**REVIEW ARTICLE** 



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#### ABSTRACT

Pulp and paper mills are categorized as a core sector industry and are the fifth largest contributor to industrial water pollution. Pulp and paper mills generate varieties of pollutants depending upon the type of the pulping process. Pulp and paper mill effluents pollute water, air and soil, causing a major threat to the environment. Although the physical and chemical methods are on the track of treatment, they are not on par with biological treatment because of cost ineffectiveness and residual effects. The biological treatment is known to be effective in reducing the organic load and toxic effects of kraft mill effluents. None of the available conventional methods are permanent eco-friendly disposal solution. Biological methods have been acknowledged for the degradation of pulp and paper mill effluents. Biological methods involve microorganisms capable of degrading pulp and paper waste in natural environments. The biological colour removal process uses several classes of microorganisms- bacteria, algae and fungi-to degrade the polymeric lignin derived chromophoric material. Several methods have been attempted by various researchers throughout the world for the removal of colour from pulp and paper mill effluents.



**KEY WORDS** 

Pulp, paper, effluents, microorganism

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### [I] INTRODUCTION

Pulp and paper mill is a major industrial sector utilizing a huge amount of lignocellulogic materials and water during the manufacturing process, and release chlorinated lignosulphonic acids, chlorinated resin acids, chlorinated phenols and chlorinated hydrocarbon in the effluent [1]. The highly toxic dibenzo-p-dioxin and recalcitrant compounds, and dibenzofuran, are formed unintentionally in the effluent of pulp and paper mill [2, 3]. The untreated effluents from pulp and paper mills discharged into water bodies, damages the water quality. The undiluted effluents are toxic to aquatic organisms and exhibit a strong mutagenic effect. Several physical, chemical and biological methods are used for the removal of colour from the pulp and paper mill effluents. Physical and chemical processes are quite expensive and remove high molecular weight chlorinated lignins, colour, toxicants, suspended solids and chemical oxygen demand. But BOD and low molecular weight compound are not removed efficiently [4]. The biological colour removal process is particularly attractive since in addition to colour and COD it also reduces BOD and low molecular weight chlorolignins [5, 6]. Microorganisms rapidly degrade a few chemicals and eliminate them from the environment, but there are other chemicals that are degraded slowly, accumulate in the environment and occasionally exhibit toxicity [7]. Biodegradation of hazardous harmful substances in the environment embody significant prospective methods, when complex and ecologically unsound pollutants are decomposed into simpler substances (sound ones) by the action of microorganisms. The principle of biodegradation technologies is an optimization of nutrient ratios

(to support the growth of selected microorganisms able to degrade the target contaminants) and an application of suitably selected isolated microorganism strains with relevant degradation abilities [8]. Treatment of pulp and paper mill effluent has not proved successful due to lack of suitable microorganism, loss of genetic potentiality in adverse environmental conditions, formation of recalcitrant compounds of various structural formulation and poor process optimization for treatment at large scale. Although the physical and chemical methods are on the track of treatment, they are not on par with biological treatment because of cost ineffectiveness and residual effects. The biological treatment is known to be effective in reducing the organic load and toxic effects of krafts mill effluents [9]. The microorganism treats the effluents mainly by two process; action of enzymes and biosorption [10]. The various enzymes involved in the treatment of pulp and paper mill effluent are lignin peroxidase, manganese peroxidase and laccase [11]. Microorganisms showing good production of these enzymes have the potency to treat the effluent.

#### [II] PULP AND PAPER MILL

The manufacture of papers dates to the ancient Egyptians before 3000 B.C., while the 'modern' method of pulping plant material for paper production was developed by the Chinese in the first century A.D. The utilization of plant fiber for paper production is one of the oldest manufacturing industries and is built upon age-old technologies. It was not until this became mechanized and the scale of production escalated in the early part of last

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century that many of today's environmental problems associated with the pulp and paper industry emerged. For example, in the industrial manufacture of paper from wood fiber, it was known that natural compounds released during processing caused harm to aquatic population [12]. Pulp and paper are manufactured from raw materials containing cellulose fibers, generally wood, recycled paper, and agricultural residues. In developing countries, about 60% of cellulose fibers originate from nonwood raw materials such as bagasse (sugar cane fibers), cereal straw, bamboo, reeds, esparto grass, jute, flax, and sisal. In World Bank studies [13], pulp and paper manufacturing with unit production capacities greater than 100 metric tons per day. As per the Ministry of Environment and Forest (MoEF), Government of India, the pulp and paper sector is in the "Red Category" list of 17 industries having a high polluting potential. Pulp and paper production is a major industry in India with a total capacity of over 3 million tons per annum [14].

#### [III] CHARACTERISTICS OF PULP AND PAPER MILL EFFLUENTS

The pulp and paper industry produces effluents with large BODs and CODs. One of the specific problems that yet not been solved is the strong black brown color of the effluent, which is primarily due to lignin and its derivatives released from the substrate and discharged in the effluents, mainly from pulping, bleaching and chemical recovery stages. The brown color of the effluent may increase water temperature and decrease photosynthesis, both of which may lead to decreased concentration of dissolved oxygen [15].

The generation of waste water and characteristics of pulp and paper mill effluent depends upon the type of manufacturing process adopted and the extent of reuse of water employed in plant. Effluent depends upon type of manufacturing process adopted and the extent of reuse of water employed in plant. Effluent of kraft pulping is highly polluted, and characterized by parameters unique to these wastes such as colour, adsorbable organic halides (AOX) and related organic compound. The alkaline extraction stage of bleach plant effluent is the major source of colour and is mainly due to lignin and derivatives of lignin [16]. Lignin wastewater is discharged from the pulping, bleaching and chemical recovery sections. Lignin is a heterogeneous, three dimensional polymer, composed of oxyphenylpropanoid units. The high chlorine content of bleached plant reacts with lignin and its derivatives formed into highly toxic and recalcitrant compounds and the responsible for high biological and chemical oxygen demand. Trichlorophenol, tetrachloroguicol, trichloroguicol, dichlorophenol dichoroguicol and pentachlorophenol are major contaminats formed in the effluent of pulp and paper mill [17]. The pollutants at various stages of the pulping and paper making process are presented in Figure- 1[18].

Owing to its serious pollution threat, it is mandatory for pulp and paper mills to take appropriate measures to comply with the discharge standards set by the Central Pollution Control Board (CPCB) [19], which is the national agency responsible for environmental compliance. The minimum national standards for pulp and paper mills wastewater discharge according to CBCP are shown in **Table-1**.

#### Table: 1. Minimum national Standards for pulp and paper mills wastewater discharge (CPCB, 2000)

| PARAMETER                     | LARGE PAPER MILLS | SMALL PAPER MILLS |
|-------------------------------|-------------------|-------------------|
| РН                            | 6.5-8.5           | 5.5-9.0           |
| SUSPENDED SOLIDS (MG/L)       | 100               | 100               |
| BOD AT 27°C(MG/L)             | 30                | INLAND: 30        |
|                               |                   | Land: 100         |
| COD (MG/L)                    | 350               | -                 |
| TOTAL ORGANIC CHLORINE (TOCL) | 2.0               | -                 |
| (kg/ton paper 1992 onwards)   |                   |                   |
| SODIUM ABSORPTION RATIO (SAR) | -                 | 26                |

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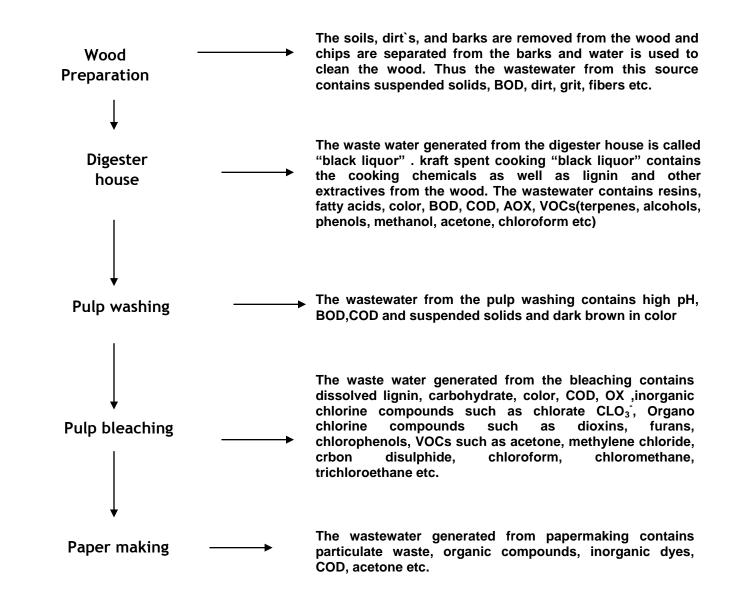


Fig: 1. Pollutants from various sources of pulping and papermaking (US EPA, 1995)

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#### [[V]] **TECHNOLOGIES** USED FOR TREATMENT OF PULP PAPER MILL AND **EFFLUENTS**

Recent developments in treatment of pulp and paper mill wastewater showed successful application of physical, chemical and biological treatment methods as well as combination of different methods in series. Commonly used physical and chemical treatment methods are electrocoagulation [20], ultrasound [21], reverse osmosis [22], photocatalytic systems using titanium dioxide (TiO<sub>2</sub>) and zinc oxide (ZnO) under UV/solar irradiation [23], hydrogen peroxide, Fenton's reagent  $(H_2O_2/Fe^{2+})$ , UV,UV/  $H_2O_2$  photo-Fenton (UV/  $H_2O_2/Fe^{2+})$ ,

ozonation and peroxon (ozone/ $H_2O_2$ )[24]. Some of these studies have optimized the operating conditions for effluent treatment [24-26]. Biological treatment methods involved the use of fungi, bacteria, algae and enzymes [27] as a single step treatment or in combination with other physical and chemical methods [28-30]. The biological treatment studies have confined themselves to the evaluation of microorganism, basic mechanism behind treatment and changes in the effluent after treatment. Not even a single study has optimized the process of effluent treatment. The microorganism treats the effluent mainly by two process: action of enzymes and biosorption as shown in Figure-3 [31]. The various enzymes involved in the treatment of pulp and paper mill effluent are lignin peroxidase, manganese peroxidase, and laccase [11]. Microorganism showing good



production of these enzymes have the potency to treat effluent. Biological treatment systems are particularly attractive, since in addition to colour they also reduce the BOD and COD of the effluent [27].

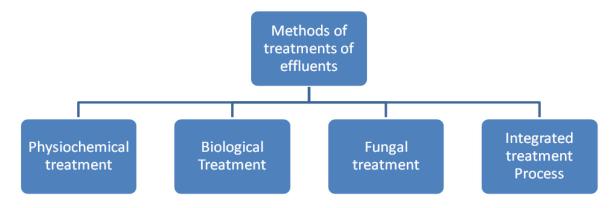


Fig:2. Figure showing different techniques used in the treatment of pulp and paper mill effluents

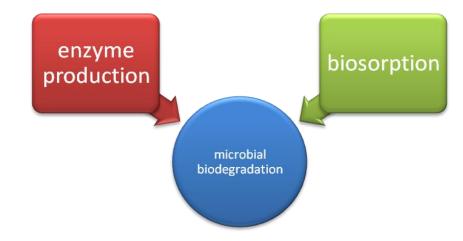


Fig: 3. Figure showing the two main process of microbial biodegradation of effluents

# [V] ENVIRONMENTAL IMPACT OF PAPER AND PULP MILLS

The environmental impact of paper and pulp mills is of particular concern since these units generate 150-200 m<sup>3</sup> effluent/ton paper with a high pollution loading of 90-240 kg suspended solids /ton paper,85-370 kg biochemical oxygen demand (BOD)/ton paper and 500-1100 kg chemical oxygen demand (COD)/ton paper [32]. Apart from the pollution, there is a growing water scarcity and deterioration in water quality in many parts of India [33]. Thus, in the context of reduced freshwater availability, declining water quality and environment pollution from inadequately treated effluent, there is an urgent need for efficient water management in pulp and paper mills. About 500 different chlorinated organic compounds have been identified in paper mill effluents [34]. The high chemical diversity of these pollutants causes a variety of clastogenic ,

carcinogenic, endocrinic and mutagenic effects on fishes and other aquatic communities in recipient water bodies [35-36].

# [VI] FATE AND AFFECTS OF PULP AND PAPER MILL EFFLUENTS

Various studies have reported detrimental effects of pulp and paper mill effluent on animals living in water bodies receiving the effluent. The effects are in form of respiratory stress, oxidative stress, liver damage and geno-toxicity [37-39]. A study in 1996 reported health impacts such as diarrhea, vomiting, headaches, nausea, and eye irritation on children and workers due to the pulp and paper mill wasterwater discharge to the environment [40]. The effluent has high chemical diversity of organic chemicals present in it. Many of them are carcinogenic, mutagenic, clastogenic and endocrinic disrupters. A study on *B.subtilis* reported the mutagenic effects of the sediments contaminated by the effluent of kraft paper mill [41]. REGULAR ISSUE Sharma et al.

Another study reports the toxic and mutagenic effects of pulp and paper mill effluent contaminating lake Baikal [42]. Exposure to the effluent adversely affects diversity and abundance of phytoplankton, zooplankton and zoobenthos, disrupting benthic algal and invertebrate communities [36]. Therefore it is obligatory to treat the effluent before disposal.

### [VII] NEED TO SEARCH A NEW TECHNOLOGY

In recent past, the colour of effluent discharge into waterways has become important problem. Pulp paper mill effluent has recognized as environmental hazards and categorized one of the twelve most polluting industry in our country. The dark brown colour of the effluent is mainly due to their high contents of oxidized and partially degraded lignin. Reducing this colour before the effluent is mainly due to their high contents of oxidized and partially degraded lignin. Reducing this colour before the effluents are discharged into natural water is an important goal. Other toxic contaminants of pulp and paper mill industry are chlorinated compounds [43, 27]. Physical and chemical methods undertaken to study colour removal from the effluent is not found to be cost-effective technology. Hence, biological treatment has been applied for the decolourization of effluent of pulp and paper mills. An important strategy for effluent treatment is the isolation and characterization of genetically significant microorganisms together with designing and optimization of process parameter to deal with specific environment pollutants [44].

# [VIII] ROLE OF MICROBES IN THE DEGRADATION OF PAPER MILL EFFLUENT

Microbial biodegradation is carried out by different organisms like Bacteria, Fungus, and Algae [45-46]. Effective Microorganism (EM) is the consortia of valuable and naturally occurring microorganisms which secretes organic acids and enzymes for utilization and degradation of anthropogenic compounds [47]. These days, microbes are collected from the waste water, residual sites and distillery sludges which are believed to have the resistance against the hazardous compounds. This is particularly due to their tolerance capacity even at the higher concentrations of xenobionts [48]. Bioremediation process involves detoxification and mineralization, where the waste is converted into inorganic compounds such as carbon dioxide, water and methane [49]. When compounds are persistent in the environment, their biodegradation often proceeds through multiple steps utilizing different enzyme systems or different microbial populations [50, 51].

### [IX] CONCLUSION

This review article may therefore serve as a challenge to researchers to continue developing better methods to degrade the effluents. Although decolourization is a challenging process

Y treatment of textile industry waste waters. However, potential of the strain needs to be demonstrated for its application in treatment of effluents. Environmental problems caused by the industrial effluents are mainly due to accumulation of pollutants having toxic compounds. There is a quick need to degrade these toxic compounds in an eco-friendly way. Microbial degradation technique has no negative impact on the environment. They degrade the toxic compounds in their own ways. Various techniques like microbial remediation, phytoremediation and photoremediation and their subtypes have been used as a ecofriendly methods. Although slow, on the whole microbial bioremediation was found to cover wide range of recalcitrant degradation and is known to be a better choice because of its nature of degradation.

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to the waste water treatment of pulp and paper mill, the result of

this findings and literature suggest a great potential for

microorganism to be used to remove color from wastewaters.

The microorganisms are adaptive in nature and can degrade

contaminants. The ability of the strain to tolerate, decolorize the

toxic effluents at high concentration gives it an advantage for

#### **CONFLICT OF INTEREST**

Author declares no conflict of interest.

#### FINANCIAL DISCLOSURE

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