



iJRASET

International Journal For Research in
Applied Science and Engineering Technology



INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 6 Issue: IV Month of publication: April 2018

DOI: <http://doi.org/10.22214/ijraset.2018.4335>

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Biodegradability Studies on Pulp and Paper Mill Wastewater: A Review

Ravichandran P¹, Balaji K², Karthik C³

^{1,3}Department of Civil Engineering, FEAT, Annamalai University, Annamalai Nagar, Tamil Nadu, India-608002

²Department of Civil Engineering, University College of Engineering, Anna University, Panruti Campus, Tamil Nadu, India-607106

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 and agro based pulp and paper mill effluents. A comparison of all treatment processes is presented. Combinations of anaerobic and aerobic treatment processes are found to be efficient in the removal of soluble biodegradable organic pollutants. Colour can be removed effectively by fungal treatment, coagulation, chemical oxidation, and ozonation. Chlorinated phenolic compounds and adsorbable organic halides (AOX) can be efficiently reduced by adsorption, ozonation and membrane filtration techniques.

Keywords: Biological treatment, COD removal, Colour removal, Pulp and paper industry, Wastewater

I. INTRODUCTION

Pulp and paper mill is a major industrial sector utilizing a huge amount of lignocellulosic 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 and recalcitrant compounds, dibenzo-p-dioxin 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. This review, therefore, would examine the pollution control systems and compare the performance of the effluent treatment measures in use [50].

A. 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 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].

B. Process for mill

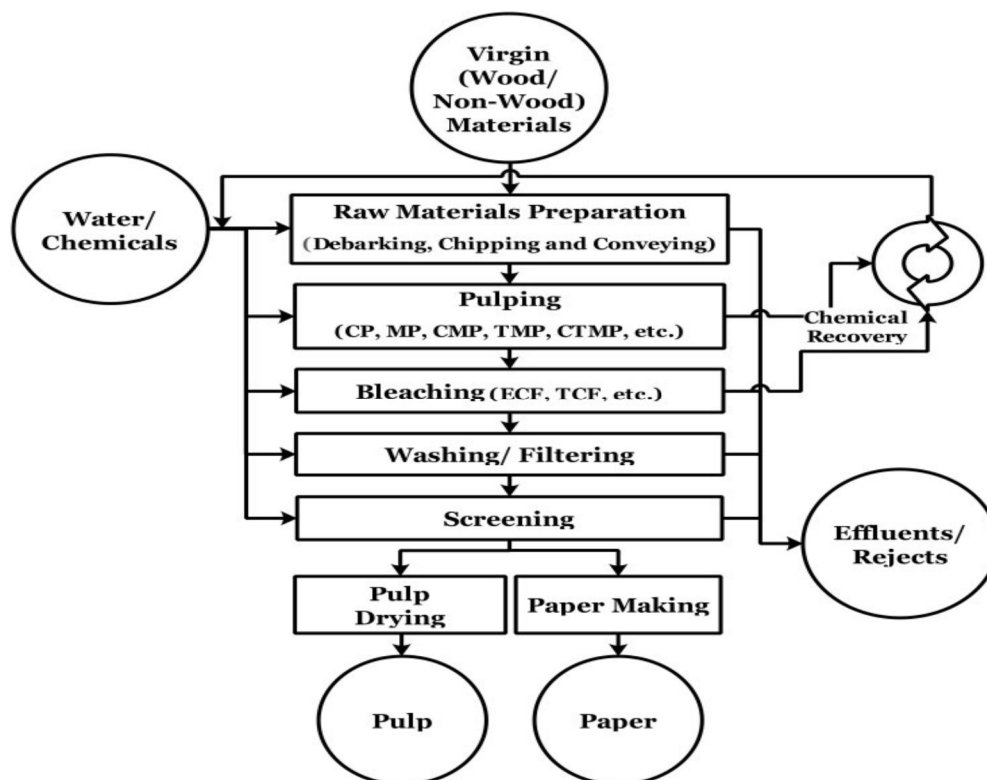


Fig. 1 Manufacturing process of pulp and paper industry

C. 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,

trichloroguilcol, tetrachloroguilcol, dichlorophenol, dichloroguilcol and pentachlorophenol are major contaminants formed in the effluent of pulp and paper mill [17].

TABLE I
Characteristics Of Wastewater At Various Pulp And Paper Processes

Process	Parameters						References
	pH	TS (mg/l)	SS (mg/l)	BOD ₅ (mg/l)	COD (mg/l)	Color (Pt-Co)	
Large mills (India)	11.0	5250	1233	983	2530	black	D. Pokhrel et al., (2004)
Small mills (India)	12.3	15,120	4890	2628	6145	DB	
Digester house	11.6	51,589	23,319	13,088	38,588	16.6 ^a	
Combined effluent	7.6	3318	2023	103	675	1.0 ^a	
TMP whitewater	4.7	–	91	1090	2440	–	
TMP whitewater	4.7	–	105	1125	2475	–	
Kraft mill	8.2	8260	3620	–	4112	4667.5	
Pulping	10	1810	256	360	–	–	
Kraft mill	8.2	1200	150	175	–	250	
Bleached pulp mill	7.5	–	1133	1566	2572	4033	
Bleaching	2.5	2285	216	140	–	–	
Pulp and paper	7.8	4200	1400	1050	4870	DB	
News air and land	8.3	450	400	16	78	–	
paper deinking							
Paper making	7.8	1844	760	561	953	Black	
Paper mill	8.7	2415	935	425	845	DB	
Paper mill bagasse	4.85	3226	1059	565	3403	LB	

^a Unit [Optical Density (O.D) at 465 nm]; ‘DB’ means dark brown; ‘LB’ means light Brown.

D. 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 m³ 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 [30]. Apart from the pollution, there is a growing water scarcity and deterioration in water quality in many parts of India [31]. 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 [32]. 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 [33, 34].

E. 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 [35-37]. 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 wastewater discharge to the environment [38]. 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 [39]. Another study reports the toxic and mutagenic effects of pulp and paper mill effluent contaminating lake Baikal [40]. Exposure to the effluent adversely affects diversity and abundance of phytoplankton, zooplankton and zoobenthos, disrupting benthic algal and invertebrate communities [34]. Therefore it is obligatory to treat the effluent before disposal.

F. Technologies Used for the Treatment of Pulp and Paper Mill 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 [19], ultrasound [20], reverse osmosis [21], photocatalytic systems using titanium dioxide (TiO₂) and zinc oxide (ZnO) under UV/solar irradiation [22], hydrogen peroxide, Fenton’s reagent (H₂O₂/Fe²⁺), UV,UV/ H₂O₂, photo-Fenton (UV/ H₂O₂/Fe²⁺), ozonation and peroxon (ozone/ H₂O₂) [24]. Some of these studies have optimized the operating

conditions for effluent treatment [23-25]. Biological treatment methods involved the use of fungi, bacteria, algae and enzymes [26] as a single step treatment or in combination with other physical and chemical methods [27-29]. 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 processes, either aerobic or anaerobic as shown in Figure 1. 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 [26].

G. 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 discharged into natural water is an important goal. Other toxic contaminants of pulp and paper mill industry are chlorinated compounds [41, 26]. 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 [42].

II. BIOLOGICAL TREATMENTS

Aerobic treatment

A. Activated Sludge Process

The performance variation of the activated sludge due to the changes in pH, temperature, and H_2O_2 and DTPA was reported by Ginkel et al. (1999), Norris et al. (2000), and Larisch and Duff (1997, 2000), respectively. Knudsen et al. (1994) reported a high reduction of BOD and soluble COD by a two-stage activated sludge process. Shere and Daly (1982) claimed that TMP wastewater was readily degradable by the activated sludge process. Hansen et al. (1999) suggested upgrading the activated sludge plant by the addition of Floobeds (floating biological bed) in series that increased COD and BOD removal from 51% to 90% and 70% to 93%, respectively. Chandra (2001) reported efficient removal of color, BOD, COD, phenolics, and sulfide by microorganisms such as *Pseudomonas putida*, *Citrobacter* sp., and *Enterobacter* sp. in the activated sludge process. Mohamed et al. (1989) reported removal of chlorinated phenols, 1,1-dichlorodimethyl sulfone (DDS), and chlorinated acetic acids in an oxygen activated sludge effluent treatment plant. Demirbas et al. (1999) reported AOX removal by the activated sludge process. Junna and Ruonala (1991) reported 90% BOD₇, 70% COD, 40–60% AOX, and 60–95% chlorinated phenols removal by the activated sludge process. Bryant et al. (1992) reported AOX removal of 46% on average from two activated sludge plant to improve the sludge settlability problem. Raghuvver and Sastry (1991) reported that a minimum of mixed liquor suspended solids (MLSS) of 2000–2500 mg/l and an aeration time of 6–8 h were required to remove 83–88% of BOD. High removals of BOD, COD, AOX, and chlorinated phenolics have been achieved in the activated sludge process (Saunamaki, 1997; Schnell et al., 2000a). Kennedy et al. (2000) reported that the activated sludge was successful in removing nearly all detectable Microtox toxicity from bleached kraft pulp mills at low level whereas the PACT was slightly better in removing highly toxic concentrated effluents. ludge systems studied. Andreasan et al. (1999) suggested the addition of an anoxic selector before the activated

TABLE II

DIFFERENT TREATMENT PROCESSES FOR PULP AND PAPER INDUSTRY WASTEWATER

Treatment Process	TSS		BOD		COD		AOX		Chlorinated phenolics	
	Influent (mg/l)	% Removal	Influent (mg/l)	% Removal	Influent (mg/l)	% Removal	Influent (mg/l)	% Removal	Influent (mg/l)	% Removal
Paper mill	1									
	4									
	3		51	94.			-	-	-	-
Paper mill	5	90.6	2	2	1210	82.4				
	7	76.4	33	93.8*	1192	57.1	11.7	55	-	-
Pulp mill	3		6							
	8									
Kraft mill (period 1)	-	-	27	>9	660	60	22.5	36	0.25	74
	-	-	0	5*	(F)				5	
Kraft mill (period 2)	-	-	27	>98	660	70	22.5	40	0.25	83
	-	-	0		(F)				5	
Pulp and paper mill	-	-	-	96.63	-	96.8	-	-	-	96.92
										D. Pokhrél et al.,(2004)
Paper mill			10	99	1533	85				
<i>Aerobic stabilization basin</i>										
Kraft mill (period 1)	-	-	27	>95	660	62	22.5	53	0.25	8
	-	-	0		(F)				5	5
Kraft mill (period 2)	-	-	27	>98	660	73	22.5	55	0.25	8
	-	-	0		(F)				5	6
Kraft mill	-	-	-	-		20-65	-	17-	-	-
								70		

- 1) ‘F’ means fraction of COD or soluble COD.
 - 2) Period 1: operating conditions for activated sludge-HRT 2 days, SRT 25 days, Temp. 30 °C, VSS 1800 mg/l.
 - 3) Period 1: operating conditions for aerated stabilization basin-HRT 15 days, SRT 15 days, Temp. 30 °C, VSS 60 mg/l.
 - 4) Period 2: operating conditions for activated sludge-HRT 1 day, SRT 25 days, Temp. 30 °C, VSS 2800 mg/l.
 - 5) Period 2: operating conditions for aerated stabilization basin-HRT 15 days, SRT 15 days, Temp. 20 °C, VSS 70 mg/l. ^a
- Means soluble COD and * means BOD₇

B. Aerated lagoons

Stuthridge and Mcfarlane (1994) stated that 70% removal of the AOX from the aerated lagoon was attributed to a short residence time section of the treatment system where the chlorinated stage effluents were mixed with general mill wastewaters. The effect

of simple mixing was reported to be responsible for 15–46% removal. Bryant et al. (1997) reported 67% removal of ammonia from black liquor spill at temperatures of 22–35 jC, pH near 7.3 in an aerated lagoon. Chernysh et al. (1992) reported large variations in AOX and TOC removal in a controlled batch study of bleached kraft effluent in an operating lagoon under both aerobic and anaerobic conditions. Welander et al. (1997) reported COD removal of 30–40% in a full-scale lagoon and 60–70% in a pilot-scale plant. Stuthridge et al. (1991) reported 65% removal of AOX from bleached kraft pulp and paper mill effluent. Junna and Ruonala (1991) reported removal of BOD₇ ranging between 50% and 75% and chlorinated phenolics 10–50% by an aerated lagoon. Achoka (2002) reported that an oxidation pond removed chemical compounds greater than 50%. Schnell et al. (2000a) reported removals of BOD, AOX, chlorinated phenolics, and polychlorinated phenolics respectively from an aerated lagoon.

C. Aerobic biological reactors

Many authors have reported high removals of organic pollutants of kraft mill wastewater by sequencing batch reactor (SBR) treatment (Franta et al., 1994; Franta and Wilderer, 1997; Milet and Duff, 1998). Reid and Simon (2000) reported 100% removal of methanol and 90% removal of COD_{sol} by SBR. Substantial removal of COD, TOC, BOD (Magnus et al., 2000a), lignin and resin acids (Magnus et al., 2000b) of TMP wastewater using high rate compact reactors (HCRs) at a retention time of 1.5 h had been reported. Removal of COD by a moving bed bifilm reactor (MBBR) had been demonstrated (Jahren et al., 2002; Borch-Due et al., 1997). Magnus et al. (2000c) reported 93% and 65% removal of BOD and COD, respectively by a biological compact reactor. Berube and Hall (2000) showed that approximately 93% removal of TOC could be achieved by a membrane bioreactor. Asselin et al. (2000) concluded that suspended carrier biofilm reactor (SCBR) was highly efficient in removing chronic toxicity from the effluent. Rovel et al. (1994) achieved 76%, 62%, 81%, and 48% removal of BOD, COD, SS, and AOX, respectively, using a biofilter. Rudolfs and Amberg (1953) demonstrated that aerobic treatment of whitewater (high strength) was able to achieve 70–80% removal of BOD. Typical efficiencies of aerobic systems are presented in Table 8.

D. Anaerobic treatment

An anaerobic process is considered more suitable to treat high strength organic effluents. Before 1980s, the treatment of pulp mill effluents by anaerobic means was limited, as most of the pulp mill effluents at that time were less concentrated (300–2000 mg/l BOD) (Bajpai, 2000) and were not suitable for anaerobic treatment. Anaerobic filter, upflow sludge blanket (UASB), fluidized bed, anaerobic lagoon, and anaerobic contact reactors are anaerobic processes, that are commonly used to treat pulp and paper mill effluents. Pretreatment of the kraft mill black liquor was investigated by Poggi-Varaldo et al. (1996) and they reported that continuous anaerobic treatment of wastewater contaminated with black liquor was feasible at low to medium loading rates, with a total COD removal of 48–80% and biodegradable COD reduction of 87–96%. Jahren et al. (1999) compared anaerobic and aerobic treatment for TMP mill effluent and found that 84% and 86% removal of COD from anaerobic and aerobic treatment systems, respectively, was achieved. Rajeshwari et al. (2000) reported that chlorine bleaching effluents were not suitable for anaerobic treatment due to their low biodegradability and presence of toxic substances that affects methanogens. Sandquist and Sandstrom (2000) developed a new treatment technology [the process consists of three steps: (1) stripping of sulfides and other volatile components from condensate; (2) regenerative thermal oxidation of stripper off gases; (3) adsorption of sulfur oxide] to treat foul condensate (sulfide) from the black liquor. Removal efficiency for foul condensate was reported to be more than 99% at a pH of 4 and removal of methanol was 90% at a low liquid/gas ratio. Jackson-Moss et al. (1992) found 50% removal of COD and color by anaerobic biological granular activated carbon. Dufresne et al. (2001) observed that undiluted foul condensates at Windsor mill were toxic to anaerobic biomass. Chen and Horan (1998) stated that COD, and sulfate removals of 66% and 73%, respectively, were obtained using a UASB reactor with a hydraulic retention time of 6 h. Peerbhoi (2000) investigated anaerobic treatability of black liquor by a UASB reactor in her study at the University of Roorkee, India. The author concluded that anaerobic biological treatment of black liquor was not feasible, as the pollutants were not readily degradable. Perez et al. (1998) evaluated two anaerobic systems (anaerobic filters and fluidized bed) in laboratory-scale reactors and reported that 81.5% organic removal efficiency was obtained in the case of fluidized bed with porous packing and 50% removal was obtained in the case of anaerobic filters on corrugated plastic tubes. Rajeswori et al. (2000) reported a 50% reduction of BOD of debarking wastewater by a fluidized bed reactor. Thompson et al. (2001) reported that COD removal efficiency of 80% was constantly achievable but the residual COD was around 800 mg/l meaning that additional treatment was essential. Schnell et al. (1992)

concluded that anaerobic treatment systems were less suitable for treatment of sulfite-spent liquor compared to an aerobic system. The anaerobic treatability of different processes [52].

TABLE III
SELECTED ANAEROBIC PROCESS PERFORMANCE (BAJPAI, 2000)

Mill location	Wastewater source	Loading rate (kg COD/m ³ /d)				BOD5	COD
			BOD5 (mg/l)	COD (mg/l)	TSS (mg/l)	Removal %	Removal %
Anaerobic contact reactor							
	TMP,	2.5	1300	3500	520	71	67
Hylte Bruk AB, Sweden	Ground wood, deink						
SAICA, Zaragoza, Spain	Waste paper alkaline cooked straw	4.8	10,000	30,000	-	94	66
Hannover paper, Alfred, Germany	Sulfite effluent condensate	4.2	3000	6000	-	97	85
Niagara of Wisconsin of USA	CTMP	2.7	2500	4800	3300	96	77
SCA Ostrand, Ostrand, Sweden	CTMP	6	3700	7900	-	50	40
Alaska Pulp Corporation, Sitka	Sulfite condensate, bleach caustic and pulp whitewater	3	3500	10,000	-	85	49
Upflow anaerobic sludge blanket							
Celtona, Holland	Tissue	3	600	1200	-	75	60
Southern paper converter, Australia	Wastepaper	10	-	10,000	-	>80	> 80
Davidson, United Kingdom	Linerboard	9	1440	2880	-	90	75
Chimicadel, Friulli, Italy	Sulfite condensate	12.5	12,000	15,600	-	90	80
Quesnel River Pulp, Canada	TMP/CTMP	18	3000	7800	-	60	50
Lake Utopia Paper, Canada	NSSC	20	6000	16,000	-	80	55
EnsoGutzeit, Finland	Bleached TMP/CTMP	13.5	1800	4000	-	75	60
McMillan Bloedel, Canada	NSSC/CTMP	15	7000	17,500	-	80	55
Anaerobic filter: Lanaken, Belgium	CTMP	12.7	4000	7900	-	85	70
Anaerobic fluidized bed: D' Aubigne, France	Paperboard	35	1500	3000	-	83.3	72.2

III. FUNGAL TREATMENT

Taseli and Gokcay (1999) isolated fungal specie (*Penicillium* 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. 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*. Zhang et al. (2000a) examined the removal of most of the detrimental organics from whitewater by combined enzyme and fungal treatment. The removal of lignin was >90% whereas resin and fatty acids were reduced by 20%. 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. Mendonca et al. (2002) suggested fungal pre-treatment of *P. taeda* wood chips by *C. subvermispora*. The performance of fungal treatment is summarized.

IV. INTEGRATED TREATMENT PROCESSES

An integrated or hybrid system is designed to take advantage of unique features of two or more processes. A combination of coagulation and wet oxidation removed 51% of COD (Verenich et al., 2001); and 83% of color and 75% of lignin (Verenich and Kallas, 2001). A combination of ozone and biofilm reactor removed 80% COD (Helble et al., 1999). A combination of chemical oxidation with ozone removed 90% of wood extractives and 50% of the COD from TMP wastewater at 150 jC (Laari et al., 1999). Athanasopoulos (2001) suggested post treatment methods such as electrolysis or ozonation to reduce COD, and $\text{NH}^+ - \text{N}$ concentration to the permitted level. Nakamura et al. (1997) reported on efficient degradation of lignin using a combined treatment of ozone and activated sludge process. Jokela and Keski-talo (1999) reported that a combination of dissolved air flotation and chemical precipitation removed 93% SS, 50% BOD₇, 57% COD, 92% phosphorus, and 52% nitrogen.

A combination of activated sludge and with ozonation (as tertiary treatment) removed 87 – 97% COD, and 97% BOD (Schmidt and Lange, 2000). Kabdash et al. (1996) showed that a combination of chemical and biological methods (bioferic) resulted in 40–50% additional removal of COD compared to the activated sludge system. Jahren and Oedegaard (1999) found that Kaldnes (anaerobic followed by aerobic) moving bed biofilm reactor at 55 removed about 60% of soluble COD from TMP whitewater. A combined anaerobic – aerobic treatment system was suggested to treat bleached kraft pulp and paper mill effluents (Duncan and Thia, 1992; Wang et al., 1997). Lescot and Jappinen (1994) showed that a combination of an aerated lagoon and a secondary clarifier was able to treat bleached kraft mill effluent in Finland resulting in 87%, 96%, 65%, 53%, and 22% removal of SS, BOD₇, COD, AOX, and color, respectively. Carlson et al. (2000) reported that 77%, 98–99%, 72%, and 81% removal of COD, BOD, TN, and TP, respectively, was achieved after upgrading the aerated basin at Monsteras mill. The system comprised of an anoxic selector, an aerated basin, and a secondary clarifier in series. The removals of extractives, resin and fatty acids were 96% and 98%, respectively, whereas the system reduced Microtox_K by 99%. Welander et al. (2000) reported on the performance of an aerobic biological process called LSP (low sludge production) to lower the biological sludge by 80 – 90%. The system configuration was primary clarifier, aeration basin, and secondary clarifier. A combination of physicochemical, biological, and effluent polishing in the aerated lagoon removed 98 - pulp and paper mill in Brazil (Foelkel, 1989). Rusten et al. (1994) reported that a combination of a biofilm reactor followed by one anaerobic and two aerobic reactors was found to remove 50% COD, 80–90% BOD₇, 50% AOX, 90% ClO_3 . Shaw et al. (2002) showed that a combination of aerobic reactor followed by anaerobic reactor removed 94% color, and 66% TOC. Schnell et al. (1997) found that 87–95%, 70–77%, and 80–94% removal of BOD, COD, and resin and fatty acids was provided by biological treatment. Tardif and Hall (1997) reported 100%, 96%, 76%, and 34% removal of resin acid (RA), fatty acid (FA), dissolved chemical oxygen demand (DCOD), and total dissolved solids (TDS), respectively at temperatures 20–40 jC by an SBR. An MBR removed 100% RA and FA, 84% DCOD, and 37% TDS at 40–50 jC. Malmquist et al. (1999) reported a COD removal of 70–90% of wastewater by biological treatment. Badar (1996) suggested a number of methods to improve the integrated paper mill wastewater effluent treatment: (1) increasing the capacity of the aeration basin; (2) installing an extra dissolved air flotation clarifier; (3) adding chlorine gas to improve bulking of sludge problem and (4) injecting oxygen to treat BOD during heavy rain and flooded conditions. Graves and Joyce (1994) reviewed the ability of biological treatment systems to remove chlorinated organic compounds discharged from pulp and paper industry. AOX removal of 32% (aerated lagoon) and 10–65% by activated sludge plant was reported. Gupta et al. (2001) isolated bacterial specie *Aeromonas formicans* suitable to treat black liquor from kraft pulp and paper mills. Performances of various treatment processes are summarized.

V. ROLE OF MICROBES IN THE DEGRADATION OF PAPER MILL EFFLUENT

Microbial biodegradation is carried out by different organisms like Bacteria, Fungus, and Algae [43-44]. 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 [45]. 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 xenobiotics [46]. Bioremediation process involves detoxification and mineralization, where the waste is converted into inorganic compounds such as carbon dioxide, water and methane [47]. When compounds are persistent in the environment, their biodegradation often proceeds through multiple steps utilizing different enzyme systems or different microbial populations [48, 49].

VI. CONCLUSION

Based on the above literature review, the following conclusions are drawn:

- 1) 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 bacteria.
- 2) The anaerobic treatment of high strength wastewater requires further treatment as it contains high residual COD.
- 3) 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.
- 4) Color is removed efficiently by fungal treatment, coagulation, chemical oxidation, and ozonation.
- 5) Chlorinated phenolic compounds and AOX can be removed by adsorption, ozonation and membrane filtration.
- 6) Combinations of two or more physicochemical processes produce a high removal of toxic pollutants.
- 7) Combinations of physicochemical and biological treatment processes with optimization of the process provide a long-term solution for pulp and paper mill effluent treatment.
- 8) More studies are needed on the removal of AOX and chlorinated phenolic compounds

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