Color Removal from Pulp and Paper Mill Effluent - Methods and Industrial Applications - A Review.

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ABSTRACT

Color and odour from integrated pulp and paper mill has been a matter of concern, on aesthetic sense, which has also been addressed in the CREP guidelines for the pulp and paper industry. Though the odour problem has been taken care by installing systems for NCG collection and combustion, the color removal from effluent, on a continuous industrial scale, has been an aspect of research for several years. Many technologies and methods have been tried out successfully in bench scale and even on pilot plant scale. However there is no proven method for color removal from pulp and paper mill effluent, so far, on an industrial scale. There has been several promising methods demonstrated, which need a combination of techniques. This paper reviews the color removal techniques so far studied. Color reduction at source is the most practical.

Introduction:

Pulp and paper industry being categorized under the Red category of polluting industries, it has been under tremendous environmental pressure, to improve the performance related to pollution. Water consumption being large, the effluent volume generated is also large. The effluent treatment processes adopted guarantee the achievement of parameter values below the Pollution control board norms, including specific effluent discharge. Mills have changed over to Elemental Chlorine Free (ECF) bleaching resulting in substantial improvement in effluent quality with regard to TDS, Color, COD and AOX. However, as a treatment process for continuous scale removal of color from effluent, no viable method has been demonstrated so far. Studies have been carried out on color removal of pulp and paper mill effluent, which include Chemical decolorisation, Coagulation, adsorption, membrane separation, Electro coagulation, fungal decolorisation, Chemo-Autotrophic Activated Carbon Oxidation (CAACO) process etc. All these processes have no doubt proved to be efficient in removing color from pulp and paper mill effluent. The crux of the issue lies in translating these methods on industrial scale, for an effluent volume as high as 2000-3000 m3/hour. Many of the references on color reduction focus on reducing the color at source of generation, rather than adopting end-of-pipe treatment methods. Controlling the color at source through control of spillages, washing losses, overflows, brown loop closure, reducing kappa number through Oxygen delignification, Ozone bleaching has been commercially successful. The industry is still on the look out for a viable color removal method, on a large scale. Various color removal methods studied so far, have been discussed which warrants combination of techniques.

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Source of Color in pulp and paper mill effluent

The pulp and paper mill effluent color is derived mainly from lignin and its derivatives removed during pulping and bleaching processes. The effluent generated from papermaking is almost colorless carrying a small tint of the dyes. The major source of color is from the pulp mill process. The overflows and effluent from brown stock washing area is a major source of color. The black liquor remnants getting washed during screening and thickening operations get drained imparting high color to the effluent. Recent pulp mill installations have incorporated the brown loop closure to prevent any liquor or washings finding their way to the effluent. In addition chemical recovery is also an added advantage. The other color source is from bleaching section, where very little scope is available for reuse of filtrate. The caustic extraction stage filtrate is the highest colored effluent among the effluents from different stages of bleaching. The color load from other bleaching stages is low. So the two major color inputs are from brown stock washing area and caustic extraction stage.

Color reduction at source Methods and techniques

Minimizing color load - control at source:

As discussed earlier lignin compounds, which are complex in nature are the source of color. Hence every attempt to minimize black liquor filtrates will considerably reduce the color of final effluent. Usually collection sumps are made to collect spillages and overflows in brown stock washer area, which can be then pumped back, Of course the collection sump needs a level control, so that the sump does not overflow into the effluent channel. Also periodical desludging to remove settled matter is also essential.

The second attempt to control is to

minimize alkali carryover during washing. The carried over alkali along with brown pulp gets usually removed at the screening and thickening stage and the filtrate has a high color of 4000-6000 Pt.Co. Units. The filtrate can be taken to the brown stock washer spray through heat exchanger, since Decker sprays are usually with cold water only, while brown stock washing needs a minimum of 70°C temperature for spray water. Modern twin roll presses are more efficient in COD removal during washing and thickening and specific water consumption is also lower. The conventional drum washers however require higher amount of wash water and consequently effluent generation is also more. Mills also use wash-aid chemicals to improve washing efficiency and to reduce the alkali loss in pulp. These aid to reduce the color load to the effluent.

In addition, the bleach plant effluent color load is a direct consequence of the kappa number and the alkali loss carryover. Reducing the kappa number of the bleach plant inlet pulp results is proportionate color reduction in bleach plant effluent. Techniques such as Oxygen delignification and use of Digester additives to reduce kappa number of digester outlet pulp are the common approaches to reduce kappa number. Oxidative extraction using peroxide and/or Oxygen is also adopted which reduce the extraction stage effluent color significantly.

Measurement of color:

The pulp and paper industry has adopted the standard method for color measurement, which is absorbance of 465nm light by a sample adjusted to pH 7.6 and filtered through an 80µ filter. Color is reported in standard color a unit that represents the concentration of a color standard solution producing an equivalent degree of absorbance of platinum as Chloroplatinate. (1) This has been defined under EPA/NCASI standard laboratory procedure and is reproducible.

Color removal techniques - End of pipe treatment methods-Literature references

A number of techniques have been tried for color removal from pulp and paper mill effluent. Quite a large number of publications are available on the subject- all restricted to laboratory scale/bench scale/pilot plant scale. There is no proven demonstrated technique for color removal on an industrial continuous scale from an integrated pulp and paper mill effluent.

Some of the end-of-pipe color removal methods studied are based on

- Physical - Adsorption
- Chemical- oxidative decolorisation
- Biological-fungal/Enzymatic decolorisation
- Electrochemical decolorisation
- Chemical Coagulation and precipitation
- Membrane process
- Photo oxidation
- Ion exchange

Physical adsorption method:

Color removal using fly ash and cinder

The fly ash and cinder generated in boilers have found to have color adsorbing effect. They act similar to activated carbon and adsorb the color bearing compounds when effluent is passed through. The efficiency of process depends on the particle size and surface area of the ash. The color removal by this technique could not be extended to a large scale. Also the color reduction started coming down as the ash gets saturated and regeneration of ash is not possible. As a once through system also, efficient mixing of ash and effluent necessitates mixing of ash at low concentration and then removing the ash through settling and filtration, which is not possible on an industrial scale.

Ion exchange resin Sorption system

Three processes namely DOW, ROHM and Haas process and the Uddeholm-Kamyr (Billerud) process. (2) The effluent is passed through highly cross-linked resin possessing no ion exchange properties. The resin functions best at pH of 2.0 to 2.5, which can be achieved by mixing acid and alkaline bleach effluents. Decolorisation efficiency of 85-92% have been reported. The resin regeneration using weak wash transfers color components to green liquor in smelt dissolving tank. The Billerud process also adopts ion exchange system commercially. But resin life is too short (six months). This has increased the operating costs. Kamyr installed a unit based on Billerud concept in Japan which was abandoned due to resin fouling problems.

Chemical Oxidation

This process has been to some extent practicable. Use of oxidants like Ozone, Peroxide, Peroxymonosulphate, Hypo, Chlorine di Oxide, Peracetic acid and Chlorine. Oxidizing agents can accomplish the destruction of both chromophores and toxic compounds. The cheaper oxidants being Chlorine and hypo, pose problem of organochloride by products. Others are expensive or unstable or both. So the chemical oxidation process is adopted as a pretreatment step to degrade compounds that otherwise resist biological treatment.

Ozone decolorisation has been found to be a very effective method. But the only problem is generation of Ozone at low cost. Ozone being unstable has to be generated at the point of use. Heightened interest in the Ozone bleaching has spurred improvements in ozone generator technology making it more economical. A related obstacle in successful application of ozone for effluent color removal is the quantity of carrier gas to be handled. Ozone auto-decomposition increases with increase in ozone concentration and temperature. The modern systems recycle the carrier gas to reduce its consumption, but they are economical only for largest system generator capacities. But as color levels go down, the Ozone requirement also goes down making it more affordable. (3)

Photo-oxidation:

UV irradiation laboratory studies have shown that the bleach effluent color can be completely reduced, in presence of active titanium dioxide. The rutile form of Titanium di oxide can be used, which is a photo chemically active semiconductor, which converts light energy into reactive radical .OH, which are extremely reactive. The photo catalysis has been adjudged the best potential application for color removal but has been tested only up to bench scale level. The power requirement equivalent makes it extremely expensive, though 90% decolorisation is achieved.(4)

Electrochemical process:

The electrochemical process is a REDOX process driven directly by electrochemical energy. About 80%

color removal from bleach plant effluent from Kraft process has been reported. The color removal from caustic extraction stage has been 90%. Studies have been made on several effluent streams and different electrode types. One of the process variation studied utilizes the froth produced from hydrogen bubbles to float out the suspended solids out of the system. Electrochemical systems are effective but operating cost is high since much of the electrochemical energy is consumed in non desirable side reactions. (5)

Coagulation and precipitation:

Chemical coagulants cause formation of a sludge phase that can be separated by density difference. A variety of coagulants have been studied for colour removal which include Lime, Alum, Ferric/Ferrous iron pickle liquors, Fly ash, sulfuric acid, polyamines. Good color removal has been obtained. But sludge separation, removal and disposal considerations have been a bottleneck.(6)

Membrane process, Ultra filtration

A membrane process uses a membrane to separate a fluid mixture into rich and lean fractions. Ultra filtration (UF) and Reverse Osmosis (RO) are the two most widely recognized examples. The fluid pressure is the driving force in UF/RO process. The method is efficient as color removal technique but membrane life and disposal of rejects is again a serious problem. Membrane fouling creates a marked decrease in flux rate. This can be prevented by pretreatment of effluent to remove particulate and colloidal matter. Pressure pulsing and detergent cleaning are also adopted. Zaidi et. al. presented an overview of developments of UF technology as applicable to pulp and paper industry which regards membrane process as technically feasible. But the UF/RO full scale conversions have not developed because of the following reasons

- Concentrate disposal to recovery is expensive modification
- Concentrate disposal to recovery also creates system corrosion due to increased chloride concentration
- Membrane fouling has been a problem
- BOD and acute toxicity are amenable to biological treatment

Two other obstacles reported include high operating cost and very high associated costs for capital, membrane replacement and maintenance. (7)

Biological processes:

Degradation of lignin by fungi has been elucidated by several investigators. Microbes have been engineered to produce enzymes that degrade lignin, at least under laboratory conditions. Currently there is one process MYCOR process applicable to color removal. The mycelial color removal (MYCOR) uses Phanerochaete Chrysosporium to metabolize lignin color bodies and remove color. The fungus is grown on rotating biological contactor, and effluent is decolorized. But the process is not economical because it is not self sustaining with respect to growth of fungus. This process can be used effectively in combination with physical and chemical treatments.

Color removal processes-present practices at TNPL

A hierarchical approach to color reduction is beneficial. The four levels to be considered are

1. Prevention and minimization
2. Reuse and recycle
3. Destruction
4. Separation and disposal

The most desirable level being prevention and minimization, following steps have been taken to reduce color of effluent

1. Technology updating: new fiber line for hardwood incorporating Oxygen delignification and brown loop closure. Introduction of ECF bleaching technology and installation of state-of-the-art twin roll presses for pulp processing.
2. Oxidative extraction: In old conventional bleach plant peroxide reinforce oxidative extraction was adopted to reduce color of effluent

Reuse and recycle methods:

1. Collection sump: Spillages of black liquor are collected in sump both in pulp mill and soda recovery to avoid entry of black liquor leakages into effluent stream.
2. Reuse of Decker filtrate in Brown stock washing: The Decker filtrate generated during thickening of screened pulp is used back in brown stock washing.
3. Recycle excess Decker filtrate in bagasse washing

Destruction techniques

As of now no color destruction techniques such as oxidation, biological treatment or electrochemical methods are adopted. However bench scale studies have been carried out with these techniques.

Color removal/separation system:

Alum coagulation for color removal was followed for some time, for anaerobic effluent stream. This was subsequently changed to ferrous chloride pickle liquor treatment, and is being followed continuously.

Color removal studies undertaken at TNPL so far:

1. Fly ash adsorption

Effluent decolorisation studies on bench scale were carried out with Fly ash from boiler. Cinder was also used. The color removal efficiency was found to be correlating with the surface area and Iodine absorption value of the adsorbent. Color removal efficiency of 90% could be achieved. When the adsorbent gets saturated with color bodies, the same has to be replaced. Doing this on an industrial continuous scale is difficult. Filterability of the fly ash is also slow requiring long time for filtration. When particle size is higher filtration is faster, but color removal is lower. Also the pH of the effluent was found to shift over to acidic side requiring neutralization before disposal.

2. Alum/Polymer coagulation

As a tertiary treatment option, the final treated effluent was treated with Alum which is capable of coagulating coloring bodies at pH 6.0, along with polymer combination, for faster settling of the coagulated color. The final treated effluent color of 200 Pt.Co could be reduced to 20-30 Pt.Co units, with alum dosage of 200 ppm and polymer dosage of 2 ppm. The treatment system warrants a clariflocculator type clarifier to remove the alum-color sludge which is very light and gelatinous. Filterability and disposal of sludge is again a point of concern. Also increase in sulphate content and Alumina in effluent is not desirable.

3. Zeolite based process

The process developed by National Chemical Laboratory, Pune was studied for our final treated effluent. 500 ppm dosage of Zeolite based chemical could totally remove the color of final treated effluent. The process could not be adopted as the Zeolite based product was not available on large quantity as required by the mill and also the cost economics could not be arrived based on lab scale.

4. Ferric chloride/ Ferrous Chloride

	Alum	Ferric Chloride	Ferrous Chloride
Concentration	100%	24%	24%
Dosage ppm (100% basis)	800	200	200
Initial color Pt.Co.	480	480	480
Final Color Pt.Co.	210	236	230
Color reduction %	56.0	50.8	52.1
Cost Rs/1000 KL	150	93	56

The ferric pickle liquor coming out as a by product waste was found to be effective in coagulating the color. The product was found to be suitable to remove suspended coloring bodies, in the anaerobic stream effluent. The anaerobic stream effluent after biogas generation has a blackish tint, due to suspended colloidal particles. Alum coagulation @ 1000 ppm could reduce the color from 600 Pt.Co. to 200 Pt.Co. This could be replaced with 160ppm of Ferric chloride (25% $FeCl_3$ concentration) with similar color removal efficiency, at a lower cost. The same was implemented on a continuous plant scale. Ferric chloride was added at the clarifier inlet channel and the coagulated coloring material was settled in clarifier and underflow was removed along with the primary sludge, after dewatering. The Ferric chloride treatment was subsequently replaced with Ferrous chloride. The comparative performance of Alum, Ferric chloride and ferrous chloride for anaerobic effluent treatment, in the plant, are given above.

5. Fungal decolorisation

Some of the lignin degrading enzymes that attack the raw materials during storage are found to improve the brightness of the wood. The white rot fungi are capable of removing the color associated with lignin compounds. In this regard works were carried out on laboratory scale on decolorisation of effluent using fungal culture isolated from bagasse pile.

6. Electrochemical decolorisation

Electrochemical decolorisation using Iron Cathode and Aluminium anode was tried for different effluent samples on laboratory scale. A continuous bench scale experiment was also conducted with the electrode combination. The current density was also varied. The results of the laboratory electrochemical decolorisation are presented below for the final treated effluent as a tertiary treatment step.
The current density, time, temperature and electrode pair combinations were optimized for the above experiments as a batch process.

The experiments were performed on a

Sample	pH	Color Pt.Co.	Color reduction %	Conductivity μmhos/cm	COD ppm	COD reduction %
Untreated	7.68	325		1964	133	
Treated	7.62	60	81.5	1792	98	26.3
Treated at pH 4.0	5.62	08	97.5	1994	67	49.6

bench scale continuous process also by constructing a cell of stainless steel cathode and Aluminium tube anode with a capacity of 5 litres. The effluent flow was 500 ml/min with a retention time of 10 min in the cell.

PHOTO - 1
BATCH PROCESS ELECTROCHEMICAL DECOLOURISATION CELL

PHOTO - 2
CONTINUOUS PROCESS ELECTROCHEMICAL DECOLOURISATION CELL

Continuous scale decolorisation showed 85% color reduction with a final color level of 60 Pt.Co units. (8)

The process showed poor response to extraction stage effluent and the color reduction was low (10% only). Color removal efficiency is high at 4 pH. Aluminium electrode was found to be more efficient than mild steel. The process efficiency increased with increased current density.

7. Resin decolorisation

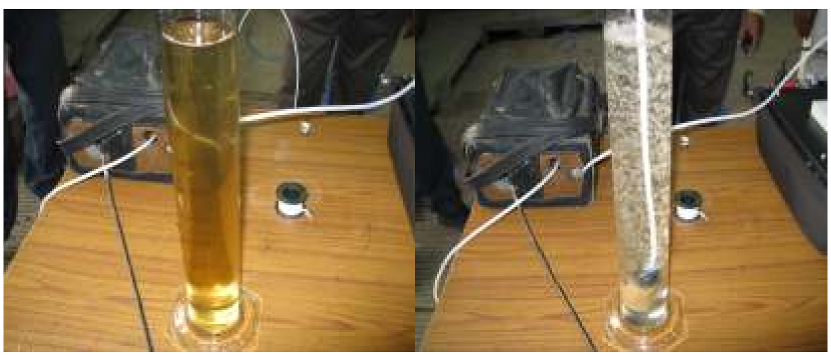
Decolorisation experiments using ion exchange resins were performed as a tertiary treatment option. A resin column was made using laboratory burette and sample of effluent was passed through the column and the color removal was studied. The results of the resin decolorisation are of final treated effluent are presented below

Resin column: 10g of 10 cm height
Effluent flow: 23 ml/min
Effluent initial color: 225 Pt.Co. units

The color started increasing after passing 600ml for 10 g of resin. No change in pH or conductivity observed. The color removal was stable. The back washing and regeneration of resin could not be established.

Volume of effluent passed through resin	Color Pt.Co.	Color reduction %	pH	Conductivity µmhos/cm
Initial	225		7.30	2400
225	20	91.1	7.00	2470
295	35	84.4	7.57	2470
345	50	77.8	7.96	2470
480	60	73.3	8.12	2470
580	60	73.3	7.96	2470
680	65	71.1	7.97	2470
780	70	68.9	7.93	2470
880	100	55.6	7.86	2470
1000	125	44.4	7.386	2470

	pH	Color Pt.Co.	**Color reduction %**	COD ppm	**COD reduction%**
Untreated effluent	7.6	220		189	
After Ozone treatment	7.6	50	**78**	161	**15**



Effluent	Technique	Color reduction%	Reject %	Reject disposal
Hardwood Decker filtrate	UF → NF	100	22% at 46 gpl	Soda Recovery
Chemical bagasse decker filtrate	UF → NF	100	18% at 39 gpl	Soda Recovery
Extraction effluent	UF → NF	100	26% at 43.5 gpl Cl^- 3.6 gpl	Soda Recovery (?)
Foul condensate	UF → NF	100	23% at 0.72 gpl	Brown stock washing
Bagasse washing	SF → µF → UF → NF	100	32% at 10 gpl	Biogas plant
Final effluent	µF → UF → RO	100	72% at 1.78 gpl TDS	Reject disposal is a problem

UF- ultra filtration, NF Nano filtration, µF Micron filter, RO- Reverse Osmosis.
Pay back 10 yrs, Membrane life not guaranteed.

8. Chemical decolorisation

a. Ozone

Ozone decolorisation of the different effluent samples was carried out in laboratory, using Ozone generator. Preliminary experiments carried out on laboratory scale have shown complete color removal from the effluent, as a tertiary treatment option. Though the Ozone removes color from different effluent streams, the consumption again depends on the COD level of the effluent, which reacts with the Ozone first, and then the color. The exact specific consumption and cost economics could not be worked out from the laboratory scale experiments. Continuous pilot plant trials have been planned to assess the cost economics of the Ozone treatment for color removal as a tertiary treatment option. The results of the laboratory experiments are presented in table on left.

Based on the above continuous pilot plant decolorisation of final treated effluent using Ozone has been carried out to assess the specific ozone requirement and color reduction obtained, so as to arrive at the cost economics. At a dosage of 50ppm Ozone color reduction of 80% could be achieved on a continuous pilot scale. Further optimization trials are underway.

9. Membrane technology

Extensive trials were carried out with different effluent streams, with membrane filtration process. A combination of Ultra filtration and reverse osmosis was also tried for some effluents. The results of the membrane filtration trials are given here for different streams studied.

Disposal of concentrate is the main aspect of concern in membrane filtration. So as a tertiary treatment step, this process is not attractive. Whereas in case of effluents like Decker filtrate and Foul condensate, the concentrate could be managed by taking them to recovery. However the life of membrane and recurring cost could not be guaranteed, which made the process very costly. The gelatinous nature of dissolved lignin poses choking of the membranes, which makes cost of membrane replacement exorbitant. Membranes usually work well while removing inorganic TDS.

	pH	Color Pt.Co.	TDS ppm	COD ppm
Final effluent	6.1	125	1248	160
CAACO treated	**3.4**	**25**	**1236**	**111**
% Reduction		**80.0**	**0.96**	**30.6**

10. CAACO process

The Chemo Autotropic Activated Carbon Oxidation (CAACO) process developed by the Central Leather Research Institute, CLRI, Chennai, for tannery effluents containing mostly tannins, involves Chemo Autotropic activated carbon oxidation (CAACO), through a reactor. The reactor is filled with activated carbon immobilised with specific bacteria to oxidize the organic matter into Carbon di oxide. Thus most of the organic TDS gets removed and thus color is also removed from the effluent. The process is being studied for pulp and paper mill effluent also. Preliminary results for the final treated effluent, are tabulated above.

The CAACO process has been adopted in commercial scale for tannery effluent color removal. The tannery effluent volumes are low compared to Pulp and paper industry. Studies are being carried out with CAACO process with a pretreatment step using Fenton's reagent. The outlet of CAACO is being studied for Ozone decolorisation subsequently.

Conclusions:

Color removal from pulp and paper mill effluent using different techniques work well in bench scale. On an industrial commercial scale, no proven technology for color removal on continuous scale is available. Studies are still on to formulate a viable method of color removal as a tertiary treatment for pulp and paper mills. Color reduction techniques such as color reduction at source, color removal of dark effluents after segregation and treatment can be adopted to minimize the color. But Color reduction at source through technology improvements is more attractive and practical than end of pipe treatment.

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