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Effect of Toxic Pollutants from Pulp & Paper Mill on Water and Soil Quality and its Remediation

[1]Pratibha Singh, [2]Noopur Srivastava, [2]Pratibha Singh,
[1]Geetha S, [1]Usharani N, [1]R.S. Jagadish, [3]Asha Upadhyay

Department of Chemistry, JSS Academy of Technical Education, Noida, U.P, India
[2]Department of Environmental Science, Bhagwant University, Ajmer, Rajasthan
[3]IGNOU Regional Centre Head Office, Jammu (Tawi)
Corresponding author

Abstract

Pulp and paper mills use a variety of bio-resources to produce paper and generate a variety of pollutants depending on the type of the production processes adopted. This chapter focuses on the paper production techniques, pollutants generation and the performance of different available wastewater treatment processes related to paper industry. The different treatment processes such as coagulation, chemical oxidation, ozonation, aerobic and anaerobic treatment for reduction of color and other pollutants from paper industry wastewater are reviewed and discussed. Further, it is concluded that the chemical coagulation, oxidation and ozonation are effective in reduction of color from paper industry wastewater. The chlorinated phenolic compounds and adsorbable organic halides (AOX) are efficiently reduced by adsorption, ozonation and membrane filtration techniques. The combinations of anaerobic and aerobic treatment processes are found to be efficient in the removal of soluble biodegradable organic pollutants.

Keywords: Pulp and paper mill, treatment methods, biological treatment, Enzyme, chemical treatment ($FeCl_3$& $KMnO_4$)

INTRODUCTION

India had 17 paper mills at the time of independence with an installed capacity of less than 0.14 million TPA (tonnes per annum). At present, there are an estimated 525 pulp and paper mills with a total installed capacity of around 6.25 million TPA (Singh 2004) with a capacity utilization of about 67%. The aggregate installed capacity by

2010 for paper and paperboard is expected to reach 8.3 million tonnes and 1.5 million tonnes for newsprint. The per capita consumption of paper in India is one of the lowest in the world at 5 kg. The present level of paper consumption in the country is 4.2 million tones. According to an estimation, the demand for paper and allied products is expected to cross 10 million tonnes by 2015 (Singh and Thakur, 2004).

PULP AND PAPER INDUSTRY HISTORY AND STATUS

The technique of paper-making is believed to have originated in China, from where it spread to the rest of the world including India. The first handmade paper mill in India was set-up in Kashmir in the 14th century. Much later, in 1832, the first mechanized paper mill based on jute and grass was established in Serampore, West Bengal. After a slow start, the growth was encouraged by the Bamboo Protection Act (1925) and Indian Finance Act (1931). More than 10 paper mills were commissioned in this period and by 1931, the production capacity had reached 45,600 tonnes (Singh and Thakur 2006).

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RAW MATERIALS AND WASTE WATER

Pulp and paper are manufactured from raw materials containing cellulose fibers, generally wood, recycled paper, and non-wood raw materials such as bagasse, cereal straw, bamboo, reeds, esparto grass, jute, flax, and sisal. The manufacturing process uses a large amount of fresh water, most of which is thrown out as wastewater. Pulp and paper industry is one of the largest and most notorious sources of industrial pollution. The Ministry of Environment and Forest, Govt. of India, has categorized the pulp and paper industry as one of the twenty most polluting industries (Singh et al. 2016).

The wastewater of from pulp and paper industries contains stray wood chips, bits of bark, cellulose fibres, dissolved ligneous material (30-45%), saccharinic acid (25-35%), formic acid and acetic acid (10%) and extractives (3-5%). The pulping and bleaching effluents are characterized by parameters unique to these wastes such as colour and organic halides (AOX). The residual lignin present in wood fibre is major coloring material, and also reacts with chlorine molecules and forms organochlorine compounds in the effluent. About 20% of the organically bound chlorine found in bleaching effluent corresponds to relatively low molecular mass (M.W 4000) products **(**Jukka et al. 1994**).**

The untreated wastewater from pulp and paper mills is generally discharged into water bodies and which cause damage to the water quality. The effluent imparts brown colour to water which is detectable over long distances. The effluents have high biological and chemical oxygen demands (BOD and COD), lignin compounds and their derivatives. The undiluted effluents are toxic to aquatic organisms and exhibit a strong mutagenic effect. Further more, some compounds in the effluents are resistant to biodegradation and can bioaccumulate in the aquatic food chain (Kumara Swamy et al. 2011).

CLASSIFICATION OF PAPER MILLS

The categorization of pulp and paper mills is based on the raw material used, plant size, and end products manufactured.

Based on the raw materials used, the paper mills are categorized as follows:

Wood/forest based mills:

These mills uses imported pulp as well as indigenous hardwood pulp from bamboo, eucalyptus, etc. The Indian paper industries, on an average, consume about 3%–4% of the total wood in India.

Agro-residue based mills:

These mills uses agricultural residues such as rice straw, wheat, sarkanda grass, bagasse, jute, etc, as raw materials. The use of agricultural residue by these mills has grown since the early 1970s partly due to the dwindling bamboo resources and partly due to the government's industrial policy encouraging investments in agro-based paper production. However, seasonal availability, transportation costs, and investments in pollution control equipment are seen as limiting factors.

Wastepaper-based mills:

These mills use imported and indigenous wastepaper, corrugated waste paper, kraft paper, and waste cuttings as raw materials. The recovery of wastepaper by these mills for paper production has increased from 65 000 tonnes in 1995 to 850 000 tonnes in 2000. However, the 20% rate of recovery is still one of the lowest, internationally. (Kumara Swamy et al. 2011)

PAPER PRODUCTION PROCESS

The pulp and paper industry converts fibrous lignocellulosic raw material into pulp and paper. The typical pulp and paper manufacturing processes involved and different waste waters generated are shown (**Figure-1**) and discussed below.

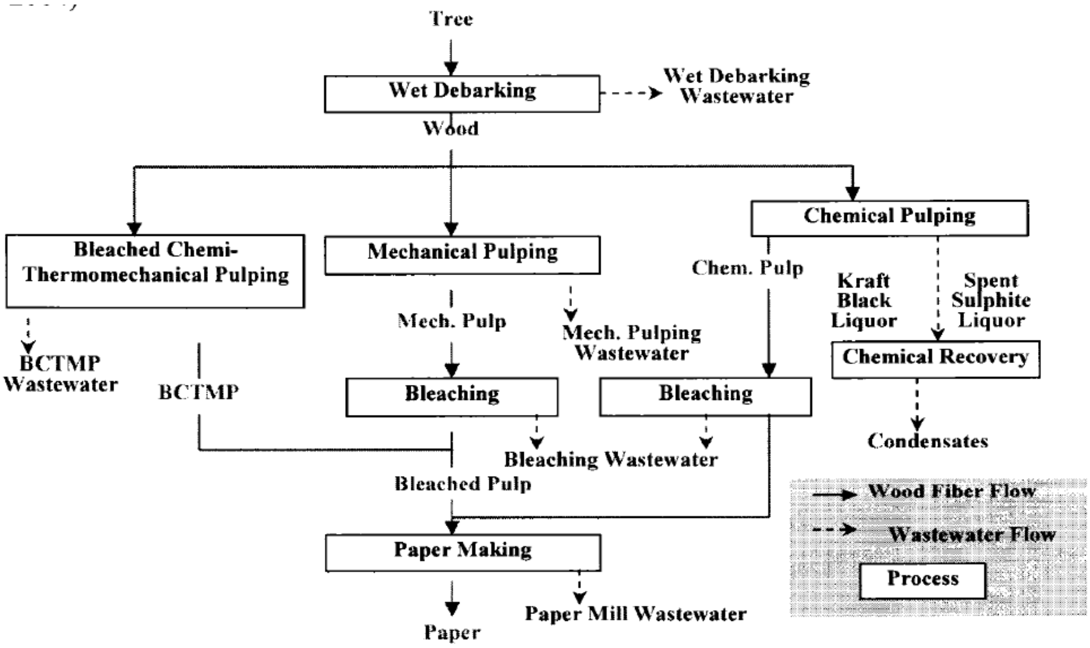

Figure-1: Different processes involved in pulp and paper production and corresponding waste waters generated (Kumara Swamy et al. 2011).

Process description of pulp and paper mill

Paper making includes five basic steps and each step can be carried out by a variety of methods. Therefore, the final effluent is a combination of waste water released from each of the five different unit processes and the methods employed therein; summarizes the main pollutants, which are normally produced during several steps of pulp and paper making process (Singh et al. 2002)

- Debarking converts the plant fiber into smaller pieces called chips and removes the bark. In this step, hard wood, softwood and agro residues are used as raw material, which results in the transfer of tannins, resin acids, etc. present in the bark to process water. For instance, softwoods contain a much higher quantity of resin acids than hardwoods.
- Pulping turns the chips into pulp. This process removes the majority of lignin and hemicellulose content from the raw material, which results in a cellulose rich pulp. Pulping can be passed out by several different methods, such as mechanical, semi chemical, kraft, sulfite pulping, etc. and once again the raw material can be utilized further.
- Bleaching is engaged on the brown pulp obtained after pulping in order to meet the desired colour dictated by product standards. Several bleaching agents, including chlorine, chlorine dioxide, hydrogen peroxide, ozone, etc.

may be used either singly or in combination. In this step, lignin, phenols, resin acids, etc. get chlorinated and transformed into extremely toxic xenobiotics.

- Washing removes the bleaching agents from the pulp. Generally, an alkali caustic soda is used to extract colour and bleaching agents from the pulp and hence, this process is also known as the alkali extraction stage
- Paper and paper products are finally produced by mixing the washed pulp with appropriate fillers (clay, titanium dioxide and calcium carbonate) and sizing agents like rosin and starch (Singh 2007)

CHARACTERISTICS OF EFFLUENT

Physicochemical Characteristics

The amount and characteristics of pollutants produced by an individual mill is an important indicator to evaluate the performance of the system. The characteristics of wastewater produced at various pulp and paper making processes varies depending on the process adopted in paper production.

The exact chemical composition of pulp and paper mill effluent is complex and unclear. The chemical compound found in pulp and paper mill effluent are mostly degrading products of lignin, cellulose, hemicellulose and wood extractives. The lignin degradation products found in the pulp and paper mil effluent include a wide variety of compounds such as manomeric phenols, enol ethers, mercaptides, stilbene, quinone derivatives, chlorinated phenols, acetic acid, formic acid, acetaldehyde, methanol, furfural and methyl glyoxal (Jukka et al. 1994). About 300 organochlorine compounds have been identified in effluent while hundred other remain unidentified. The most dangerous of these compounds are chlorophenols such as guaicols, catechols and their transformation products anisoles and verathroles. The most common chlorophenols are extremely toxic and persistant trichlorophenol (TCP) and pentachlorophenol (PCP). Dioxins (Poly chlorodibenzo-p-dioxin or PCDD) and furans (PCDF), which are the most dangerous, chlorinated compounds reported. Apart from dioxins and furans, the other chlorinated compounds found in pulp and paper mill effluent include chloroforms, chloroacetones, aldehydes and acetic acids (Jukka et al. 1994).

Absorbable organic halogens (AOX) and total organo chlorine (TOCl) are the other deadly organochlorinated compounds found in effluent. The chlorinated organic compounds are formed during chlorine bleaching stage of paper production. It is estimated that conventional chlorine bleaching of kraft pulp produces about 100-300g of chlorinated phenolic compounds per tonne of pulp (Jokela and Salkinja-Salonen 1993). In order to reduce the amount of chlorinated organic compounds produced the mills are increasingly adopting use of oxygen bleaching and use of chlorine dioxide bleach in place of chlorine gas.

Colour and Turbidity

The pulp and paper mill effluent is usually dark colored, foul odoured and turbid in nature. The dark color is caused by the presence of higher lignin and its degradation products. It is estimated that the manufacture of one tonne of bleached paper release about 40-50 kg lignin and its products to waste water (Abassi 1985).

Most of the colour to the wastewater is contributed by lignin degradation products formed during black liquor stage of pulping. The colour as high as 65,000 units is reported in literature (Srivastava and Singh, 2015). The effluent is generally turbid and opaque due to excessive presence of organic solids. The dark colour and turbidity often has serious consequences on disposal into water bodies.

Total solids (TSS and TDS)

The total solids in pulp and paper mill effluent consist of both setlable and non-setleble solids. Each category consists of both organic and inorganic substances. Chakravarty et al. (1995) revealed that the total solids in pulp and paper mill combined effluent range from 3200-6940mg/l, which is well above the minimum acceptable level (MINAS). The high-suspended solid imparts high COD, BOD and turbidity to effluent.

COD and BOD

The pulp and paper mill wastewater is mostly deficient in dissolved oxygen and associated with extreme values of BOD and COD. The high BOD is caused due to suspended low molecular weight solids. Chakravarty et al (1995) reported that in most cases, the BOD of pulp and paper mill effluent varied between 1200 to 1800 mg/l. This violates of minimum acceptable standard for BOD and also ISI limit for discharge into land for irrigation, which respectively stand at 100mg/l and 500mg/l. The literature shows reports of BOD as high as 16,000mg/l (Srivastava and Singh, 2015).

The pulp and paper mill effluents are characterized by high chemical oxygen demand. The lignin and its degradation products not only impart colour and odour to waste water but also increase its BOD and COD values. The pulp and paper mill combined effluents are reportedly contains COD values ranging from 1000 to 4200mg/l (Srivastava and Singh, 2015). The organic composition and COD characteristics of pulp and paper mill effluents from different processes are shown in **Table-1.**

Table 1: The organic composition and COD characteristics of pulp and paper mill effluents

Wastewater	COD (mg COD /l)	Organic Composition (% of COD)	Potential Inhibitory Compounds
Wet Debarking	1300-1400	Tannins 30-55; monomeric phenols 10-20; simple carbohydrates 30-40; resin compounds 5	Tannins, resin acids
Sulphite Spent Liquor	120000-220000	Lignosulphates 50-60; carbohydrates 15-25	Not Reported
Sulphite Evaporator Condensate (SEC)	7500-50000	Acetic acid 33-60, methanol 10-25, fatty acids <10	Sulphur, organic sulphur
Chlorine Bleaching	900-2000	Chlorinate lignin polymers 65-75, methanol 1-27	Chlorinated phenols, resin acids
Kraft Evaporator Condensate (KEC)	1000-33600	Methanol 60-90	Sulphur, resin acids, fatty acids, volatile terpenes
TMP Effluent	1000-5600	Carbohydrates 25-40	Resin acids
CTMP Effluent	2500-13000	Polysaccharides 10-15, lignin 30-40, organic acids 35-40	Resin acids, fatty acids, sulphur

Srivastava and Singh, 2015).

ENVIRONMENTAL CONCERNES AND DISPOSAL NORMS

Effluent Disposal Standards

The Central Pollution Control Board (CPCB) has prescribed the following effluent discharge standards for pulp and paper mills under E (P) Act 1986 (Table-2). In 2003, CPCB constituted a task force on Corporate Responsibility for Environmental Protection (CREP). Under this task force, the following action plan has been formulated and agreed upon by the industries:

Table 2: Effluent discharge standards for pulp and paper mills under E (P) Act 1986

Category	**Standard**	**Note**
Large (writing & printing) pulp and paper mills	200 m^3/tonne of paper 150 m^3/T	Standards of discharge for the large pulp & paper mills established from 1992 onward to meet standard of 100 m^3/tonne of paper
Agro-residue based	200 m^3/ tonne of paper	Agro-residue based mills established from January 1992 onward to meet the standards of 150 m^3/tonne of paper
Wastepaper based mills	75 m^3/tonne of paper	Wastewater based mills established from January 1992 onward to meet the standards of 50 m^3/tonne of paper

EFFLUENT DISPOSAL AND ITS ENVIRONMENTAL CONSEQUENCES

Pulp mill and bleach plant effluents are highly colored due to polymeric lignin degradation products and contains chlorinated aromatics. The toxic and environmentally persistent dioxin like compounds resent in the effluent of pulp and paper mill (Bumpus et al. 1988). The pulp and paper industries every year generate more than 7000 billion gallons of highly colored and toxic waste effluents mainly containing high molecular weight, modified and chlorinated lignins (Sundman et al. 1981; Huynh et al. 1985). Most pulp and paper mills dispose the effluent into water bodies such as rivers and canals or onto the barren land.

Effect on water quality

Studies demonstrated a variety of responses in fish populations living downstream of bleached kraft pulp mills These included delayed sexual maturity, smaller gonads, changes in fish reproduction and a depression in secondary sexual characteristics (Munkittrick et al. 1997). The main problem which occurred due to pulp and paper mill was growth of sewage fungus in the river receiving effluents (Webb. 1985).

The dark color and high turbidity due to suspended solids can cause the problems of both water opacity and blanketing of river or lakebeds. Severe blanketing may result in anaerobic decomposition under the blanket releasing hydrogen sulphide into aquatic ecosystems. The dark colour and blanketing can reduce photosynthetic activity in aquatic plants (Singh et al 2004). This leads to a chain of adverse effects on the aquatic ecosystem as the growth of primary consumers as well as secondary and tertiary consumers are adversely affected (Ruggicro et al. 1989). Therefore, it becomes necessary to remove color and toxicity before they can be accepted into surface waters.

Effect on land quality

Elements such as magnesium, sodium chloride and sulphur, which are also common in pulp mill wastewater can cause nutrient imbalance in crops, increase soil salinity and deteriorate soil structure and ultimately lower crop productivity in long run (Sundari and Kanakarni. 2001). The pulp & paper industry annually produces over one hundred thousand dry tones of solid waste. The most important problem which the pulp & paper industry is facing today is the disposal of tremendous volumes of waste water. This waste water is rich in dissolved solids such as chlorides and sulphates of Na, Ca & varying amounts of suspended organic materials. The effluents are generally alkaline in reaction with high chemical & biological oxygen demands. The paper mill effluent contains toxic trace elements which may accumulate in soils in excessive quantities these toxic elements may cause severe problems to human beings & animals by entering into the food chains. Untreated industrial effluents contain high concentration of heavy metals. Pulp mill effluents disturb soil quality:

- Increasing pH of soil
- Changing soil color & texture
- Imbalance of macro and micro nutrients in soil
- Negative effect on soil microbial activities & disturb all natural cycles
- Decrease in germination percentage
- Adverse effect on seedling growth.
- Increase in organic load
- Depletion of oxygen supply in soil

Effect on Crops and Livestock

Pulp and paper mill effluent is also responsible for affecting the quality of crops due to irrigation of polluted water; damages the soil, growth, quality and yield of the crop. Somashekar et al. (1984) in their study on the effect of various industrial effluents observed that paper mill wastewater has inhibiting effect in the germination of crops. Their experiment showed that 18, 14 and 13 percent germination for paddy crop respectively with 25, 50 and 100% waste water. Higher concentration of soluble salts and heavy metals present in pulp and paper mill effluents affect the seed germination of sunflower and maize (Rajamani and Oblisami 1979; Sahai et al. 1985). The inhibitory effect of the effluent increased not only with the increasing concentration but also with the increasing during of soaking (Kidd and West, 1968).

The paper mill effluents adversely affect the germination of rice seeds (Singh et al. 2002). Dutta and Boissya (1997) reported that the germination of rice seeds show a gradual decline at 50% and above concentrations of the effluent, throughout the experimental period, in comparison to control seeds. Mishra and Sahoo (1989) have shown a 44% reduction in shoot weight in 100% paper mill wastewater treated soil.

The farm animals are affected by means of pollutants in the water, soil and air. The pollutant may enter through crops and water consumed by the livestock, as the water borne contaminates accumulate in vegetation and fodder.

WASTEWATER TREATMENT METHODS

Agro residue based pulp and paper mills generally treat combined effluent. The treatment sequence involves equalization, primary settling and clariflocculation followed by secondary biological treatment (anaerobic and/or aerobic). This is followed by the activated sludge process and secondary clarification. Most of the large and a few medium and small paper mills have chemical recovery plants to recover spent pulping chemicals. The treated effluent is disposed of on land, surface water (river) or in drains. The primary sludge is dried in sludge drying beds or lagoons depending upon land availability and is generally sold to board manufacturers. The waste water treatments are broadly categorized into physicochemical and biological methods.

PHYSICOCHEMICAL TREATMENT METHODS

- Several physicochemical color removal methods such as adsorption, rapid sand filtration, chemical precipitation, membrane processes and electrochemical methods have been developed and reported in literature in the past (Srivastava and Singh 2015).
- The adsorption methods are increasingly being considered for removal of synthetic organic chemicals, color forming organics and disinfection by-products. The different adsorbates commonly used in effluent treatment include activated carbon, processed bone, char powder, activated alumina, magnesia, activated bauxite, fly ash, alum, lime etc (Srivastava and Singh 2015). Activated carbon is the main adsorbent in full-scale effluent treatment. Other naturally adsorbents are used in special cases. Activated alumina is widely used for removal of fluoride. Silica Gel is used for the separation of hydrocarbons. The polymeric resins and carbonized resins are often employed for improved removal of organic compounds from effluent.
- The membrane techniques require pretreatment and requires large capital investment. Membrane fowling is another problem associated with this method. Adsorption and membrane process are efficient but expensive (Manjunath and Mehrotra. 1981). The application of electrochemical method is another way to treat the wastewater from the cellulose paper production (Christoskova and Lazarov. 1988). This method guarantees high treatment efficiency, but its effectiveness depends on the type of electrodes, the construction of electrocoagulators and the condition under which the process is run.
- Chemical precipitation using alum, ferric chloride and lime has been studied extensively (Lathia and Joyce 1979), Despite the short detention time and low capital cost, there are some drawbacks reported, such as high cost of chemicals for precipitation and pH adjustment, voluminous sludge production due to heavy dosages, dewatering and disposing of generated sludge and high residual cation levels, The chemical precipitation methods are cheap but produce a large quantity of sludge and do not completely remove toxicity.

- The chemical aspect of colour removal of effluent from pulp and paper industry is very important. The use of calcium hypochlorite (1-2% as available chlorine) during alkaline extraction reduced the colour of effluent by 84% without affecting the quality of pulp. The use of chlorinated backwater (having 0.8% residual chlorine) during brown stock washing reduced the colour of eff1uent by 60% without affecting the quality of pulp. The combination of alum, lime and magnesium sulphate in presence of ferric acid chloride reduced the colour, BOD and COD by 97%, 68% and 52%, respectively. The combination of alum, calcium hypochlorite and ferrous sulphate in presence of chlorine water was most effective and reduced the colour, BOD and COD by 97, 71 and 64% respectively. The treatment options that have been explored till now are not cost-effective at plant level and no completely efficient method is currently available.

BIOLOGICAL TREATMENT METHODS

- Biological methods have the potential to eliminate or reduce the problems associated with physicochemical methods. Several studies have been carried out concerning the decolourization and treatment of such wastewaters by biological methods. Color of paper mill effluent is largely due to lignin and lignin derivatives and polymerized tannins, which are resistant to degradation due to the presence of carbon-to-carbon biphenyl linkages. It is reported that lignin and lignin derivatives are biodegradable by some of microorganisms under proper environmental conditions. Numerous bacteria have been reported to decompose lignins and lignin derivatives and some of these being *Pseudomonas spp., Flavobacteria, Xanthomonas spp., Bacillus spp., Aeromonas spp., Cellulomonas spp., Chromobacrtia,* etc (Ebtesam El-Bestawy et al. 2008). Although numerous bacteria can decompose monomeric lignin structure models, only a few strains are able to attach lignin derivatives obtained from different pulping processes.
- Many of the past studies have focused on screening, identifying, and evaluating the ability and effectiveness of fungi on degrading lignins in situ and in vitro. A variety of fungi has been proved to be lignin degraders and are classified into white-rot, soft-rot, and brown-rot fungi based on the type of wood decay carried out by these organisms (Ebtesam El-Bestawy et al. 2008).
- The white rot fungi are a group of basidiomycetes that possess an active lignolytic enzyme system, which are most efficient of the microorganisms that degrade lignin and its modified forms (Pokhrel and Viraraghavan 2004). These fungi do not use lignin as a carbon source for their growth but use it as a secondary metabolite which is not required for their growth. The lignin degradation by white rot fungi is extensively studied and degradation is caused by three extracellular phenol oxidases namely lignin peroxidases (LiP), manganese peroxidases (MnP) and laccases (Lac)(Peng Wang et al. 2008). In addition to degrading lignin, these fungi are also capable of degrading a variety of environmentally persistent pollutants such as chlorinated aromatic

compounds, heterocyclic aromatic hydrocarbons, synthetic high polymers and various dyes (Ohkuma et al, 2001).

- Several authors reported on the capacity of different fungal species to remove color from kraft mill effluent (Gokcay and Dilek, 1994; Duran et al., 1994; Sakurai et al., 2001). Prasad and Gupta (1997) reported on a substantial reduction of color and COD by the use of white rot fungi *T. Versicolor* and *P. Chrysosporium.* Saxena and Gupta (1998) showed that white-rot fungi *P. Chrysosporium* in combination with other white-rot fungi (*P. sanguineus*, *P. ostreatus and H. annosum*) and with the use of the surfactants were able to remove color, COD, and lignin content. Choudhury et al. (1998) found that lignin, BOD, COD and color removal were achieved to the extent of 77%, 76.8%, 60%, and 80%, respectively, by the fungal specie *Pleurotus ostreatus*. Taseli and Gokcay (1999) isolated fungal specie (*Pencillium sp.*) which was able to remove 50% of the AOX, and color from the soft-wood bleachery effluents in a contact time of 2 days. Zhang et al. (2000b) showed that fungus such as *T. versicolor* and fungal culture filtrate (FCF) obtained from these organisms were able to efficiently degrade the dissolved and colloidal substances. The other white rot fungi reported to degrade effluent color under optimum conditions include *Tinctoporia borbonica, Schizophyllum commune, Aspergillus fumigatus, Pleurotus ostreatus* among others (Singh and Thakur, 2004).

  On the basis of above information following research study has been conducted on laboratory scale to find remedies of pulp and paper mill waste water treatment..

Methodology

The study was conducted with the effluent released from Pulp and Paper mill, Chattishgarh. The factory uses cane molasses as the raw material. The effluent flows out into a 'nala' for about 10 km, which passes through the villages. The villagers use this effluent for the irrigation.

Sampling

The effluent sample from the Pulp and Paper mill were collected at the main outlet point where combined effluents from the factory are being disposed of into mill influent water. Water samples at the point of discharge were collected in clean plastic container from the main outlet. The sample was collected i.e. April 2016 from pulp and paper mill, Chattishgarh. Immediately after collection the water samples were brought to the laboratory and kept in the refrigerator at 4^0C till used for analysis.

Analytical methods

Electrical conductivity (EC) of the effluent was measured using a pocket type digital EC meter (Hanna Instruments Co.) calibrated at 20^0C. The reading was taken in milli siemens (ms m^{-1}). pH of the effluent sample was measured by a pH meter (model PR 8404) using glass electrode.

For total suspend solids 100 ml of the sample was centrifuged at 2000 rpm for 10 minute. The supernatant was removed and the residue was washed three times by resuspending it in distilled water and recollecting by centrifugation. The residue was finally transferred quantitatively to preweighted dish (X1g). The dish was weighed again after drying (X2g) to a constant weight (X1g). The dish was weighed again after drying (X2g) to a constant weight at 105^0C. TSS was calculated by using the following formula.

$$\text{TSS (ppm)} = \frac{(X_2 - X_1) \times 1000 \times 1000}{\text{ml of sample}}$$

The TDS was calculated as the difference between the total solids (TS) and total suspended solids (TSS), TDS (ppm), TS (ppm)-TSS (ppm).

COD and Colour unit was calculated by according to the standard method [6]. The sample was centrifuged at 1000 rpm for 30 minutes to remove all the suspended matter. The pH was adjusted to 7.6 with 2 M NaOH (CppA standard method) and then used for the measurement of absorbance at 465 mm. The absorbance values were transformed into colour unit (CU) using the following relationship.

$$\text{CU} = 500 \times \frac{A_2}{A_2}$$

where

A_1= Absorbance of 500 cu platinum cobalt standard solution (A_{405} = 0.132) and A_2 = Absorbance of the effluent sample [6]

Effects of different chemicals on pulp and paper mill individually and in combination

Three sets of three 100 ml sterilzied Erlenmeyer flasks were filled with 50 ml of sample effluent. In one set of flask $Al_2(SO_4)_3$ was added at the rate of each 1 g/l, 2 g/l and 5 g/l whilst in second set $KMnO_4$ was added at the rate of 1 g/l, 2 g/l and 5 g/l. The entire flasks were shaken at 150 rpm and 25^0C for 2 hrs. Thereafter, all the samples were centrifuged at 5000 rpm for 10 min. After that pH, EC, TSS TDS, COD and colour were measured.

Results

Pulp and paper mill Effluent was collected i.e. April 2016 from Pulp and Paper mill, Chattishgarh. The physico chemical analysis of spent wash (raw effluent) was highly acidic in nature with high BOD (32000 ppm), COD (45000 ppm), TDS (9566.66 ppm), TSS (97686.66 ppm), phenol (5.1ppm), sulphate (3800 ppm), nitrogen (299 ppm), phosphorus (767.66 ppm), potassium (481.33 ppm) and low content (Table 1). Raw pulp and paper mill effluent contains metal viz. Mn (3.68 ppm), Zn (3.781 ppm), Cu (0.31ppm), Ni (0.86 ppm) Fe (72.07 ppm) and Na (498 ppm). However, the pH of treated pulp and paper mill effluent was acidic and other parameters including metals were high in comparison of **MINAS** value. Physiochemical characteristics were analyzed and the data are given in Table 1.

The colour of the effluent was dark brown and colour unit was recorded 6287.87CU, whilst pH was in acidic range 5.1, (Table 4.1, Plate No. 1). The biochemical oxygen demand (32000 mg l^{-1}) and chemical oxygen demand (45000 mg l^{-1}) were also recorded.The pulp and paper mill also contained a good amount of N, P and K and chlorine content (Table 1)

From Table 4, pH was found to increase from 7.8 to 8.4 on increasing concentration (1 gl^{-1} to 5 gl^{-1}) of $KMnO_4$. Similarly colour, COD and BOD were decreasing with increasing concentration of $KMnO_4$. Maximum colour, COD and BOD reduction were recorded 21.25%, 93.79% and 81.48% respectively at 5g l^{-1} concentration of $KMnO_4$ (Table 2, Plate No. 1).

From Table 3, Decrease in pH was recorded from 3.3 to 2.0 on increasing concentration (1 gl^{-1} to 5 gl^{-1}) of $FeCl_3$ (Ferric chloride). Decrease in colour, COD and BOD were also observed with increasing concentration of $FeCl_3$. Maximum colour, COD and BOD reduction were recorded 99.10%, 54.16% and 85.92% respectively at 5g l^{-1} conc. of $FeCl_3$ (Table 3).

Table 1: Physico chemical analysis of pulp and paper mill effluent

Parameters	Mean value
BOD	32000± (577.35)
COD	45000 (±946.48)
Nitrogen	299 (±9.46)
Phenolic compounds	5.1 (±0.06)
Phosphorus	767.66 (±26.26)
Sulphate	3800 (±57.73)
Total suspended solids (TSS)	97686.66 (±566.10)
Total dissolved solids (TDS)	9,566.66 (±88.19)
Chlorine	2800(±26.83)
Colour	6287.87 (± 97.85)
Total organic carbon	2880(±22.30)
K	481.33 (±28.93)
Na	498 (±16.83)
Cu	0.31 (±0.03)
Fe	72.07 (±12.76)
Mn	3.68 (±0.64)
Ni	0.86 (±0.01)
Zn	3.781 (±0.06)

All the values are in ppm means (n=3) ± standard error.

Table 2: Effect of $KMnO_4$ on pH, CU, COD and BOD of the pulp and paper **effluent**

Conc. Of $KMnO_4$ / Parameters	**1g l^{-1}**	**3g l^{-1}**	**5gl^{-1}**
pH	7.8±0.34	8.1 ±0.17	8.4 ±0.11
CU	5835.47±1347.57 (7.19%)	5005.44±634.06 (20.39%)	4951.40±557.38 (21.25%)
COD (mgl^{-1})	28400±2338.80 (11.25%)	23866.66±2808.51 (25.41%)	1986.66±2313.96 (93.79%)
BOD (mgl^{-1})	17666.66±881.91 (60.74%)	12000±2390.40 (73.33%)	8333.33±1452.96 (81.48%)

Table 3: Effect of $FeCl_3$ on pH, CU, COD and BOD of the pulp and paper effluent

Conc. Of $FeCl_3$ / Parameters	**1g l^{-1}**	**3g l^{-1}**	**5gl^{-1}**
PH	3.3±0.31	2.3±0.57	2.0±0.15
CU	123.73±34.87 (98.03%)	134.24±15.27 (97.86%)	56.16±4.00 (99.10%)
COD (mgl^{-1})	22666.66±4745.68 (29.16%)	16000±1454.70 (50%)	14666.66±1763.83 (54.16%)
BOD (mgl^{-1})	14000±881.91 (68.88%)	10666.6±2309.40 (76.29%)	6333.33±1452.66 (85.92%)

All the values are in ppm mean (n=3) ± standard error

Significant correlation can be seen between colour unit, COD and BOD of the effluent. The result of the study also supports the findings of this study. Linear relationships amongst these parameters were observed . Most of these parameters are found to exceed beyond permissible limit and warrants treatment. The pattern of colour removal by chloride and sulphate salts of aluminium and iron were more or less similar. Per milli equivalent of metal ion for coagulation is based on percentage colour removal.

It was observed that ferrous sulphate alone was not effective in reducing the colour of effluent as it does not form floe with pulp and paper mill waste water. The other flocculant i.e. alum, ferric chloride, lime were found effective for colour removal. But these chemicals also depend on the pH of the waste water. Ferrous sulphate in combination with alum was effective to some extent in reducing colour of effluent due to producing of more acidic chemicals. While COD reduction is comparatively lower.

Thus, initial pH, molecular size and electrical charge have profound influence on the efficiency of colour removal and the chemical dosage required. The coagulant dose required to maximum colour removal was 5000-7000 mg/l in case of ferric chloride and almost double (12000 mg/l) in case of alum. In all cases, colour removal decreased beyond coagulant level (optimum coagulant dose). Percentage colour removal was significantly higher in the case of treated pulp and paper mill waste.

Colour causing substances present in pulp and paper mill waste are microcolloids which are hydrophilic in nature like proteins and other biopolymers. Stability of these colloids depends mainly on the hydration shell and high concentrations of colloids naturally required to withdraw the solvent from the hydration shell.

Potassium permanganate, hydrogen peroxide and bleaching powder were screened for removal of calcium from raw and treated pulp and paper mill waste. Only potassium permanganate and bleaching powder yielded good removal. Highest colour removal was attained 78%, the reduction in COD was of the order of 25-30% only. Similar results of 80% colour removal and 36% and 32% COD and BOD reduction from sugar fermentation process waste water by oxidation with chloride gas were reported by Swamy et al.

Potassisum permanganate react with a variety of organic substances which results in a net transfer of an oxygen atom from the manganate ion to the organic substrate. It has been reported that oxidation of organic compounds by potassium permangnate rarely results in complete destruction of molecule. It may, therefore, be inferred that chemical oxidation of colour causing substances results in chromophoric group rather than complete degradation of colour causing substances H_2O_2, Alum, other chemicals show similar reaction mechanism as $KMnO_4$.

CONCLUSIONS

Based on above studies the following conclusions are drawn:

(i) The pulp and paper mills use various plant bio-resources as raw materials such as bamboo, eucalyptus, agricultural waste residues such as rice straw, wheat, sarkanda grass, bagasse, jute/rags, etc as the raw materials. However, the raw materials used vary from mill to mill depending on the end product desired.

(ii) The chemical compounds found in pulp and paper mill effluent are mostly degrading products of lignin, cellulose, hemicellulose and wood extractives such as manomeric phenols, enol ethers, mercaptides, stilbene, quinone derivatives, chlorinated phenols, acetic acid, formic acid, acetaldehyde, methanol, furfural and methyl glyoxal. About 300 organochlorine compounds have been identified in effluent while hundred other remain unidentified.

(iii) Color is imparted to effluent by chromophoric compounds such as lignin and tannin, and the decolorization is efficiently achieved through fungal treatment, coagulation, chemical oxidation, and ozonation techniques.

(iv) Chlorinated phenolic compounds are produced during pulp bleaching stages. Chlorinated phenolic compounds and AOX can be removed by adsorption, ozonation and membrane filtration techniques. However, more studies are needed on the removal of AOX and chlorinated phenolic compounds.

(v) Physical and chemical processes are quite expensive to remove only high molecular weight chlorinated lignins, colour, toxicants, suspended solids and COD. However, BOD and low molecular weight compounds like alcohols and acids appreciably are not removed efficiently by these methods.

(vi) Aerobic processes such as Activated sludge process and Areated logoons are effective in removal of BOD and chlorinated phenolic compounds. The anaerobic treatment of high strength wastewater is not effective as it leaves high residual COD.

(vii) Both aerobic and anaerobic treatment systems are feasible to treat wastewater from all types of pulp and paper mills except that bleaching kraft effluents are less suitable for treatment by anaerobic means, as they are more toxic to anaerobic bacteria.

(viii) A combination using an anaerobic process followed by an aerobic treatment system is a better option, as it can make use of the advantages of both the treatment processes. Combinations of physicochemical and biological treatment processes with optimization of the process provide a long-term solution for pulp and paper mill effluent treatment and are the need of the hour to develop the technology which will allow mills to operate with zero effluent.

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