

Colour removal from kraft mill effluents a review

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The problem of color removal from pulp and paper mill waste waters has been a subject of study in the last few decades. Discharge of substantial ratios of untreated mill effluent into stream has long been recognised 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.

The color in kraft mill waste waters is mainly due to lignin and its derivatives. 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 large volume of effluents contain both dissolved organic and inorganic solids along with a high chloride content. These properties rule out disposal by evaporation and subsequent incineration in the recovery furnace. Therefore a number of internal and external techniques have been developed to reduce these pollutants.

Measurement of Effluent And Receiving Water Color Levels

Standard procedure involves visual observation of color samples with standard potassium chloroplatinate-cobaltous chloride solution. Color is usually expressed as APHA units.

Methods recommended for color measurement includes

- (a) Adjustment of sample to pH 7.6
- (b) Filtration of less than 50ml of sample through a 0.8 micron membrane filter and

- (c) Comparison to Platinum—Cobalt colour standard at a 4.65μ wave length.

This standard method does not recommend removal of turbidity.

Status of State And Federal Effluent Color Regulations

Although tolerance limits for discharge of industrial effluents into surface waters (ISI report 1974) do not quantitatively stipulate any limits for colour they state that the effluents should not have a COD of more than 250mg/lit. If kraft lignin alone is the COD contributing material in the treated effluent, then 250mg/lit. of COD will be equivalent to 140 mg/lit. of lignin. This effluent at 7.0 pH will exhibit about 1400 units of color on platinum cobalt scale. It becomes therefore necessary to remove color before they can be accepted into surface waters.

Source of Color Effluent in Kraft Mill

A survey indicates that about 80% color load is from the bleach plant effluents. Other sources of color effluent in a kraft mill are—

	Percentage Color Load
1. Kraft pulping and Recovery	.. 9%
2. Chlorination	.. 5%
3. Bleach caustic extraction stage	.. 76.2%
4. Paper mill sewer	.. 1.2%
5. Combined mill sewer	.. 8.6%

Internal Color Load Control Without Major Technology Change

With indications that the pulp mill accounts for between 65-85% of the total mill color load which is mainly due to pulping liquor losses, attention to the following measures should produce significant improvement.

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(a) **More Extensive Pulp Washing :**

Achievement of 98% efficient liquor separation certainly a realistic goal should reduce color load to the great extent. Closure of screening system losses and further attention to pulp washer system optimization from a BOD load stand point as well should prove beneficial. Moves in this direction includes in digestion diffusion washing as well as addition of external washing stages.

(b) Prevention of evaporator carry over and recycling of evaporator boil out.

(c) Retention of pulping liquor spills and leakages.

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

While continuous color measurement has not reached the application stage, it should be possible in its absence to develop useful correlation with other measurable parameters such as conductivity, which would lead to detection and prevention of color load losses again in terms equivalent to the basic problem of BOD load control.

Physical Methods :

Adsorption:—Among the different adsorbents, such as slag, flyash, activated carbon and soils used for color removal only activated carbon seems to hold promise. A no. of reports are available [(1) Dorica & Wong, 1979, (2) Grossman et al., 1979, (3) Gahin & Drause, 1979] on the application of activated carbon in treating various pulp mill wastes. In the light of high costs involved in decolorising, it is considered appropriate to use activated carbon treatment as a polishing step after lime decolorisation process (4). This step may prove economical only if reuse of treated effluent for mill processes is considered.

Results are now available from a four year pilot plant programme of St. Regis Paper Company, USA in which staged treatment involving : a Primary clarification, (b) bio-oxidation, & (c) Lime treatment and carbon adsorption was studied in various configurations. The most economical process was found to involve low lime addition followed by carbon adsorption in down flow granular carbon beds (5). Carbon adsorption in continuous, counter-current stairred contactors was also believed to have promise of lower operating costs and

substantial lower capital costs. Activated carbon treatment preceded by massive lime treatment may make it economic.

Resin Separation Processes :—The resin separation approaches which have been considered include (a) Reverse osmosis membrane separation, (b) Ultrafiltration, (c) Electrodialysis, (d) Ion exchange, and (e) granular resin separation through non-ion exchange processes. Dynamically formed membranes are also currently under study. Reverse osmosis, ultrafiltration and electrodialysis are the three forms in which membrane techniques have been applied for colour removal (RHC report, 1971). The main disadvantage is the fouling of the membranes requiring their frequent replacement. The power requirements are also high prohibiting the use of membrane techniques on a commercial scale. The results of an extensive laboratory and field study in reverse osmosis processing a number of pulp and paper waste streams were reported in 1972 [(6) Kowalczyk, 1979, (7) Sanks 1973]. Color rejection from kraft caustic bleach effluent was in excess of 99% using cellulose acetate membranes.

Reduction of color from pulp mill effluents by ultrafiltration has been examined by Champion International Corporation, USA. The pilot plant consisted of a five stage circular mould cellulose acetate membrane unit. High color removal (90-97%) was demonstrated when operating at water recovery ratios of 98.5 to 99%. Pilot plant capacity (membrane flux) was 600-800 lit/day/m², when operation proceeded smoothly. However, plugging of the membrane cartridges by residual particulates even after precoat filtration was found to be troublesome⁵.

Several specialized resins have offered encouraging results. Included among these are the processes developed by Rohm & Hass & Uddeholm-Kamyr.

Rohm & Hass Process :—This is based on use of a special polymeric absorbent, Amberlite XAD-8, a highly cross linked 20-60 mesh resin possessing no ion exchange proportion⁸. The process functions best at pH 2-2.5, so that mixing of acid and alkaline bleaching effluents proves favourable. Higher decolorization efficiency is noted for hardwood than for softwood effluents (75-85% for softwood and 85-92% for hardwood). It is claimed that adequate protection against resin fouling

is provided by hydrosieve filtration and that resin life of at least 5 years can be expected. Resin regeneration is effected using weak wash which then transfers the colored components to the green liquor in the smelt dissolving tank. Alternatively, white liquor is proposed for regeneration. Chloride accumulation is not held to be sufficient to produce pulping and recovery system problems.

Uddeholm Kamyr Process :—This process appears to combine both adsorption and ion exchange mechanisms⁹ possibly based on a weakly anionic resin. The resin is regenerated using 1-2N caustic. It then requires an acidic reactivation using either sulfurous or spent sulfuric acid from ClO_2 production. The regenerants are recoverable and the eluted colored material is ultimately burned in the recovery furnace. Chloride separation is accompanied using sodium sulfate displacement so that chlorides do not appear to present problems.

Soil Media

Soil as a medium for colour removal can be used successfully. The land requirement is however high in most cases. The study conducted by Blosser and Owens 1964¹⁰ on land disposal of pulp and paper mill wastes revealed that color removal varied with the type of waste applied and the type of soil used. It was observed that clay looms are most effective in retaining color, followed by silt loam and sandy loam. Most of the soil leached out the absorbed color at one stage or the other. The studies conducted by the National Environmental Engineering Research Institute, Nagpur¹¹ on color removal employing pulp mill wastes and a few soils from Amlai, M. P., revealed that color removal is directly proportional to the cation exchange capacity of the soil. It is estimated that about 90 hectares of land will be required to dispose of 18,200 cu.m/day of pulp mill waste.

Chemical Methods

These include various lime treatment methods, coagulation methods, oxidative treatment and radiation methods, and electro-chemical methods.

Massive Lime Treatment :— Although laboratory studies using several coagulants have been reported, the most popular coagulant is lime. Lime has proven in

pilot plant and full-scale operation to be able to remove more than 90% of color¹². The sludge is thickened, dewatered and burnt for recovery. Large doses of lime are necessary for effective color removal. The effluent is neutralised with flue gas. A number of mill scale variations on the lime precipitation process have evolved in the last 30 years including :

- (a) the massive lime process involving slaking of reburnt lime in caustic extract followed by the resolution of the precipitated color in the recausticizing process and ultimately burning of the colored organics in the recovery furnace,
- (b) addition of minimal lime dosage of total unbleached kraft effluent in the primary clarifier, precipitating the color and dewatering, the sludge in admixture with the lime mud and burning the color in the lime kiln and
- (c) precipitation of colored substances in the caustic extract or other specific colored effluents using minimal amounts of lime slurry followed by dewatering in admixture with lime mud and burning of the colored organics in the lime kiln, or use of lime mud, fortified with additional reburnt lime or hydrate, to precipitate color and again destruction in the kiln⁵.

Massive lime treatment process was initiated by Maggi and improved by Berger. The process involves application of high doses of lime (3,000—10,000mg/lit.). The Massive lime process consists of slaking and allowing all the lime, used in the mill for recausticizing the green liquor to react with the highly colored effluent, settling and dewatering sludge. This sludge is used for recausticizing the green liquor. This is possible as only a small quantity of lime will react with color bodies and practically most of it will settle as sludge along with the absorbed and precipitated color.

The colored sludge when used for recausticizing will render the color bodies to dissolve in the white liquor which then attains a black or dark brown color. On passing through digestion, the color ends up in the black liquor which in turn is concentrated and burnt in the recovery furnace. The dissolved calcium in the decolorised effluents is reclaimed by carbonating with

lime kiln gas under controlled pH conditions and settling out the calcium carbonate. This along with the calcium carbonate produced in recausticizing process are burnt in lime kiln to get back lime.

A modified lime treatment for color removal and sludge disposal has been worked out in recent years. It is based on the hypothesis that soluble calcium hydroxide could affect color precipitation at satisfactory rates by utilising other solid phase surfaces for deposition. This process employs lime dosage of 1000mg/lit. as CaO on the total in clarified kraft pulp and paper mill effluent with a lime recovery system¹³. Massive lime treatment for color will be possible only if lime mud or sludge is recovered. Srivastava et al, 1984¹³ found that 1300 mg/lit. of lime plus 30 mg/lit. of MgSO₄ removed color from pulp mill wastes better than 3000mg/lit. of lime alone. Color removal achieved was 90% at a pH between 10.8—11.7

Coagulation:—Alum and ferric salts have been tried in lignin removal. Mittal and Mehrotra 1981¹⁴ showed that an alum dose of 245 mg/lit. and clay of 500 mg/lit. reduced the color by 95%. Thickened sludge is obtained on coagulating color by alum and clay. Optimum alum dose needed to decolorise waste is reduced by lowering the pH of the waste. Fuller, 1971¹⁶ has patented a process for alum precipitation of effluent color after secondary treatment in the presence of alum mud. Thickened sludge is blended with primary and secondary sludges and dewatered to 30-40% solids in pressure filters before incineration in a multiple hearth furnace. Recovery of alum for reuse is accomplished through acidification with sulphuric acid. Over 90% decolorisation is achieved.

A pilot plant work on alum and polymer treatment of individual waste streams has been reported¹⁷. The streams tested were unbleached kraft effluents, screen room effluent, bleach kraft effluent and spill overflows consisting largely of pulping liquor. The results of these studies were that alum coagulation and settling removed 81-93% of the color. Sludge dewatering was enhanced considerably by acidification of the sludge to a pH of 2 to 2.5 and heating to 80°C. Timpe et al 1973¹⁸ reported color removal from caustic extraction effluent by aluminium chloride, aluminium sulphate and ferric sulphate. Polyelectrolytes and silica were added in some trials. It was found that

neither silica nor organic polyelectrolytes had any significant effect on color removal but promoted flocculation and settling.

Christman and Smith 1969¹⁸ reported that coagulation of kraft wastes with alum and ferric chloride resulted in a dense rapidly settling coagulum. Optimum pH was found to be 3.9 for ferric chloride and 5.3 for alum whereas optimum dose was found to be a linear function of the initial color. At optimum pH and dose 92% and 95% color removal was achieved by alum and ferric chloride respectively. Olthof and Eckenfelder 1975¹⁹ described the results of the laboratory coagulation studies that the use of the iron salts for color removal from pulp and paper mill waste treatment can be an attractive alternative for lime treatment as the dose of the iron salts required is only 25-33% of the lime dosage. Polyethylene oxide has been tried and has been reported to be promising at jar test level²¹.

From the available information, it can be concluded that since the waste volume is large and highly colored, large quantities of the coagulants will be required. Adjustment of pH prior to chemical treatment will also be necessary. Further the sludges obtained will offer problems of dewatering and disposal.

Oxidative Treatment and Radiation Methods:—The possibility of decolorising kraft mill effluents by exposure to ozone, chlorine, hydrogen peroxide, radiation sources was tried by many workers. NCASI laboratory trials have demonstrated the capability of ozone for decolorising pulp mill waste waters (NCASI report, 1974 a). But ozone is difficult to handle and is costlier in terms of installation as well as operational costs. Hydrogen peroxide was reported to be very slow. Even at a dosage level of 300mg/lit. and after a contact time of 24hr., the decolorisation by Hydrogen peroxide is very low¹³. Use of chlorine dioxide for removal of color from pulp mill waste waters was studied²⁴. A preliminary investigation of radiation enhanced oxidation of pulp mill effluents for color reduction indicated that exposure to 10⁷ Roentgens in the presence of 350 mg/m² oxygen can achieve 90% decolorisation. The addition of Propyl alcohol to nitrogen saturated solution will produce increased color removal in 2000 mg/lit. at discs of 1.1 Mrad/hr²⁵.

Electro chemical Methods:— Serdobolskii et al (1979a)²⁶ described a 2.4—3 cu. m/hr pilot plant for the electro-chemical treatment of kraft bleach plant and caustic extraction effluents. Anodes used were Al, Fe with generally better results obtained with aluminium anodes. Reduction achieved COD 82.4-19.4%, color 94-98% and chlorolignin 93.9-99%. Bochkarev et al 1978²⁵ investigated electrochemical coagulation of kraft mill effluents based on formation of metal hydroxides during anodic dissolution of electrodes. Steel electrodes with a surface of 0.1 to 0.04 m² served as anodes at a current flow of 100-300 amp h/cum. Color removal of 70-90% and phenol removal of 50-60% obtained. Serdobolskii et al (1979 b) investigated electrochemical treatment of various kraft mill effluents that had been biologically treated using lead, titanium and graphite electrodes. Increasing current densities to 300-400 amp/m² sharply reduced BOD. Depending upon the electrode material electro conductive additives and effluent composition, 40-99.5% color removal, 78-100% phenol and complete lignin removal is achieved.

Biological Methods:— Steam volatile compounds like alcohols ketones, phenolics mercaptans and terpenes present in foul condensates and pulp washing waste waters are readily biodegraded by mixed population of microbes present in biological treatment systems. Resin acids and their sodium salts are also biodegradable³⁰. Biodegradation of chlorinated compounds occurs very slowly. Tetrachloroglucol could be degraded by an inoculum of activated sludge in 5 day³¹. Fungi like *Teichoderma koningi* easily degrade methyl catech.

Several attempts have been made to biodegrade lignin bacteria, yeast and fungi. A number of bacteria *Pseudomonas*, *Flavobacterium*, *Xanthomonas*, *Acromonas*, *Nocardia*, *Arthobacterium* species have been shown to utilize C-14 labelled lignin. Kawakmi 1975²⁹ found that *Pseudomonas ovalis* degraded alkali lignin more readily than kraft lignin sulphionate. A mixed population of bacteria and protozoa derived from lake bottoms sediment near the effluent of a sulphite paper mill, was shown to degrade by some 10% lignin sulphionate at 1% concentrations when supplied as sole carbon source (33). *Microsuronsp* and *candida sp.* were reported to utilize carbohydrate free sulphite waste liquor. During microbial attack of lignin, a no. of simple aromatic compounds, like vari-

llic acid, P. hydroxy benzoic acid, ferulic and syringic acids, coniferaldehyde, etc, are produced³⁴.

The most promising organism for delignification appears to be white rot fungi can remove 60% of color from kraft bleach plant effluent in 2-4 days. The most important among the white rot fungi that degrade lignin considerably are *Phanerochaete* *Ce Chrysosporium*, *Polyporus versicolor*, *Coriolus versicolor* and *Sperotrichum puluerlumentum*. White rot fungus are shown to degrade modified lignins and lignin derivatives present in pulp mill wastes. This fungus is found to give out extracellular enzymes which break down lignin into simple aromatic compounds which are metabolised intracellularly. Attempts are being made to modify lignin molecule by photooxidation using U. V. light which renders the modified lignin molecule bio-degradable³⁵.

The biggest drawback of lignin bio-degradation so far has been its slowness and incompleteness.

Color Load Control With Technological Changes in Bleaching Process

(a) Elimination of The Caustic Extraction Stage :

This already enjoys limited use at several mills and involves substitution of a hypochlorite stage for the conventional caustic extraction stage. Since the latter contributes at least 75-80% of bleach plant color load, its elimination can result in major load reduction. Recently this modification has been proposed as an "antipollution sequence" yielding a 62-82% color reduction. It involves using large amount of chlorine dioxide immediately before the chlorination stage and substitution of sodium hypochlorite for the caustic extraction stage (36).

(b) Use of Oxygen Bleaching and Effluent Recycling to Pulp Chemical Recovery :

Oxygen bleaching has already reached commercialization in several countries with provision for oxygen stage effluent recycling to chemical recovery. A current study³⁷ has shown that while a modest 10% color load reduction may result from inclusion of the oxygen stage; an 87% reduction can be foreseen if the oxygen stage effluent is completely reduced. These results are for softwood bleaching and are even more

encouraging for hardwood, where a 95% average reduction was observed.

(c) Intensive Infra Stage Recirculation and Organic Matter Precipitation

Recent surveys, particularly of five and six stage CEDED and CEHDED sequence mills, have identified major savings in effluent flow and steam use through use of counter-current washer flow; with one mill reporting an effluent flow of 8000 gal/ton against average of 22000 gal. (38). Recent studies have suggested that in addition to counter-current flow, extensive recirculation around the chlorination stage can reduce bleach plant flow to 1600 gal/ton, achieving 40% color reduction, possibly due to precipitation of concentrated color bodies³⁸.

(d) Rapson Closed Cycle Recovery Process

One of the most intriguing approaches to be presented is that by Rapson³⁷. The change proposes use of chlorine dioxide in place of chlorine in the first stage; along with total counter-current recirculation from bleaching directly through the brown stock washing system. Accumulated chlorides could be removed by evaporative crystallization of sodium chloride from white liquor. The recovered sodium chloride could be used for electrolytic production of needed pulping and bleaching chemicals. A special chlorine dioxide production process is proposed employing hydrochloric instead of sulfuric acid to maintain the desired chemical balance. Organic components of the bleaching effluents are in essence disposed off through the recovery furnace.

The wide ranging nature of the work of effluent decolorization reviewed briefly in this report represents a major investigative and interpretive challenge to the technical leadership of paper industry. There is no other portion of the industry's environmental protection programme in which present and proposed manufacturing technology are so closely intertwined with environmental considerations as in the definition and solution of individual mill decolorization problems. There is a need to include decolorization considerations in the growing use of optimization approach to establish in process retention goals for coloured organic effluent streams. As a matter of choice, investigative efforts in the decolorization area should continue to focus on those approaches which can be integrated with existing pulping and bleaching technology.

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