Some Chemical Aspects Of Color Removal From Effluents Of Paper Industry

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Pulp and Paper industry is one of the highest polluting Industries. The wastewater from this industry has very high propo :ion of organic pollutants and significant color loads. Although there is no stringent legislation to the tolerance limits for discharged color in effluents, by Central Pollution Control Agencies but some state pollution control authorities have imposed tolerance limits for the color in discharged effluents. The present practice of color removal involves precipitation and coagulation of colored substances using aluminium salts. Although such chemical treatment methods are expensive but the industry has perforce adapted these methods to contain the tolerance limits for color discharge.

Central Pulp and Paper Research Institute took the research project on color removal from effluents of paper industry with the main thrust to understand chemistry and response of various techniques viz. chemical precipitation, photo oxidation, electroflocculation etc. with an objective to evolve an economic treatment method. Studies were also directed towards the identification of different sources of color bearing components and their relative colloidal stabilities. From the studies, it was observed that extractives and lignin are major sources of color. In newsprint industry the color load is mainly due to extractives leached out during preseteaming and refining operations and in other pulp mills the color is mostly due to lignin. In small pulp mills the color load was due to spent pulping liquors discharged.

Studies on chemical treatment included different inorganic salts of Al, Ca, Fe etc. and polyelectrolytes like polyethylene oxide (PEO) and polyacrylamide (PAA). Studies reveal that lignin and extractives differed significantly in their colloidal stability and showed varying response towards precipitation and chemical coagulation on addition of electrolytes. Combination of Alum and was found to be effective in removing the color over 90%. The present paper highlights the colloidal chemistry of color bearing component and their response towards different techniques. The paper also discuss how the ionic strength, particle size of colloids, concentration of colloidal molecules influence the efficiency of color removal.

INTRODUCTION

Paper industry is one of the highly polluting Industries. The industry uses on an average 150 to 200 cubic meters of fresh water per ton of paper and nearly 75% of which is discharged as effluent. The effluent of paper industry contains highly polluting organic components. The Central Pollution Control Board has made tolerance limits for pollutional parameters like pH, Temperature, TDS, BOD, COD, etc. 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 agency but some states have imposed tolerance limits for discharge of the color.

The color load varies from mill to mill depending upon the raw material used, process employed, type of the end products and extent of closure of the system. In newsprint industry, the major color load comes from extractives leached out during presteaming and refining operations . In paper mills producing cultural papers the color load is attributed to discharge 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.

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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. The color can be categorized into two groups:

- Color due to colloidal particles (Dissolved color)
- Color due to relatively large colloidal macromolecules (suspended color)

It is easy to remove the color due to large 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 dose of chemical coagulants for precipitation and subsequent flocculation. In such a case the chemical treatment process becomes un- economical and some of the mills are spending nearly Rs. 800 - 1000 per ton of paper for removal of color alone.

Central Pulp And Paper Research Institute undertook the studies on color removal with the main trust on identifying the color bearing compounds in the effluents and their relative colloidal stabilities. The studies also include color removal using different electrolytes and polyelectrolytes and new emerging techniques eg. photooxidation and electroflocculation. The present paper highlights the chemical aspects of color removal and prospects of various techniques for economic removal of color.

SOURCES AND MAGNITUDE OF COLOR IN PAPER INDUSTRY

Pulp and paper mill effluents have a characteristic brownish black color, which is mainly due to lignin's, tannins and other extractives bearing, chromophoric groups. The magnitude of color depends on the raw material used process employed and type of end products. Lignin and extractives are highly polymerized substances and are difficult to bio degrade. Major sources and magnitude of color are given in Table - 1. The color in small mills is mainly due to lignin going through spent liquors. It is estimated that the quantity of lignin going through spent liquors varies from 300-400 kg/ ton of pulp, generating color load of about 1400-1500 kg PCU / ton of pulp. It was estimated that 90% of the color was due to lignin.

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

In alkali extraction stage effluent only about 50-60 kg of lignin / ton of paper (1) is going into effluents and the combine effluents will have color load of about 1500 PCU (2). In newsprint mills where eucalyptus constitute the raw material for production of mechanical pulp component, very high color load are noticed in the effluents. Eucalyptus contains about 3-6 % extractives, mostly tannins, which are leached out during pre steaming and refining stages. The washing of CMP pulp is highly colored and the color intensity is several times higher when compared to color due to lignin compounds. Hindustan News print Ltd. At Kerala state, today is facing serious problems due to high color loads in its effluents and the mill is incurring heavy expenditure for color removal, in order to meet the tolerance limits imposed by state authorities. Small mills with heavy lignin concentration in there effluents may find this difficult task to contain the color limits. Although central pollution authorities have not imposed the tolerance limits for color loads, but in the long run these mills will have to think seriously to contain the color loads. Similarly big mills although have relatively low color loads, will be looking forward to economic treatment methods for removal of color.

RESULTS & DISCUSSION

1. Chemistry of Color Removal

The particle charge, particle size and concentration color colloids play very vital role in the color reduction process, when the interaction is allowed with various electrolytes. The Fig. 1 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 ionise, adsorb and attract low molecular weight ions to its surface, which are held tightly to the colloidal surface, which is known as the stern layer. The remaining ions will be attracted to the particle and extend into the solution in the diffused layer also called Gauy-Chapman layer, until electron neutrality is established (Fig 2). The net charge on the colloidal particle is the strongest force inhabiting their removal. It is the interparticle repulsion that prevents colloids from colliding and forming large masses. By partial or complete neutralisation of their 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 large 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.

- Destabilization involving charge neutralisation
- 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 3 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 neutralises surface charge but also forms an insoluble complex with the colloid for destabilisation. In destabilised colloidal system collision 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 macrofloc. A portion of the colloids are removed by being physically entrapped in microflocs already formed. Fig. 1, Fig. 2 & Fig. 3 are depicted below:

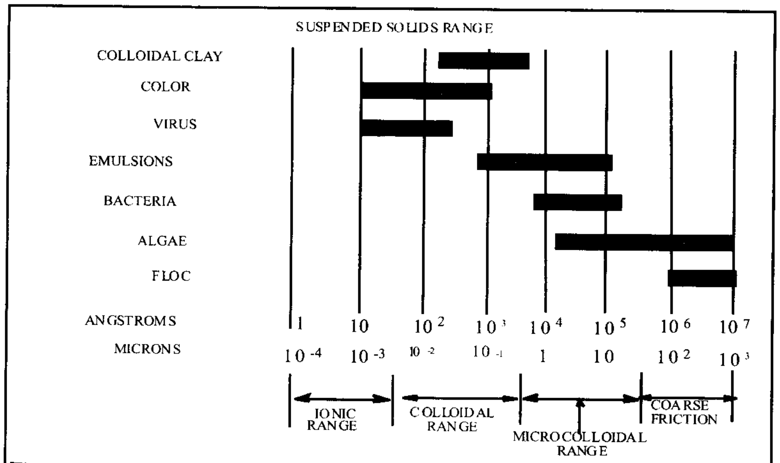

Fig. 1: Particle size of some common suspended particles

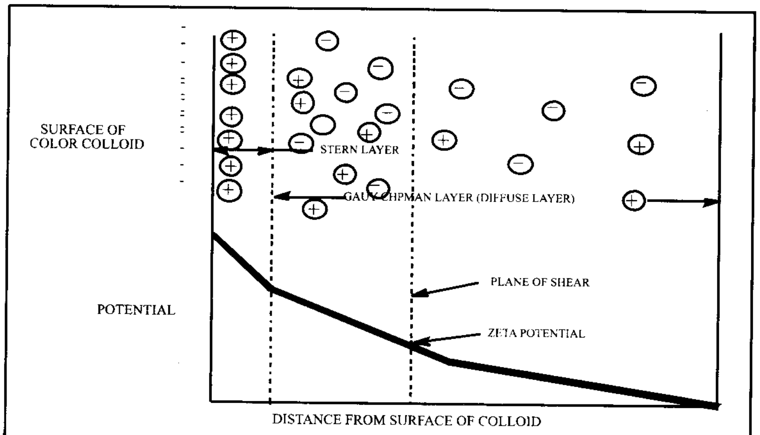

Fig. 2: Illustration Showing Charge Neutralization

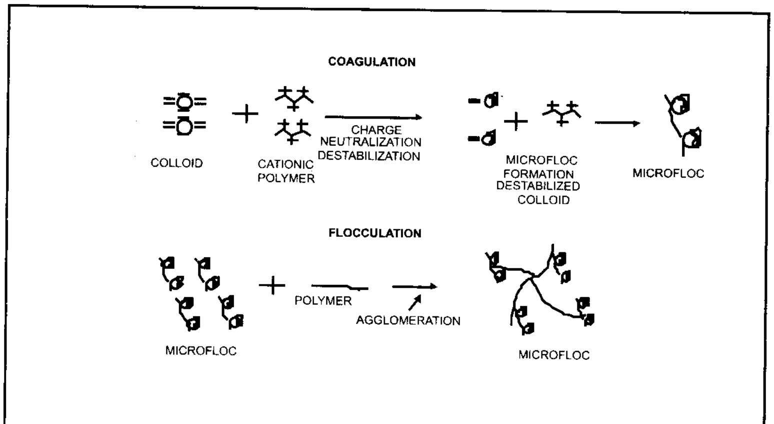

Fig. 3: Mechanism of Coagulation and flocculation

2. Present Practices and Chemicals used for Color Removal

The most commonly employed method for removal of suspended and colloidal particles is chemical treatment in clariflocculators. Some mills employ one stage clarification and some adopt two-stage clarification. Alum is the most commonly used chemical coagulant, because it is relatively cheaper than other chemicals. After removal of suspended matter the clarified effluent is sent for subsequent secondary treatment involving biological methods. Some mills segregate the high color, high solids effluents which are treated separately before mixing with low solids, low color effluent. However, present chemical treatment is capable of partial removal of color, COD and BOD. The dissolved color with micro colloidal particles enters the effluent stream. For instance, Hindustan Newsprint Limited (HNL) at Kerala state, a newsprint unit, is using massive quantities of alum to precipitate and coagulate the color bearing substances, mostly extractives.

Further such colloidal components precipitate as gelatinous and voluminous precipitate and are very difficult to dewater. After looking into various problems faced and heavy operational cost involved it is inferred that till today we do not have an economically viable treatment system for removal of color. Major challenges are to bring down the operational costs methods for dewatering of precipitated matter and possible utilization of sludge rich in organic matter.

CORPORATE RESPONSIBILITY FOR ENVIRONMENTAL PROTECTION IN PULP AND PAPER INDUSTRY (CREP)

In the year 2003 Ministry of Forest and Environment (MOFE) promulgated a directive and formulated charter on CORPORATE RESPONSIBILITY FOR ENVIRONMENTAL PROTECTION (CREP), where in effluent color have been identified as one of the pollutant for both small agro waste and large integrated mills. As per the directive industry has been asked to bring down the color load of the discharged effluent to a minimum practical limit by 2008. CPPRI had been entrusted with the task force of identification / development of an appropriate and economically viable technology.

The introduction of CREP has brought a major revolution in the pulp and paper industry both in large as well as in small sector with respect to technological upgradation and environmental management. CREP is going to have a significant impact on overall sustainability, technological and environmental status as well as competitiveness of our pulp and paper industry.

TABLE - 3

EFFECT OF VARIOUS ELECTROLYTES ON COLOR REMOVAL OF CMP WASHING EFFLUENT

Electrolyte	Dosage, g/l	Color Reduction, %	End pH
Alum	1.0	47.8	5.2
	1.5	92.7	4.8
	2.0	97.3	4.2
Calcium Chloride	1.0	35.0	6.4
	2.0	62.5	6.3
	3.0	60.4	6.3
Polyaluminium Chloride	1.0	74.5	5.5
	1.5	96.7	5.1
	2.0	99.0	4.6

Initial pH: 8.3 *Initial Color: 27260 PCU*

PH during addition of electrolytes: 6.5

STUDIES CONDUCTED AT CPPRI ON VARIOUS EOP OPTIONS

Keeping in view the CREP guidelines, CPPRI focused its R&D initiatives on identification and development of appropriate technology for color reduction and in the year 2003 initiated the R&D activities on identification and development of an appropriate technology for color removal. An exhaustive data search conducted, revealed that there was a wide variation in the color loads of liquid effluents generated by pulp and paper mills, India. This is mainly due to wide variation in the raw material usage and also in the process technologies, which varied from mill to mill. Table 2 summarises the magnitude of the color loads in the different pulp and paper mill 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)	8928	Extractives (Poly phenols & tannins)
Effluent from Agro based Mill	14,808	Lignin & Its degraded products

Among various EOP options, CPPRI extensively studied the chemical precipitation method, photo oxidation process and electroflocculation process to reduce the color loads in liquid effluents.

1. Chemical Precipitation

CPPRI had done extensive research on chemical precipitation methods for removal of color from liquid effluents. Initially studies were started with alum, $CaCl_2$ and PAC as chemical coagulant. The effectiveness of these chemicals are summarized in Table 3.

The results in Table 3 clearly indicate that the aluminium salts are more effective in color removal due to the fact that these aluminium ions from trivalent metal complexes with eater and these complexes contain number of repeating ion units which facilitate the destabilization step.

A good coagulation should also be proceeded by good settling, so that treated effluent is free from suspended precipitate. In Table 4 results of settling properties of

TABLE – 4

EFFECT OF ALUM & CALCIUM CHLORIDE COMBINATION IN SETTLING

Alum added, gpl	3.0	4.0	2.0	1.0
Calcium chloride added, gpl	-	-	1.0	2.0
Color Reduction, %	98.9	99.5	97.9	97.4
Volume of sludge, %	70	69	56	50

Initial pH: 8.51 *Initial Color: 32560 PCU* precipitate have been recorded which reveal that good settling could be obtained when calcium chloride was used in combination with alum. When alum alone was used the sludge was not compact and separation of clear supernatant could be hindered and this property of sludge did not improve even when alum dosage was improved from 3 to 4 gpl. With introduction of calcium chloride the sludge was more compact and this could facilitate phase separation more effectively.

All of these chemicals have found to be very effective but were sensitive to pH control. A feasibility study conducted by CPPRI at Hindustan Newsprint limited has revealed that the cost of treatment for CMP effluent with Alum is around Rs. 300/ ton, however the problems associated with are

- High sludge generation with poor stability
- Carry over of sludge due to lighter flocs.

The poor stability of the sludge was improved with the addition of polymers but with additional cost to the tune of Rs. 500/ton to achieve a residual color of 200 PCU from a initial color load of 10,000 PCU. The cost of treatment would however vary from case to case depending upon the initial color loads. Chemical precipitation method using polymer only has in practice in US mills but the treatment costs are pretty high. Keeping in view the limitation of chemical precipitation methods CPPRI during the last three years have focused its R&D activities on new emerging technologies for color reduction. The technologies studied are:

- Photo oxidation or UV irradiation process
- Electro flocculation process1.

leads to the complete mineralisation of the color substances to H_2O and CO_2 or biodegradable material. The mechanism for photooxidation is as below:

For Photooxidation, the source of UV radiation is UV lamps of different

$$H_2O_2 \longrightarrow 2HO^{\bullet}$$

$$\text{Organic Pollutant} + OH^{\bullet} \longrightarrow CO_2 + H_2O + \text{mineral acids}$$

(Complete decomposition of Organic pollutants)

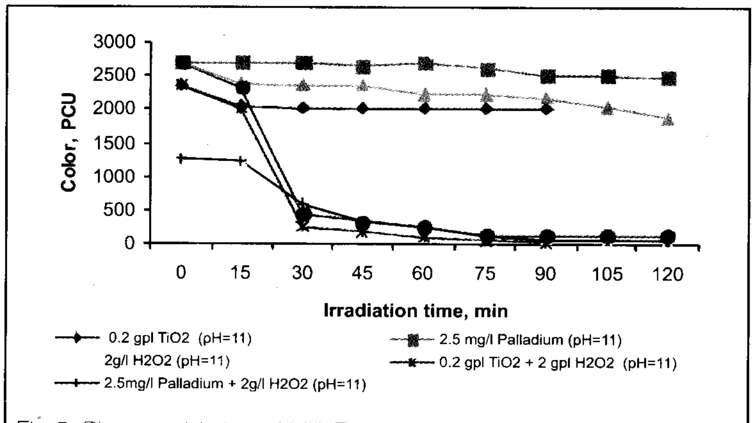

Fig.5: Photo -oxidation of Mill Effluent with different Catalyst

Source CPPRI Data

1. U.V. IRRADIATION OR PHOTO-OXIDATION PROCESS

U.V. 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 effluent.

The process is based on the generation of very active hydroxyl radicals (OH), which attracts organic compounds and initiate a series of oxidative reactions and ultimately wavelength. The results have shown that at 254nm wavelength, maximum degradation of colored component has taken place compared to UV radiation at 300nm and 350 nm. The results are depicted in Fig. 4.

The process is flexible at a pH range of 3 to 11 however essentially requires presence of oxidant (H_2O_2 / O_2 / O_3) for release of active hydroxyl groups. The studies revealed that presence of a catalyst reduces the reaction time drastically with improved efficiency. The findings are shown in Fig. 5. Fig.

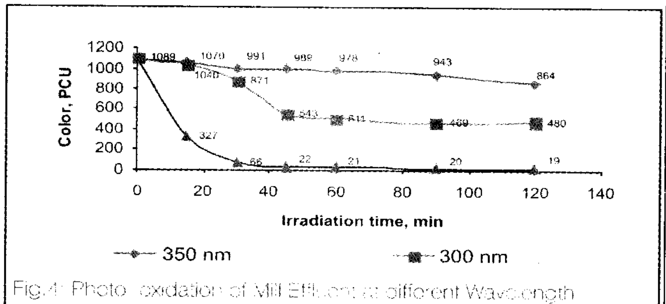

Fig.4: Photo oxidation of Mill Effluent at different Wavelength

Source CPPRI Data

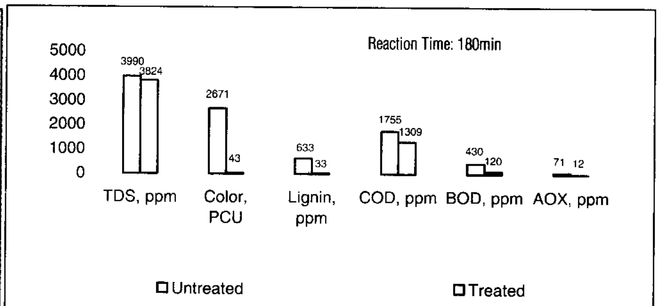

Fig.6: Process Effn of Photooxidation Process – E Stage

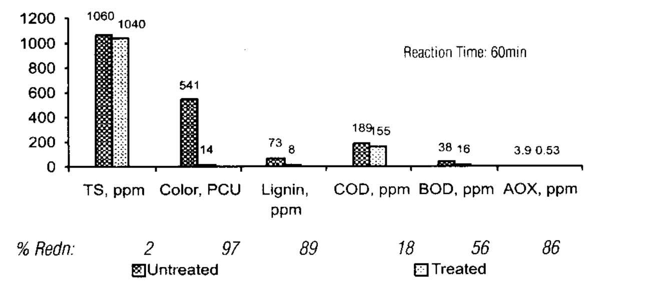

Fig.7: Process Effn of Photooxidation Process – Discharge Effluent

Source CPPRI Data

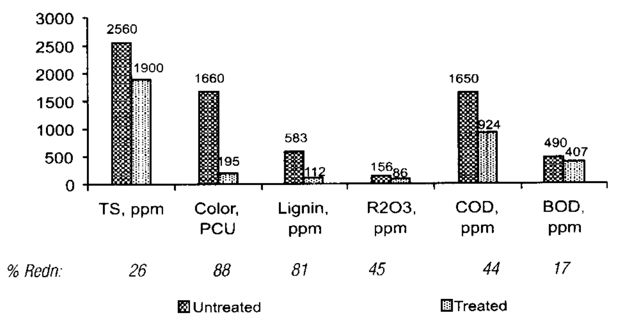

Fig.8: Pilot Scale Trials on Electroflocculation Process – Case I

Source CPPRI Data

6 & 7 depicts the efficiency of the process in reducing the pollution loads in E-stage effluent and final discharged effluent. The process is capable of reducing the brown color to absolute colorless effluent.

Advantages

- Very good for absolute color reduction
- Total elimination of organic components to CO2 and H2O and therefore no sludge generation
- A combination of catalyst and oxidant significantly improves the process kinetics

Limitations

- Best suited for tertiary treatments only
- Higher volume of effluent will need large contact area or more contact time
- Energy and cost intensive

2. ELECTROFLOCCULATION PROCESS

During the last two years CPPRI has done extensive R&D research in development of electroflocculation process from lab scale research to pilot scale research. The process have been found to be effective as primary treatment for removal of color from liquid effluents.

The process involves application of an electric current to sacrificial metal electrodes like Al, Fe or Mg having coagulating properties, generating metal ions and gas bubbles, simultaneously. The metal ion released, combines with pollutant and gas bubbles generated capture the coagulated agglomerates resulting in most of the pollutant being floated to the surface. The mechanism of the process is given below:

1st Step

At Anode $$M \longrightarrow M^{3+} + 3e$$

At Cathode $$2e + 2H_2O \longrightarrow 2OH^- + H_2$$

2nd Step

$$M^{2+} + OH \longrightarrow M(OH)_2 . MOH^+$$

(Insoluble)

$$M(OH)_2 . MOH^+ + \text{Color Bodies}^{(-)} \longrightarrow \text{Flocs}$$

3rd Step

$$\text{Flocs} + H_2 \longrightarrow \text{Floats}$$

Present Status

Encouraged with the findings of process on lab scale, CPPRI decided to demonstrate the technology on pilot scale. Jointly funded by CPCB and Industrial Partner (M/s Century Pulp & Paper Mills, Lalkuan), the project was executed by CPPRI and a

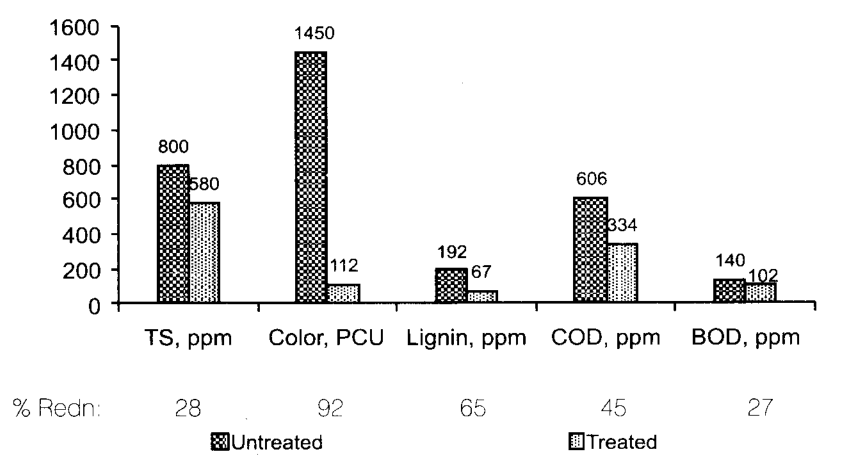

Fig.9: Pilot Scale Trials on Electroflocculation Process – Case II

pilot plant of 1 m^3/hr capacity was fabricated, installed and successfully commissioned at CPPM, Lalkuan. The plant is operating on continuous mode. The results of process efficiency are depicted in Fig. 8 & 9.

Pilot scale trials conducted on continuous mode has revealed that electroflocculation process is technically feasible and presently economic viability of the process is being studied for different colored streams

CONCLUSION

1. The positive response of color colloids with the cationic coagulants like Alum, Calcium Chloride, Polyaluminium chloride, Ferrous sulphte, etc. where the trivalent Al & Fe and divalent Ca are predominant show that coloring bodies are negatively charged.
2. The color is present in the effluent as true color in the form of micromolecules or suspended color as macromolecules. It is easier to precipitate the macromolecules by addition of electrolytes as compared to the color due to micro-molecules which need a higher dosage of electrolyte to precipitate.
3. Chemical precipitation method is presently being practiced in many mills using a combination of coagulants and flocculants but the process has certain limitation.
4. Besides the cost, the sludge generation is very high and disposal of such huge volumes is a problem. It also increases the anionic concentration of the effluent.
5. In view of CREP guideline and the limitations of chemical precipitation methods, CPPRI did extensive studies on new technologies viz, Photo-oxidation & Electrofloculation.
6. Photo-oxidation is a promising technology as it eliminates the organics to CO_2 and H_2O resulting to absolute reduction of color. The process has been well established on lab scale and need to be evaluated on Pilot scale for its techno economically feasibility. This treatment is however suitable for tertiary treatment only.
7. Electrofloculition process developed by CPPRI has been found to be promising as a primary treatment for color removal. The technical feasibility of the process on continuous operation has been established. The economic viability is being studied for different colored effluents with respect to different levels of final achievable color.

REFERENCES

1. Subrahmanyam, P. V. R., Parekh, R.C. and Mohan Rao, j. G., Ippta, Vol. 9, No. 1, 1972, p. 14.
2. Sharma, G. D., Singh, M.N. and Agarwal, N.R., Ippta , Convention: 124(78).
3. 'Pollution Engineering practice Handbook' Ann Arbor Science Publishers. p. 419-426 (1975).
4. Hillis, W. E., Wood extractives and their significance to pulp and paper industry. p.59, Academic Press, New York-1962.
5. Kulkarni A.G., Mathur R. M., Gupta Abha and Pant, Rajesh. Ippta, Vol. 24, No. 3, !987.
6. Metijevic, E. and Janauer, G. E., J. Colloidal Interface Science, 21:68 (1966).
7. Matijevic, E. and Stryker, L. J., J. Colloidal Interface Science, 22:68 (1966).
8. Fernandes, J. D., Thampi, K. P., Prahaladhan, V. M. Singh, Sarju, Ippta, Vol. 22, No. 2, June 1985.
9. Kulkarni, A. G., Mathur, R. M., Tandon Rita, Naithani, S. and Pant, Rajesh, Ippta, Vol.25, No. 1, 1988.
10. Kulkarni, A. G., Mathur, R. M., Abha Gupta, Naithani, S. and Pant, Rajesh, Ippta, Seminar, 1989.