EXECUTIVE SUMMARY

OF

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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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:

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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

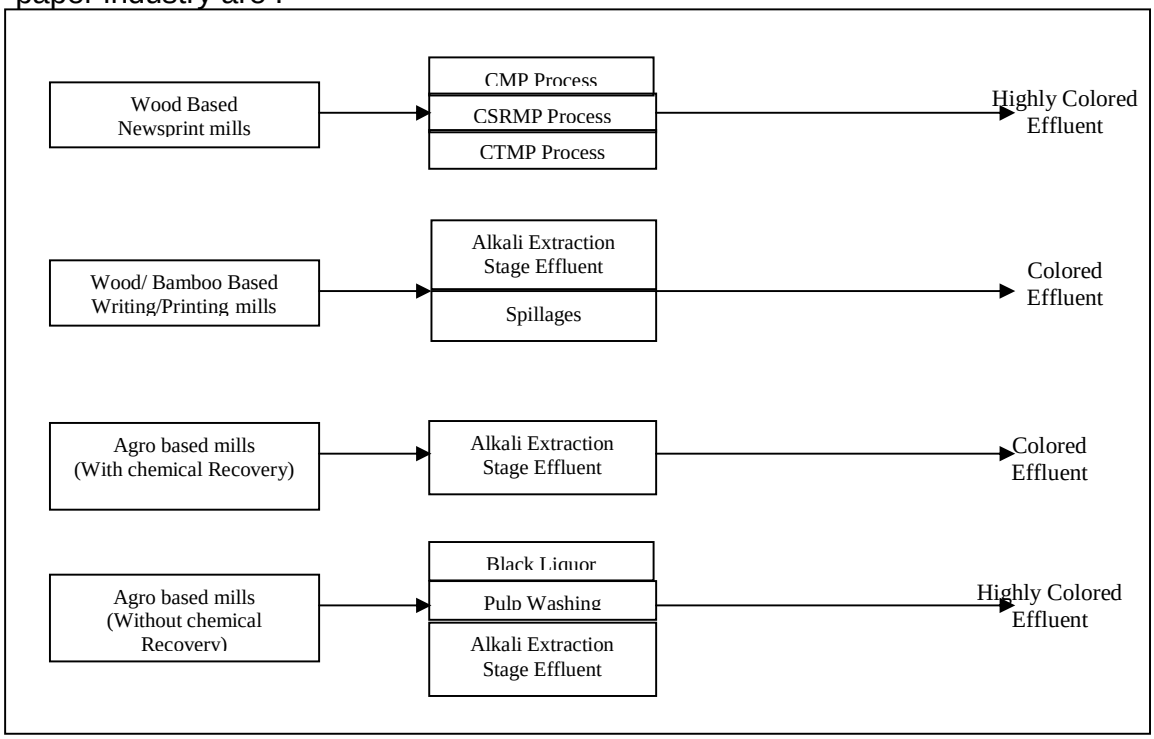
The Indian paper industry uses on an average 100 to 250 m^3 of fresh water/ton of paper and nearly 75% of which is discharged as effluent. In addition to high proportion of inorganics and organic pollutant the effluent from paper industry contains significant color loads. Although there is no stringent 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.