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Reduction of Pollutants in Hardwood Pulp Mill Bleach Effluent

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This study focused on the removal of the pollutants from high coloured hardwood kraft pulp mill bleach effluent. The reduction efficiency of colour and chemical oxygen demand (COD) is evaluated at the optimum dosage of polyaluminium chloride with cationic polyacrylamide. The pollutants caused functional groups get de-linked from wastewater and which is present in treated wastewater sludge was proved through the FTIR spectrum. At the optimized pH attained from these coagulants treat the wastewater, the flocs formation/settling and the pollutant removal efficiency is encouraging and the resulting colour of the wastewater is to 55 PtCo units from 1100 PtCo units and chemical oxygen demand to 659 mg/L from 1935 mg/L.

Keywords: Cationic polyacrylamide, Chemical oxygen demand, Colour, FTIR, Polyaluminium chloride.

INTRODUCTION

In pulp and paper industries, the pulping process and subsequent bleaching method are designed with huge quantity of water. The pulping and bleaching process generate most of the liquid, solid and gaseous wastes. Bleaching of wood pulp is a chemical process carried out on various types of wood pulp to decrease the colour of the pulp, so that it becomes whiter. The main use of wood pulp is to make paper where whiteness (similar but not the same as "brightness") is an important characteristic. The kraft process in which the raw material is treated mechanically or chemically to eliminate lignin in order to facilitate cellulose and hemicelluloses fiber separation and to get better paper making properties of fibers. During this process, it consumes large volume of fresh water, sodium hydroxide, sodium sulfide, sodium carbonate, chlorine dioxide, sulphuric acid, *etc*.

The dissolved lignin and other organic and inorganic components are washed by a counter current system from the pulp, concentrated by evaporation and subsequently burned in the recovery boiler to generate energy and spent chemicals. Up to this stage, it is possible to close loop process without discharging any wastewater using modern pulping and bleaching technology. Chlorine dioxide is sometimes used as a combination with chlorine, but it is used alone in elemental chlorine free (ECF) bleaching sequences. It is used at moderately acidic pH 3.5 to 6. Chlorine dioxide (elemental chlorine free technology) currently is the most important bleaching method worldwide. About 95 % of all bleached Kraft pulp is made using chlorine dioxide in elemental chlorine free bleaching sequences. During alkaline pulping the chromophores of native wood was degraded. Chromophore is an organic structure which gives rise to colour. In bleaching stage using chlorine dioxide for brighten the pulp and it generated acidic effluent. During bleaching, chromophoric and highly oxidized polymeric lignin derivatives are formed that give rise to a dark colourization in the wastewater. Light basic colour of wood derives from certain structures of lignin and dark colour derive from certain extractives *i.e.* aromatic extractives; all the extractives are also not coloured, for example fats, waxes, monoterpenes, resin acids and strerols are colourless. This coloured wastewater contains several toxic and non-biodegradable organic materials, which include organic acids, chlorinated lignins, resin acids, phenolics, unsaturated fatty acids and terpenes. The bleaching process yields unruly organic compounds in the effluent, which are not easily degraded by biological wastewater treatment. All bleaching agents used to delignify chemical pulp, with the exception of sodium dithionite, break lignin down into smaller, oxygen-containing molecules (many of the products are carboxylic acids). These materials must be removed between bleaching stages to avoid excessive use of bleaching chemicals since many of these smaller molecules are still susceptible to oxidation.

The main forms of treatment of effluents from pulp mills have been invested heavily in the technology of anaerobic treatment, a process favoured by the high concentrations of organic matter usually found in industrial effluents [1]. Chlorine-based bleaching processes are responsible for the majority of environmental problems. Related effluents normally contain a large amount of chlorophenols as well as a trace of toxic substances such as DDT, polychlorinated biphenyls and polychlorinated dibenzodioxines [2]. Also, dioxins, furans, halogenated polycyclic aromatic hydrocarbons, chlorinated lignosulfonic acids and chlorinated resin acids are found to be produced during the bleaching process [3].

The use of inorganic metal salts for coagulation-flocculation has been well documented. Now the trend is also towards to this technique as fashion for pulp mill wastewater treatment. Mahesh *et al*. [4] had investigated a comparative study for colour removal of pulp bleach plant effluent with three different decolourizing agents: fly ash, high molecular weight amine (Kemamine T 1902D) and lime, showed 90 % or more colour removal. Fly ash treatment offered a promising way for colour removal (94 %); amine treatment yielded better colour removal than fly ash.

Mehna *et al*. [5] had investigated a small pulp mill utilizing agri residues were characterized for their pollution load and were decolourized with the white rot fungus *Trametes versicolor* strain B7. They found that maximum colour reduction of 92 % with a chemical oxygen demand reduction of 69 % at optimum pH 4.5-5.5.

Nagarathnamma and Bajpai [6] found 92-95 % of the colour reduction and 50 % of the chemical oxygen demand reduction at pH range of 3 to 5 by *Rhizopus oryzae* from extraction stage effluent from chlorine bleaching of kraft pulp. Tantemsapya *et al*. [7] found that the variation in pH of lignin containing wastewater at the levels of 2 to 10 had no influence in removal of colour (89-93 %) and chemical oxygen demand (66-70 %) when white wood ash was used. The highest removal of colour (42.2 %) and chemical oxygen demand (29.7 %) was found when the initial pH was adjusted to 2 and such removal was gradually decreased when pH was raised.

Most of the researches show that the treatment of pulp mill bleach effluent by biological method and it takes minimum 2 days incubation for lignin breakdown and also mostly based on anaerobic treatment. Pulp mill effluent using a biological method is found to be low, whereas the treatment efficiency of the effluent using chemical coagulation processes is good in short reaction time.

Coagulation and flocculation are not only the economic but also the effective method for removal of pollutants. In present work, an endeavor has been made to treat the huge volume of high strength hardwood pulp mill bleach effluent through coagulation-flocculation method by composite coagulants and flocculants. The removal of pollutants was achieved through two simultaneous mechanisms, which included coagulation by charge neutralization and flocculation by bridging. The removal of pollutants was confirmed through FTIR spectrum.

EXPERIMENTAL

The effluent sample collected from the pulp mill Hardwood Elemental Chlorine Free Bleaching (HWECF) bleach plant in Tamilnadu, India. The sample was characterized and the analysis by using IS 3025 standard methods are given in Table-1.

TABLE-1
CHEMICAL CHARACTERISTICS OF THE TREATED AND UNTREATED HARDWOOD ELEMENTAL CHLORINE FREE PULP MILL BLEACH PLANT EFFLUENT

Particulars	Untreated effluent	Treated effluent
pH	3.7-5.3	6.7-7.1
Colour (PtCo)	1100	55
Chemical oxygen demand (mg/L)	1935	659

pH: For measuring pH, 100 mL of the sample taken in a clean dry beaker, stirred well and checked reading in the pH meter until getting stable reading. Chemical oxygen demand: [Standard reference: IS 3025 (Part 58):2006].

Placed 0.4 g of mercury(II) sulphate in a reflux tube. An aliquot of sample diluted to 20 mL with demineralized water and mixed well (simultaneously for blank, used 20 mL of demineralized water). Then pipetted out 10 mL of 0.25 N standard potassium dichromate solution to the sample containing reflux tube. Finally 30 mL of concentrated sulphuric acid, which already contains silver sulphate (prepared by 10.12 g silver sulphate was added to 1 L of concentrate sulphuric acid, kept overnight for dissolution and shook well after dissolution) was slowly added and mixed well. Refluxed the contents of the flask for 2 h at 150 ± 2 °C. Then cooled and washed down the condensers with 60 mL de-mineralized water. Then it was titrated against 0.1 N standard ferrous ammonium sulphate using ferroin as indicator. The end point is attained colour changes sharply from green blue to wine red. Colour: [Standard reference: IS 3025 (Part 4): 1983].

Platinum cobalt method: Colour is measured by visual comparison of the sample with platinum-cobalt standards. One unit of colour is that produced by 1 mg of platinum per litre in the form of chloroplatinate ion. Prepare standard solutions having colour units of 5, 10, 15 and up to 70 as prescribed above said reference. The clear supernatant solution was taken for analysis. If the colour exceeded 70 units, the sample was diluted using demineralized water until the colour is in the range of the standard solutions.

Methods: The coagulants and flocculants were chosen by depends on the nature of the effluent. Normally pulp mill bleach effluent has strong anionic nature due to the major source of lignin/chromophore derivatives. Jar test procedures carried out using 1000 mL of the Hardwood elemental chlorine free bleach plant effluent samples with the milk of lime (MOL), polyaluminium chloride and cationic polyacrylamide used for quick settling. The selected coagulants were added to 1000 mL of wastewater and it was stirred for a period of 3 min at 100 rpm and it was followed by further slow mixing of 10 min at 30 rpm. The flocs formed were allowed to settle for 30 min. After settling, the pH, colour and chemical oxygen demand were analyzed. The analysis was repeated for 4 times for getting average values using Indian standard IS 3025 methods.

RESULTS AND DISCUSSION

The nature of the hardwood pulp mill bleach plant effluent is acidic medium. For this study using milk of lime, the pH has increased to neutral medium. The dosage of coagulants and flocculants will be varying based on the level of coloured wastewater strength. At pH 6.7 to 7.1 the colour has reduced to 55 from the untreated effluent value 1100 PtCo units and chemical oxygen demand reduced from 1433 to 659 mg/L and it has been shown in Table-1.

Effect of coagulants-flocculants: pH of the wastewater plays an important role when aluminium compounds used for coagulation process. This hardwood kraft pulp mill has acidic medium. By the addition of milk of lime to the effluent sample getting neutral medium. Moreover, Ca^{2+} ion also contributes the attraction of negatively charged particles from the wastewater. The pH of the wastewater plays an important role when aluminium compounds used for coagulation process. Because, the solubility of the aluminium species in effluent is pH dependent and it is generally present in the form of positive ions [*i.e.* $Al(OH)^{2+}$, Al^{3+}, $Al_2(OH)^{4+}$ *etc.*]. The Aluminium species may act as an adsorbing agent for the condensate polymer/lignin complex. When applied to the wastewater, it may hydrolyze to aluminum hydroxide forming a large, insoluble particulate with a large surface area. Concurrently, cationic polyacrylamide may bind to the hydroxyl or methoxyl groups of the lignin to create an insoluble complex. The lignin has methoxyl ($O-CH_3$) groups, hydroxyl groups of primary and secondary aliphatic, phenolic hydroxyl groups, carboxyl (-COOH) groups and carbonyl functional groups. This complex may then be adsorbed into the hydrolyzed aluminum hydroxide and become bound forming the insoluble agglomerate and removing the colour from the effluent without re-solublizing.

The advantage of cationic polyacrylamide is the pH intensive and functioning well over a broad pH range. The cationic charge in this polymer is derived from nitrogen in the form of a secondary, tertiary or quaternary amine group and the charge can be located on a pendant group or may be in the backbone of the polymer chain. The addition of the milk of lime, polyaluminium chloride and the cationic polyacrylamide reacts with the lignin in the wastewater to form flocs and remove chemical oxygen demand and colour from the effluent, thus reducing the true colour of the effluent. The chemical oxygen demand is generated from various complex organic compounds, which could not be all precipitated with added coagulants and flocculants. So that the removal of chemical oxygen demand was lower than that of colour.

FT-IR spectral analysis: Every lignin IR spectrum has a strong wide band between 3500-3100 cm^{-1} assigned to OH stretching vibrations. This band is due to the presence of alcoholic and phenolic hydroxyl groups involved in hydrogen bonds. The spectrum (Fig. 1) of pulp mill bleach plant wastewater sample shows broad band at 3325 cm^{-1} assigned for carbonylated and hydroxylated functional groups *i.e.* O-H bond of hydrated phenols, poly(vinyl phenol), poly(ethylene oxide), poly (vinyl isobutylether) and the wavenumber 1635 cm^{-1} assigned for N-H bond of hydrated primary amines, amino acids, C=C non-cyclic alkenes and cyclic alkanes, C=O stretching of poly-peptides and urease NO_2 asymmetric stretching of nitrates.

After treating this wastewater, the pollutants were reduced due to the above said functional groups are broken and get delinked from wastewater along with the added coagulants and flocculants.

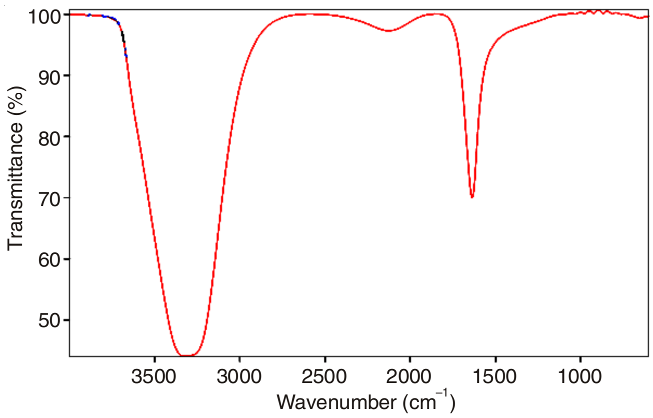

Fig. 1. FTIR spectra of untreated hardwood pulp mill bleach plant effluent

It was noticed that main functional group is carboxylic group from lignin is cause of colour and another significant functional group of the –OH bond from hydrated phenol subsequently one more NH bond from hydrated primary amines were segregated from the wastewater sample. These are made bond with the additives like milk of lime, polyaluminium chloride and cationic polyacrylamide formed flocs. The broad band of the untreated sample spectrum at 3325 cm^{-1} is referred to mainly alcoholic and phenolic hydroxyl groups in lignin. After treating, these functional groups are delinked from the wastewater and it appears in the treated wastewater sludge. After removal of the above pollutants from the pulp mill bleach effluent wastewater, the resulting water was taken for colour and chemical oxygen demand analysis and the results are given in Table-1.

The removed functional groups have been presented in treating wastewater sludge were proved through the FTIR spectrum (Fig. 2). The FTIR spectrum of treated wastewater sludge shows a band at 1250-900 cm^{-1} which referred to the stretching vibration of cyclic ethers caused by the combination or overlapping of C–O as a result of several deformations in lignin by the action of the chemicals used in the processes. The band 1369-1316 cm^{-1} show the stretching vibration of aromatic nitro compound (NO_2) and aromatic C–N stretching caused by agricultural residues and the chemicals used in the treatment system. The band 1395 cm^{-1} assigned to asymmetric stretching of SO_2 groups appears due to the pulping process chemicals and get delinked from the wastewater due to the added coagulants. Bands appear in 1424 and 1458 cm^{-1} for asymmetric deformation of C–H in lignin and C=C stretching vibration. There are also a stretching vibration of aromatic nitro compound NO_2, secondary C=O and C–N groups at 1540-1515 cm^{-1}. The band 1648 cm^{-1} for secondary amide C=O stretching, primary amide NH_2 bending, α,β-unsaturated aromatic oximes/imines and intra molecular hydrogen bonded carboxylic acid groups. The functional groups like C=O stretching of α-amino acids, aryl aldehydes, α,β-unsaturated acids, carbamates, amide-I band, -CO-NH-CO-, α,β-unsaturated aldehydes, aryl carboxylic acids at 1699 cm^{-1}. The band at 1744 cm^{-1} for C=O stretching vibrations of saturated aliphatic ketones, α halogen ketones and dicarboxylic amino acids. The removal of colour causing pollutants is strongly evidenced by these significant bands appeared in the sludge. The stretching

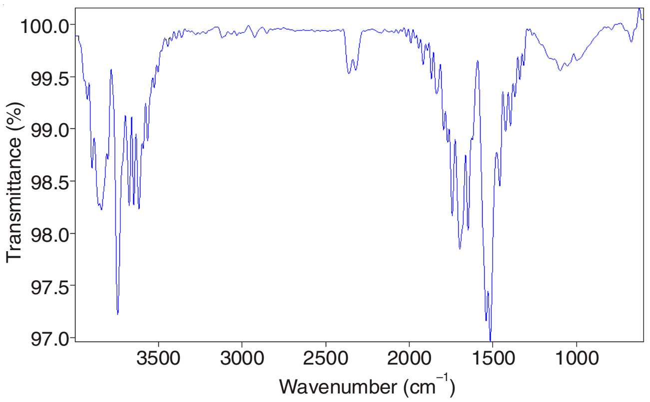

Fig. 2. FTIR spectra of treated pulp mill bleach plant effluent sludge

vibrations of NH^+, CH, SH, PH, SiH functional groups appear in 2700-2250 cm^{-1} range. Another significant functional groups like O-H stretching vibration chloro phenol at 3600-3550 cm^{-1} and the O-H free carboxylic acid groups at 3580-3500 cm^{-1}. This also confirm for removing the pollutants from the wastewater after treatment. There is also a stretching vibration of oximes O–H and Si–H at 3700-3200 cm^{-1}. The groups like tertiarybutyl phenols at 3650-3640 cm^{-1} and O–H stretching alcoholic groups shows that the phenolic/alcoholic groups are getting delinked due to the effectively treated this wastewater. These are the evidences for removal of pollutants from the wastewater.

Conclusion

The purpose of this work to overcome the problem in disposal of coloured high chemical oxygen demand bleach plant effluent generated from pulp and paper industries. This research work achieved by reducing the pollution caused chemicals like phenol, aromatic primary amines, carboxylic acids and lignin, *etc*. from this pulp mill bleach effluent. Moreover the same research work is highly useful to come out from the problem of discharging coloured wastewater generated from integrated pulp and paper industries. Because of this work, the colour and chemical oxygen demand reduction were achieved by maximum removal of pollutants like hydrated lignin (C=O), phenolic hydroxyl groups, chlorinated phenols, carboxylic acid groups and inorganic functional groups like sulphur, phosphorous compounds, *etc*. can be highly appreciable and valuable along with it is applicable for pulp and paper industries to solve the effluent problem with quick reaction time.

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