatest intensity of color comes from kinos followed by ellagitannins. Gallic acid also contributes to appreciable amount of color followed by catechin, ellagic acid and stilbenes. The presence of air also considerably increases the intensity of color.

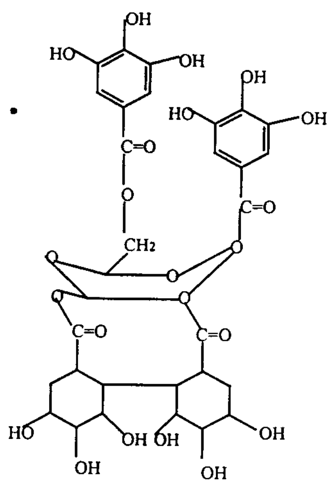
It was further showed by W.E.Hillis that the molecular constitution of the polyphenols also has a considerable impact on their chromogenic properties and the chromogenic properties vary within a class. Leucodelphinidines with pyrogallol moities contribute more than leucocyanidines with catechol moities and leucopelagronidens with phenol moities. Also catechin (with catechol moieties) forms less color than leucoanthocyanins showing that the flavandiol nucleus is an important feature of color. In addition, the chromogenic nature of extractives depends on the pulping liquors for instance Kraft liquor gives darker and browner color than NaOH solution of same pH.

3.1.1 Chemistry of Color Generated from Extractives

The extractives commonly present in the heartwood of eucalyptus species are the gallic acid, ellagic acid ellagitannins and kinos. Literature shows that under alkaline conditions, ellagitannins which contain an ester linkage with the anomeric glucose carbon are most sensitive to hydrolysis producing ellagic acid. The ellagitannins which are more susceptible to hydrolysis have the following structures **(Fig.-4)**.



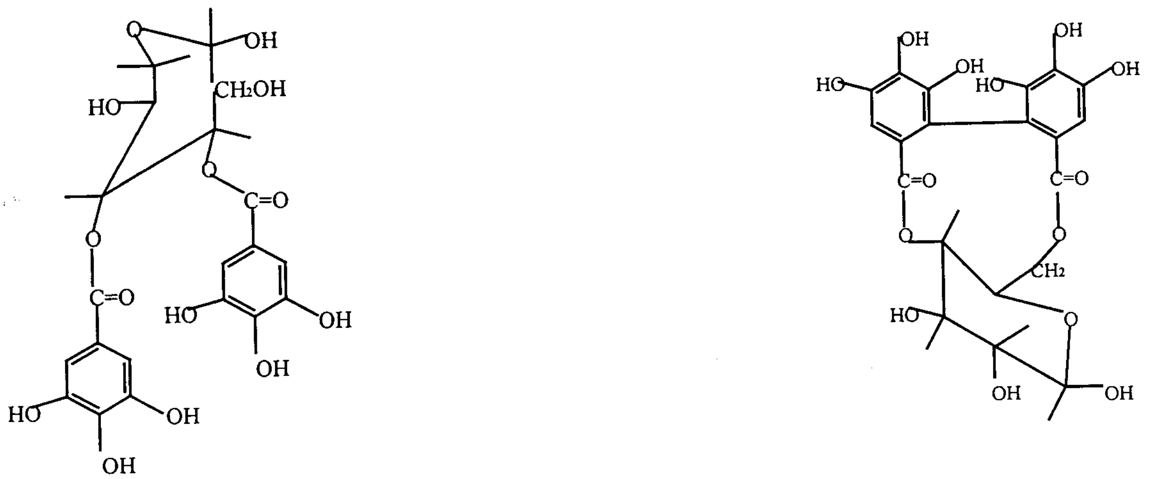
(A)



(B)

FIG. 4: Ellagitannins Susceptible to Hydrolysis

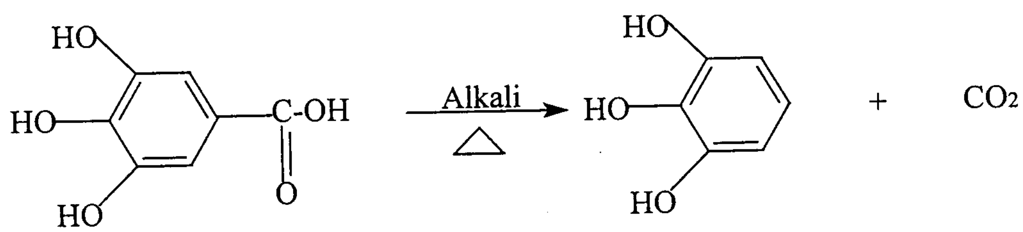
However compounds like C & D are more resistant to hydrolysis **(Fig.-5)**.



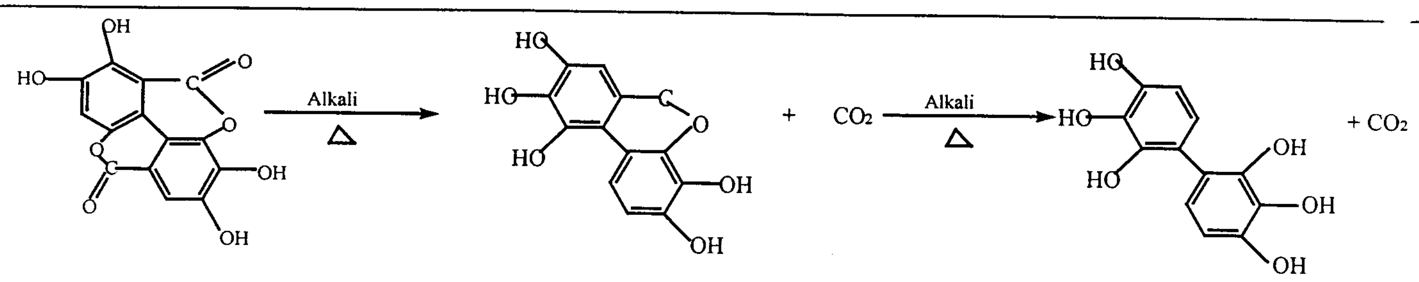
(C) (D)

FIG. 5: Different Types of Ellagitannins Resistant to Hydrolysis

Further heating of gallic acid and ellagic acid in alkaline solution under conditions comparable with those of Kraft, soda and NSSC pulping process produced the following products.



Gallic Acid Pyrogallol



2,3,3',4,4' Pentahydroxy-diphenyl methyloid

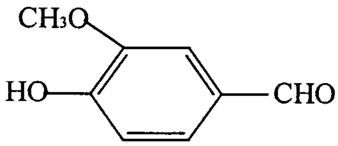
Hexahydroxydiphenyl (Brown Color)

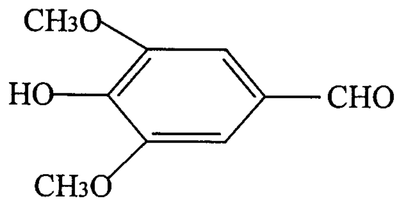
Ellagic acid is extensively decarboxylated to hexahydroxy diphenyl, which rapidly oxidizes to dark brown products, which contribute considerably to color. The rate of decarboxylation of ellagic acid depends to a large extent on the pH of the solution. The rate of decarboxylation reaction increases as the pH of the solution increases.

3.2 LIGNIN AS THE SOURCE OF COLOR

Lignin is the principal source of color for chemical pulping processes. Lignin, which is separated from the cellulose fibre and gets dissolved into the process liquid, reacts with the pulping and bleaching chemicals and leads to the formation of light absorbing compounds like quinones. These light absorbing compounds are generally responsible for the characteristic brown color of the spent pulping liquor and the bleach effluents.

Alkali treatment of wood lignin results in the formation of vanillin and syringaldehyde, which darken upon exposure to air. The main source of color from lignin therefore appears to be from its degradation products and their reaction with air. Aulin-Erdtman showed that though absorption maxima for vanillin and syringaldehyde is around 300 in alkaline solution the absorbance maxima shifts to longer wavelengths i.e. at 347-363. These shifts were attributed to the presence of both phenolic and carboxyl groups in these compounds. Further the formation of compounds like quinone and pyrogallol from the demethylation of vanillyl and syringyl moities of lignin are responsible for the color reaction of lignin.


Vanillin


Syringaldehyde

4.0 SOURCE OF COLOR FROM PULP & PAPER MILLS

The main source of colored wastewaters in the pulp and papermaking process includes the debarking plants, pulp mills and the bleach plants. The following figures **(Fig.-6)** illustrate the different sources of waste water discharge points in a pulp & paper mill.

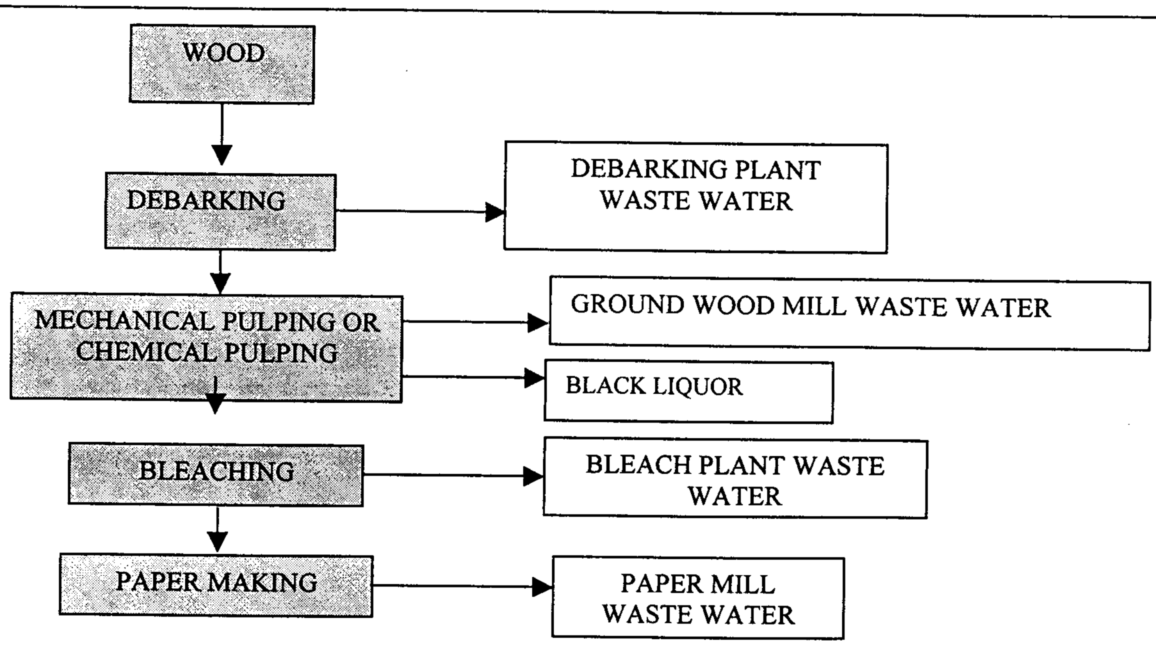


FIG.6: Sources of Wastewaters Emanated from the Pulp & Paper Industry- A General View

4.1 DEBARKING OF WOOD

The effluent generated from debarking of wood contains colored phenolic compounds emanated from barks. These colored effluents however form only a small fraction of the combined effluent stream from the whole process.

4.2 PULPING

A review of sources of color in liquid effluents indicate that approx. 30-50% of the color in the liquid effluent may result from the pulp mill. A typical kraft pulping process can generate as much as 230-270 kg color / ton of pulp. Depending upon the pulping process (Kraft, NSSC, sulfate, mechanical or TMP) the effluent color load can vary significantly.

The principal source of color from paper making process is the lignin. The amount of lignin separated and removed from the cellulose fibre is different for different pulping process. The amount of color discharged from each source is further dependent upon the process conditions such as temperature, pH, mechanical action and reaction with process chemicals.

4.2.1 Chemical Pulping

Chemical pulping processes are the major sources of color in effluents because they separate and remove more lignin than any other pulping processes. The kraft pulping process is the dominant pulping process and also the major color producing process. Typical mill effluent color discharges for selected process are as follows.

Bleached Kraft mill	-	135 kg color/t
Bleached sulfite mill	-	55 kg color/t
Bleached TMP mill	-	50 kg color/t

However the black liquors from the Kraft process and the spent sulphite liquor from the acid bisulphite process are utilized in the recovery process after concentration in the evaporators & subsequent combustion in the recovery system. Hence such liquors do not contribute to the problem of effluent color.

On the contrary, the small and medium sized mills, which are not equipped with any chemical recovery system, the chemical pulping process may contribute significantly to color.

4.2.2 Mechanical Pulping

Generally mechanical pulping generates wastewater containing low molecular mass lignin and polyphenolic compounds, which give the effluent their characteristic brown color. Since the solid concentration is low, it is not economically feasible to concentrate the liquor by evaporation and burn it in furnace to destroy the color bearing organic compounds, as a result the mechanical pulping effluents which contain low molecular weight lignin and polyphenolic compounds contributes significantly to effluent color.

4.2.3 Bleaching

Pulp bleaching is done primarily to remove the colored substances from the pulp and improve its brightness. The method of bleaching mechanical pulps however differs from those of chemical pulp bleaching because in mechanical pulps the lignin fraction is retained and constitutes an important part of total yield. Thus the objective of bleaching mechanical pulps is to decolorize the lignin and other components without dissolving them. Mechanical bleaching only transforms the colored components to colorless phenolics without degrading the compounds to the point of solubilization. On the other hand, the objective of chemical pulp bleaching is to completely remove the lignin residue from the pulp. This removal of lignin from the pulp however results in highly colored bleach effluents.

The major contribution to effluent color load in the chemical pulp mill is the alkaline extraction stage wastewater, which contributes to approximately 50 % of the total color load. The acidic wastewater from chlorination stage also has significant quantities of color. The objective of bleaching chemical pulps is to remove all the lignin by oxidizing it to small molecules which are soluble either in water or aqueous alkali by multi stage chemical treatments, such chemical treatments result in the oxidative degradation of the lignin into compounds like tetrachloroquinones and mucenic acids during the chlorination stage and in the formation of hydroxychloroquinones during the alkali extraction stage. The formation of such compounds with extended conjugated systems and chromogenic properties are chiefly responsible for the color of the acidic and alkaline bleach effluents.

A significant fraction of dissolved organic in acidic and also in alkaline bleach plant effluent are high color mass (> 10,000). The high molecular mass materials are primarily composed of dissolved lignin fragments, generally referred to as polychlorinated oxylignins. These high molecular mass components carry the bulk of chromophores (color bodies) and are mainly responsible for the color of the bleach plant effluents.

The low molecular mass fraction is composed of dissolved chlorinated fatty acids, resins and other dissolved components. **Fig.- 7** depicts the effluent color loads from different section of a bleached kraft mill.

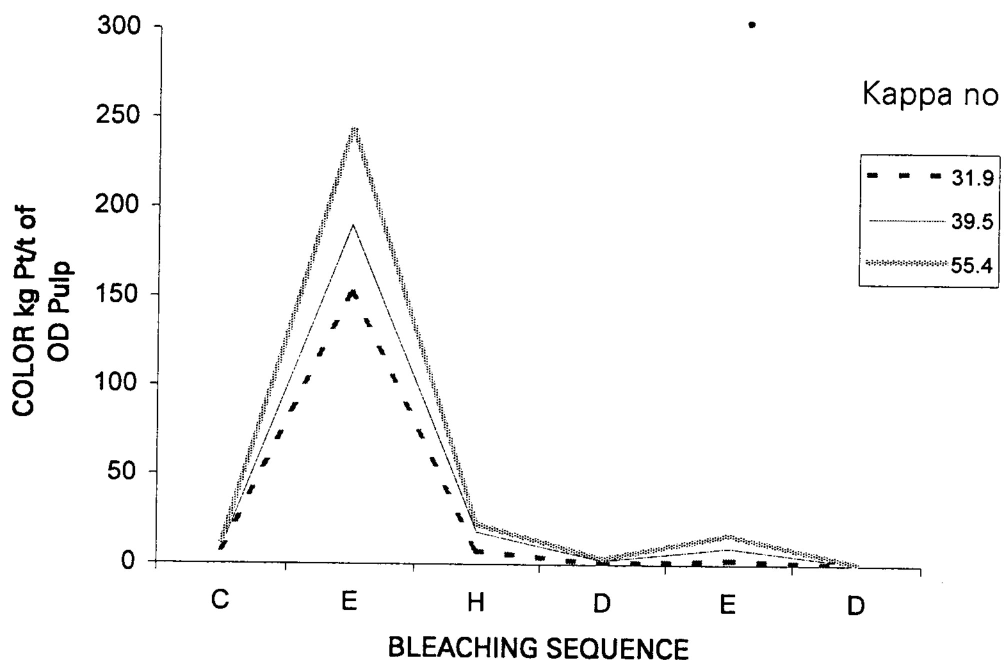


FIG. 7: Color of Bleach Effluent

In one of the study report carried out by the Swedish Enveron Care Project have showed that as much as 90% of the color removed in Swedish Kraft bleaching system occurred in the caustic extraction stage and 62% in the sulphite bleaching system. The amount of color generated during bleaching depends upon the degree of cooking of the pulp prior to bleaching. The **Table- 3 and Fig.- 8** below show that the amount of color generated during bleaching increased with increasing kappa no. of unbleached pulp.

TABLE- 3

Color of Effluent from Bleaching Spruce Kraft Pulp

(Data Generated By Halmora & Balhar)

Kappa no	31.9		39.5		55.4	
Color	mgPt/t	Kg Pt/t	mgPt/t	Kg Pt/t	mgPt/t	KgPt/t
Bleaching Sequence						
C	300	8.27	300	8.27	450	12.41
E	8,000	152.00	10,000	190.0	12,800	243.20
H	400	7.60	950	18.05	1,200	22.80
D	40	0.76	125	2.38	180	3.42
E	150	2.85	500	9.50	900	17.10
D	5	0.09	40	0.76	50	0.95
TOTAL		171.57		288.96		299.88

The effluent color loads from different section of a bleached kraft mill are shown in **Fig.- 8**.

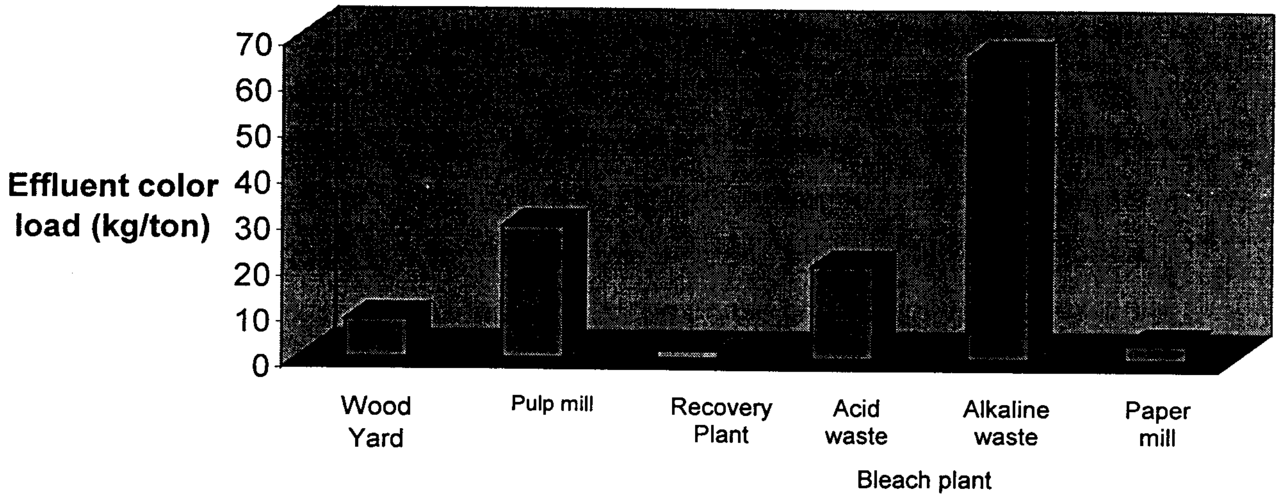


FIG. 8: Effluent Characteristics from CEDED Bleached Kraft Mill

5.0 COLOR REMOVAL STRATEGIES

As a rule, color bodies are resistant to removal by conventional wastewater treatment process and for this reason suitable alternative technologies are sought. Following approaches can be adopted to reduce the problem of effluent color and this includes:

- Inplant control measures without major technology change.

- Process modification/ technology innovation to control the generation of these highly colored components.

- End-of-pipe treatment methods.

5.1 INPLANT CONTROL MEASURES WITHOUT MAJOR TECHNOLOGY CHANGE

In a pulp mill, spent pulping liquor is the only source of color load and any loss through spillages or inefficient washing would lead to effluent color load. If practiced, following measures should significantly reduce the problem.

a) **More Extensive Pulp Washing:**

Since the spent liquors from hardwood and softwood kraft pulping may contain 2700 kg and 1800 kg of color, respectively, achievement of 98% efficient liquor separation, certainly a realistic goal, should reduce color to 55 and 35 kg, respectively. Closure of screening system losses and further attention to pulp washer system optimization, from a BOD load standpoint as well, should be beneficial. Steps taken in this direction include in-digester diffusion washing as well as addition of external washing stages.

b) **Prevention of Evaporator Carryover and Recycling of Evaporator Boil-Outs:**

The evaporation system itself must be reexamined as a source of color load. Both these control approaches can be expected to yield significant further load reduction, as in the case of BOD load itself.

c) **Retention of Pulping Liquor Spills and Leakage:**

Provision of spillage and leakage retention facilities around process, storage, and pump transfer equipment has become necessary from color load control viewpoint.

d) **Instrumental Detection of Intermittent Sewer Losses:**

In absence of color measurement monitoring facilities, useful correlations with other measurable parameters, such as conductivity, which would lead to detection and prevention of color load loss again in terms equivalent to the basic problem of BOD load control, should be developed.

5.2 PROCESS MODIFICATION

One approach used to reduce the discharge of chlorinated organics as well as color in effluents is to decrease the amount of residual lignin in pulp entering the bleach plant. This is achieved by selective extended delignification during pulping. By adopting modified cooking cycles and rapid displacement heating (RDH) as much as 40% to 60% reduction in bleach plant effluent color can be accomplished in a kraft mill using hardwood. Oxygen delignification, with its filtrate flowing counter currently through the screen room, washroom, evaporators, and recovery, significantly reduced the bleach plant effluent color. Only 60% of the lignin remained to be bleached out after the oxygen stage.

Other methods being produced to reduce effluent color are partial or total substitution of the molecular chlorine by chlorine dioxide, reinforcement of the alkaline extraction stage with oxygen, and sequences involving oxygen prebleaching.

A modern bleaching sequence (ODCEDED) with 50% lignin removal in the oxygen stage and 65% ClO_2 substitution in the chlorination stage could achieve substantial reduction in effluent color. Significant reduction in effluent color loading is also possible with other bleaching sequences.

Fig.-9 gives the bleach plant effluent color load for different bleaching sequences for hardwood. Both oxygen bleaching and substitution of chlorine by chlorine dioxide have a positive influence on effluent color reduction.

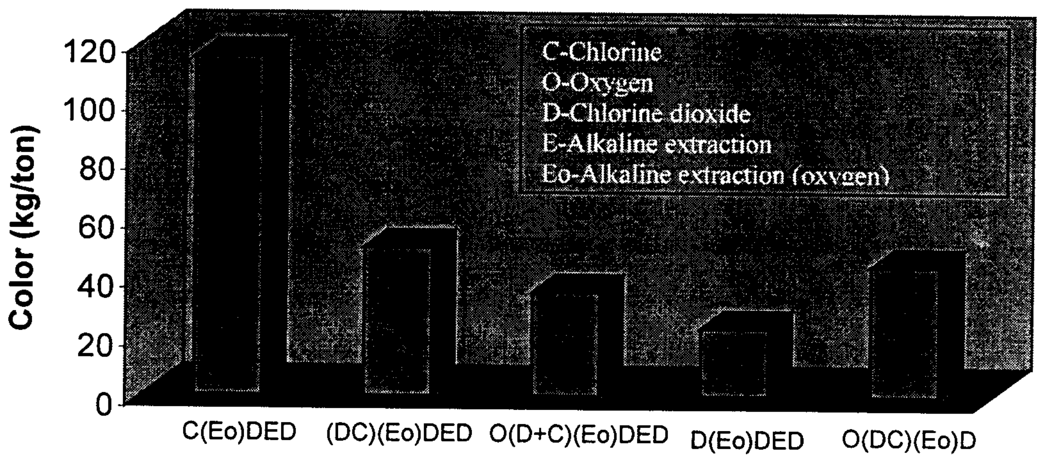


FIG. 9: Relative Color Loads in Effluents from Different Bleaching Sequences for Hardwood

For the Integral newsprint mills, chemi (thermal) mechanical pulping has been suggested as a low polluting pulping alternative for chemical pulp mills. It is however a well-known fact that water pollution from a chemi-mechanical pulping line can be severe. The CMP effluent, unlike other mechanical pulping (SGW, TMP & CTMP) effluents is characterised by high color load. Color loads are specially high for Newsprint mills that employ eucalyptus for the production of mechanical pulp component. Eucalyptus contains 3-6% extractives, mostly polyphenols (such as tannins, which leach out during presteaming and refining stages.

These extractives and their hydrolysis products known for their highly chromophoric nature are mainly responsible for the color in mechanical pulping effluents.

Laboratory scale studies carried out on CTMP pulping of Pine & Spruce chips at Helsinki Institute of Technology using Na_2SO_3 charge as the pretreatment chemical has indicated that color depends to some extent on pretreatment condition. High temperature and extended retention time increases color but higher Na_2SO_3 charge decreases it.

Thus for the Newsprint mills effluent color reduction can be achieved either by a proper selection of the raw material or by modification of the pretreatment process. A review of literature however revealed that the area of color reduction through process modification remains largely unexplored.

5.3 END-OF-PIPE TREATMENT

Due to small particle size and chemical structure of the lignin residues, traditional primary and secondary effluent treatment processes have been only partially effective in limiting effluent color. Specific treatment for color has generally focused on pretreatment of bleach plant filtrates as well as supplemental or tertiary treatment at the effluent plant.

Early methods to remove color from pulp mill wastewaters include limited & massive lime treatment, alum co-precipitation and precipitation with iron, salts and lime. More recent methods employ techniques like chemical oxidation with $KMnO_4$, oxygen & ozone or H_2O_2; adsorption and absorption on activated charcoal, reverse osmosis & electro dialysis; iron flotation or foam separation techniques & biological treatment. Most of these color reduction procedures can be broadly categorized as-

(i) Chemical treatment methods, which indicates chemical coagulation methods & chemical oxidation method.

(ii) Physical treatment methods, which include Adsorption methods & membrane processes.

(iii) Irradiation Process

(iv) Biological Treatment Methods

(v) Electrolytic Methods

6.0 BASIC ELEMENTS OF EFFLUENT COLOR REMOVAL DEFINITION

6.0.1 Measurement of Effluent and Receiving Water Color Levels

Selection of method for measurement of pulping and bleaching derived color has always proceeded from the observed similarity in hue between so called natural water color of swamp or decaying vegetation origin and that of mill effluents. Starting with color wheel visual comparators, a method was evolved (Published in NCASI tech. Bull. No. 253, Dec.1971) with single- wavelength spectrophotometric measurements in the spectral range of 450-480nm, where both effluents and the cobalt-chloroplatinate standard display flat adsorption curves.

This procedure involves pH adjustment to 7.6 followed by filtration through an 0.8 µm porosity membrane filter so as to produce a high clarity sample without significant removal of nonfiltrate color. Color is then determined by light absorption measurement at 465nm and expressed in standard color units, reading against a calibration curve prepared with the above standard. The procedure has been recognized by EPA in its effluent color standard.

The detail procedure for measurement of color is annexed which is a part of CPPRI publication on **"Laboratory Manual of Testing Procedures"**. The procedure is based on the standard methods for the examination of water and wastewater published jointly by American Public Health Association, American Water Works Association and Water Pollution Control Federation.

6.0.2 Detectable Changes in Receiving Water Color

The definition deficiency for determination of the variability in level of color detectability in different receiving waters and at different points along or overlooking such waters still continues to exist. There is a need for professionally screened observer panels to determine (a) absolute thresholds of detectable color level; (b) perceptible changes from a given, visually observable, reference color level; and (c) the influence of lighting conditions, water depth and quality, and observer angle. The importance of such information in establishing rational water-quality color standards and ultimately defining the goals of decolorization technology research are seemingly obvious.

6.1 CHEMISTRY OF COLOR REMOVAL

The particle charge, particle size and concentration of color colloids play a very vital role in the color reduction process, when the interaction is allowed with various electrolytes. The **Fig-10** shows the sizes of different particles falling within the category of suspended solids. Normal color bearing substances lie within the range of ionic to colloidal dimension i.e. $10^{-3} - 10^{-1}$ microns. Particles of the colloidal nature when dispersed in water, can ionize, adsorb and attract low molecular weight ions to its surface, which are held tightly to the colloidal surface, which is known as Stern Layer.

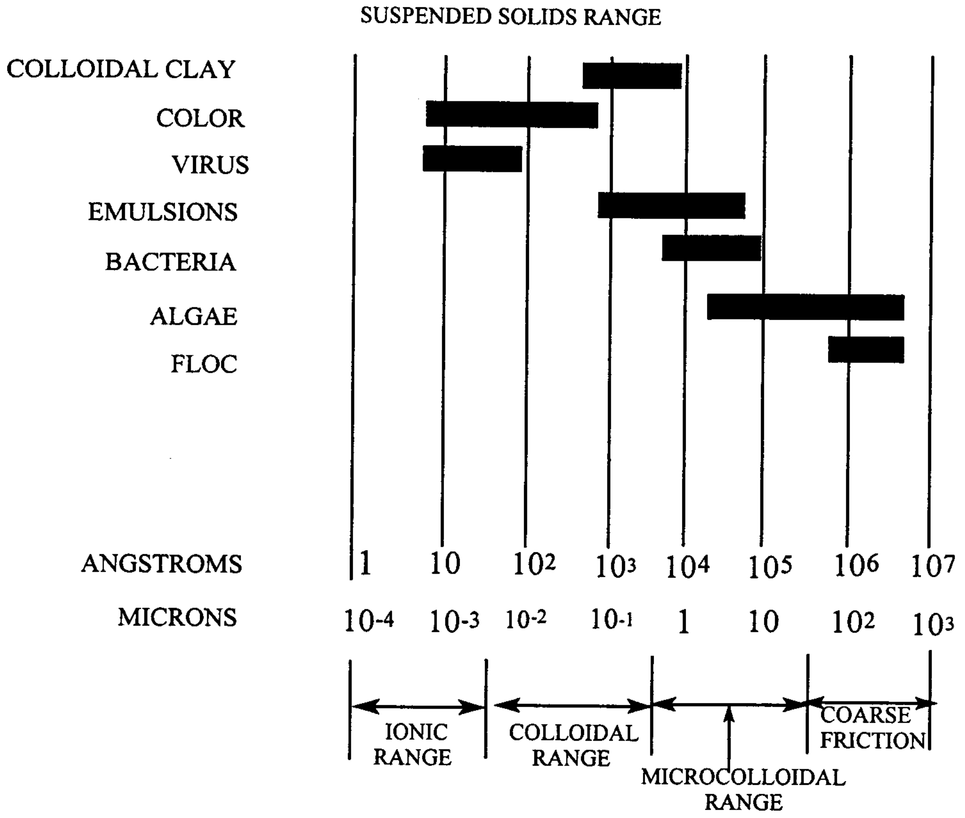


FIG. 10 : Particle Size of Some Common Suspended Particles

The remaining ions will be attracted to the particle and extend into the solution in the diffuse layer also called Gauy-Chapman Layer, until electroneutrality is established. **(Fig-11)**.

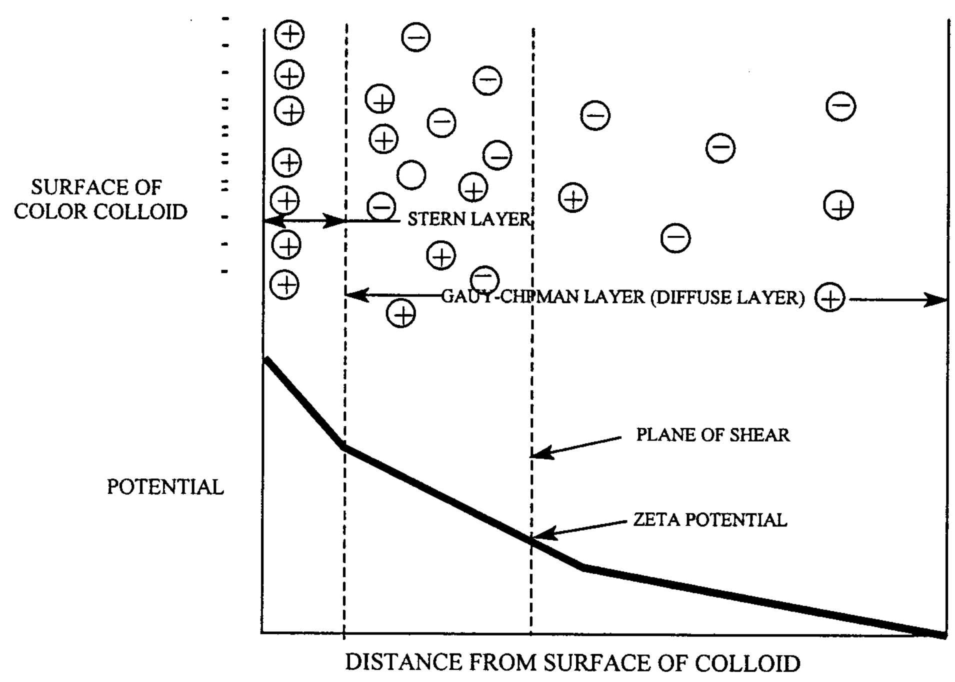


FIG.--11: Illustration Showing Charge Neutralization

The net charge on the colloidal particle is the strongest force inhibiting their removal. It is the interparticle repulsion that prevents colloids from colliding and forming large masses. By partial or complete neutralization of this surface charge, colloids can collide through Brownian motion and mixing, and can be attracted to each other by hydrogen bonding and Van-der-Waal's forces, enabling them to form larger masses. It is also important to consider the degree of hydration, as the particles that are hydrophilic are much harder to remove than those, which do not get hydrated or are hydrophobic. Thus the removal of colloidal particles is accomplished in four steps, namely-

- Destablization involving charge neutralization
- Microfloc formation
- Agglomeration of microflocs, and

- Physical entrapment by macrofloc formation.

The first three steps are known by familiar terms of coagulation and flocculation. **Fig.-12** illustrates this phenomenon very distinctly. In a hydrophilic colloidal system, where colloids are strongly hydrated, it may be necessary to add a chemical that not only neutralizes surface charge but also forms an insoluble complex with the colloid for destabilization.

In a destabilized colloidal system collisions can occur and through chemical bridging, hydrogen bonding and Van-der-Waal's forces of attraction, the color bearing particles can form microflocs, which on continuous mixing again combine to form macroflocs. Portions of the colloids are removed by being physically entrapped in microflocs already formed.

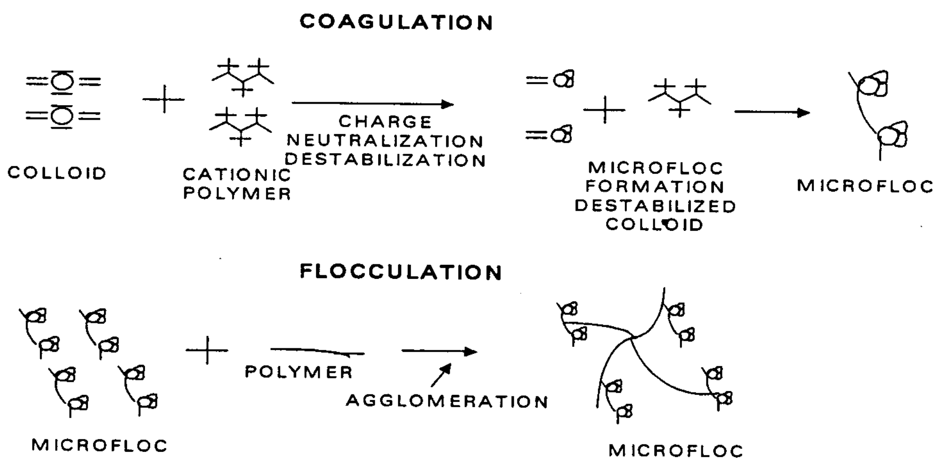


FIG. 12: Mechanism of Coagulation & Flocculation

7.0 AN OVERVIEW OF EFFLUENT COLOR REDUCTION TECHNOLOGIES

Conventional method of effluent treatment such as primary sedimentation clarifier followed by biological methods are effective in reducing biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC) and suspended solids (SS). However these methods do not have any significant effect on effluent color. Process modification and / or end of pipe (EOP) treatment methods for color removal are becoming necessary to satisfy pollution discharge limits.

7.1 PROCESS MODIFICATION

Till recently, most of the technological innovations/process modification that has taken place worldwide, to contain color loads in liquid effluent were in and around pulp mill and bleach plant only. To reduce the discharge of chlorinated organics as well as color in the effluents, the amount of residual lignin in pulp entering the bleach plant must be reduced. This is achieved by selective extended delignification during pulping.

By adopting modified cooking cycle and RDH as much as 40-60% reduction in bleach plant effluent color can be accomplished. Oxygen delignification preceded by an extended cooking process also helps in partial dissolution of residual lignin in unbleached pulp. Other methods being practiced to reduce color are partial or total substitution of molecular chlorine by ClO_2, reinforcement of the alkaline extraction stage with oxygen and sequences involving oxygen prebleaching. Overview of technological changes in bleached kraft fibre line in last few decades is summarized below-

(i) **Technology in the 1970s: Fig.-13** Illustrates the color produced in five major processing areas of a bleached kraft mill typical of those built in the 1970s. These mills were not engineered with color discharge minimization as a primary design consideration. The bleach plant had a CEDED sequence with no possibility for countercurrent filtrate flow to recovery. Color discharge from the bleach plant was 70% of the total mill effluent color.

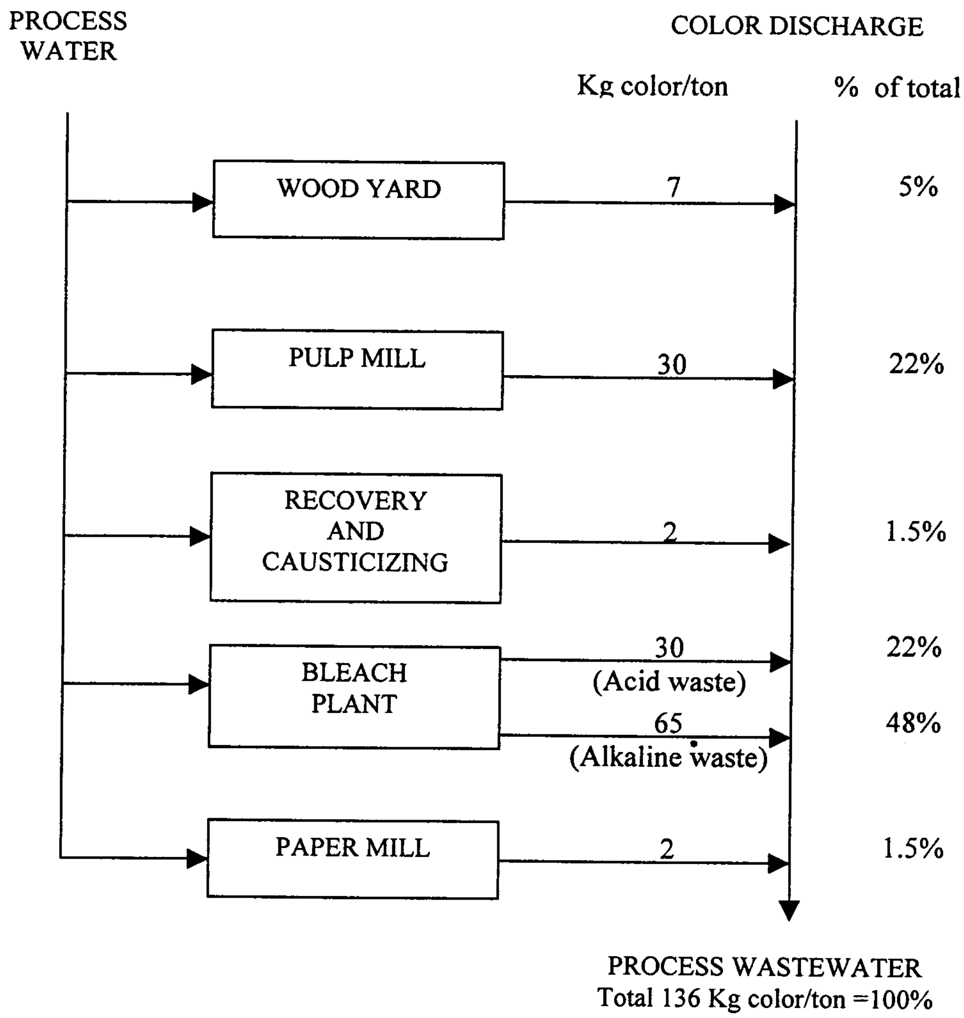


FIG. 13: Effluent Characteristics of a Bleached Kraft Mill of 1970's Designed with a CEDED Bleaching Sequence

The pulp mill had minimal spill control, and the screen room was operated with continuous purge to mill effluent. This area accounts for more than 20% of total mill color.

The wood yard was designed for dry debarking, but "small quantities" of wash water added for cleanliness contributed to the color discharge from this area. The recovery and causticizing areas drained to the mill waste with their color contribution. The paper mill did have considerable recycling, however a continuous purge was included in the design.

(ii) **Technology of the 1980s: Fig.- 14** illustrates the color produced in the same five major processing areas of a typical 1980s bleached kraft mill. These mills achieved a dramatic reduction in mill color discharge as a result of design, which was directed principally towards operating cost optimization and environmental improvement. Oxygen delignification, with its filtrate flowing countercurrently through the screen room, wash room, evaporators, and recovery, significantly reduced the bleach plant effluent color. Only 60% of the lignin remained to be bleached out after the oxygen stage.

The screen room was designed to be operated essentially closed. Only rejects from screens and cleaners were carried to mill effluent. Spill containment systems were designed to handle major spills and to return liquids to the fiber line.

Evaporators were sized approximately 20% larger to process the additional wash water, which was now required, along with the returned process spills. Recovery furnaces were sized 6% to 10% larger to process the additional organic and inorganic solids at lower heating value returned from the oxygen stage.

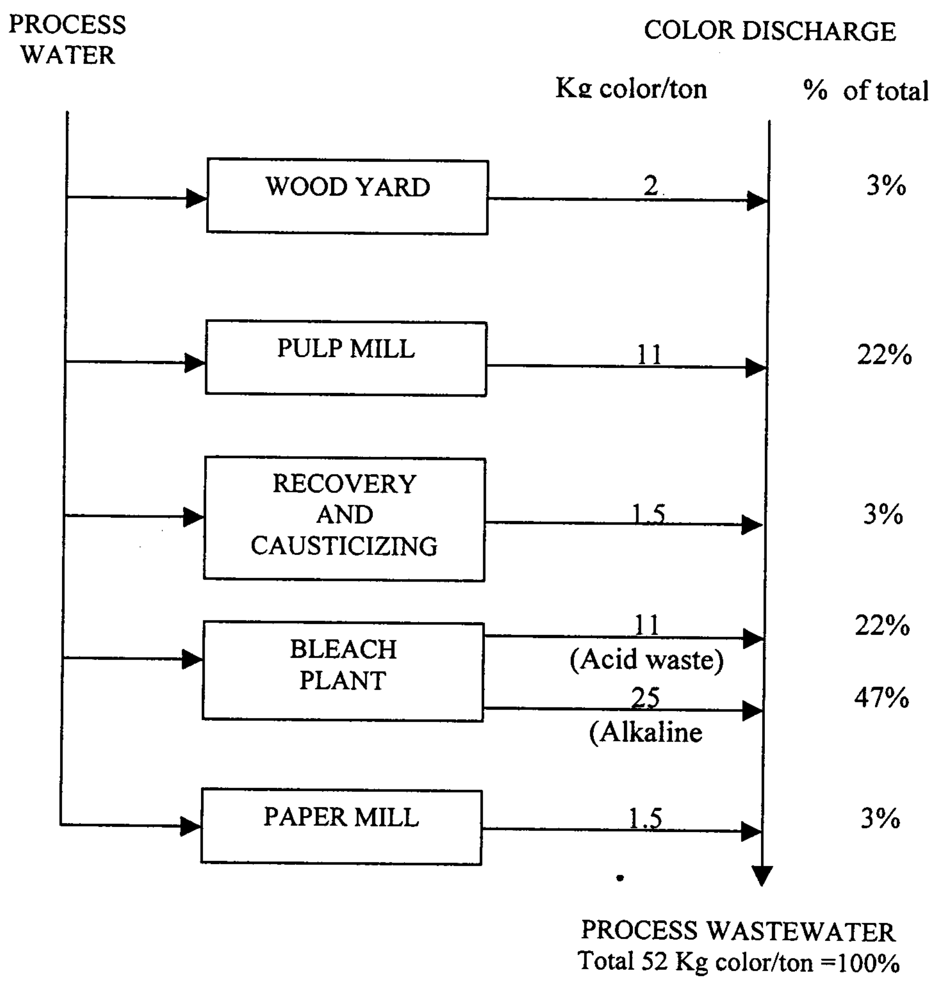


FIG. 14: Effluent Characteristics of a Bleached Kraft Mill of 1980's Designed with a O-C_DED Bleaching Sequence

Causticizing systems were sized 6% larger to supply the oxygen stage and were designed for total spill containment. The paper mill was designed to recycle a greater percentage of whitewater.

(iii) Technology of the 1990s: During this period, the emphasis was on bleach sequence modification. Potential process modifications available in the bleach plant are:

- High ClO_2 substitution for chlorine
- Use of oxidative extraction stage
- Use of hydrogenperoxide

Till date most of the studies concentrated on effluent color reduction in chemical pulp mills evaluating highly colored bleach plant effluents and very little attention was given to contain effluent color loads from mechanical pulping process. The reason is attributed mainly to worldwide trend of producing mechanical pulps using TMP process. In developed countries due to TMP being the predominant pulping process and use of softwood species as raw material for mechanical pulping production, the effluent color is not a major issue. On the contrary in India, out of three newsprint mills having mechanical pulping street, only one is based on TMP process based on bagasse and other two mills using E.hybrid are based on CMP process. The effluent generated from these mills employing CMP process have very high color loads. For these mills, adoption of APMP (Alkaline Peroxide Mechanical Pulping) is one alternative to contain effluent color loads, however, economic feasibility needs to be worked out.

7.2 END-OF-PIPE (EOP) TREATMENT OPTIONS

The nature and composition of the effluent, degree of treatment required, operating costs and efficiency of treatment plants are some factors to be considered when deciding on the type of treatment needed for effluent color reduction. Various EOP treatment options, which have been tried, are confined to bleach effluents only. These methods included physico-chemical treatment method, physical separation method, UV irradiation methods, biological method etc. An overview showing the status of these technologies is summarized in **Table- 4** and are briefly discussed in following sections.

TABLE-4

Status of Various EOP Treatment Technologies

TREATMENT TECHNOLOGY	STATUS
Chemical Precipitation Alum Lime Polymer addition followed by air flotation	**Full Scale application** On mill effluent On bleach & mill effluent On unbleached kraft mill effluent
Membrane Filtration	Mill scale application in E-stage effluent
Ozonation	Bench scale application with bleach effluents
UV Irradiation	Bench scale trials on bleach effluents
Electro-flocculation	Lab scale trials on bleach effluents
Biological Process Mycor Process Lacasse Treatment	 Bench Scale Development trial stage

7.2.1 Chemical Treatment Methods

This includes chemical coagulation methods and chemical oxidation method.

(i) Chemical Coagulation Method

Color imparted to pulp & paper mill effluent is due to the presence of colloidal particles which exists as negatively charged particles. Removal of suspended color bodies having high molecular weight fraction can therefore be easily removed by charge neutralization by introducing metal ions with high charge densities. Treatment of negatively charged particles begins with neutralizing the charge to allow particles to bond into larger and larger particle structures until removal by sedimentation can be achieved. The first part of the process, the charge neutralization is called coagulation while the second part involving particle growth is termed flocculation.

A typical treatment system would include a rapid mix tank (1 to 2 minutes detention time), a flocculation tank (5 to 15 minutes detention time) and a liquid/solid separator (standard reactor or flotation type clarifier), since this treatment results in a considerable volume of sludge that typically is difficult to handle, auxillary facilities for sludge dewatering and disposal must also be provided.

For the pulp and paper industry, principally three chemicals have been used for color removal which are lime, alum and polymers. Though the use of alum is established, the use of lime and ferrous sulphate have been found economically preferable in many cases.

The disadvantages of these systems are the necessity to maintain absolute pH control and problems encountered in sludge handling.

a) Treatment with Massive Lime

The process was developed for color removal from pulp mills effluents, during the 1950's by the National Council of Air and Stream Improvement (NCASI) of U.S. and was patented in 1964.

The significant difference between the massive lime process and the earlier process of treating pulp mill effluent with lime, is the amount of lime used. In earlier work, lime usage was closely related to the stochiometric requirements but produce voluminous sludge, which did not densify on settling. Efforts to concentrate the sludge using centrifuges and other methods were also unsuccessful.

Massive lime process utilizes a large excess of lime to produce a heavy and readily settable sludge. The process removes 90-99% of the color and 35-50% BOD from pulp mill effluents.

- **The Process**

The process involves slaking of lime with part of the total effluent and remaining colored effluent is then treated with heavy doses of slaked lime (approximately 20000 ppm). A detention time of 5-10 min. is given during which colored compounds react to form insoluble calcium compounds, which is separated form the treated effluent in primary clarifier. Clarified decolorized effluent is then treated with CO_2, calcium carbonate as precipitate, which settles out in the carbonator clarifier and is removed, then combined with the sludge from primary clarifier in the sludge storage tank. Clarified decolored effluent, with most of the calcium compounds removed overflows from carbonator sludge clarifier. **Fig.- 15** shows a schematic diagram of the massive lime process.

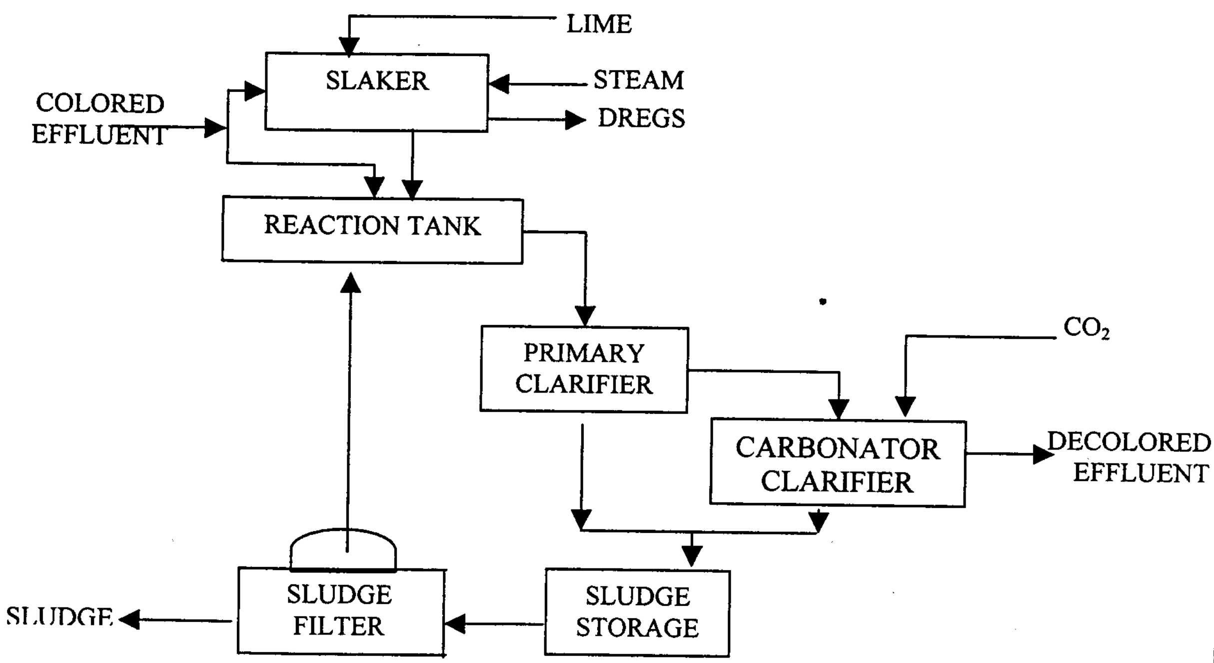


FIG. 15: Massive Lime Treatment

Sludge having a solid content of 18-22% is pumped to a rotary vacuum filter and concentrated to about 50% solids. Filtrate from the vacuum filter is returned to the massive lime treating system because of its high content of dissolved and suspended solids. Sludge at approximately 50% solid is removed from the process, and the lime in the sludge is recovered by using the sludge in the mills causticizing process. Lime produced in the kiln can be recycled to the massive lime process. CO_2 from the limekiln flue gases can be used for carbonation step of the massive lime process.

Colored compounds removed from the massive lime process with the sludge are, to a large extent, soluble in caustic and dissolve in the white liquor as it is produced in the causticizing process. Therefore, the white liquor produced with this process is black. This process was demonstrated at International Paper Company's mill at Springhill La, to determine the effectiveness and feasibility of using massive lime treatment (20,000 ppm) to decolorize kraft pulp mill effluent. The plant was designed to treat 2 m^3/min of wastewater. Color removal ranged from 90 to 97% with overall color reduction between 94-95%.

Major operating problems were –

- Foaming and carryover of suspended solids from the primary clarifier.
- Scaling and mechanical problems with the carbonator system.
- Poor pH control in the carbonator.

b) Treatment with Alum

Two full-scale attempts at color removal using alum to treat mill effluent have been made: one in the US and other in the USSR. Ninety percent removal was obtained at the US mill, but operation could only be intermittent because of sludge handling and alum recovery problems. The mill is no longer in operation. Alum treatment evidently is still in operation at the Soviet mill. However, alum recovery and reuse is not in operation as planned.

In India HNL is using alum to treat the colored effluents. The operating costs are very high besides operational problems. This has been discussed in detail as one of the case study in the chapter II.

c) Treatment with Polymers

Certain organic polymers such as polyamines have been used to precipitate color from effluents. The mixed-liquor suspended solids present in secondary clarifiers do not seem to interfere with the precipitation of color bodies. With a 600 mg/l polyamine dosage, more than 85% color reduction can be achieved in bleach plant effluent. On the other hand, alum dosage of 600 mg/l brought about 54% reduction in color. Precipitation of color bodies using polyamines was more effective than alum but more expensive. Again, sludge handling and disposal poses problems in both.

Polymer treatment for color removal is being successfully applied at several mills in the US. At stone Container Corp.'s unbleached kraft mill in Hodge, la., 90% color removal was obtained by polymer addition followed by air flotation. Reportedly, the sludge can be treated for partial coagulant recovery and disposed off in the recovery system.

- **Commercial Status**

At a Lauisiana mill in the early 1970's, massive lime or high-dosage lime treatment of bleach plant filtrate and mill effluent was tried. High color removals (>90%) were obtained, but full – scale efforts were abandoned because of lime consumption and corrosion in the chemical recovery system from cycle of chlorides. Lower dosage lime treatment was also tried at several mills. Approximately 75% to 90% color removals were obtained. However, operation at these facilities was also halted because of difficulties in handling the lime sludge.

(ii) Chemical Oxidation

Chemical oxidation alters the structure of the color bearing groups in such a manner that they no longer absorb radiation in the visible range. The chemicals which are capable of removing color by chemical oxidation include $KMnO_4$, H_2O_2 and O_2/O_3. The color removal efficiency of these oxidants is greatly influenced by their oxidation potential is summarized in **Table-5**.

TABLE- 5

Various Chemical Oxidants Used for Reducing Color in Bleach Plant Effluents

Sl.No.	Oxidant	Oxidation Potential	Dosage, g/l	Color reduction efficiency, %	Status	Advantage	Limitation
1	Potassium Permanganate ($KMnO_4$)	0.59	7	66	Lab Scale	Large settling flocs	High dosage increases the color in supernatant Reacts with low molecular weight component only Eliminates O_2 from waste water
2	Hydrogen Peroxide (H_2O_2)	0.68	N.A.	20-50	Lab Scale	Suitable for small volume of easily oxidisable colors.	Requires long contact time Removes color of easily oxidisable components only.
3	Ozone (O_3)	2.07	6.0 or 1g/l H_2O_2 + 3 g/l O_3	90 90	Lab Scale studies with effluents Increasingly used for waste water treatment	Very effective in removing color	High cost of Ozone generation Operation limits the commercial installation

Other chemical oxidants, which have been tried on laboratory scale, are the use of Per Acetic Acid (PAA) Caro's acid (Persulfuric acid) combination of ozone and H_2O_2 and combination of potassium permanganate ($KMnO_4$) and ozone (O_3) for kraft mill effluent decolorisation.

Chemical oxidation with Fenton's Reagent (H_2O_2 and Ferrous) which have been tried for treating wastewater from dye industry (red wastewater) gave color reduction efficiency of 91% in 0.5 hr. oxidation time with H_2O_2 dose of 5g/l, Fe^{2+}/H_2O_2 ratio of 0.1 and pH 5. However this has not been tried for pulp & paper mill effluent so far.

7.2.2 Physical Treatment Methods

(i) Adsorption Method

a) Carbon Adsorption Method

Carbon adsorption is an advanced treatment process widely used in water treatment but with limited applications in wastewater treatment in general and pulp & paper color removal in particular. The process functions by virtue of the high surface area of the carbon particle and the numerous sites for absorption of organic molecules. The process is effective in removing certain types of dissolved and colloidal organics, but it is nonselective in the sense that color-causing as well as non-color-causing organics can be removed.

There are two types of carbon: granular and powdered. Granular activated carbon is used in gravity and pressure applications in structures similar to those used in sand filtration. For mill effluent, the process typically would be applied after secondary treatment and after pretreatment by filtration. At this point, the penetrated wastewater can pass through a bed of granular carbon for residual organics removal. Eventually, the absorption capacity of the carbon will be exhausted, and the bed must be regenerated. This can be done using caustic as an interim measure but with thermal decomposition eventually needed.

Numerous studies have been conducted to investigate color removal with granular activated carbon on both bleach plant and entire mill effluents. Although removals in excess of 90% have been obtained, carbon requirements can be high, and full-scale applications of the process for color removal have not been tried. Anticipated problems center around economic regeneration and disposal of the spent carbon.

Powdered activated carbon is used in a different fashion, generally as an additive to aeration basins or other well-mixed tanks for supplemental organic removal. Some laboratory testing has been done to investigate carbon dosages for color removal, but as with granular carbon, this technology is not arousing much interest.

b) Use of Coal Fly Ash & Coal Cinders

Substantial quantities of fly ash and cinder are produced in the P&P industry where coal is burnt in boilers. Fly ash and cinder if utilized are capable of reducing color load of the effluents due to their adsorptive properties.

Laboratory scale experiment undertaken have revealed that both these solid wastes with particle size of 325 microns act as good adsorbents for color bodies and result in 95% color removal, 30-40% BOD, 75-85% COD. 50 gm of cinder was required for treating one litre of alkali extraction effluent with an initial color of 4000 Pt. Co. Unit.

The optimum conditions are:

Particle size	-	325 microns
Treatment time	-	30 minutes
pH	-	5
Temperature	-	45°C

INITIAL COLOR	QUALITY OF CINDER, gms	COLOR REDUCTION EFFICIENCY, %
9000	10.7	95 maximum
4000	6.1	95 maximum
BOD Reduction at 90% color removal		30-40%
COD Reduction at 90% color removal		75-85%

➢ **Theoretical Considerations**

Different sample of cinder show variation in their color adsorptive properties. Attempts were made to determine the mechanism of color removal by adsorption so as to explain the variation in adsorptive properties. Determination of fixed carbon content, volatile matter and ash content, chemical composition and particle size determination by sedimentation method was carried out.

However no correlation between these properties and color removal efficiency was established.

c) **Use of Amberlite XAD-8**

The process was developed by Rohm & Hass Co. Philadelphia, as a one step process for decolorizing kraft pulp bleaching effluent using the polymeric adsorbent Amberlite XAD-8. Amberlite XAD-8 which has no ionic groups and is not an ion exchange resin, functions as an adsorbent removing organics from the waste effluent by Van-der-waals forces.

Unlike other decolorization processes such as lime and ion exchange treatment, which treat only caustic extract, the Amberlite process is capable of treating all or part of the bleach effluent. However the requirement of the process is that (a) the pH of the effluent should be below 3.0 or preferably below2.5 that can be readily achieved by blending the caustic extract effluent with the highly acidic chlorination effluent and (b) pre-filtration of effluent.

The process is capable of achieving decolorization levels of 70-95 with corresponding removal of BOD (33%), COD (43%) and S.S. and pulp fibre (78%).

➢ **Commercial Status**

Demonstrated in 1973 in a mobile plant at an Eastern United State mill using combined caustic extracts and chlorination effluent. The volume of the effluent treated was 6.874 million gal/day at treatment flow rate of 12 Bed volume (BV)/hour to achieve 76% decolorization.

(ii) **Application of Membrane Technologies**

Membrane process includes ultra filtration, reverse osmosis, dialysis and electro dialysis. Reverse osmosis and ultra filtration are advanced water treatment processes that use membrane technology. The process operates by use of pressure and a semi permeable membrane. The pressurized feed is filtered, producing a product solution and a smaller quantity of rejects. The openings in the membrane are very small in the range of 10°A to 0.1 μ for ultrafiltration and 5 to 20°A for reverse osmosis. In ultrafiltration, membranes operate at low pressure (10 to 20 psi) and the separation of high molecular mass color materials depends on the pore size of the membrane. The pore size, in turn, is based on the degree of contaminants removal desired.

Reverse osmosis can be visualized as an extension of ultrafiltration, where a higher reduction of solute is achieved along with purification of the effluent from inorganics. Reverse osmosis operates at higher pressure (500 to 1,000 psi). Color removal of 80% to 95% is possible by use of these processes.

Depending on the application, numerous types, sizes, and configurations of membranes can be selected. For color removal applications, the membrane size would nominally fall in the ultrafiltration range.

Currently, there are several full-scale applications of membrane technology at pulp and paper mills. Quite a few mills in Japan reportedly have installed ultrafiltration systems on E-stage filtrate for effluent chemical oxygen demand control. Color removal data are not available, but other investigators in laboratory and pilot plant trials have found removals in the 80% to 90% range.

A large-scale ultrafiltration pilot plant test for color removal was performed on E-stage filtrate at a Swedish kraft mill in 1978. This provided 87% reduction in color after 2,000 hours of continuous operation. The results of trial are shown in **Table- 6**.

TABLE- 6

Ultrafiltration at Iggesunds after 2000 hours of Continuous Operation

	E. stage filtrate	U/F concentrate	U/F filtrate	% Reduction
Volume, m^3	12	0.6	11.6	95
Color, kg/t of pulp	150	130	20	87
BOD_7, kg/t	5.6	1.3	4.3	25
COD, kg/t	44	27	14	70
Total organic carbon, kg/t	14	9.7	4.4	70
Total organic solids, kg/t	30	19	11	65
Total inorganic solids, kg/t	43	7	36	20
Organic chlorine, kg/t	2.3	2.0	0.3	87
Inorganic chlorine, kg/t	13.4	0.5	12.9	4
Acute toxicity, %	17	-	35	≈50

This operation produced data for the design of a full-scale plant in Sanyo, Japan. The ultrafiltration system went online in 1981, operating at approximately 90% color removal. Prefiltration is required to remove residual solids.

In ultrafiltration system the E- stage effluent is split into a concentrate with high molecular mass lignin and low color and low COD permeate containing a small amount of lignin of the original pollutants. The permeate carries 10% of the color, 20% of the COD and 60% of the BOD. Ozonization of the permeate can further reduce the BOD and COD toxicity. The concentrate can be used for brown stock washing or go directly to the evaporators. Alternatively the concentrate can be used as a raw material for adhesive production.

- **Process Drawbacks**

Ultrafiltration is in itself not a solution to the pollution problem. It can split the waste liquor into a low color permeate which may be reused or dumped and a high color concentrate but the latter must be treated further because ultrafiltration does not remove color, BOD, COD and toxicity. It only divides the waste stream into two waste streams with different characteristics, **Fig.-16** summarizes the possible further treatment of permeate and concentrate.

Through ultrafiltration and concentrate incineration offers the cheapest solution in terms of capital costs, combustion of concentrate with higher chloride levels could result in increased recovery boiler corrosion and enhance the danger of explosions. The other disadvantage is the fouling of the membranes, which result in the frequent replacement of the costly membranes.

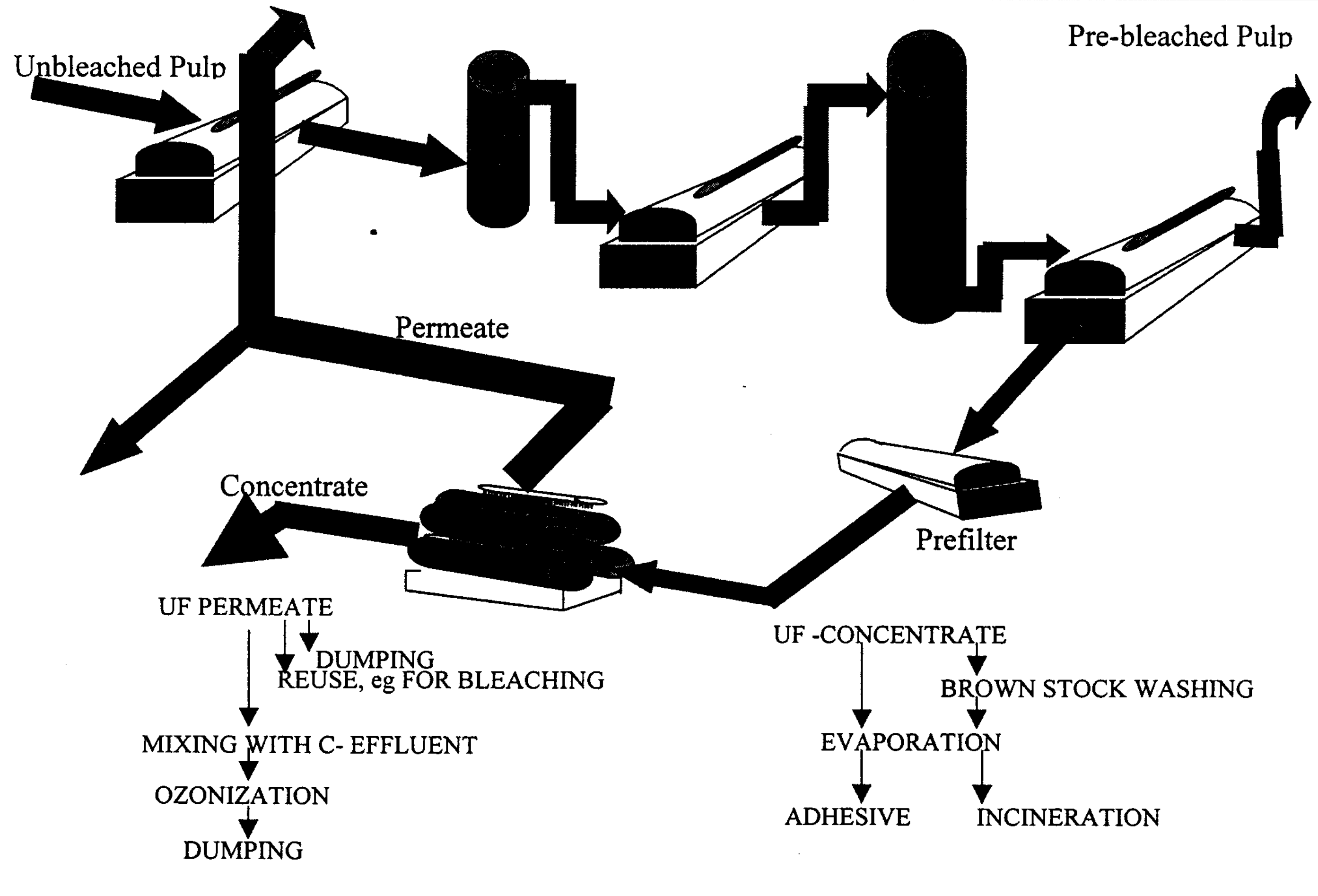


FIG. 16: Treatment of Ultrafiltration Permeate and Concentrate

7.2.3 Irradiation Process

Irradiation of the effluents in the presence of oxygen and/or hydrogen peroxide has also been found promising for significant reduction in effluent color and total organically bound chlorine (TOCL) in bleach plant effluents. Effectiveness is demonstrated by bench scale studies. Extensive research is being carried out to further investigate the feasibility of this process for industrial application.

Heterogeneous photo-oxidation using TiO_2 catalyst can greatly accelerate the decomposition of aqueous pulp mill effluent organic constituent in both concentrated form (as resulting from ultrafiltration) and in untreated effluent. The first demonstration of heterogeneous photo-oxidation by TiO_2 of pulp mill effluent was reported over a decade ago in which organic chlorine content was efficiently reduced but aquatic toxicity remained unchanged.

In a more recent development, the efficacy of enhanced photo-oxidation of BKME (Bleached kraft mill effluent) for the reduction of TOCl, toxicity and color was investigated on bench scale. Aqueous catalytic photo-oxidation by TiO_2 particles require photon energies in excess of 3ev or in practice corresponding to wavelengths <380nm. In order to assess the basic efficiency of TiO_2 catalyzed degradation of BKME, experiments were conducted using 365 and 254nm peak irradiation lamps.

Under optimum conditions, the dark brown mill effluent can be converted by enhanced photo-oxidation to a clear, colorless and odorless solution.

- **Commercial Status** :

The efficacy of enhanced photo-oxidation of BKME for color reduction has been demonstrated on bench scale. The scale up of this technology to pilot plant scale is still awaited. The effectiveness and versatility of photo-oxidation method has given rise to the development of various process alternatives employing $UV/O_2/H_2O_2/O_3$ + H_2O_2/fentons reagent and various combination of these. Preliminary experimental results have demonstrated the potential of photo-assisted catalytical oxidation of organic contaminants and have shown promise of being developed into a viable process for commercial application.

7.2.4 Biological Process

Decolorisation through the use of white rot fungi, or the Mycelial color removal (MyCOR) process has been shown to be effective in removing color. However, the longer treatment time required and the short active time of the reactor were constraints for continuous operation.

7.2.5 Electrolytic Process

Electro-coagulation and electro-flocculation are two techniques involving the electrolytic addition of coagulating metal ions directly from sacrificial electrodes. These ions coagulate with pollutants in water, in a similar manner to the addition of coagulating chemicals such as alum and ferric chloride and allow the easier removal of the pollutants. There is no addition of anions meaning no increase in salinity of the treated water. The system produces half to one third of the sludge. Greater activity means less metal ions required and a wider range of pollutants can be removed. In electro-flocculation the pollutants are removed by the bubbles which are generated during the process, capturing the coagulated pollutants and floating to the surface.

The process has been successfully tried on small industrial scale for waste water treatment containing pollutants like fats, oils, grease (POG's) suspended solids, dissolved solids, bacteria, algae, heavy metal, cations, anions, BOD's, nutrient etc. However, lab scale experiments were conducted by Allan.M.Springar. etal and Kerala Pollution Control Board on bleach plant effluents using electro-flocculation process, which has resulted in color reduction to the tune of more than 85% with operational costs relatively much lower than any other treatment process. However, since the application of this process to pulp & paper mill effluent has not been investigated thoroughly, there is a need to conduct prefeasibility studies to demonstrate the technology on plant scale.

C

Current Scenario

CONTENTS

PART– II : CURRENT SCENARIO OF NEWSPRINT MILLS IN INDIA

PART –II

CURRENT SCENARIO OF NEWSPRINT MILLS IN INDIA

1.0 BACKGROUND

The magnitude of problem related to effluent color in newsprint mills is relatively more severe as compared to mills producing cultural grades of paper. The reason is mainly attributed to the type of raw materials used and pulping process employed in these mills.

Newsprint by definition is a paper product containing not less than 50% fibre obtained by mechanical pulping with ash content not exceeding 8%. In India presently there are 62 newsprint mills. Among all these, only three mills viz. Hindustan Newsprint Ltd. (HNL), Kerala, Mysore Paper Mills (MPM), Bhadravati and Tamil Nadu Newsprint Ltd. (TNPL), Tamilnadu are producing mechanical pulp from wood/non-wood employing mechanical pulping process for Newsprint production, while rest of the mills are either waste paper based mills or bamboo, bagasse based mills employing chemical pulping process. The details of these mills are covered in forgoing section.

1.1 HINDUSTAN NEWSPRINT LTD., (HNL), KERALA

HNL is located at Newsprint Nagar in Kottayam district of Kerala state. The mill was established in 1980, with an installed capacity of 80,000 tpa of standard Newsprint, as one of the subsidiaries of Hindustan Paper Corporation Ltd (HPC) and commenced production from 1982. At present the mill is producing about 1,05,000 tons per annum of newsprint.

Chemi-mechanical pulp (CMP) from eucalyptus and chemical pulp (CP) from reed with a furnish mix of 75:25 was the target furnish for manufacture of newsprint. In the initial years the mill had faced problems with this furnish mix and had to resort to using imported pulp to maintain the production targets.

However, since commissioning the mill has been steadily improving and optimizing its operations resulting in reduction in consumption of imported pulp. Presently the furnish mix constitutes of 65-68% CMP, 22% CP and 10% Imported CTMP pulp.

The mills performance over the past few years has been extremely good and this has logically led the mill to consider an expansion programme. By 2004 the mill has a plan to go for a 100 tpd deinking production line based on recycled fibre from Imported/Indigenous ONP/OMG furnish. In 2001 the CMP pulp production was around 200 tpd, constituting about 65% in the furnish mix, by 2004 with the expansion of paper machine the CMP share will come down to 140t/day. The furnish mix will be 40% DIP, 40% CMP and 20% CP.

1.1.1 Details of Chemi-Mechanical Pulping Street

The mill is presently using Eucalyptus hybrid, E.grandis and Acacia as a raw material for mechanical pulp production, employing chemi-mechanical process. The most ideal ratio of wood mix has been found to be 60% E. grandis and 40% E.hybrid for production of quality newsprint. This ratio however may gradually change with a shift towards more use of Eucalyptus hybrid and Acacia as E. grandis is available through Kerala Government forest in higher altitudes only, which may cease after 2004. Mills own plantation is mainly on E. hybrid and Acacia as the climatic conditions where HNL owns the farmlands are not favourable for the growth of E. grandis.

E.grandis is chipped separately while other species like Acacia & E. hybrid are chipped together. The reason for separate chipping is the pulp quality obtained from E. grandis, which is very good and in order to maintain the quality, the mill prefers to keep proportion of grandis on the higher side. The alkali requirement during impregnation is also relatively lower than compared to E.hybrid (6.0% instead of 6.5%). The exact proportion is maintained meticulously with screw valve (rpm) conveyors.

The schematic of chemi-mechanical pulping process street is given in **Fig.- 1**.

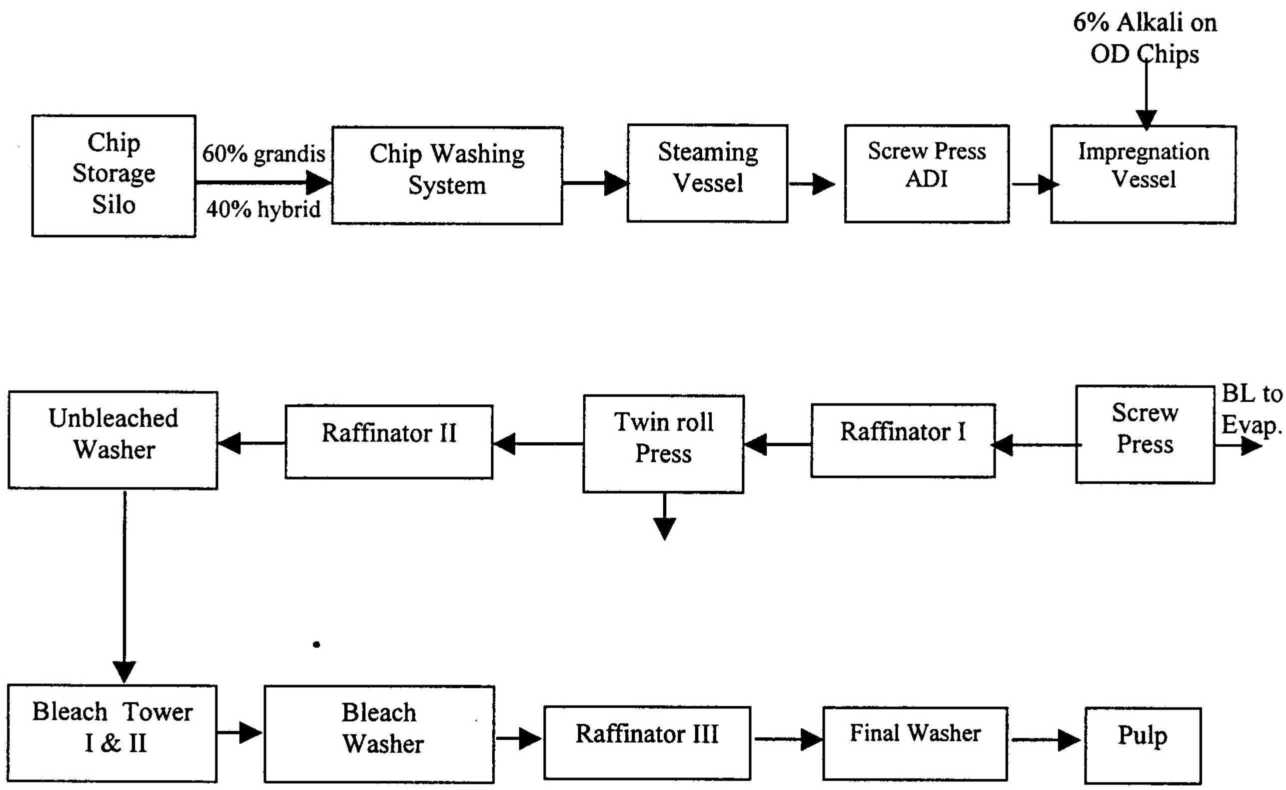


FIG. 1: Schematic of Chemi-mechanical Pulping Process at HNL

Chips from chip storage silo containing 60% grandis and 40% hybrid are delivered to chip washing unit. In chip washing unit, chips are washed with water to remove silica and dirt. Chips washing unit consists of rotary scrap separator, inclined screw drainer, hydro cyclone and drum screen. Water from chips gets drained through inclined screw drainer and goes to rotary drum screen to recover fines, which goes back to steaming vessel. The filtrate from drum screen goes to a chip washer-circulating tank. The discharge from scrap separator junk trap and from hydro cyclone is fed to scrap conveyor, while the contaminated water/filtrate gets drained.

Chips after thorough washing are discharged to the steaming vessel where the chips are heated to a temperature of 90°C. Pre steaming of chips helps in driving away the entrained air in chip capillaries, which otherwise inhibits liquor impregnation. LP Steam at a pressure of 3.5 kg/cm^2 is injected at four points at the bottom periphery of the vessel and also through a concentric pipe inside the vessel. Retention time in the steaming vessel is 20-25 minutes.

Chips after steaming are discharged through a chute to plug screw feeder to convey the chips to the bottom zone of impregnation vessel. The impregnation vessel is a stainless steel 304 construction, supplied by Sunds Defibrator. Bottom/Top diameter of the impregnation vessel is 1170 mm/1800 mm and the height of the vessel is 13775mm. Caustic at strength of approximately 60g/l is fed to the bottom zone of the impregnation vessel and liquor level in impregnation vessel is maintained at 90%. Chips in the form of column move from bottom of the impregnation vessel to its top. Chips get impregnated with liquor during their upward motion. A temperature of 75°C and a retention time of 45 minutes are maintained in the impregnation vessel.

Impregnated chips, travel to the top of the impregnation vessel from where the chips are scraped and delivered to a screw conveyor, which further delivers it to the live bottom vessel, feed screw conveyor. From live bottom vessel chips are discharged to a twin screw feeder which feeds the chips to a screw press where the liquor is squeezed out of the chips and discharged into a liquor collection tank.

From the screw press, chips through a feeding screw are discharged to raffinator-I. In raffinator-I chips are defibrated by mechanical action to pulp and are discharged by gravity to mixing screw conveyor where unbleached washer filtrate is added to bring down the consistency of the pulp. Pulp is further diluted at the suction of MC Pump with UB Washer filtrate and is pumped to the vat of a twin roll dewatering press. Dewatering press filtrate tank is provided with two pumps. One pump feeds black liquor for dewatering press roll cleaning showers and other pump feeds liquor for the dilution of pulp at mixing screw conveyor and at the suction of the MC Pump and a part of the liquor is pumped to liquor tank # 3. From dewatering press thickened pulp at a consistency of 30-35% is discharged to the shredder where the pulp is shredded and screw conveyed to the feeding chute of raffinator-II. From raffinator-II refined pulp at freeness of around 450-570 ml CSF is discharged by gravity to raffinator-II chest from where the pulp is pumped to a unbleached pulp washer for washing.

The extracted black liquor from the screw press after passing through DSM screen comes to a liquor tank #3. From liquor tank # 3 this combined liquor is pumped to a lut filter of slusher type where fines coming along with liquor is further removed.

Filtrate black liquor is discharged to a spent liquor tank from where it is pumped to the recovery section. A part of this liquor is also used for screw press flushing.

Pulp from raffinator-II is pumped to the suction of the pump of unbleached washer filtrate chest. Here the pulp is further diluted to a consistency of 1-1.5% and is pumped to a rotary vacuum drum type unbleached pulp washer having 4115mm drum dia. X 6705 mm face width with a filtration area of 87.5 m^2. Washer is run at an rpm of 1.5. Unbleached pulp washer filtrate passes through a barometric leg to an unbleached pulp washer filtrate chest of 130 m^3 capacity. Unbleached pulp washer filtrate is used for screw feeder flushing, chip washing unit and for raffinator-I and eye dilution. In unbleached washer, washing is done with bleached filtrate.

1.1.2 Problem of Effluent Color in Chemi-Mechanical Pulping Process

Initially the mill was not designed to control the effluent color problem. In the beginning 70% grandis and 30% E.hybrid was the raw material furnish. The production of CMP was around 140 t/d and since all the system was new, the mill was able to control the effluent color using poly aluminium and rare earth chlorides available as an industrial by product. Gradually with increase in the M/c capacity, CMP production was increased to 200 tpd. Over the years due to limited availability of E.grandis the proportion of hybrid was increased. Presently the ratio of grandis: hybrid works between 60:40 or 50:50. However, at all times whenever E.hybrid was used 100%, the effluent color load was very high.

With increased production and raw material changes, it was felt that rare earth chlorides will not help further to control the color problem. In 1993 the mill took an expansion plan for ETP by putting one more clarifier for treating colored and non-colored effluents separately, the details of which are given separately.

(1) For Non- Colored Stream. (New Clarifiers)

Clarifier Size	- 50m dia, 4m side wall
Effective Volume	- 3500 m^3
Quantity of effluent treated	- 15, 500 m^3/day
Retention time	- 5.5 hr

(2) Colored Stream. (Old Clarifier)

Clarifier Size	- 30m dia, 6m side wall
Effective Volume	- 2100 m^3
Quantity of effluent treated	- 7500 m^3/day
Retention time	- 6.5 hr

The complete schematic of ETP plan is shown in **Fig.-2.**

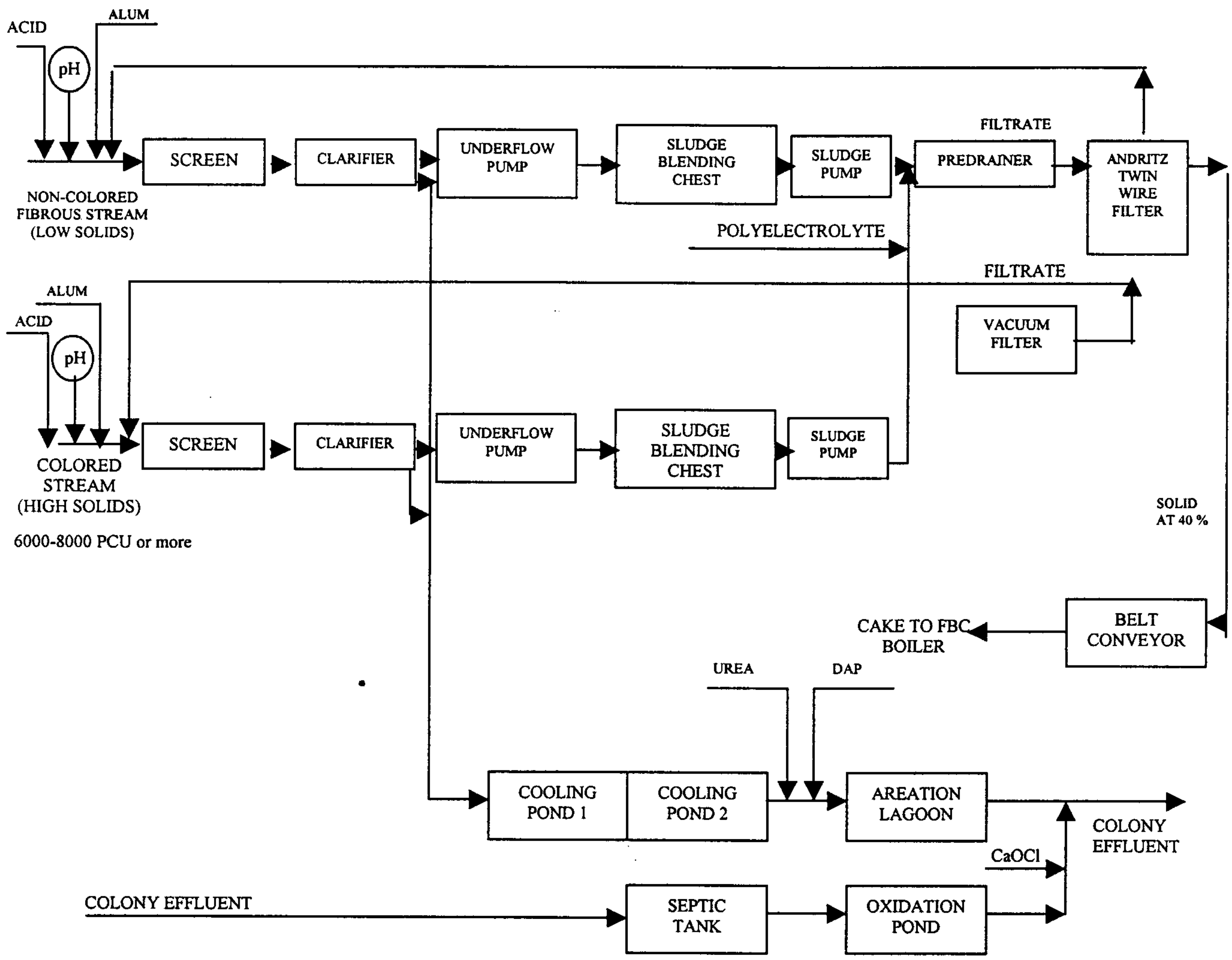


FIG. 2: Schematic of ETP at HNL

Table- 1 indicates the effluents characteristics of different effluent streams at HNL.

TABLE-1

Pollution Loads of Different Effluent Streams at HNL

Parameters	Colored Effluent	Non colored Effluent	Clarifier Outlet	Combined Effluent
pH	10.1	8.8	6.3	8.8
TDS, mg/l	1000	1080	2440	2160
TSS, mg/l	260	627	517	475
Color, PCU (at 7.6 pH)	8816	1064	2126	5567
COD, mg/l	3682	882	1325	2078
BOD, mg/l	1565	208	441	740

In the colored stream color variation ranges between 6000 to 8000 PCU and some times even more due to plant upsets. The fluctuations are more due to plant upsets only and since the mill does not have any equalization tank or stabilizing pond, the fluctuation directly affects the primary clarifier performance.

1.1.3 Measures Taken by Mill to Control Effluent Color Problem

The mill has initiated steps for effluent color reduction by adopting inplant measures for at source reduction as well as End-of-Pipe (EOP) treatment methods. The mill has adopted cross recovery of CMP liquor extracted from screw press and dewatering press.

(a) Problems in Cross Recovery of CMP & CP Liquor

Despite of having a cross recovery system for CMP & CP liquor the mill is unable to run the recovery boiler with CMP: CP liquor ratio beyond 20:80 limit. The reason is attributed to poor swelling volume ratio of CMP liquor. A study conducted at CPPRI with mix black liquor having CMP: CP ratio has revealed that increasing the CMP ratio in the mix liquor significantly decreases the resultant swelling volume ratio of mixed black liquor, and this limits the increase of CMP proportion in the mix liquor beyond 20-25% which otherwise upsets the boiler operation.

(b) End-Of-Pipe Treatment of Colored Effluent Employing Chemical Precipitation Method Using Alum as a Coagulant

The colored effluent is separately treated employing alum precipitation method to bring down the color loads. **Table-2** shows the alum requirement for effluent color reduction at mill site.

TABLE-2

Effluent Color Reduction by Alum Treatment

Volume of effluent, m^3/day	Initial color, PCU	Alum required *, t/day	Final Color, PCU
7500	10,000	45	400-600
7500	5000	12-15	400-600

* **pH of the effluent brought to 7.0 pH from 10.0 by adding HCL before alum treatment**

As already mentioned the fluctuation in effluent color load is too high ranging from 5000-10,000 PCU and mill is using around 10-15 t/d of alum for treatment. However, with high initial color loads due to plant upsets the system performance goes down significantly.

The mill is using low grade alum for treatment and has also tried with mixed sulphate salt which is a by product of a nearby industry. The comparative data on cost of treatment using both the grades of alum are given in **Table-3**.

TABLE-3

Comparative Cost Data on EOP Treatment for Color Reduction With Different Grades of Alum

Type of Alum	Dosage g/l	Quantity t/d to treat 7500m^3/day effluent	Cost of chemical Rs./t	Total Operating cost for Alum Rs./t	Cost per annum incurred in Rs., crores
Low grade Alum	2.5 (currently used)	18.7	2250	133	1.38
*Low grade Alum	6.0 (actual requirement for high color i.e. 10000 PCU)	45.0	2250	318	3.3
Mixed Sulphate Alum	3.5	26	1290	105	1.1

* **Irrespective of initial color loads, greatly varying between 5000-10,000 PCU the mill is using low Alum dosage i.e. 2.5 g/l to keep the operating cost 1/3 of the actual cost of Alum treatment requiring 45 t/day of alum to bring down the color loads from 10,000 to 400 – 600. Most of the time the color load remains on the higher side.**

1.1.4 Process Limitations

(a) Clarifier Efficiency:

There has been a wide variation in initial effluent color loads and in absence of any equalization tank, there is a tremendous shock load, which lowers the clarifier efficiency. To absorb the shock loads the mill essentially needs an equalization tank, which will improve the clarifier efficiency.

(b) Sludge Handling:

The sludge obtained after alum precipitation contains lighter flocs and is a slow settling sludge. It is experienced that with alum dosing of 10-15 t/day, bulking of sludge take place which results into increased SS in the clarifier overflow. Around 80% sludge is removed with the clarifier underflow and 20% remain with the clarifier overflow. Sometimes suspended solid in clarifier overflow goes upto 250mg/l.

(c) With the adoption of Alum precipitation, 80% color reduction is normally achieved however reappearance of color has been observed in the aerated lagoons.

1.2 MYSORE PAPER MILLS LTD., (MPM), BHADRAVATI

MPM is located at Bhadravati village of Shimoga district in Karnataka state. The mill was established in the year 1936 with a small capacity of 4,000 tons/annum of writing & printing grades of paper. The mill grew gradually and undertook a large expansion cum modernization program in the year 1972 with a view to increase the capacity from 24,000 tons to 37,000 tons/annum of writing & printing and cultural varieties of paper and further installing new equipment to produce 75,000 tons of newsprint per annum. The mill was encouraged by the government of India to install facilities to produce newsprint in view of country's substantial dependence on import of newsprint.

Presently the mill is producing 250 t/day of newsprint using Acacia cold soda refiner mechanical pulp (CSRMP) and 100 t/day of writing and printing grades of paper using bagasse/bamboo and hardwood chemical pulp. The mill also uses 45-50 t/day of imported CTMP pulp to maintain the strength properties of finished newsprint. The mill is sourcing most of its raw material from its own captive plantations except bamboo, which is sourced from state forests.

1.2.1 Details of Chemi-Mechanical Pulping Street

The mill is employing cold soda refiner mechanical pulping process (CSRMP) for the production of mechanical pulp using Acacia. Initially Eucalyptus was used but due to high effluent color loads, it has started using Acacia which is sourced from captive plantations. Though most of the time 100% Acacia is used however sometime Eucalyptus is also mixed.

Acacia, Eucalyptus chips washed in situ are conveyed pneumatically to a steamer and then to M&D (continuous digester) in which they are soaked in a dilute solution of NaOH (50%) for 2 hrs. after chemical impregnation in a soaking bin for 1 hr the chips are conveyed through bucket elevators to two pressafiners where consistency is increased from 30% to 52%.

Liquor extracted in the pressafiner is partly recirculated in the system with replenishment of caustic soda and partly sent back for cross recovery in chemical recovery system.

To control the effluent color problem the mill has made internal modification by introducing a bleaching stage before BSW and secondary refining. This has enabled the mill to control the effluent color problem to some extent. The schematic of process layout before and after modification is given in **Fig.-3 & 4**.

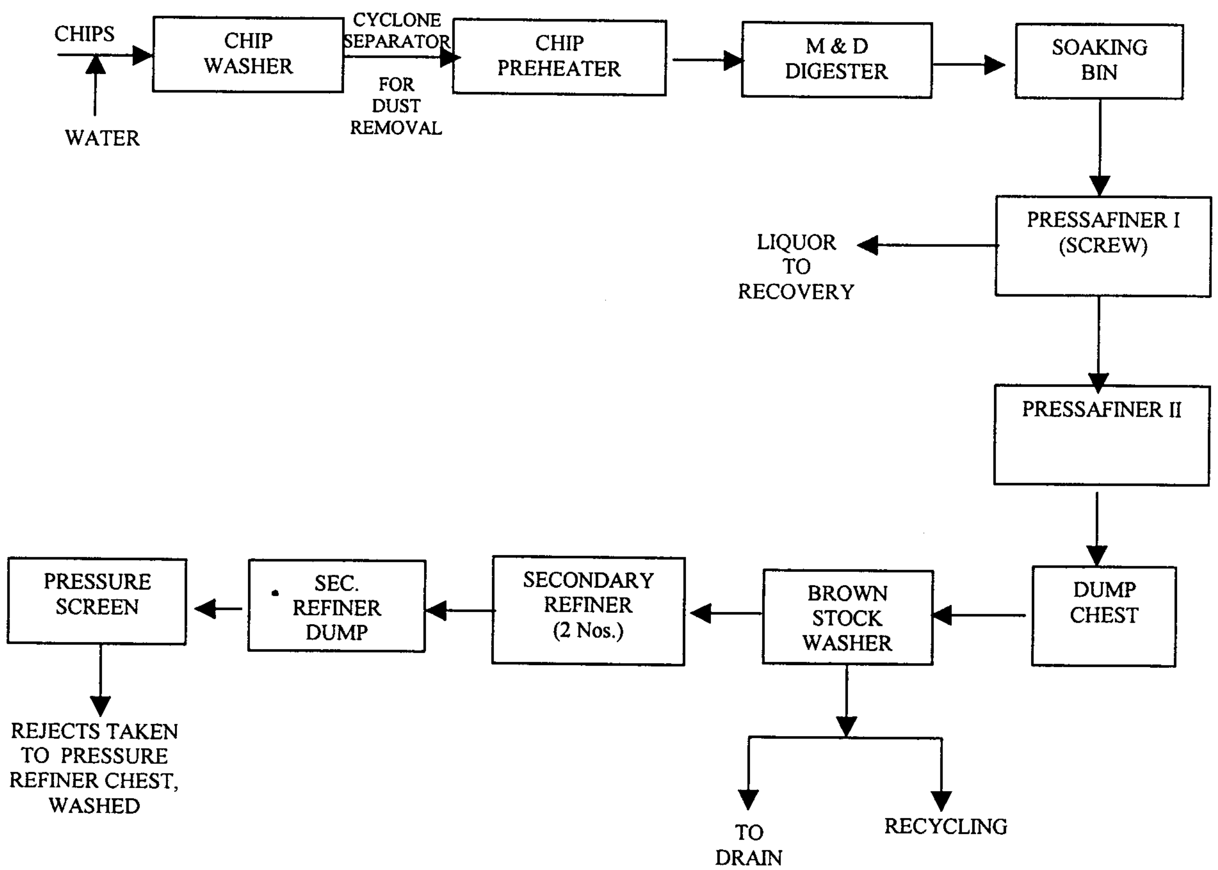


FIG. 3: Mechanical Pulping Street at Mysore Paper Mills (CSRMP)

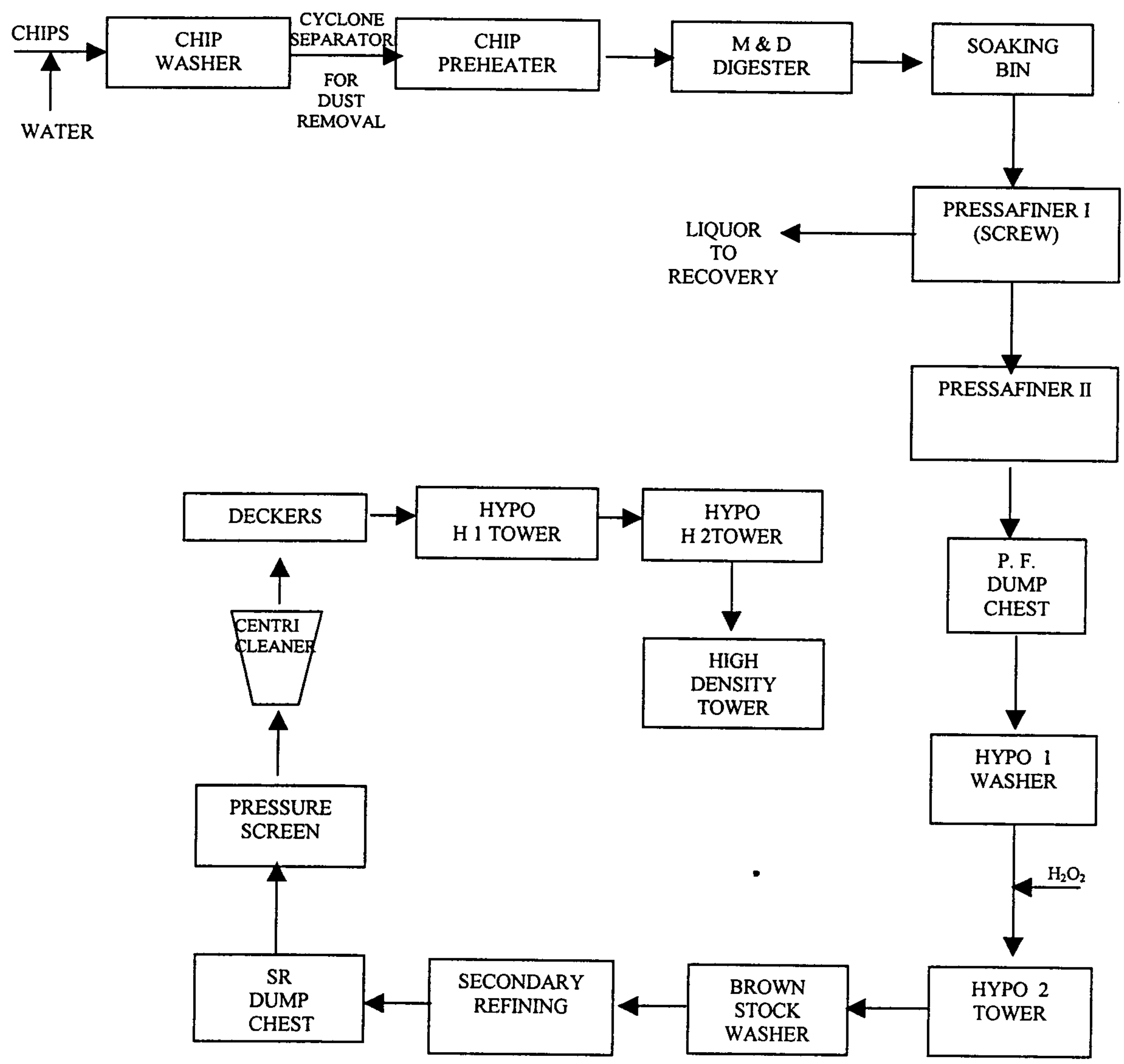


FIG.4: Mechanical Pulping Street at Mysore Paper Mills (After Modification to Control Effluent Color)

1.2.2 Problem of Effluent Color in Mechanical Pulping Process

Unlike HNL, the problem of effluent color is relatively less. The prime reason attributed is the raw material. MPM is using Acacia, which is a low colored wood species compared to E.Hybrid. Initially when the mill was using E.hybrid the effluent color from mechanical pulping street was very high. The mill has a combined ETP plant due to which use of alum as EOP treatment method has not found to be economically feasible.

Therefore to control the effluent color problem, following measures have been introduced.

(i) The mill has switched over to the use of Acacia, a light colored wood species, which has helped to control effluent color problem to a large extent.

(ii) As an inplant measure, the mill has undertaken modification in mechanical pulping street by introducing a bleaching stage (H_2O_2) between pressafiner and brown stock washer/secondary refiner, which has resulted in generation of low colored effluent and can be recycled within the process. The schematic of process indicating the effluent flow rates are shown in **Fig.-5**.

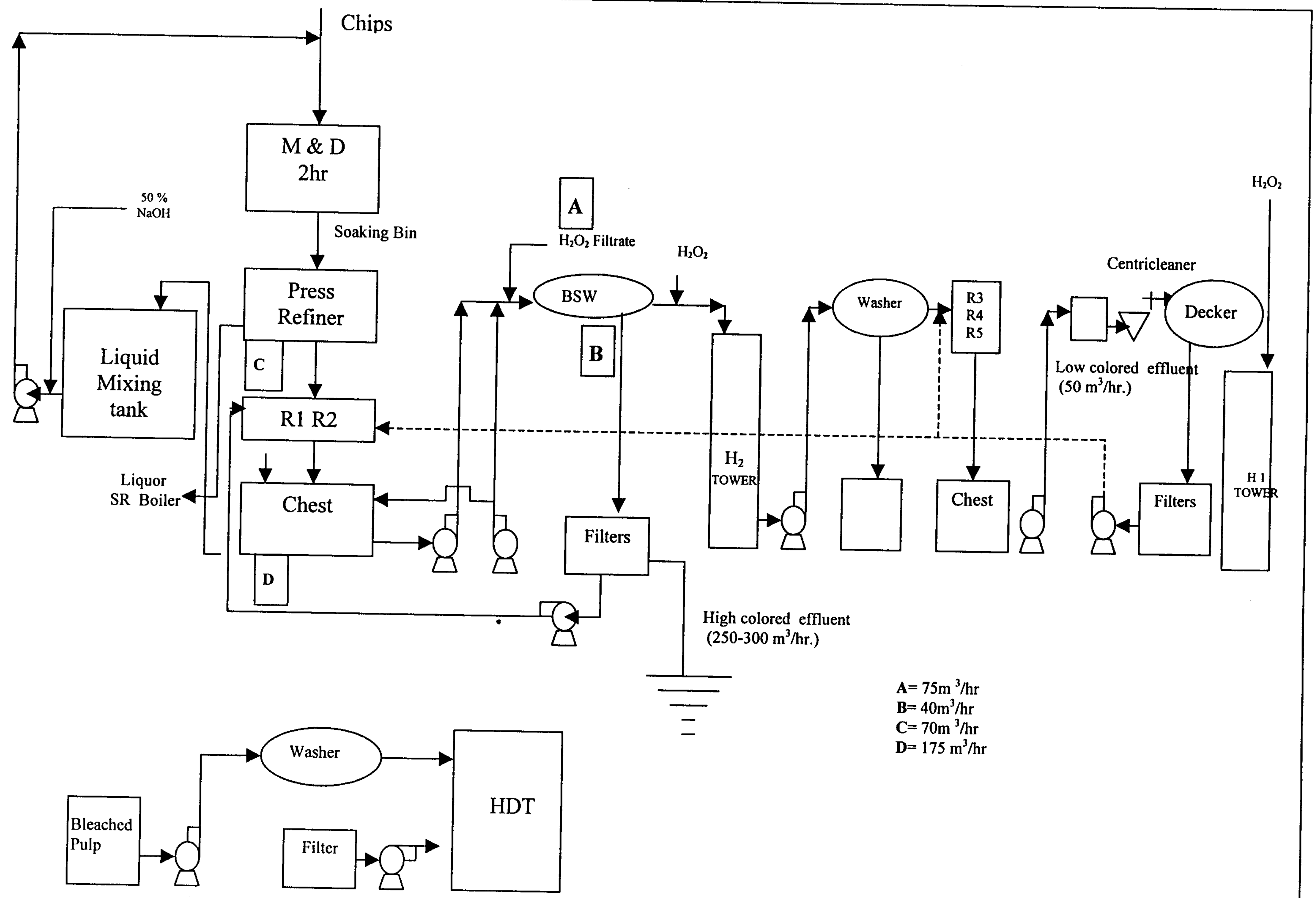


FIG. 5: Schematic Showing Recycling and Discharge of Colored Effluent in CSRMP Street at MPM

1.2.3 Treatment of Colored Effluent

The ETP layout does not have a provision for separate treatment of colored effluent. The schematic of ETP layout is shown in **Fig.-6**.

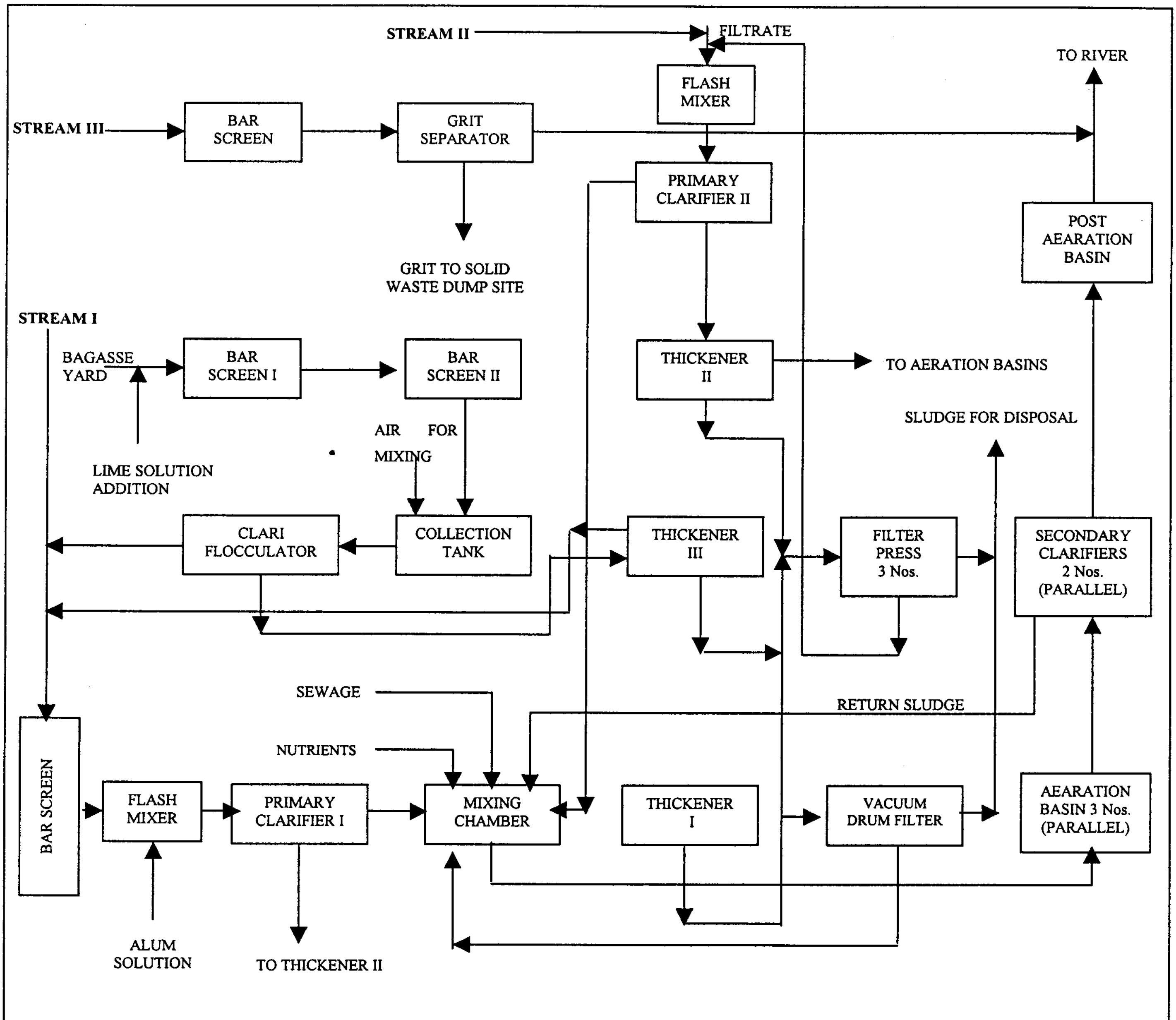


FIG. 6: Schematic of Process Layout of ETP at MPM

The total combined effluent generated is 1000 m^3/hr including CSRMP, CMP 1 & 2 and bleach plant effluent. The flow of each stream is as follows:

Effluent from CSRMP - 250-300 m^3/hr

Effluent from Chemical Pulping I (Bagasse) - 300 m^3/hr

Effluent from Chemical Pulping II (Hard wood) - 400 m^3/hr

The mill is using around 7t/day of alum only to remove the suspended solids in the effluent, which does not help in reducing the effluent color loads.

Having done the modification with incorporating hydrogen peroxide stage before secondary refining has proved beneficial in reducing the color, as part of the bleach feed is going to chest, which further helps in reducing the color. Before modification H_2O_2 was being added at final stage only.

Presently the mill does not practice any EOP treatment method to control effluent color load as treating 22000 m^3/day of combined effluent employing chemical precipitation method would not be a techno economically viable option.

The advantage obtained after modifications on BSW filtrate color & effluent characteristics are indicated in **Table-4 & 5.**

TABLE- 4

BSW Filtrate Color & Effluent Characteristics at ETP (for Eucalyptus)

Sl.No.	Parameters	Before Modification	After Modification
1	**CSRMP BSW Filtrate**		
	Color, PCU	61920	31655
2	**Phase II**		
	Color, PCU	5583	5955
	COD, mg/l	2807	2233
	BOD_3, mg/l	844	826
3	**Final Effluent**		
	Color, PCU	2527	1348
	COD, mg/l	773	586
	BOD_3, mg/l	223	146
4	**H_2O_2 Consumption, tons/day**	0.042	0.056

TABLE- 5

BSW Filtrate Color & Effluent Characteristics at ETP (for Acacia)

Sl.No.	Parameters	Before Modification	After Modification
1	**CSRMP BSW Filtrate**		
	Color, PCU	10175	5785
2	**Phase II**		
	Color, PCU	2335	1642
	COD, mg/l	2035	1766
	BOD_3, mg/l	742	531
3	**Final Effluent**		
	Color, PCU	1110	811
	COD, mg/l	577	451
	BOD_3, mg/l	106	60

1.3 TAMIL NADU NEWSPRINT LTD., (TNPL), TAMIL NADU

Tamil Nadu Newsprint & Papers Ltd. (TNPL) is one of the world's largest bagasse based paper mills, located at Kagithapuram in Karur District of Tamil Nadu. TNPL was established in 1979 by the Govt. of Tamil Nadu under a world Bank supported project for increasing the National Production of both Newsprint and writing and printing paper and for utilization of bagasse, a renewable non- conventional raw material.

Initially Mill was designed to produce 50,000 tpa of Newsprint and 40,000 tpa of writing and printing paper. Bagasse pulp accounted for over 70% in the Newsprint furnish and 75% in writing and printing furnish, while hard wood (Eucalyptus) and other tropical imported wood pulp accounted for the balance.

The capacity was increased in 1995 to 1,80,000 tonnes of Newsprint Paper annually from the earlier level of 90,000 tonnes. At present 100% bagasse pulp is used for production of Newsprint. The furnish of Newsprint consists of 60% Chemical bagasse pulp and 40% Mechanical bagasse pulp. Writing & printing paper is manufactured using 75% chemical bagasse pulp and 25% chemical wood pulp procured from locally available hard woods. However, as on today the mill produces more of writing & printing grades of paper accounting to 85% of total production and remaining 15% goes for newsprint production.

1.3.1 Details of Mechanical Bagasse Pulping Street

Mechanical bagasse pulping street has two nos. 56" unimount pressurized refiners for thermo-mechanical pulping and one atmospheric refiner for chemi-mechanical pulping. Each refiner is driven by 6000 HP motor and operates at 1.5 kg/cm^2.

Washed bagasse is fed to TMP refiners by positive feed through a ribbon feeder. Pulp after refining is blown continuously in to a blow tank. Small amount of cooking liquor consisting caustic and sodium sulfate is added to get load reduction on the refiner. The pulp from blow tank is subjected to secondary stage refining in a 56" atmospheric unimount refiner. The refined pulp is then screened and cleaned in three-stage pressure screen and centicleaning system.

After screening and cleaning pulp is bleached to a brightness of 50 % ISO using hydrogen per oxide at high consistency. After reaction time of about 2 hours the pulp is neutralized with H_2SO_4 for pH correction and transferred to a storage tank.

During visit the mechanical pulping street was shut for maintenance and therefore data could not be collected for mechanical pulping.

1.3.2 Problem of Effluent Color at TNPL

The problem of effluent color at TNPL is relatively much less than HNL and MPM. The primary reason is the type of mechanical pulping process employed and the raw material used. As already mentioned the mill is employing thermo-mechanical (TMP) process using bagasse for mechanical pulp production. Since the chemical addition is almost negligible, (small amount of cooking liquor consisting of caustic and sodium sulphate is added to get load reduction on refiner) and bagasse being a light color non-wood species the effluent color is very low compared to other two mills.

The color in effluent is mainly contributed from bagasse washings during raw material handling. To keep the bagasse in moist condition, the mill uses secondary clarifier overflow. The wet bagasse is dumped on the yard and the effluent drains into the channel, which is recirculated. As the color of the effluent is high, a part of this is purged and is collected in the bagasse clarifier. For bagasse washing, the mill uses decker filtrate overflow. Foul condensate from chemical recovery evaporation plant is used as a shower water in decker filter. The decker filtrate water is stored in a chest and a part of which is used for screening & centri-cleaning dilution water. Remaining water i.e. about 160 m^3/hr from all the three pulp mill is used for bagasse washing. Of the nearly 300 m^3/hr water purged from washing system, 160 m^3/hr is make up from decker water filtrate water and the remaining 140 m^3/hr is from secondary clarifier outlet (final discharge). The secondary clarifier carries nearly 160 PCU color & with only 50 ppm lignin and major color intensity & lignin is due to decker filtrate. The decker filtrate has been the major source of color in effluent. The average color level of decker washer is about 3500 PCU and after bagasse clarifier outlet the color level comes to about 2000 PCU. The colored effluent generated in bagasse washing is around 5000 m^3/day, which goes to bagasse clarifier followed by anaerobic lagoon. To this effluent mill is using 1.2 g/l alum to achieve a discharge color load of 200 PCU. The schematic of existing bagasse washing system is shown in **Fig.-7.** The characteristics of different colored effluent stream are given in **Table-6.**

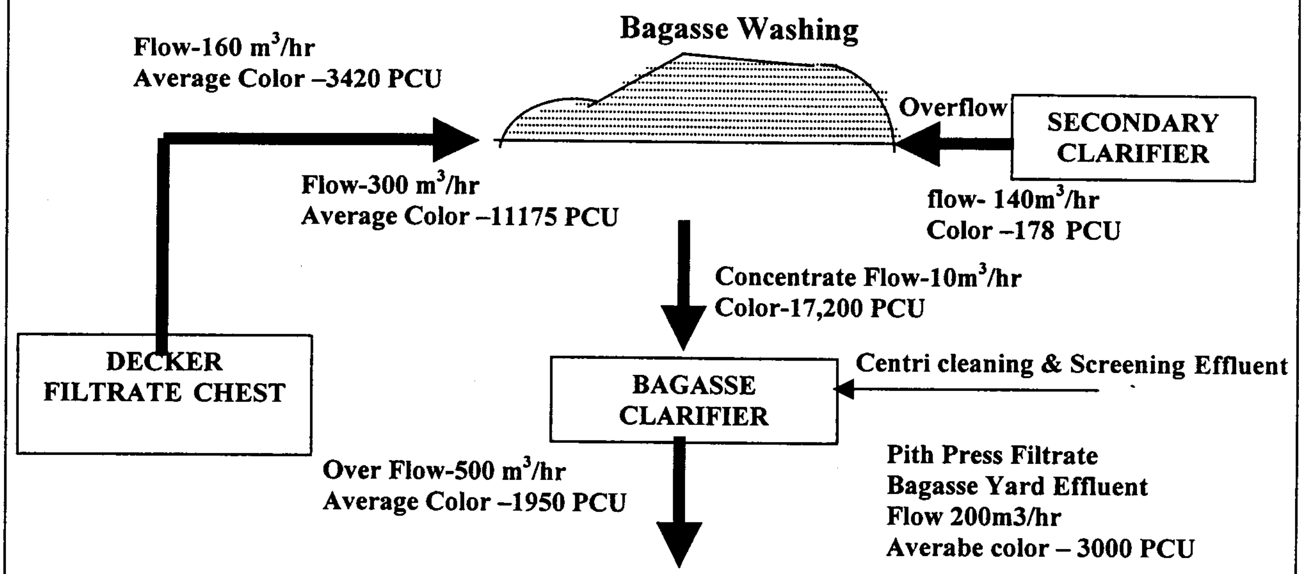


FIG.-7 EXISTING BAGASSE WASHING SYSTEM AT TNPL

TABLE – 6

Characteristic of the Effluent Stream at TNPL

Parameter	Values (Range)		
	Bagasse Washings	Decker Filtrate	Alkali Extraction Filtrate
pH	4.6-5.1	7.6-10	9.1-10.1
Suspended Solids, ppm	170-802	162-430	20-42
Total dissolved solids, ppm	2772-3958	2790-4368	1728-1904
Color at 7.6 pH, PCU	1060-3150	2500-3650	1700-1925
Lignin, ppm	351-644	880-1610	294-324

The company has a commitment to environment and to prevent particulate emissions during raw material preparation & storage, practice of wet depithing and wet storage has been followed. However, despite of relatively low color loads, the mill is facing lot of public opposition in the form of legal notice on this issue.

2.0 CONCLUSION

Evaluation of the current status of all the three newsprint mills viz. HNL, MPM and TNPL, clearly indicates that effluent color problem is more severe for HNL followed by MPM and TNPL due to variation in raw material type and species used for mechanical pulp production. E. hybrid being a highly colored wood species, the color problem will continue to persist for HNL. Secondly, the mill presently do not have adequate ETP lay out to treat colored effluents separately, due to which whatever technology is adopted will become economically unviable due to high operating costs.

D

Feasibility Studies
&
Recommendations

CONTENTS

PART– III : FEASIBILITY STUDIES ON COLOR REDUCTION FROM MECHANICAL PULPING EFFLUENTS

PART –III

FEASIBILITY STUDIES ON COLOR REDUCTION FROM MECHANICAL PULPING EFFLUENTS

1.0 INTRODUCTION

A detailed overview of current scenario of newsprint mills in India, based on non-wood/wood and employing mechanical pulping process, clearly indicates a wide spectrum of effluent color problem in these mills. Besides the mechanical pulping process employed, the other reason identified as a major cause for high color intensity in discharge effluents is the raw material species, used for mechanical pulp production. During the course of study and mill visits undertaken, the samples of various raw materials being used in these mills were collected and evaluated at CPPRI laboratory to study the intensity of color generation by different wood species under alkaline conditions.

As already discussed in Part I of this report the organic chemical constituents present in wood, particularly the extractives and lignin are responsible for color generation in liquid effluents. Under neutral conditions these organics having chromophoric groups show lower color intensities, however, subject to alkaline conditions the increase in intensity is manifold.

2.0 IMPACT OF RAW MATERIAL SPECIES ON EFFLUENT COLOR REDUCTION

(i) Quantification of Extractives

The result summarized in **Table –1** quantifies the soluble extractives in different wood species. The alcohol soluble (percent) extractives generally represent the group of color-bearing compounds like phlobanes, tannins and stilbens (discussed in detail in Part I of the report). The result clearly shows that E.hybrid and Acacia has relatively higher amounts of extractives having chromophoric groups compared to bagasse and E. grandis.

TABLE-1

Quantification of Soluble Extractives in Different Solvent Medium for Different Wood Species

WOOD SPECIES	ALCOHOL/BENZENE SOLUBILITY, % w/w	ALCOHOL SOLUBILITY, % w/w	0.1 NaOH SOLUBILITY, % w/w
Eucalyptus Hybrid Mill I	0.83	5.78	12.5
Eucalyptus Hybrid Mill II	5.12	6.36	8.97
Eucalyptus Grandis Mill I	0.78	0.38	11.01
Acacia Mill I	8.76	8.34	9.78
Acacia Mill II	4.64	7.59	14.4
Bagasse Mill III	2.33	1.84	40.0

This has been further confirmed when these extractives extracted under different solvent mediums were subjected to alkaline conditions (treated with 0.1 N NaOH Solution). The findings are depicted in **Table-2**.

TABLE-2

Magnitude of Color Generation in Different Solvent Extract Under Alkaline Condition (0.1 N NaOH)

WOOD SPECIES	ALCOHOL/ BENZENE EXTRACTION IN 0.1 N NaOH Soln.			ALCOHOL EXTRACT IN 0.1 N NaOH Soln.			0.1 N NaOH EXTRACT		
	COLOR PCU at 1 % Conc.	Extr. %	Lignin %	COLOR PCU at 1 % Conc.	Extr. %	Lignin %	COLOR PCU at 1 % Conc.	Extr. %	Lignin %
Eucalyptus Hybrid Mill I	3756	91.5	8.5	16376	73.7	26.3	16393	75.8	24.2
Eucalyptus Hybrid Mill II	2289	94.8	5.2	12400	83.3	16.7	13685	85.2	17.8
Eucalyptus Grandis Mill I	1754	90.9	9.07	3482	89.0	11.0	5245	92.8	7.2
Acacia Mill I	5795	82.3	17.7	5917	84.2	15.8	2400	85.7	14.3
Acacia Mill II	3517	92.8	7.2	3949	89.1	10.9	994	93.7	6.3
Bagasse Mill III	725	89.4	10.64	964	88.2	11.8	877	89.4	10.6

The results showed that the color intensity was highest for E.hybrid followed by Acacia, Grandis and Bagasse in all cases. One interesting findings was that wood species grown in Kerala State (E.hybrid & Acacia Mill I) showed higher effluent color intensity than one's grown in Karnataka State (Mill II).

3.0 IDENTIFIED TECHNOLOGIES FOR COLOR REDUCTION FROM MECHANICAL PULPING EFFLUENTS

Extensive literature review conducted on color reduction technologies have revealed that till date only two technologies have been tried on commercial scale for color reduction in liquid effluents. The technologies are:

- Chemical Precipitation with Alum and Poly-electrolytes
- Physical Separation employing Ultra-filtration

Both these technologies, however have been tried on bleach plant effluents and no data is available on mechanical pulping effluents using these two technologies elsewhere. In India however only Hindustan Newsprint Ltd., Kerala has adopted chemical precipitation method using alum alone as an EOP treatment method for color reduction. The process has several limitations, which has been discussed in previous chapter.

Keeping in view that not much of R&D work has been done in the area of color reduction in mechanical pulping effluents, a feasibility study was undertaken to evaluate the techno-economic feasibility of chemical precipitation and ultra-filtration techniques towards color reduction in mechanical pulping effluents.

4.0 STUDIES ON COLOR REMOVAL FROM MILL EFFLUENT

Table-3 summarizes the characteristics of color streams at Mill I. The mill is based on Eucalyptus employing CMP process and the effluent generated carries high color loads. The effluent from screw press and dewatering press carrying highest color load is sent to chemical recovery for cross recovery. The effluent from unbleached washer is partially recycled and partially purged out which goes to drain to ETP, which is the final discharged effluent having color load of 13,000 PCU. The total effluent generated is 7500 m^3/day.

TABLE-3

Characteristics of Various Colored Streams Emanated from Mechanical Pulping Street at Mill I

	SCREW PRESS	DEWATERING PRESS	UNBLEACHED WASHER	DRAIN
pH	12.4	12.1	10.5	10.5
Total Solids, % w/w	8.1	7.0	2.4	1.4
Total Dissolved Solids, % w/w	7.7	7.2	1.7	1.6
Suspended Solids, g/l	7.8	7.8	12.4	0.1
Residual Alkali, g/l as NaOH	7.8	1.8	0.68	0.74
Total Sodium as Na, g/l	18.2	10.0	3.6	3.0
Color PCU, (7.6 pH)	58,890	74,440	93,330	19,165
Lignin, g/l	8.9	18.8	2.4	3.0

Table-4 summarizes the characteristics of various colored streams at Mill II. The mill is based on Acacia employing Cold Soda Refiner Mechanical Pulping (CSRMP). In the CSRMP street the highest color load effluent is generated from pressafiner, which is sent to chemical recovery for cross recovery. The effluent generated from centricleaner reject stream has very low color loads 533 PCU and with the flow rate of 50 m^3/hr the total effluent generation is only 1000 m^3/day. The effluent generated from BSW has the highest color i.e 6420 PCU, which goes to ETP at a flow rate of 300 m^3/hr. The total effluent generated from BSW is around 6000 m^3/day. In Mill II, which is based on Acacia the color load is nearly 50% less than Mill I, which is based on E.hybrid.

TABLE-4

Characteristics of Various Colored Streams Emanated from Mechanical Pulping Street Mill II

	BLEACHED FILTRATE	PRESSAFINER EFFLUENT (CSRMP)	CENTRICLEANER REJECT STREAM (CSRMP)	BSW FILTRATE (CSRMP)
pH	9.0	12.3	8.4	9.9
Total Solids, g/l	0.36	15.4	0.4	0.76
Suspended Solids, g/l	0.48	7.85	1.87	0.75
COD, mg/l	2657	-	-	5180
BOD, mg/l	930	-	-	2069
Color PCU,	2122	2,60,416	533	6421

4.1 FACTORS INFLUENCING THE EFFICIENCY OF COLOR REMOVAL

Removal of color due to colloids is a multistep process and careful understanding of these factors influencing each step would therefore be necessary.

a) Role of pH

pH has a strong influence on the precipitation of colloidal particles. In alkaline solution, the colloidal particles whether lignin or extractives exist in the form of sodium salts and possess a strong electrical charge. For destabilization it is essential to bring down the pH. Usually this step is accomplished by addition of mineral acids or alum. For instance, the color in CMP effluents could be precipitated only at pH levels around 5.0. The dosage of chemical coagulant would depend on the initial pH of the colored solution. The effect of pH vis-à-vis chemical dosage is discussed in detail in following sections.

b) **Relative Stabilities of Colloidal Particles**

Lignin and extractives exist as colloidal particles and they possess different molecular size and electrical charge. The colloidal stability would depend upon both molecular size and charge carried by colloidal particles.

During color removal studies it was observed that at same concentration of solids, extractives and lignin required different dosage of electrolyte for precipitation. The results are given in **Table-5**.

TABLE-5
Relative Colloidal Stabilities of Lignin and Extractives

Electrolyte dosage $CaCl_2$, ppm	Lignin solution (1%)		Extractives Solution (1%)	
	Absolute color, PCU	Color reduction, %	Absolute color, PCU	Color reduction, %
Nil	21240	-	38570	-
100	12950	40	30812	20
200	8937	58	31250	19
500	8937	58	30812	20
3000	1725	92	5000	84

The extractives were isolated by methanol extraction of wood chips and lignin was extracted by treating with NaOH solution. The $CaCl_2$ was chosen due to the fact that calcium salts have ability to form water insoluble complexes with extractives.

The above results clearly show that extractives were much more colloidally stable compared to lignin macromolecules. In one of the studies conducted at CPPRI for effect of molecular size on colloidal stability have shown that the bagasse black liquor required 10% lower electrolyte dosage than rice straw black liquor for removal of 86 % color from black liquors. Thus initial pH, molecular size and electrical charge have profound influence on the efficiency of color removal and also influence the chemical dosage required for desired amount of color removal.

c) **Role of Electrolytes and Polyelectrolyte**

Various electrolytes and polyelectrolytes are used to coagulate color in the effluents, with an aim to achieve a good reduction of color with minimum dosage of easily available non-toxic electrolyte.

Most widely used inorganics are the di and tri-valent metal salts of calcium, aluminium and iron. The principal difference between calcium, aluminium and iron salts is their hydrolysis product. When calcium salts are added to water, the calcium ion is formed. When aluminium or iron salts are added, they form trivalent metal complexes with water. These complexes contain a number of repeating metal ion units and can more properly be referred to as polyaluminium or polyferric hydrates. Polymetal hydrates of significant lengths have been reported. They are cationic and can destabilize a colloidal suspension. They also have a sufficient chain length to bridge the distance between particles. In addition, their strong hydrogen bonding ability enables them to form large macroflocs that can trap other stable colloids.

From the literature search, it was found that hydrolysed aluminium ions behave in a manner consistent with the formula $A_{18}(OH)_{20}$ at pH 5.2, which is close to the optimum flocculation point. Organic polyelectrolytes can be either natural or synthetic. Natural products such as starches or gums have been used for years as flocculants or aids to improve treatment with inorganic coagulants. Synthetic organic polyelectrolytes have become predominant in solid/liquid separation. They are generally used in conjunction with inorganic electrolytes and considerably improves both performance and treatment cost. The organic polyelectrolytes have a high molecular weight and contain a variety of ionisable groups that are placed along the polymer chain. These synthetic polyelectrolytes are classified as non-ionic, anionic & cationic. Polyacrylamide & polyethylene oxide are commonly used polyelectrolytes, which are non-ionic. Co-polymers of acrylamides and acrylic acid from anionic polyelectrolyte, which has an advantage of having large chain length. Thus when an anionic polyelectrolyte is dissolved in water the negative charges repel each other and unwinding of coil occurs, and thus large available chain length makes a more effective bridging agent when charge neutralization is not an important factor in removal of suspended solids. However, the cost prohibitiveness limits the scope of application of such polymers.

4.2 COLOR REDUCTION WITH ALUM PRECIPITATION METHOD

The results of the studies conducted on alum precipitation with and without the acid addition are depicted in **Table- 6, 7 & 8**. Based on the findings the technoeconomic feasibility of the process has been evaluated.

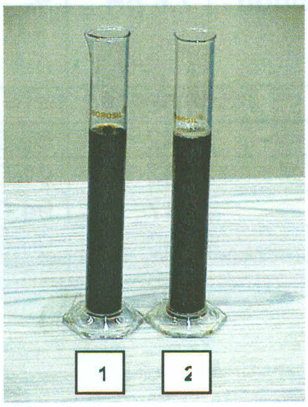
TABLE-6

Studies on Color Reduction by Alum Precipitation

Only Alum Used

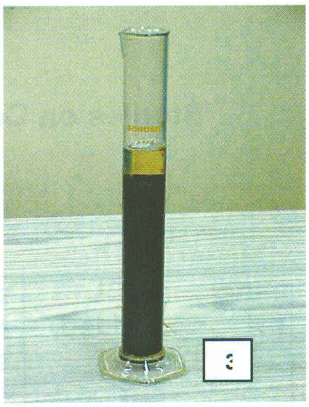
S.No.	Initial pH	Alum dose, g/l	pH after Alum addition	Color, PCU at 7.6 pH	Color reduction, %	Settle Sludge Volume, %, after 3 hrs.
1	8.74	-	-	6116	-	-
2	9.4	3.9	5.0	367	94.0	50 (2Hr.)
3	9.4	4.42	4.8	245	96.0	60
4	9.4	4.78	4.6	198	96.7	62

Color Reduction in Mechanical Pulping Effluent (E-hybrid) by Alum Precipitation Process

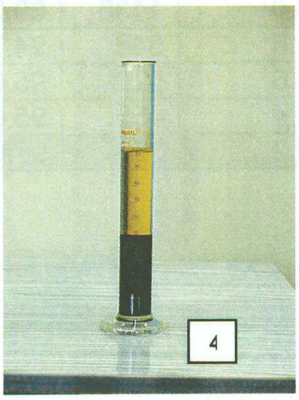


1 - Original Liquor
Color = 28,000 PCU(at 7.6pH)

2 - After Alum Treatment, 0 Hour



3 - After Alum Treatment,
Settling Time = 0.5 Hour



4 - After Alum Treatment,
Settling Time = 3.0 Hours
Color = 800 PCU (at 7.6 pH)

TABLE-7

Studies on Color Reduction by Alum Precipitation

Combination of HCl + Alum
Alum added at pH 8.0

S.No.	Initial pH	HCL added, g/l	pH after HCl addition	Alum dose, g/l	pH after Alum Addition	Color, PCU at 7.6 pH	Color reduction, %	Settle Sludge Volume, %, after 3 hrs.
1	10.8	-	-	-	-	7089	-	-
2	10.8	0.44	8.0	3.18	5.0	742	89.5	50
3	10.8	0.44	8.0	3.64	4.8	633	91.0	24
4	10.8	0.44	8.0	3.81	4.6	417	94.0	30
5	10.8	0.44	8.0	4.42	4.4	290	96.0	30
6	10.8	0.44	8.0	5.34	4.2	246	96.5	40

TABLE-8

Studies on Color Reduction by Alum Precipitation

Combination of HCl + Alum
Alum added at pH 7.0

S.No.	Initial pH	HCL added, g/l	pH after HCl addition	Alum dose, g/l	pH after Alum Addition	Color, PCU at 7.6 pH	Color reduction, %	Settle Sludge Volume, %, after 3 hrs.
1	10.8	-	-	-	-	10526	-	-
2	10.8	0.88	7.0	2.11	5.0	1136	89.2	25
3	10.8	0.88	7.0	2.62	4.8	548	94.7	38
4	10.8	0.88	7.0	3.13	4.6	520	95.0	35
5	10.8	0.88	7.0	4.0	4.4	455	95.6	40
6	10.8	0.88	7.0	4.2	4.2	313	97.0	40

4.2.1 CASE I - ONLY ALUM IS USED

Pulp Production, t/day	-	318
Volume of colored effluent, m^3/day	-	7500
Initial Color, PCU	-	6116
Final Color, PCU	-	198-245
Optimun pH for precipitation	-	4.8-4.6
Color removal efficiency, %	-	96.0
Dose of Alum, kg/m^3 (Avg.)	-	4.6
Alum required to treat 7500 m^3/day effluent, t/day	-	34.5
Cost of Alum, Rs./ton	-	2250
Cost of treatment, Rs./ day	-	77,625
Cost of treatment, Rs./ ton of pulp	-	**244**
Cost of treatment, Rs./ Annum	-	**2.56 Crores**

4.2.2 CASE II - ALUM IN COMBINATION WITH HCl ALUM ADDED AT pH 8.0

Pulp Production, t/day	-	318
Volume of colored effluent, m^3/day	-	7500
Initial Color, PCU	-	7089
Final Color, PCU	-	290
Optimun pH for precipitation	-	4.4-4.2
Color removal efficiency, %	-	96.5
Dose of Alum, kg/m^3 (Avg.)	-	4.4
Alum required to treat 7500 m^3/day effluent, t/day	-	33.0
Cost of Alum, Rs./ton	-	2250
Cost of treatment due to alum, Rs./ day	-	74,250
Cost of treatment due to alum, Rs./ ton of pulp	-	**233**
HCl required to bring pH to 8.0, kg/m^3	-	0.44
Acid requirement, t/day	-	3.3
Volume of Acid required per day, m^3/day	-	3.47
Cost of HCl, Rs./Lit.	-	3.50
Specific gravity of HCl, t/m^3	-	0.95
Cost of treatment due to acid, Rs/day	-	12158
Cost of treatment due to acid, Rs./ ton of pulp	-	**38.2**
Total cost of Alum + Acid, Rs./t of pulp	-	**271**
Total cost of treatment, Rs./t of pulp	-	**2.84 crores**

4.2.3 CASE III - COMBINATION OF ALUM AND ACID. ALUM ADDED AT pH 7.0

Pulp Production, t/day	-	318
Volume of colored effluent, m^3/day	-	7500
Initial Color, PCU	-	10526
Final Color, PCU	-	313
Optimun pH for precipitation	-	4.2
Color removal efficiency, %	-	97.0
Dose of Alum, kg/m^3 (Avg.)	-	4.2
Alum required to treat 7500 m^3/day effluent, t/day	-	31.5
Cost of Alum, Rs./ton	-	2250
Cost of treatment due to alum, Rs./ day	-	70,785
Cost of treatment due to alum, Rs./ ton of pulp	-	**223**
Acid requirment, kg/m^3	-	0.88
Acid requirement, t/day	-	6.6
Volume of Acid required per day, m^3/day	-	6.94
Cost of HCl, Rs./Lit.	-	3.50
Specific gravity of HCl, t/m^3	-	0.95
Cost of treatment due to acid, Rs/day	-	24316
Cost of treatment due to acid, Rs./ ton of pulp	-	**76.4**
Total cost of Alum + Acid, Rs./t of pulp	-	**299.4**
Total cost of treatment, Rs./t of pulp	-	**3.13 crores**

The comparative operating cost data of all the three cases are summarized in **Table-9**.

TABLE -9

Average Production, t/day = 318

Volume of Effluent generated, m^3/day = 7500

Cost of Alum, Rs/t = 2250

Cost of Acid, Rs./Lt. = 3.50

	Chemicals Added	Chemical Dose, Kg/m^3	Optimum pH for precipitation	Color reduction, %	Chemical requirement, t/day		Final Color, PCU	Cost of treatment, Rs./t		Total cost, Rs./t	Cost, Rs. (crores)/ annum	Settled sludge volume, %, after 3 hrs.
					Alum	HCl		Alum	HCl			
CASE I	Alum	4.6	4.8-4.6	96.0	34.5	-	200-245	244	-	244	2.56	60
CASE II Alum added at 8.0 pH	Alum + HCl	4.4 + 0.44	4.4-4.2	96.0	36.0	3.3	246-290	233	38.0	271	2.84	40
CASE III Alum added at 7.0 pH	Alum + HCl	4.2 + 0.88	4.2	97.0	31.5	6.6	313	223	76.0	299	3.13	40

4.2.4 Observations

(i) An overall 96.0% color reduction efficiency is achieved.

(ii) When alum is used alone, the cost of treatment is relatively less but the sludge settleability is poor.

(iii) The mill is using HCl to bring down the initial pH to 7.0 in a view that it will reduce the cost of treatment by reducing the alum consumption. The, studies carried out at CPPRI have indicated that the cost of treatment is relatively higher however the additional benefit is that the settleability is slightly improved.

(iv) Over all alum precipitation is not recommended for treating mechanical pulping effluents having high color loads due to

- High alum consumption, increases the treatment cost significantly, i.e. to the tune 3.0 crores to achieve a residual color of 200 PCU.

- The sludge obtained contains very light flocs which are hydrophilic and slimy in nature and showed very poor settleability.

4.3 COLOR REDUCTION USING PHYSICAL SEPARATION METHOD EMPLOYING ULTRA-FILTRATION TECHNIQUE

4.3.1 CASE I- Effluent having high color load

Bench scale trials were conducted on colored effluent using membrane filtration technique.

The system works on the principle of separation of low molecular weight and high molecular weight fractions under high pressure using membrane with micro pores. The permeate with low molecular weight fraction is effectively separated out. As the color of the pulp mill effluent is mainly due to high molecular weight lignin present in colloidal form, the resultant color is substantially reduced in permeate. Bench scale trials were conducted on ultra filtration DDS Model-35 having a surface area of membrane 4.5 m^2. The schematic flow sheet of membrane filtration process is illustrated in **Fig.- 1**.

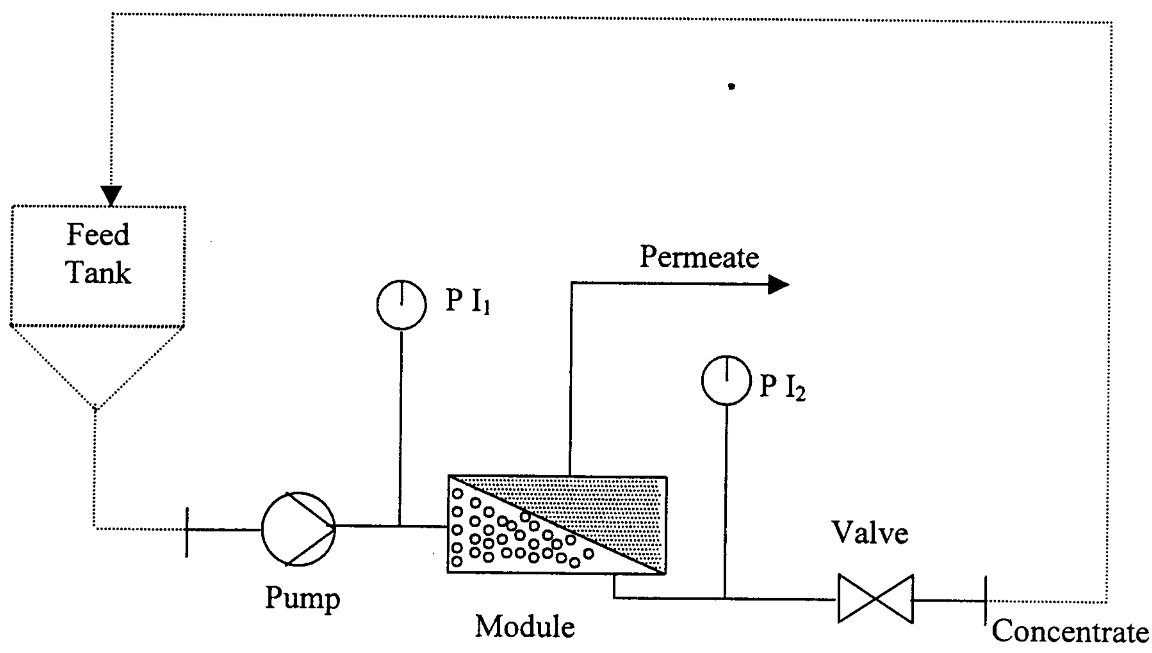


Fig. –1 Schematic of Ultra-filtration Process

The unbleached washer filtrate was passed through a cartridge filter to remove all suspended solids. After filtration effluent was received in feed tank and pressure of 0.4 mpa was applied. Results obtained for trials on unbleached washer filtrate are given in **Table- 10.**

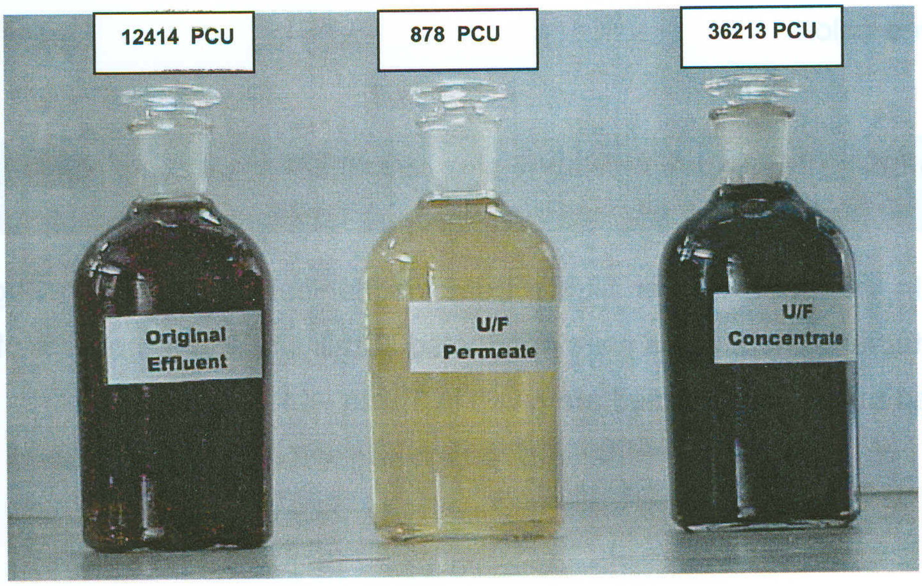
TABLE-10

Studies on Color Reduction Using Ultra-Filtration Technique

(Bench Scale Trials)

Sample Taken	-	60 Litr.
Time Taken	-	55 Minutes
Initial Color, PCU	-	14900

PARAMETERS	U/F FEED	U/F CONCENTRATE	U/F PERMEATE
Total Solids, % g/l	0.66	1.0	0.53
Lignin, g/l	1.56	4.57	0.28
Sodium, g/l	0.013	0.002	0.031
Color, PCU (7.6)	12414	36213	878
Color reduction efficiency, %	-	-	93.0



Treatment of Mechanical Effluent (Eucalyptus) by Ultra-Filtration Process

4.3.2 Observations

(i) The effluent color, which is due to soluble extractives and lignin, was reduced to a level of 800 PCU indicating a color removal efficiency of 93.0%.

(ii) The membrane filtration is effective in removal of color by separating lignin. In absence of any technoeconomically viable solution a combination of alum treatment to remove suspended color followed by ultra-filtration to remove dissolved color will be more effective solution to reduce the color level in final effluent however the cost of treatment will be high.

4.3.3 Limitation

The process is expensive and energy intensive. Since the process involves separation of organic & inorganic constituents through membrane, it is sensitive towards solids concentration. A colored effluent having high color loads due to high molecular weight lignin and extractives may limit the process performance due to fouling of polysulphones membrane, which eventually will increase the process downtime due to frequent cleaning/replacement of membranes. It is therefore recommended that ultra-filtration technique should be adopted in combination with alum precipitation in the primary stage to remove suspended color followed by ultra-filtration at the tertiary stage to remove the dissolved color.

4.3.4 CASE II- Effluent Having Low Color Load

In this case decker filtrate from mechanical pulping using bagasse has been studied. The studies were conducted at mill site and the results of the study obtained on trials conducted are given in **Table –11**.

TABLE -11

Results of Membrane Filtration of Decker Washing Effluent

Trial No.	Color at 7.6 pH(PCU)			Lignin, ppm		
	Inlet	Permeate	Reduction, %	Inlet	Permeate	Reduction, %
1	3650	413	89	1610	328	80
2	3000	433	86	1440	320	78
3	2500	580	77	875	310	65
4	3250	490	85	882	228	74
5	2700	350	87	956	294	69

The effluent flow & color at various points before & after membrane filtration in Decker filtrate is shown in **Fig-2**.

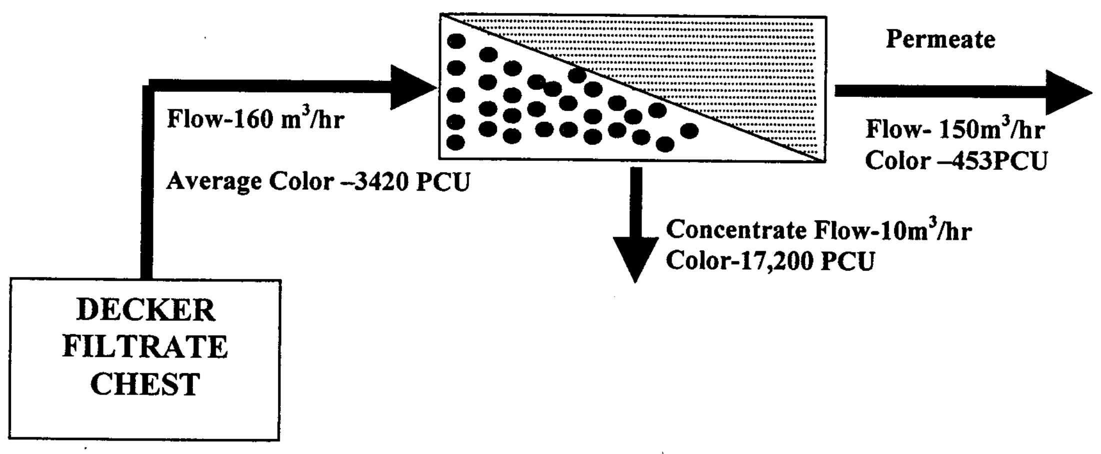


FIG. 2 Membrane Filtration Applied at Decker Filtrate

4.3.5 Observation on Ultra-filtration Trials on Decker Filtrate Water

(i) An average color reduction of about 85% was achieved with an average reduction of lignin content by about 73%.

(ii) COD reduction of 60% is achieved. Volume of concentrate to Permeate is in the ratio 6: 94.

(iii) A permeate flux of 150 LPH was maintained

(iv) TDS reduction is in the range of 40-50%.

(v) Continuous trials have shown that with decker filtrate, the membrane filtration was running quite smoothly and did not require much of the back washing.

(vi) On an average, it is possible to separate nearly 2 tons of lignin per day as concentrate which about 200 m^3/day. Utility of this concentrate containing high concentration of lignin is to be ascertained as to where it can be utilized.

(vii) Although membrane filtration is highly effective in removal of color from decker filtrate but considering its volume i.e. 3200 m^3/day, it is concluded that under the existing ETP system it may not be effective in reducing the color of the total mill effluent. Nevertheless there is a need for further deep.probing of application of membrane filtration technique only for the color reduction keeping in view of the capital cost, overall impact on color and the operating cost.

5.0 EMERGING TECHNOLOGIES

From the extensive literature review, three emerging technologies have been identified, which are promising in reducing the effluent color load. These technologies have been studied at lab scale using bleach effluents. The technologies are:

- UV/Photo Irradiation Process
- Ozonation
- Electroflocculation

Of these, preliminary lab scale studies were conducted at CPPRI on electro-flocculation using mechanical pulping effluent. The findings have been found to be very encouraging. The process involves, passing of low voltage current through metal electrodes to release metal ions at anode which coagulate with colloidal colored particles and subsequently floats on the surface with the help of gas generated at cathode. The findings of the study are depicted in **Table-12**.

TABLE-12

Color Reduction in Mechanical Pulping Effluents Employing Electro-Flocculation Process (Lab Scale Studies)

Temperature - 40°C

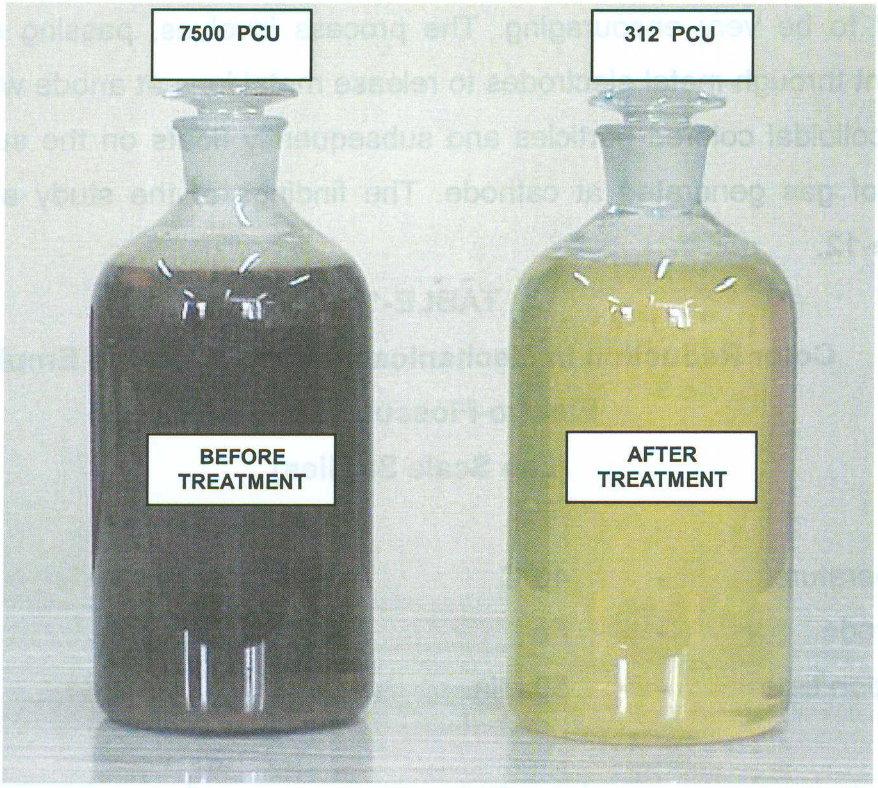
Electrode - Fe

Reaction time - 50 min.

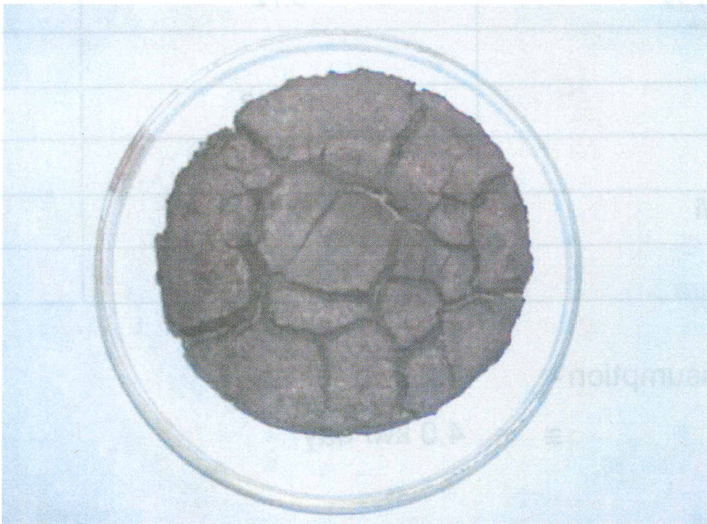
Parameters	**Before Treatment**	**After treatment**
pH	6.0	10.0
Conductivity, mS/cm	4.0	4.5
Total Solids, %	0.72	0.58
Redn. η, %	-	19.4
Color, PCU	10642	333
Redn. η, %	-	97
Organics, g/l	1.76	0.54
Redn. η, %	-	69

Power consumption - 0.2 kwh

$\cong$ 4.0 kw/ day



Treatment of Bagasse Effluent by Electro-Flocculation Process



Organic Components (Lignin & Extractives) Separated During Electro-Flocculation Process

(Shown After Filtration)

There is a need to carry out extensive research on these technologies to establish the techno-economic feasibility for removing color from mechanical pulping effluents.

In view of this CPPRI has taken up project on "Demonstration of color reduction Technology" to evaluate the techno-economic feasibility of these emerging technologies in removing color from pulp & paper mill effluents.

6.0 RECOMMENDATIONS

1. With the growing public concern over the discharge of colored effluents to the river, the problem of effluent color has become a prominent issue for the Pulp & Paper Industry. The problem is more serious for newsprint mills based on wood. For newsprint mills effluent color reduction can be achieved either by a proper selection of the raw material or by adopting a suitable pretreatment process in order to extract out the extractives from the wood. A systematic study would be required.
2. In the existing system when the mills do not have an option to change its raw material, the mills should look into the possibility of adopting new pulping technology i.e. Alkaline Peroxide Mechanical Pulping Process (APMP) for mechanical pulp production to reduce effluent color load.
3. For EOP treatment technology it is essential that mill should have a separate street for treating the colored effluents and then combine it with other effluents for conventional treatment.
4. The EOP treatment facility should essentially have an equalization tank prior to treatment to absorb the shock loads due to variations in color loads. This will improve the overall performance of the treatment plant.
5. Feasibility studies conducted at CPPRI on Chemical precipitation method using alum have clearly indicated the alum precipitation is not a viable option for treating mechanical pulping effluents due to the following reasons:

   - Highly colored effluents require high alum dosage leading to higher costs.

- Formation of very light flocs of precipitate having poor settleability, which leads to carryover of precipitated color with supernatant.
- The addition of acid to bring down Alum consumption may further increase the treatment cost, however some improvement in sludge settleability is obtained.
- The addition of polymers in combination of Alum to improve settleability will substantially increase the treatment cost.

6. Studies conducted employing ultra-filtration technology clearly indicates that the technique is viable only for effluents having low color loads. For high color load effluents, a combination of alum precipitation followed by ultrafiltration is more suitable option for higher efficiency, however the cost of treatment will be substantial.
7. From the literature review three emerging technologies have been identified which are
   - UV Irradiation Process
   - Ozonation
   - Electro-flocculation

   Of these three technologies, preliminary studies on lab scale have been conducted on electro-flocculation process using mechanical pulping effluents. A color reduction efficiency of 97% with 50% reduction in COD and 70% reduction in organic components is achieved. The process is technically feasible and needs to be studied on pilot scale to establish the economic viability of the process.
8. Also there is need to take up detailed R&D activities to study ozonation and irradiation process for treating mechanical pulping effluent.
9. In view of this, CPPRI has already taken up a project as one of the plan schemes in which identified technologies will be studied on lab scale and pilot scale to evaluate the techno economic viability of the process for treating mechanical pulping effluents.

E

Bibliography

SELECTED BIBLIOGRAPHY

1. **Color & COD reduction of bleach effluents**

Kapoor, S.K., Pant, R., Roy, T.K., Mathur, R.M.

Ippta, Vol. XVII, No. 2, P. 42, June 1980

Abstract: This paper highlights the use of calcium hypochlorite was added in the extraction stage of bleaching sequence of bamboo and mixed hard wood pulp, for color and COD reduction. Optimum doses of hypo for maximum color and COD reduction have been determined. Color was measured directly from the standard chloroplatinate color unit curve, which was prepared with the help of U.V. Spectrophotometer absorbance at 465 nm. It was observed that the color load of extraction stage effluent could be reduced to the extent of 80%by adding during extraction stage 0.4% calcium hypochlorite on O.D. pulp in case of mixed hard woods and 0.6% in case of bamboo.

2. **Color removal from kraft mill effluents a review**

Gautam , M., Dixit, M. K., et al.

Ippta, Vol. 24, No. 2 (Suppl), P-16-22, June 1987

Abstract: The article describes that the lignin and its derivatives impart an offensive color which inhibit the natural process of photosynthesis in the stream due to absorbance of sunlight. This affects the whole aquatic ecosystem adversely. The paper also discuss the technology changes in bleaching process for reducing the color load in effluent. Discharge of substantial ratios of untreated mill effluent into stream has long been recognized as dangerous to fish and other aquatic life. While the pollution load of the effluents with respect to other parameters can be reduced to acceptable levels using existing technologies the treatment with respect to color removal continues to defy economically viable solution.

3. **Color reduction of kraft bleach effluent by – The addition of hypochlorite**

Kaul S.S Bist, D.P.S., Jangalgi N. R.,

Ippta, Vol. XVII, No. 4, P. 1-5, Dec. 1980

Abstract: Experiments have been carried out to see the effect of addition of calcium hypochlorite on the color of the alkali extraction stage effluents of bamboo and mixed hard woods. The main objective of this article is to reduce color of caustic extraction stage effluent so that it may be recycled again in the process by mixing with grade II effluent. Results of present study showed that by the addition of only 1% calcium hypochlorite in the extraction stage of C/E/H bleaching sequence, color can easily be reduced by 80%. It is also found out that further addition of hypochlorite beyond 1.5% on pulp basis, has no significant effect on the color removal of the effluent.

4. **An approach to in plant color reduction of bleach plant effluent using Calcium hypochlorite**

Bhargava, G.G., Dwivedi, R.P., Jangalgi N.R., Kaul,S.S.

IPPTA, Vol. XVIII, No. 3, P. 58-66, Sept. 1981

Abstract: The findings of the paper shows the effluent, which is high in colour, presents an aesthetic problem and impairs the process of photosynthesis which in turn retards biological activity and transmission of sunlight into water. The present study was undertaken to reduce the color and pollution load of the caustic extraction stage effluent by inplant process. The bleaching sequences studied were C/EH/H sequences are excellent in removal of 76-80% color, BOD 40-50% and COD 40% can be removed.

Bleached pulp obtained by HC/EH/H/Sequenced is slightly inferior compared to C/E/H sequence. The C/EH/H sequence is preferred over HC/EH/H sequence in view of cost of chemicals and quality of pulp. Advantages of this inplant color reduction process is saving of nutrients used in an anaerobic and aerobic treatment by 30% and possibility of reusing the water back in chipper house and coal ash disposal after treatment.

5. **Decoloration of kraft pulp mill effluent studies at OPM, Amlai**

Sharma , G.D. et al.

IPPTA , Convention Issue 1987, P. 124 -140

Abstract: The paper describes the various methods for treating kraft pulp mill effluents with using flocculating agents and degrading agents at laboratory and plant level. It was found that degradation of coloring matter with calcium hypochlorite gave very encouraging results.

This paper covers the reduction of Kraft pulp mill effluents at Orient Paper Mills, Amlai. The effluent from the wash plant and alkali extraction stages of bleach plant along with contaminated gland cooling water and miner spillages from the digester house and soda recovery plant are separately diverted together for treatment and is termed as Grade III effluents. It is blackish brown in color and is non-biodegradable in nature. The results of the decoloration of Grade III untreated effluent with calcium hypochlorite alone and combination with alum liquid chlorine and ferrous sulphate are recorded. In addition of calcium hypo chlorite at the inlet of the polishing pond may reduce the color to an appreciable extent and also reduce the BOD_5 & COD. The remaining effluent is further treated in aerobic lagoons and stabilized in the polishing pond having retention period of about 7-8 days.

6. **Color removal from kraft pulp mill effluents by massive lime treatment.**

Robert, S., Wright, John L Oswalt, and Joseph G. Land, Jr.

Tappi, Vol. 57, No. 3, P. 126-130, March 1974

Abstract: This article describes the effectiveness and feasibility of using massive lime treatment (20,000ppm of lime) to decolorise kraft pulp mill effluents. Objective of this project were to determine the effectiveness of color removal design and performance of massive lime system equipment; effect on normal pulp operations; effect on pulp quality and operation costs. Impact of the massive lime system on a hypothetical 1000 t/d bleached kraft pulp and paper to treat 4 million gal of effluent per day, cost would be approximately $ 1.8 / t of bleach

pulp. Treatment of the most highly colored effluents will remove 72% of the mills total color load.

7. **Decolorizing dye wastewater with low temperature catalytic oxidation**

Daewon pak & Wonseok Chang

Wat. Sci. Tech., Vol. 40, No. 4-5, P. 115-121, 1999.

Abstract: A novel oxidation technology developed to decolorise dye wastewater and the feasibility of color removal with Fe/MgO catalyst fluidizing in a reactor under continuous flow was demonstrated at room temperature. Through the catalytic oxidation those dyes can be degraded to molecules with lower molecular weight and than a part of them can be mineralized based on TOC analysis. The catalytic oxidation rate is dependent on hydrogen peroxide and catalyst dosage. The catalytic oxidation rate increased with increasing hydrogen peroxide and catalyst dosage. Fe/MgO catalyst fluidizing in the reactor operated at room temperature was tested to decolorize the wastewater from a dye manufacturing industry. In the fluidized bed reactor, the wastewater was completely decolorized and about 30% of COD removal was obtained during 30 days of operation.

8. **Decolorisation of kraft mill effluents with polymeric adsorbents.**

Moven L. rock, Alexender Bruner, and David C. Kennedy

Tappi, Vol. 57, No. 9, P. 87-92, Sept. 1974

Abstract: The article describes the use of Amberlite XAD-8 adsorbent fordecoloration of kraft mill effluent.. Decolorisation levels of 70-95% were achieved with corresponding removal of BOD (33%), COD (43%) and suspended solids and pulp fibers (78%). the optimum method of achieving a total mill color of 200 APHA (76% decolorization) is to decolorize the total chlorination and caustic extract effluents by 84%, the capital investment would be $1,495,000 with an operating cost of $0.70/t. In order to reach a total mill color of 300 APHA (64% colorization) a slightly modified approach was used, the system is

estimated to have a capital investment of $940,000 and operating costs of $0.42/t of pulp bleached.

9. **Modern methods for the analysis of extractives from wood and pulp : review.**

B. Bruce Sithole

Appita , Vol. 45, No. 4, P. 260-264, 1992.

Abstract: This paper describes the use of modern methods to analyse the extractives. The methods vary depending on among other things, the sample matrix, the complexity of the analysis and the type of information required from the analysis. Modern analytical procedures encompass techniques such as thin layer chromatography, HPLC, gel permeation chromatography, capillary gas chromatography and FT-IR spectroscopy.

10. **Treatability study of organic and color removal in designing / dyeing wastewater by UV/US system combined with hydrogen peroxide.**

P.C.Fung, Q. Huang, et al.

War. Sci. Tech., Vol. 40, No. 1, P. 153-160, 1999.

Abstract: This paper describes the treatability of model dye, cuprophenyl yellow RL, in wastewater by the UV/H_2O_2/ultrasonication (Us) process. The process was studied on a bench scale using a UV/US combined reactor. The dye degradation was found to follow pseudo first order kinetics at different pH and H_2O_2 dosages. The effect of pH, hydrogen peroxide dosage and US on the oxidation process were investigated and performance of the process on color removal were evaluated.

11. **Design of an efficient tannin extract effluent treatment system.**

L. Etiegni, M. Wakoli and K. Ofosu-Asiedu.

Wat. Sci. Tech., Vol. 39, No. 10-11, P. 321-324, 1999.

Abstract: Study has shown the possibility of reducing the color of a tannin extract effluent in two stages of coagulation for pH adjustment. The effluent had BOD-2350mg/l, COD-4600mg/l, suspended solids- 0.43–4.20 mg/l, phosphorous- 2078 mg/l, free ammonia –2982mg/l and color index of 50-150^{0}H. Three potential treatment processes were considered. VITOX system using pure O_2 lagoon evaporation process using wood ash leachate for pH adjustment.

12. **Decolorisation of extraction stage bleach plant effluent by combined hypochlorite oxidation and anaerobic treatment.**

T. Clark, M. Bruce and S. Anderson

Wat. Sci. Tech., Vol. 29, No. 5-6, P. 421-432, 1994.

Abstract: This paper shows the hypochlorite treatment of E-stage effluent at high pH can reduce effluent color by about 80-90%, using chlorine dosage of 0.1kg active chlorine per kg color, although the AOX concentration of the waste water increased by about 50%. Subsequent anaerobic treatment of the decolorized wastewater was able to reduce the AOX concentration to close to its original level. Anaerobic treatment of untreated E-stage effluent had no effect on the concentrations of AOX or color.

13. **Application of ferrous hydrogen peroxide for the treatment of H-acid manufacturing process wastewater.**

Zhu Wanpeng, Yang Zhihua and Wang Li

Wat. Res. Vol. 30, No. 12, P. 2949-2954, 1994.

Abstract: H-acid (1-amino-8-naphthol-3, 6-disulfonic acid) is one of the important dye intermediates. A pretreatment method, ferrous ion peroxide oxidation combined with coagulation has been studied. The method of ferrous – hydrogen peroxide oxidation is also known as Fenton's reagent method. The results shown that the optimum pH between 2- 4 and ferrous ion dosage is 200 mg/l. The overall COD removal can reach 90% or more when the concentration of ferrous ion is 200mg/l, the dosage of hydrogen peroxide is 3g/l and the ferric chloride dosage of two stage coagulation treatment is 15g/l and 5g/l respectively.

This method not only removes COD effectively, but also improves the biodegradability of the wastewater by combining with coagulation process. During the oxidation of H-acid by Fenton's reagent, first, hydroxyl radical substitutes passive groups on naphthalene ring. It makes naphthalene ring activable. Secondly naphthalene is oxidized and broken down producing elementary unsaturated fatty acid.

14. The influence of solution matrix on the photocatalytic removal on color from natural wastes.

M. Bekbolet, Z. Boyacioglu and Ozkaraova

Wat. Sci. Tech., Vol. 38, No. 6, P. 155-162, 1998.

Abstract: The results of the present study shows the photo catalytic color removal of humic acid in the presence of common inorganic ions: namely, chloride, nitrate, suphate and phosphate ions at pH 6.8 retard the photocatalytic removal rate provided that the removal rate is explained in terms of Langmuir-Hinshelwood kinetics. The authors reported that an initial 50% removal was observed due to adsorption during the equilibrium period when distilled water was used instead of Millipore water.

15. Treatment efficiency of land application for thermo mechanical pulp mill effluent constituents.

Hailong Wang, Gerty J. Gielent, Maurice L. et al.

Appita Journal, Vol. 52, No. 5, P. 383-386, September 1999.

Abstract: Results from this study show that the land irrigation was highly efficient in the treatment of organic contaminants from thermo-mechanical pulp effluents. Removal rates through the soil core were greater than the 90% for TOC, COD, BOD, turbidity, resin acids, phenols and phytosterols and in the TMP effluent were actively removed by a 750mm high soil column. The broader objectives of this study were to examine the effectiveness of the system in removing contaminants from TMP effluents during land application impacts on soil fertility and groundwater quality.

16. **Color removal from kraft mill effluent by an improved lime process.**

Metthew Gould

Vol. 56, No. 3,P. 79-82, March 1973

Abstract: This paper covers the removal of Kraft pulp mill effluents treated with approximately 2000 ppm of lime before entering a solids contact clarifier. The lime reacts with the color bodies, precipitating them at a settleable sludge that is continuously removed from the clarifier. Operating on the highly colored, caustic extract stage, the system results in 90% reduction in color and approximately 45% BOD removal.

17. **A convenient method for the determination of wood extractives in paper making process waters and effluents.**

F. Orsa and B. Holmbom

Jl. of pulp & paper science (JPPS), Vol. 20, No. 12, December 1994

Abstract: An analytical method has been developed, the rapid determination of lipophilic extractives, lignans, and lignins in paper mill process waters and effluents. The method comprises centrifugation to remove fibers, fines and other non colloidal particles from dissolved and colloidal substances, extraction with methyl ter.-butyl ether (MTBE), silylation gas chromatography (GC) to determine the amount of extractives and amount of dissolved lignins is determined from the UV absorption value at 280nm of the extracted water sample.

18. **Fly ash and cinder from coal for the treatment of paper mill effluents.**

Subhash Maheshwari, Nayak, R.G., et al.

Ippta, Vol. XVI, No. 2, P. 97-104, June 1979

Abstract: This paper shows the fly ash and cinder obtained as waste from coil fired boilers were effective for the treatment of the effluents for reducing 90-95% color, 30-40% BOD, 75-85% COD of the alkali extraction stage effluent could be reduced.

19. **Toxic constituents in mechanical pulping effluents**

J.M. Leach and A.N. Thakore

Tappi, Vol. 59, No. 2, P. 129-132, February 1976

Abstract: This paper shows the toxic constituents fractionated from mechanical pulping effluent using chromatographic techniques were identified by spectroscopic comparison with authentic samples obtained through chemically synthesized materials. The predominant toxicants were the resin acids, dehydroabietic, isopimaric, abietic, pimaric, neoabietic palustric, sandaracopimaric which together accounted for 60-90% of overall toxicity in the mechanical pulping effluents studied. The total resin acid concentrations, range from 12-62 mg/l in mechanical pulping effluents measured by gas chromatography.

20. **Studies on the removal of color from paper mill effluent.**

Ratna Kumar Srivastava & K.C.Mathur

Indian Pulp & Paper, P. 5-7, June-July 1985

Abstract: This study has shown the possibility of reducing the color of a paper mill effluent. Using Dolomite a new coagulant (a mineral of magnesium), which been used successfully for 90% color removal. The effluent had high amount of solids, BOD, COD, per ton of paper. Further about 50-55kg of lignin which imparts dark brown color is also released per ton of paper.

21. **Ultrafiltration for removing color from bleach plant effluent.**

Eka AB, Surte,

Tappi, Vol. 63, No. 4, P. 97-101, April 1980.

Abstract: The paper describes an ultrafiltration method that effectively decolorizes effluent from the alkali extraction stage of a conventional kraft pulp mill. In a E-stage effluent contributing 140-150kg of color per ton of pulp and 5-6 kg of BOD_7 per ton, ultrafiltration will reduce the color by 90%, COD by 80%, and BOD_7 by 25-50%. The overall effect on total mill effluent is a 65-70% reduction in color, 40% reduction in COD and 10% reduction in BOD_7.

22. **The efficacy of enhanced photo oxidation for the reduction of TOCl, Color, and toxicity in mill aqueous effluents.**

Rechard M. Higashi, Gary N. Cherr, Donald G. Crosby

Tappi proceedings, Environmental conference, P. 73- 83, 1991.

Abstract: The paper describes that 365nm irradiation with TiO_2 catalyst functioned very efficiently degrade a model resin acid but failed to cause any spectral degradation or change in TOCl, possibly due to the dominance of non degradable high molecular mass material in mill effluent. The experiments have shown that degradation of title pollution parameters in whole mill effluent, when irradiated at 254nm in the presence of the catalytic oxidant TiO_2 is increased with elevated temperature, increased light intensity and low pH.

23. **Ozonation and wet oxidation in the treatment of thermo mechanical pulp (TMP) circulation waters.**

A.Laari, S. Korhonen, T. Tuhkanen et al.

Wat. Sci. Tech., Vol. 40, No. 11-12, P. 51-58, 1999.

Abstract: This study has shown two objectives: to reduce concentration of lipophilic wood extractives and to treat the concentrated residues from evaporation and membrane filtration by low-pressure catalytic wet oxidation. Chemical oxidation with ozone for the removal of lipophilic wood extractives (LWEs) from circulation waters in TMP production. The oxidation was found to be selective against the lipophilic extractives over the reduction of COD. However, the necessary ozone dose to remove 90% of the LWEs was found to be rather high, from 500-800mg/l. Wet oxidation removed about 50% of the COD of the waste water at 150^{0}C.

24. **Coagulation and precipitation of a mechanical pulping effluent –1 Removal off carbon, color, and turbidity.**

Robert J. Stephenson and Sheldon J.B.Duff.

Wat. Res. Vol. 30, No. 4, P. 781-792, 1996

Abstract: This paper shows the iron and aluminum salts were able to remove up to 88% of the total carbon and 90-98% of color and turbidity from mechanical pulping effluents. In terms of minimizing the total carbon, color and turbidity levels, the optimum adjusted pH ranges were 4.0-6.5 for ferric chloride, above 7.4 for ferrous sulphate, 5.0-6.0 for aluminum chloride and 5.8-6.8 for aluminum sulphate.

25. The color and UV visible absorption spectra of mechanical and ultra high yield pulps treated with alkaline hydrogen peroxide.

David G. Holah

Tappi proceeding, International mechanical pulping conference, P. 177-182, 1991

Abstract: The paper shows during the initial stages of alkaline hydrogen peroxide bleaching chromophores that absorb light at wavelengths in the range 360-460nm are oxidized to chromophores, coniferaldehyde and quinoid that absorb light at wavelength < 300nm to increase ISO brightness and whiteness and decrease yellowness. . However alkaline hydrogen peroxide bleaching of SGWD and TMP decreases yellowness. Most of the brightness increase during alkaline hydrogen peroxide bleaching of SGW, TMP, and CTMP occurs in the first 240 minutes. As the time of bleaching approaches 240 minutes, the brightness increases at a slower rate than the initial rate and eventually ceased to increase with time. The highest brightness levels attainable were dependent on the pulp type and decreased in the order of SGW>TMP>CTMP.

26. Electrochemical removal of color and toxicity from bleached kraft effluents.

Allan M. Springer, Vincent C. hang, and Timothy S. Jarvis

Tappi Journal, Vol. 78, No. 12, P. 85—92, Dec. 1995

Abstract: The main objective of this paper is to confirm that electrochemical treatment and decolorise pulp and paper effluent and determine an optimum set of conditions to run the electrochemical cell and also determine the economical feasibility of electrochemical treatment. A laboratory scale flow through

electrochemical process reduced color from mill effluents as much as 90%. The process variables are increasing cell current, decreasing solution pH and increasing solution temperature each increased the rate of color removal. The optimum conditions to run the electrochemical cell are pH of 6, current of 1A, and temperature of 50^{0}C.

27. Color Removal of high strength paper and fermentation industry effluents with membrane technology

I. Koyuncu, F. Yalcin and I. Ozturk

Wat. Sci. Tech., Vol. 40, No. 11-12, P. 241-248, 1999.

Abstract: This paper presents the pilot plant studies on the biologically treated effluents from the pulp & paper and fermentation industry effluents by using two stage membrane treatment (Ultrafiltration, UF) and (reverse osmosis, RO). In the first part of the study the combination of UF and RO treatment resulted in very high removals of COD, color and conductivity for the pulp and paper industry effluents. The overall removal efficiency of COD, color, conductivity, NH_3-N were found as 90-95%, 95-97%, 85-90% and 80-90% respectively with 85-90% recovery after UF and RO membranes for all these waste water streams.

28. Determination of total lignin and polyphenol in eucalypt woods.

D. E. Bland and M. Menshun

Appita, Sept. 1971, Vol. 25, No. 2, P. 110-115,

Abstract: Milled wood lignin has been used to determine the absorptivity of several eucalypt lignins. It has been shown that the customary sulfuric acid determination of lignin in eucalyptus wood does not include all the lignin but that an appreciable amount remains in the acid solution. These do not obey Beer's law but evidence is given that the absorptivity of milled wood lignin at infinite dilution is equal to the absorptivity of acid solution lignin.

29. Current status of the effluent decolorisation problem

Isaiah Gellman and Hebert F. Berger

Tappi, Vol. 57, No. 9, P. 69-73, September 1974

Abstract: In this paper, methods are both reviewed and proposed for determining color intensity, sources and distribution of effluent color load, and levels of receiving – water color change noticeable and therefore possibly objectionable to significant groups of human observers.

30. Color reduction studies at a bleached kraft pulp mill.

Acker Smith and William H. Malloy

Tappi Journal, Vol. 73, No. 4, P. 87-90, 1990

Abstract: Experiments have been carried out to see the effect of pH for the color removal. The optimum pH for inorganics is around 4.5-5.0. At pH values higher than this the coagulants are not being used effectively. The lower the pH of the bleach plant effluent, the higher the color removal efficiency at the same polyamine dose. The main objective of the paper is to reduce color to minimize adverse impact it may have on the aesthetic appeal of the river.

31. Characterisation of lignin and carbohydrate residues found in bleach effluents.

J.W. Collins, A.A. Webb, and L.A.Boggs

Tappi journal, Vol. 54, No. 1, P. 105-110, January 1971

Abstract: The studies were concerned with chlorination, alkaline, extraction and hypochlorite effluent from sulphite and kraft pulps predominantly soft wood in makeup. The sulfite alkaline extraction effluent was found to contain fractions with fluorescent properties. Kraft alkaline extraction effluent was investigated for hydroxy carboxylic acids by gas chromatography of their trimethylsilyl derivatives. Effluent concentrates obtained by reverse osmosis and/or vacuum evaporation were fractionated by gel chromatography, and the fractions were characterized

for lignin by ultraviolet absorption and ionization difference absorption spectroscopy and for carbohydrate by the phenol sulphuric acid test.

32. **Reuse of wastewater from pulp & paper industries**

Garg. S.L., Kaushal deepa

Ippta, Vol. 9, No. 2, P. 53-60, June 1997

Abstract: Studies have been made to treat wastewater being discharged to river body from pulp and paper industry, so as to bring its parameters near by those as suggested by pollution control boards. Enormous amount of wastewater from pulp and paper industry cannot be reused as it is discharged with high color load, high BOD, COD alkalinity etc. Treating this water with some chemicals such as alum, lime cat- floc (T), PAC & through sand and coal ash columns, color is removed to appreciable extent and hence treated water can be further reused for land applications.

33. **Ozonation – An important technique to comply with new German laws for textile wastewater treatment.**

Frank Gahr, Frank Hermanutz and Wilhelm Oppermann

Wat. Sci. Tech., Vol.30, No. 3, P. 255-263, 1994.

Abstract: Ozonation is a high efficient decoloration procedure for separated wastewaters containing unfixed reactive dyes. An ozonation treatment of the total wastewater for complete decoloration can not be recommended but ozone can be used in this case as a polishing step to reduce refractory substance s before or after biological treatment. Ozonation being a sludge free method to decompose dyestuff, finishing products, and other organic materials is of increasing importance because of the limited space for disposal of sludges. Other advantages of this treatment are the improvement of biodegradability, reduction of aromatic and halogenated organic compounds and also a significant decrease of chemical oxygen demand.

34. **Spectrophotometric determination of lignin in polyphenol-containing eucalyptus woods by the acetyl bromide method**

Kenji Iiyama and Adrian F. Wallis

Appita, vol. 41, No. 6 442-446, November 1988

Abstract: The paper shows the effect of various wood polyphenols on the lignin determination by the acetyl bromide method was therefore tested. The modified acetyl bromide method is thus proposed as a facile, rapid alternative to the more tedious conventional method to obtain at least approximate lignin contents of polyphenol – containing woods of E. diversicolor and E. marginata species.

35. **Decolorisation of wastewater from bleached kraft pulp& paper mill using alum & clay**

Manjonath D.L., Kumar Pradeep, Mehrotra Indu

Ippta, Vol. XVII, No. 3, P. 16-23, September 1980

Abstract: The paper discusses the approach incorporated in the present investigation, aims at improving alum coagulation has been shown to yield flocs which settle faster and forms a more compact sludge. The work embodied in the present project also incorporates the continuous treatment of colored wastewater in a sludge blanket clarifier. The performance of the model has been evaluated with reference to alum coagulation and alum along with two different doses (500 & 800mg/l) of clay.

36. **Effect of tertiary coagulation and flocculation treatment on effluent quality from a bleached kraft mill.**

Andrew T. Hodgson, Alan J. Hitzroth, et al.

Tappi Journal Vol. 81, No. 2, P. 166-172, February 1998

Abstract: The paper shows the tertiary treatment (coagulation and flocculation) can produce excellent color removal over a broad range of temperature, pH, and BOD. Tertiary coagulation and flocculation technologies have the potential to help mills without state-of-art process equipment to meet

today's stringent regulations limiting effluent discharge. The tertiary treatment system reduced COD, AOX, 2,3,7,8-TCDF and mixed function oxygenase induction by 24%, 23%, 80%, and 18% respectively.

37. **Some recent advances in the chemistry of condensed tannins (proanthocyanidin polymers) relevant to their use as industrial chemicals.**

L. Yeap Foo and Lawrence J. Porter

Appita , Vol.39, No. 6, P-477-480, November 1986

Abstract: Studies have shown conclusively that condensed tannins consist of chains of flavanoid units. The reactions of condensed tannins with alkaline bisulphate is now understood in chemical terms. Caustic soda has been suggested as an extraction medium by some workers for bark tannins. Therefore this must be taken into account when the phenolic properties of the A-ring are being utilized such as cross-linking with formaldehyde. This contrast in reactivity leads to much faster cross linking of formaldehyde and the phloroglucinol –type tannins with consequent adhesive formulations difficulties. Use has been made of this greater reactivity by the development of cold settling adhesives involving condensation of the depolymerised tannin with resorcinol.

38. **An enzymatic pretreatment to enhance the lime precipitability of pulp mill effluents.**

R.I. Scmidt & T.W.Joyce

Tappi, Vol. 63, No. 12, P. 63-67, December 1980

Abstract: This paper shows the effectiveness of color removal by lime precipitation depends in part upon the molecular weight distribution of the color bodies. The enzymatic pretreatment can be used both to increase the limits of color removal which are presently attainable as well as to reduce the quantities of lime required to achieve lower levels of color removal. Removal of color by this process roughly 90%, using lime concentrations of 1500mg/l Ca $(OH_2)_2$.

39. **The determination of extractives and pitch by chromic acid oxidation**

John A. Lloyd and Len M. Stratton

Appita, Vol. 39, No. 4, P. 287-288, July 1986

Abstract: Paper shows the determination of small amounts of extractives and pitch using chromic acid oxidation of extractives, and absorbance measurement of reduced chromic acid solution. The method was used to determine the amount of extractives adsorbed by talc in a laboratory test of talc efficiency.

40. **Use of new oxidizing agents in a refiner: A route to high brightness pulp**

Celine Leduc. Mohini M. sain, Claude Daneault. R. lanouette and Jacques L. Valade

Tappi Journal, Vol. 83, No. 4, P. 77, April 2000

Abstract: Objective is to assess the impact of chip length and thickness on the properties of hand sheets made from ultra high yield sulphite pulp. The best chip size distribution can help reduce strength loss during the winter months.

41. **Coagulation and precipitation of a mechanical pulping effluent –1l Toxicity removal and metal salt recovery**

Robert J. Stephenson and Sheldon J.B.Duff.

Wat. Res. Vol. 30, No. 4, P. 793-798, 1996

Abstract: This paper shows the iron and aluminum salts were able to remove the total carbon, color and turbidity from CTMP/BCTMP pulping effluent. Toxicity was completely removed from the ¼ strength effluent at the ferric chloride dose of 5g/l. Ammonium chloride was effective in decreasing the effluent toxicity, the maximum toxicity removal (EC50 of 51%) was found the highest coagulant dosage and lowest waste water strength Ferric chloride with the fixed solids recovery of approximately 82% appears to be the best candidate for coagulant recovery.

DETERMINATION OF COLOR IN EFFLUENT

TM V-A9
2001

1. Scope

The Platinum-Cobalt method of measuring color is the standard method, the unit of color being that produced by 1 mg platinum/lt. in the form of chloro-platinate ion. The Platinum-Cobalt method is useful for measuring color of the samples in which color is due to naturally occurring materials like lignin.

2. Preparation of standards

In absence of the reliable supply of potassium chloro platinate, chloro platinic acid prepared from pure metallic platinum can be used.

Potassium chloro platinate standard - Dissolve 1.246 g potassium chloro platinate ($K_2 PtCl_6$) equivalent to 500.0 mg metallic platinum and 100.0 mg crystallized cobaltous chloride ($CoCl_2.6H_2O$) equivalent to 250.0 mg metallic cobalt in distilled water with 100 ml conc. HCl and dilute to 1000 ml with distilled water. This stock standard has a color of 500 units.

Standard using metallic platinum - If K_2PtCl_6 is not available, dissolve 500.0 mg pure metallic platinum in aqua regia with heating. Remove HNO_3 by repeated evaporation with fresh portions of conc. HCl. Dissolve this product along with 1.0 g crystallized $CoCl_2$. 6 H_2O as directed above. This standard has a color of 500 units.

Prepare standards having colors in the range of 5-70, by diluting 0.5, 1.0, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, ---6.0 & 7.0 ml stock color standards to a final volume of 50 ml and measure at 465 nm.

Report sample pH. In pulp & paper mill effluents color measurement is carried out at pH of 7.6 at 25°C.

3. Procedure

Transfer a suitable portion of each standard to quartz cell of spectrophotometer and measure absorbance at 465 nm for calibrating the instrument. Measure the absorbance of sample at 465 nm. If color concentration is high, dilute the sample

4. Calculation

$$\text{Color, PCU} = \frac{\text{Sample absorbance at 465 x dilution x std. color values}}{\text{Absorbance of std. sample at 465 nm.}}$$

PCU = Platinum cobalt unit

NOTE: *The sample should be free of solids.*

ABBREVIATIONS

Part I

°A	Angstrom
APMP	Alkaline Peroxide Mechanical Pulping
BOD	Biochemical Oxygen Demand
BV	Bed volume
BKME	Bleached Kraft Mechanical Effluent
CMP	Chemi-Mechanical Pulping
COD	Chemical Oxygen Demand
CPCB	Central Pollution Control Board
CTMP	Chemi-Thermo Mechanical Pulping
EOP	End-of-Pipe
EPA	Environmental Protection Agency
ev	electron volt
gm	gram
gal/day	gallons per day
HNL	Hindustan Newsprint Limited
IR	Infrared
Kg	Kilogram
Kg / ton	Kilogram per ton
kg Pt/t	Kilogram Platinum per ton
mg Pt/t	Milligram Platinum per ton
m^3/min	Cubic meter per minute
mg/l	Milligram per liter
MyCOR	Mycelial color removal
NCASI	National Council of Air and Stream Improvement
NSSC	Neutral Sulphite Semi Chemical
PAA	Per Acetic Acid
Pt. Co. Unit	Platinum Cobalt Unit
PCU	Platinum Cobalt Unit
ppm	Part per million
RDH	Rapid Displacement Heating
SGW	Stone Ground Wood
SS	Suspended Solids
TOC	Total Organic Carbon
TMP	Thermo-Mechanical Pulping
UV	Ultra violet
μ	micron

Part II

CMP	Chemi-Mechanical Pulping
CP	Chemical Pulping
CSF	Canadian Standard of Freeness
CPPRI	Central Pulp & Paper Research Institute
CSRMP	Cold Soda Refiner Mechanical Pulping
DIP	Deinked Pulp
ETP	Effluent Treatment Plant
EOP	End-of-Pipe
g/l	Gram per liter
HNL	Hindustan Newsprint Limited
HPC	Hindustan Paper Corporation Limited
Hr	Hour
kg/cm^2	Kilogram per centimeter square
LP	Low Pressure Steam
min	Minute
mm	Millimeter
m^3	Cubic meter
m^2	Meter square
m^3/day	Cubic meter per day
m^3/hr	Cubic meter per hour
mg/l	Milligram per liter
MPM	Mysore Paper Mills
ONP	Old Newsprint
OMG	Old Magazine
PCU	Platinum Cobalt Unit
ppm	Part per million
Rs/t	Rupees per ton
SS	Suspended Solids
tpa	Tons per Annum
TMP	Thermo-Mechanical Pulping
TNPL	Tamil Nadu Newsprint Limited
t/day	Tons per day

Part III

Avg	Average
COD	Chemical Oxygen Demand
CMP	Chemi-Mechanical Pulping
CPPRI	Central Pulp & Paper Research Institute
CSRMP	Cold Soda Refiner Mechanical Pulping
ETP	Effluent Treatment Plant
EOP	End-of-Pipe
g/l	Gram per liter
kg/m^3	Kilogram per cubic meter
LPH	Liter per hour
m^3/day	Cubic meter per day
m^3/hr	Cubic meter per hour
N	Normality
PCU	Platinum Cobalt Unit
PI	Pressure Indicator
R&D	Research and Development
Rs/day	Rupees per day
Rs/ton	Rupees per ton
Rs/L	Rupees per liter
t/day	Tons per day
t/m^3	Tons per cubic meter
w/w	weight by weight