Bioremediation Approaches for Treatment of Pulp and Paper Industry Wastewater: Recent Advances and Challenges

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Vineet Kumar, Indu Shekhar Thakur, and Maulin P. Shah

Abstract

Pulp and papermaking industry is a large consumer of fresh water and also an important source of dark-brown-colored wastewater, generated during various stages of pulping and papermaking activities. The colored wastewater discharged from pulp and paper industry even after secondary treatment remains toxic and complex in nature and retains high amount of lignin, lignin residues, resins, acids, chlorinated phenols, and various persistent organic pollutants (POPs) including the adsorbable organic halides (AOXs; halogenated or organochlorine). The existing various conventional methods along with integrated processes (aerated lagoons and activated sludge plants) cannot efficiently treat pulp and paper industry wastewater due to its complex and recalcitrant nature. Hence, the discharged partially treated/or untreated wastewater are contributing to deteriorating water quality due to increasing biological oxygen deman and chemical oxygen demand and decrease of dissolved oxygen.

In a terrestrial ecosystem, the wastewater irrigated soil showed decrease of moisture content and increase of pH and toxic heavy metals content. To tackle this problem associated with hazardous waste disposal, the existing pulp and paper industry wastewater treatment process needs to be improved with better treatment outcomes. Although, several physicochemical methods are available for the treatment of such wastewater, they are more energy intensive and suffer from residual effect. In addition, they are very expensive, inefficient, and produce a huge amount of toxic sludge which is difficult to handle and also produces volatile organic compounds on burning. To combat these challenges, biological

V. Kumar (✉) · I. S. Thakur
Environmental Microbiology and Biotechnology Laboratory, School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, India

M. P. Shah
Environmental Microbiology Lab, Bharuch, Gujarat, India

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treatment using bacteria, fungi, yeasts, and algae has evolved as a preferred means to treat and reduce the toxic organic compounds loaded in generated pulp and paper industry wastewater.

Keywords
Adsorbable organic halides · Persistent organic pollutants · Phytoremediation · Chlorinated lignin · Bleaching

1.1 Introduction

Pulp and paper industry are among the most important industries in the world not only for an economical purpose but also for a social purpose. Besides, it is also one of the major polluting industry discharging a variety of organic and inorgaic pollutants such as gaseous, liquid, and solid into the environment (Ali and Sreekrishnan 2001; Lacorte et al. 2003; Singh and Chandra 2019). Consider that manufacture of paper consumes significant quantities of wastewater, as high as 200–350 m^3 $tonne^{-1}$ of paper produced, of which nearly 75% is discharged as wastewater (Nagarathnamma et al. 1999). Currently, there are 759 paper mills operating in India, out of which 30 are wood-based large-scale mills, 150 are agro-based medium-scale mills, and 579 are recycled fiber-based medium and small-scale mills, producing 3.40, 2.42, and 5.10 Mtpa paper, respectively (Rajwar et al. 2017). As per the Ministry of Environment, Forest and Climate Change (MOEF&CC), Government of India, the pulp and paper sector is in the Red Category list of 17 industries having a high pollution potential owing to its serious environmental threat. Most significant sources of pollutants in pulp and paper mills are pulping of raw materials (wood chips), pulp bleaching, and paper coating processes (Bajpai et al. 1993; Nagarathnamma et al. 1999; Yadav et al. 2010; Rocha-Santos et al. 2010; Singh and Chandra 2019). Pulping process results in dissolved forms of lignin and other wood components called black liquor (BL) due to its black color, whereas bleaching produces the mono-aromatic compounds like chlorophenols, catechols, and guaiacols and numerous high-molecular-weight organic compounds like phenols, chlorolignins, chlorophenols, adsorbable organic halides (AOXs), extractable organic halides (EOXs), and plasticizers (Mishra and Thakur 2010; Mishra et al. 2014; Chandra et al. 2011a, b). Besides, bleached effluent is heavily loaded with organic matter, having high suspended solids (SS), color, biological oxygen demand (BOD), chemical oxygen demand (COD), total organic chlorides (TOC), chlorinated resin acids, phenols, dioxins, and furans (Larsson et al. 1988; van Driessel and Christov 2001; Leadbitter 2009; Yadav et al. 2010; Malaviya and Rathore 2007). These parameters have discharge limits, laid down by various environmental regulatory authorities around the globe. The high values of COD in wastewater also indicate the recalcitrance of chemicals that have escaped biodegradation processes (Mahesh et al. 2006; Gommers et al. 2007; Chen et al. 2012a, b, c). These chemicals may be persistent in nature and may cause several problems to animals, plants, microorganisms and human healt (Singh and Chandra 2019). According to the United States Environmental Protection Agency (USEPA), 27% (wt %) of municipal solid waste is composed of paper waste, and about 100 million kg of toxic pollutants are released every year from the paper industries.

Some large-scale pulp and paper mills have recovery boilers to burn much of the BL they produce, generating steam and recovering the cooking chemicals, viz., sodium hydroxide (NaOH) and sodium sulfide (Na_2S_2) which are used to separate lignin from the cellulose fibers of wood chips needed for papermaking (Pokhrel and Viraraghavan 2004; Mishra and Thakur 2010). This chemical reaction and burning of organic materials release a considerable amount of heat energy which is recovered by transferring it through water-filled tubes in walls of the recovery boiler. However, they are inefficient, costly, and produce a huge amount of toxic sludge which is difficult to handle (Thompson et al. 2001; Mishra and Thakur 2010; Qadir and Chhipa 2015). On burning, volatile organic compounds (VOCs) like dioxins and furans are formed which are more toxic than the parental compounds. Small-scale pulp and paper mills often lack such installations due to their high operational costs and do not have satisfactory and adequate wastewater treatment facilities; as a result, unrecovered wastewater amplify the pollutant toxicity and are a cause of serious environmental concern (Oke et al. 2017; Singh and Thakur 2006; Medhi et al. 2011; Ojunga et al. 2010; Tyor et al. 2012). In aquatic system, it blocks the photosynthesis reaction processes and decreases the dissolved oxygen (DO) level which adversely affects the flora and fauna and causes toxicity to aquatic ecosystem (Poole et al. 1977; Leadbitter 2009; Hou et al. 2018), whereas in the contaminated soil, it showed the accumulation of toxic recalcitrant organic pollutants and heavy metals (Kumar and Chopra 2011; Pradhan and Behera 2011; Roy et al. 2008; Medhi et al. 2011). Several pollutants that discharged in pulp and paper mill are also reported as carcinogenic, mutagenic, clastogenic, and endocrine-disrupting in nature (Haq et al. 2017; Mishra et al. 2014). Therefore, it is mandatory for pulp and paper mills to comply with the appropriate standards set by Central Pollution Control Board (CPCB), New Delhi, India. However, potential advanced processes that are used for wastewater treatment discharged from pulp and paper industry includes chemical coagulation, flocculation, precipitation, ion exchange, advanced oxidation processes, ozone treatment, electrochemical degradation, membrane processes (especially reverse osmosis, nanofiltration, and ultrafiltration), photocatalytic degradation, and adsorption on activated carbon, as a means of removing color and turbidity from wastewater (Subramonian et al. 2017; Gonder et al. 2012; Birjandi et al. 2016; Mahesh et al. 2016; Yeber et al. 1999; Stephenson and Duff 1996; Pihlajamäki and Nyström 2002; Mahesh et al. 2006; Rodrigues et al. 2008).

However, these treatment approaches offer an economic nonviability, limited versatility, operational constraints, partial treatment, and plausible formation of secondary hazardous by-products and also generate a huge amounts of toxic sludge that limit their industrial applicability (Pokhrel and Viraraghavan 2004; Thompson et al. 2001; Zhang et al. 2009). Researchers across the globe have tried to devise innovative methods for achieving maximum reduction in the color, BOD, and COD loadings of pulp and paper mill wastewater (Gommers et al. 2007; Singh and Thakur

2006; Singhal and Thakur 2012). The conventional biological treatment methods, such as activated sludge (AS) and aerated lagoons (extended aeration methods), are ineffective in removing color and phenolics and also do not decolorize wastewater very effectively (Lerner et al. 2007; Qadir and Chhipa 2015; Erkan and Engin 2017). However, certain advanced biotechnological treatment methods, such as biodegradation using potent microorganisms, can prove to be effective for further treatment of toxic organic pollutants and decolorization of such wastewater compared to chemical treatment and conventional aerobic–anaerobic treatment, as lesser sludge would be produced, with an additional low-cost benefit (Ragunathan and Swaminathan 2004; Abira et al. 2005; Dias et al. 2005; Chandra and Singh 2012; Chandra and Kumar 2015b, 2017b). The use of microbes for biodegradation of refractory organic compounds is an efficient, relatively cost-effective, and environment-friendly tool for the treatment of industrial wastewater (Kumar et al. 2018; Kumar and Chandra 2018a, b). However, biotechnological methods using fungi, bacteria, and actinomycetes are less effective for complete decolorization and detoxification of pulp and paper industry wastewater (Latorre et al. 2007; Raj et al. 2005; Raj et al. 2014a, b; Singhal and Thakur (2009a, b). Although a plethora of information is available on biological treatment methods for BL, there is an acute shortage of efforts to make the process being implemented effective on a large scale application.

1.2 Pulp and Paper Industry Wastewater Generation and its Characteristics

Paper manufacturing process involves three steps: pulping (also called delignification), bleaching, and finally papermaking. The purpose of pulping is to extract cellulosic content from plant materials obtained from hardwood or softwood trees. Generally, three approaches like mechanical pulping, chemical pulping, and a combination of both mechanical and chemical pulping are known to produce pulp from wood (Sandstrom et al. 1988; Esposito et al. 1991; Martin and Manzanares 1994; Thompson et al. 2001). However, the main drawback of mechanical pulping is yielded low-quality pulps, unsuitable for high-strength fiber products, and high energy requirements (Stephenson and Duff 1996). Mechanical pulping causes less pollution than chemical pulping. The most important delignification (chemical pulping) processes are kraft, sulfite, and soda pulping (Abdelaziz et al. 2016; Becker and Wittmann 2019; Wong 2009). Kraft pulping is a process in which wood chips are cooked in a large pressure vessel called a digester at 155–175 °C in an aqueous solution NaOH and Na_2S_2, also known as white liquor, to dissolve lignin from cellulose and hemicellulose fibers of the wood chips. The thus formed hydroxide (OH-) and hydrosulfide (HS-) anions crack the aromatic ether bonds within the lignin structure and release low-molecular-weight thiolignin oligomers (Abdelaziz et al. 2016). Sulfite pulping is a process of cooking of wood chips at 140–170 °C in alkaline, a pH neutral or an acidic environment, depending on the added sulfite salt (Abdelaziz et al. 2016; Schutyser et al., 2018). The ether bonds within the lignin structure are thereby hydrolyzed and subsequently sulfonated by the sulfite ions

(SO_3^{-2}) in the liquor. Sulfite pulping produces fully water-soluble, highly degraded lignosulfonates with a sulfur content of 4–7 wt% (Abdelaziz et al. 2016; Schutyser et al., 2018; Van den Bosch et al., 2018). Established in 1874, sulfite pulping became the dominant process for wood delignification until kraft pulping was established in the 1930s. Similar to kraft and sulfite pulping, soda pulping involves cooking biomass at 160–170 °C in presence of soda (NaOH) and—optionally—anthraquinone, the latter increasing the efficiency by promoting reductive ether bond cleavage (Abdelaziz et al. 2016; Schutyser et al., 2018; Van den Bosch et al., 2018). The wastewater generated at the end of pulping stage called BL is a dark brown in color due to dissolved lignin and its degradation products, hemicelluloses, resins, acids, and phenols (Hermosilla et al. 2015). The BL has high COD, BOD, and TSS (Pokhrel and Viraraghavan 2004). In the pulping process, less than 50% yields are achieved, and the pulp requires further extensive bleaching. During the bleaching process, wood components such as lignin and some carbohydrates are structurally modified, oxidized, degraded and chlorinated (Thompson et al. 2001; Leadbitter 2009; Oke et al. 2017). This is followed by an alkaline extraction phase using high temperature, pH, and consistency, which transforms the oxidized products into a soluble form. In the extraction stage, chlorinated oxidized lignins, not soluble in the acidic chlorination stage, are solubilized and dissolved into the spent liquor. The final bleaching is performed by oxidizing agents: chlorine dioxide and hydrogen peroxide. In India, bleaching is still being done with chlorine. Chlorine dioxide is used by very few mills for viscosity protection in the first bleaching stage (10–15% substitution) and for brightening in the final bleaching stages (Nagarathnamma et al. 1999). The use of chlorine-based bleaching chemicals results in the generation of a large number of toxic chlorinated organic compounds. The wastewater generated at bleaching stage has toxic colored compounds, including chlorophenols, EOXs, AOXs, and a small proportion of extremely toxic DDT, polychlorinated biphenyls (PCBs), and polychlorinated dibenzodioxins (PCDDs) (Savant et al. 2006; Chandra and Kumar 2015b; Lacorte et al. 2003; Rocha-Santos et al. 2010; Singh and Chandra 2019). In addition, chromophoric and highly oxidized polymeric lignin/chlorolignin derivatives are formed giving rise to the characteristic dark color to BL (Fig. 1.1; Nagarathnamma et al. 1999; Esposito et al. 1991; Chedchant et al. 2009; Chandra et al. 2011a, b; Mishra et al. 2014). A large number of pulp and paper mills are reluctant to recycle bleach plant wastewater to the chemical recovery system due to the corrosive nature of chloride ion and the substantial dilution of the chemicals to be recycled. Acid precipitation of lignin is a commonly applied treatment to BL after precipitation of more than 90% of lignin is removed from the solution as solid material. In addition, the precipitated lignin generates large volumes of sludge, which requires further treatment and disposal (Thompson et al. 2001; Pokhrel and Viraraghavan 2004). Nevertheless, the remaining soluble percentage is composed of oxidized and partially degraded lignin (predominantly composed of oligomeric lignin compounds) chlorinated organics responsible for the mutagenicity of the effluent. The high-molecular-weight persistent chlorinated organic compounds along with residual lignin generated during pulp bleaching are the major contributor to effluent color, COD, and chronic toxicity (Ali and Sreekrishnan 2001; Pandey

Fig. 1.1 Pulp and paper industry wastewater. (**a**–**c**) the huge volume of complex brown color wastewater generated during pulping and bleaching process and discharged into the environment after secondary treatment; (**c**, **d**) a large view of the collected pulp and paper industry wastewater

et al. 2012; Verma 2008; Maheshwari et al. 2012; Thompson et al. 2001). Finally, the brown/black color effluent generated during pulping and bleaching processes is a complex mixture of hundreds of compounds like lignin, tannin, chlorinated phenol compounds, suspended solids, diterpene alcohols, waxes, fatty acids, resin acids, fatty acids and their degraded products, phenols, dioxins, furans, chlorinated resin acids, chlorinated phenol, chlorinated hydrocarbons, various surfactants, dibenzo-p-dioxins, and dibenzofurans (Fig. 1.1; Ali and Sreekrishnan 2001; Rocha-Santos et al. 2010; Savant et al. 2006; Lacorte et al. 2003). While some of these pollutants are naturally occurring wood extractives (e.g., tannins, resin acids, stilbenes, lignin), others are xenobiotic compounds that are unintentionally generated formed during the process of pulping and papermaking processes (Thompson et al. 2001; Lacorte et al. 2003).

Thus, effluents discharged from industries are heavily loaded with organic matter containing 200 organics and 700 kinds of inorganic compounds (Table 1.2; Chandra and Singh 2012; Chandra and Abhishek 2011; Chandra et al. 2011a, b; Haq et al. 2016; Haq et al. 2017; Karrascha et al. 2006). Table 1.1 summarizes the physico-chemical characteristics of different kinds of influent generated during pulp and paper making process in pulp and paper industry. Some of the pollutants notably polychlorinated dibenzodioxins and dibenzofurans (dioxins and furans) are

Table 1.1 Physicochemical characteristics of wastewater discharged from various industries (Chandra and Abhishek 2011; Chandra et al. 2011a, b; Arivoli et al. 2015)

Parameters	BL	RGPPME	PPME	PPME
pH	8.8 ± 0.2	9.0 ± 0.2	8117.50 ± 185	7.80 ± 0.012
Color (Pt/co)	3100 ± 22.32	6100 ± 3.5	–	877.29 ± 4.65
EC (μS cm^{-1})	–	–	–	3.87 ± 0.06
Turbidity (NTU)	–	–	–	274.36 ± 1.04
BOD (mg L^{-1})	5100 ± 167.6	7360 ± 153	5850 ± 50.12	230.18 ± 2.75
COD (mg L^{-1})	12,245 ± 439.5	18,700 ± 440	16,400 ± 120	981.75 ± 4.29
TDS (mg L^{-1})	402.68 ± 53.92	1402 ± 1.5	840 ± 32.45	2129.17 ± 37.16
TSS (mg L^{-1})	–	–	100 ± 4.00	1179.17 ± 30.43
TS (mg L^{-1})	–	–	940 ± 2.71	3316.67 ± 39.56
Total phenol (mg L^{-1})	38.54 ± 2.61	38.5 ± 2.8	1272 ± 30.45	4.93 ± 0.07
AOX (mg L^{-1})	4.7 ± 0.2	–	–	–
Total nitrogen	–	–	571 ± 25.12	–
Lignin (mg L^{-1})	663 ± 4.23	1000 ± 1.1	614 ± 8.13	–
Sulphate (mg L^{-1})	1762 ± 41.11	1800 ± 14	–	73.67 ± 1.43
Tannin (mg L^{-1})	–	–	–	42.38 ± 0.49
PCP (mg L^{-1})	–	–	145.11 ± 4.56	
Phosphate (mg L^{-1})	BDL	BDL		2.65 ± 0.05
K+ (mg L^{-1})	–	12.2 ± 1.33	86.52 ± 2.58	–
Na + (mg L^{-1})	–	102 ± 11	136.56 ± 4.56	–
Cl^{-} (mg L^{-1})	–	–	31.42 ± 0.86	–
Nitrate (mg L^{-1})	–	3 ± 4.5	41.52 ± 3.56	–
Heavy metals				
Cd (mg L^{-1})	0.06 ± 0.03	BDL	0.2078 ± 0.09	–
Cr (mg L^{-1})	0.255 ± 0.04	BDL	0.2020 ± 0.01	–
Cu (mg L^{-1})	0.105 ± 0.05	0.105 ± 0.013	0.5110 ± 0.10	–
Fe (mg L^{-1})	3.99 ± 0.91	3.990 ± 0.47	1.203 ± 0.04	–
Ni (mg L^{-1})	2.84 ± 0.06	2.840 ± 0.38	0.1500 ± 0.02	–
Zn (mg L^{-1})	1.5 ± 0.30	1.500 ± 0.17	0.3330 ± 0.01	–
Hg (mg L^{-1})	–	–	0.8750 ± 0.03	–
Pb (mg L^{-1})	–	–	0.0148 ± 0.00	–

BL black liquor, *RGPPME* rayon grade pulp paper mill effluent, *PPME* pulp paper mill effluent, *BDL* below detection limit, *Cd* cadmium, *Cr* chromium, *Cu* copper, *Fe* iron, *Ni* nickel, *Zn* zinc, *Hg* mercury, *Pb* lead, *BOD* biological oxygen demand, *COD* chemical oxygen demand, *TSS* total suspended solid, *TS* total solid, *TDS* total dissolved solid, *TOC* total organic carbon, *TVS* total volatile solids, *EC* electrical conductivity, *PCP* pentachlorophenol, K^+ potassium, Na^+ sodium, Cl^- chloride, *AOX* adsorbable organic halides

recalcitrant to degradation and tend to persist in nature (Mishra and Thakur 2010). They are thus known as POPs and have been classified as "priority pollutants" by the USEPA as well as the "dirty dozen" group of POPs identified by the United Nations Environment Program. It is well-established that many of these contaminants are

Fig. 1.2 Wastewater discharged from the pulp and paper industry after secondary treatment. (**a**, **b**) deposition of sludge in aquatic bodies

acute and/or chronic toxins (Nestmanna and Lee 1985; Costigan et al. 2012). This has resulted in a growing concern about the potential adverse effects of genotoxicants on aquatic biota and public health through the contamination of drinking water supplies, recreational waters, or edible organic species.

Eventually, pulp is used to produce paper, but the short fibers are not retained within the paper production and are returned to the wastewater (Jenkins et al. 2003). These residual sludge fibers and other materials detrimental to paper production (e.g. filler, ink) are separated from the wastewater by decantation in the clarifier. Then, the sedimentation material is directed to the press where it becomes the sludge. The sludge is called primary sludge when it originates from the production of virgin wood fiber or deinked paper sludge when it is produced by removing inks from postconsumer fiber. The secondary sludge formed after treatment of wastewater by activated sludge process (Fig. 1.2). Paper production generates around 45% of wastewater sludge. The wastewater sludge is enriched with various fiber wood compounds such as lignin, carbohydrate polymers (cellulose and hemicellulose), and other extractives (lipids and others) in addition to some potentially toxic compounds such as chlorinated organics, resin acids, and heavy metals (Raj et al. 2007a). The heavy metals (HMs) in wastewater sludge are of major concern from the ecotoxicological risk perspectives. A variety of odorous compounds generated by secondary treatment units have also been reported, including sulfur compounds, wood-derived terpenes, and organic acids. These compounds contribute to the pungent stack emissions of total reduced sulfur and other compounds from pulp and paper mills (Watson et al. 2003).

1.3 Distribution and Structural Components of Lignin

Lignin is a major component of lignocellulosic biomass, and processed in enormous amounts in the pulp and paper industry worldwide. It is a complex heteropolymer, of para-hydroxyphenyl propane units linked together via a variety of ether and C–C bonds. Lignin is basically formed by the random coupling of radical species arising

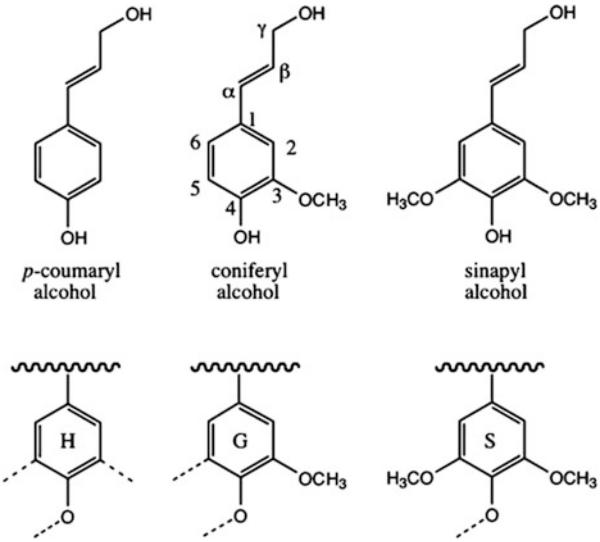

Fig. 1.3 Primary lignin monomers and corresponding unit (Wong 2009)

from the peroxidase-mediated dehydrogenation of three cinnamyl alcohol derivatives: p-coumaryl, coniferyl, and sinapyl alcohols. The corresponding phenylpropanoid units in the lignin polymer (known as lignin polymer units) are denoted as p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, respectively, based on the methoxy substitution on the aromatic rings (Fig. 1.3). The content of these three immediate biosynthetic precursor alcohols varies not only in different plant species but also in the different tissues of the same plant. In gymnosperms, the primary lignin precursors are the two monolignol conifery and p-coumaryl alcohols, while in angiosperms, sinapyl alcohol is also present (Garg and Modi 1999). It is closely associated with cellulose and covalently attached to hemicelluloses. The ether and C–C linkages present in lignin are not susceptible to hydrolytic attack, and therefore, lignin is highly resistant to breakdown (Bugg et al. 2011). Approximately 50–80% of all interunit bonds are β-O-4 ether bonds. In addition, subunits are connected by α-O-4 linkages, β-5 linkages, β-β linkages, 5–5 linkages, and biphenyl and diaryl ether structures. The double bond, conjugated with the aromatic ring, quinone methides, and quinone groups, is responsible for the color of their solution (van Driessel and Christov 2001). These chemicals are responsible for the dark color and toxicity of the wastewater discharged from the pulp and paper industry (Fig. 1.3). Lignin present in wood is converted to thio-lignin and alkali lignin in the kraft pulping. Chlorophenols from the pulp bleaching process are found both in free and bound forms in dissolved organic matter and particles; high- and low-molecular-weight chlorinated compounds are produced by complex reactions between chlorine and lignin in the wood pulp. Under natural conditions, these compounds are slowly degraded to various chlorinated phenolics which may be methylated under aerobic conditions. The low-molecular-weight phenolics and their methylated counterparts (which are more lipophilic) cause toxicity and bioaccumulate in fish. The dark brown color not only is aesthetically unacceptable but also could inhibit the process of photosynthesis in natural aquatic environments due to the barrier effect of sunlight. To minimize the impact of effluents on the environment, several treatment technologies have been employed, although little is known on their efficiency to eliminate the toxicity attributed to the presence of organic compounds.

1.4 Environmental Fate of Pulp and Paper Industry Wastewater

The wastewater discharged from pulp and paper industry remains toxic and complex due to retaining of high color, BOD, COD, TDS, TSS, and also consisting of potentially toxic chlorinated compounds even after conventional secondary wastewater treatment processes (Raj and Chandra 2004; Emeka et al. 2011; Mishra et al. 2013; Wu et al. 2005). Due to high pollution load and color-contributing substances, pulp and paper wastewater poses a serious aquatic and soil pollution (Fig. 1.4). In aquatic ecosystem, the dense brown color of this wastewater inhibits the natural process of photosynthesis due to reduced penetration of solar radiation and decreases the dissolved oxygen level, which adversely affects flora and fauna and causes toxicity (Hall et al. 2009; Ojunga et al. 2010; Hewitt et al. 2008; Swamy et al. 2011; Ali and Sreekrishnan 2001). The toxicity assessment of pulp and paper wastewater on fish reproductive system has been reported by various workers (Parks et al. 2001; Orlando et al. 2002; Oakes et al. 2005; Wartman et al. 2009; Orrego et al. 2011; Martel et al. 2017; Hou et al. 2018). The short-term exposure of pulp paper mill wastewater to the flora and fauna of aquatic and terrestrial ecosystem has been observed by Verma (2008). Pathan et al. (2009) also showed the behavioral changes in freshwater fish *Rasbora daniconius* exposed to paper mill wastewater and further higher concentration created an adverse effect on fish. Tyor et al. (2012) also tested the toxicity of pulp and paper industry wastewater by using the *Daphnia* test model. Similarly, Pandey et al. (2012) showed the comparison of fish toxicity and Microtox toxicity of luminescence bacteria due to bleach plant effluent released from agro- and wood-based pulp and paper mills and also showed the impact of pulp paper mill wastewater on survival and hatchability of *Cyprinus carpio*. The result showed that paper mill effluent treated eggs hatch susceptibility and adverse effect and development stages are badly affected and effluent showed ultimately lethal effect. The color-causing organic compounds have also been implicated in the appearance of algal blooms (Dileká et al. 1999). The physicochemical properties of river water were analyzed by Emeka et al. (2011); Lacorte et al. (2003) attempted an overview of organic compounds that contribute to the toxicity of pulp and paper industry wastewater. Presence of organic compounds in the wastewater has contributed to deterioration of water quality due to the mixing of organic compounds in the recipient ecosystem, i.e., aquatic and terrestrial ecosystem. The effect of different pollutants present in pulp paper mill wastewater in long-term study at a multi-tropic level in aquatic communities receiving water bodies in the United States

Fig. 1.4 Environmental impact of secondary treated wastewater discharged from pulp and paper industry. (**a**–**c**) A view of the contaminated site showing aquatic pollution due to discharging of colored complex wastewater. (**d**, **e**) Irrigation of agricultural field through discharged effluent affecting the crop as well as soil microflora and texture

has been also evaluated. The study has shown the toxic effect on fish macrovertebrate, phytoplankton, and other flora and fauna (Hall et al. 2009). The primary reproductive effects in fish due to being exposed to pulp and paper wastewater were reported by Hewitt et al. (2008). The toxic effect of pulp and paper mill wastewater on phytoplankton and macroinvertebrates in River Nzoia, Kenya was studied by Ojunga et al. (2010). This study has concluded that the wastewater produce changes in both physicochemical parameters of the receiving water and contribute to nutrient loading, especially phosphorus and nitrate, on the deteriorating water quality and eutrophication eliminates some taxa of both phytoplankton and macroinvertebrates, whereas others such as *Microcystis* sp. and *Chironomus* sp. appear to thrive in contaminated environment due to their tolerance to changing water quality. The genetic disturbance by pulp paper mill wastewater on large mouth bass (*Micropterus salmoides*) was reported by Denslow et al. (2004).

In a terrestrial ecosystem, the wastewater irrigated soil showed the decrease of moisture content and increase of pH as well as accumulation of heavy metals, i.e., Zn, Cu, Cd, Cr, and Pb in soil. The studies revealed that mill effluent has a deleterious effect on seed germination and growth parameter of rice and mustard and pea. It also has been noted that the effluent concentration above 50% was found inhibitory for plant growth parameter. Accumulation of contaminants into the terrestrial ecosystem is due to gradual percolation of contaminants which in turn changes the soil texture (Roy et al. 2008; Pradhan and Behera 2011; Kumar and Chopra 2011). In many developing countries, farmers irrigate their crop plants with water bodies which might be severely exposed to industrial effluents. This leads to risks of bioaccumulation of toxicants in the food chain. Thus, it is important to treat the industrial effluents before their final discharge. This continuous practice of irrigation of agricultural field through discharged effluent affecting the crop as well as soil texture (Medhi et al. 2008, 2011; Devkumari and Selvaseelan 2008). Pathan et al. (2009) reported that the toxicity of paper mill wastewater to fish *Rasbora daniconius* and its LC_{50} values were assessed for different concentration of effluent for 24–96 h exposure periods. In addition, the impact of paper mill wastewater on the survival and hatchability of eggs of *Cyprinus carpio* was reported by Tyor et al. (2012). However, the health hazards of polluted underground water due to pulp paper mill effluent in the vicinity of the pulp paper industry are not known so far.

These compounds, mostly complex aromatic in nature, also impart heavy toxicity to the aquatic systems, thus entering the food chain. Many researchers have reported that the mixing or direct entry of pulp paper mill effluent into the recipient ecosystem (aquatic and terrestrial ecosystem) is responsible for potential health hazards as mill wastewater mixing consequently increases the organic or inorganic compounds, i.e., enhancing or supporting the growth of numerous *total coliform*, *fecal coliform*, *Klebsiella* spp., *E. coli*, *Enterobacter* spp., *Klebsiella* spp., *Enterobacter* spp., *Salmonella*, *Vibrio cholerae*, *Shigella* spp., *Citrobacter* sp., etc. (Huntley et al. 1766; Clark et al. 1992; Liss and Allen 1992; Megraw and Farkas 1993; Gauthier and Archibald 2001; Chandra et al. 2006). Beauchamp et al. (2006) investigated the thermotolerant coliform population of one paper mill effluent and two paper mill sludges and wood chips screening rejects using chromogenic media. Large numbers of thermotolerant coliforms, i.e., 7,000,000 MPN g^{-1} sludge (dry weight; d.w.), were found in combined sludges. From this first series of isolations, bacteria were purified on the MacConkey medium and identified as *Citrobacter freundii, Enterobacter* sp.*, E. sakazakii, E. cloacae, Escherichia coli, K. pneumoniae, K. pneumoniae* subsp. *rhinoscleromatis, K. pneumoniae* subsp. *ozaenae, K. pneumoniae* subsp. *pneumoniae, Pantoea* sp.*, Raoultella terrigena,* and

R. planticola. Second, the presence of thermotolerant coliforms was measured at more than 3700–6000 MPN g^{-1} (d.w.) sludge, whereas *E. coli* was detected from 730 to more than 3300 MPN g^{-1} (d.w.) sludge. The presence of thermotolerant coliform bacteria and *E. coli* was sometimes detected from wood chips screening rejects in large quantities. Also, indigenous *E. coli* were able to multiply into the combined sludge, and inoculated *E. coli* isolates were often able to multiply in wood chips and combined sludge media. This study points out that the coliform bacteria are introduced by the wood chips in the wastewater, where they can survive through the primary clarifier and regrow in combined sludges. Furthermore, Emeka et al. (2011) reported the variation in physicochemical dynamics due to the impact of paper mill wastewater that discharge into the Owerrinta River, Eastern Nigeria. Long et al. in 2012 from the United States have reported the characterizing paper mill wastewater using indicators and source-tracking methods. This study examined potential public health implications of *E. coli* in a Wisconsin river that receives paper mill wastewater upstream of a public beach. Furthermore, the effects of solid wood waste discharge on the physicochemical and microbial identification of the Warri River were reported by Idise et al. in 2012 from Nigeria. Lee et al. (2012) carried out some significant work where they have conducted a survey and reported the effect on the skin and health of children living in upstream and downstream villages from a pulp and paper mill. This study has reported that the ill effect on children who drank water directly from the river was compared with those who never did. River water analysis has shown physicochemical variation within the acceptable range except for fecal coliform (6 MPN/100 mL). Moreover, Lee et al. (2012) surveyed and observed that the pulp and paper mill wastewater has created health-related problems to the downstream population of the river.

1.5 Biological Treatment Methods of Pulp and Paper Industry Wastewater

Pulp and paper industry is a very water-intensive industry in terms of freshwater use. Currently, the increasing needs to reduce water consumption and to satisfy tightened discharge standards in stringent environmental regulations have forced pulp and paper industries to treat their effluent for safe disposal in environment using advanced treatment processes. Most wastewater treatment processes (WWTPs) use aerobic and/or anaerobic biological processes to remove organic contaminants in wastewaters (Singh and Thakur 2006). The commonly available biological treatment methods adopted in the pulp and paper industry to lower the pollution load indices like BOD and COD include anaerobic lagoon, stabilization pond, aerated lagoon, activated sludge process, or its modification depending on the local conditions. Aerobic processes are preferably used in most pulp and paper mills because of their ease of operation as well as the relatively low capital and operating costs.

1.5.1 Aerobic Treatment Process

Among aerobic technologies, AS and aerated lagoons are commonly used wastewater treatment approach applied in pulp and paper industry (Fig. 1.5; van Ginkel et al. 1999; Erkan and Engin 2017; Pokhrel and Viraraghavan 2004; Lerner et al. 2007). Despite the widespread usage, these technologies still suffers from instability, high sludge production, and high operating cost. The most important operational difficulty associated with activated sludge is the separation of sludge from the clarified wastewater. Implications of conventional AS process used for pulp and paper industry wastewater with modification to a low sludge production (LSP) process have been studied for treating (Talat Mahmood et al. 2006). The LSP system produced 36% less sludge than the base case system, while both systems removed 96% BOD, 73% COD, and 56% AOXs from a bleach kraft mill wastewater. The LSP system required approximately 25% higher aeration than the conventional activated sludge system. The LSP sludge settled much better than the conventional activated sludge and had superior dewatering properties. This could lead to settling and dewatering chemical cost savings. The odorous compound released from pulp and paper mill wastewater and their reduction were also investigated by Watson et al. (2003). They reported that the AS may be helpful for reduction of odorous gases. However, the AS and aerated lagoons are not able to effectively mitigate the pollution load of pulp and paper mill wastewater. Because the microorganisms present in the conventional activated sludge system are not effective in degrading compounds like lignin, therefore, complete treatment of such wastes remains elusive.

Fig. 1.5 A view of the aerated activated sludge treatment of pulp and paper industry wastewater

1.5.1.1 Bioaugmentation/Biostimulation Process for Efficient Treatment of Pulp Paper Effluent

Bacterial Bioaugmentation/Biostimulation

In the recent past, biotechnological approaches for the remediation of contaminated environment have gained worldwide attention (Chandra et al. 2018a, b, c, d, e; Kumar and Chandra 2020a, b; Perestelo et al. 1989; Morii et al. 1995; Thakur 2004). Bioremediation is considered a cost-effective and environment-friendly technology with great potential to remove target compounds from contaminated sites or for treatment of wastewater (Malaviya and Rathore 2007; Raj et al. 2014a, b; Kumar et al. 2018; Kumar and Chandra 2020a, b; Chandra and Kumar 2017a, b). It is a set of techniques that improve the degradation capacity of contaminated areas (Chandra and Kumar 2015b). They use bioaugmentation strategy (introduction of specific degradable strains or consortia of microorganisms) (Yu and Mohn 2002; Yadav et al. 2016) or biostimulation strategy (introduction of nutrients, inducers, and oxygen) (Chandra et al. 2018a). Bioaugmentation is the introduction of a group of natural or genetically engineered microorganisms to decontaminate soil and water (Chen et al. 2012b). Comparing with the common biotreatment process, the inoculated indigenous or allochthonous microbial strains can enhance the biodegradation of target pollutants, serving to strengthen or complement the metabolic capabilities of the indigenous microbial community (Mishra et al. 2014). An important factor for successful bioaugmentation is the selection of potential bacteria that can not only degrade contaminants but can also adapt to an adverse environment, usually higher toxicity of the contaminated area (Dudášová et al. 2014). The major bacterial species successfully used in bioaugmentation and biostimulation processes for kraft lignin degradation and decolorization of pulp and paper industry wastewater are *Paenibacillus* sp., *Aneurinibacillus aneurinilyticus, Bacillus* sp. (Raj et al. 2007a, b, 2014a), *Serratia marcescens*, *Citrobacter* sp., *Klebsiella pneumonia* (Raj et al. 2007a, b; Chandra and Abhishek 2011), *Pseudomonas, Bacillus, Pannonibacter, Ochrobactrum* (2011), *Bacillus megaterium*, *Pseudomonas aeruginosa* (Tiku et al. 2010), *Novosphingobium* sp., *Aeromonas formicans* (Gupta et al. 2001), *Pseudomonas fluorescens* (Chauhan and Thakur 2002), *Comamonas* sp. B-9 (Chen et al. 2012a) *Pseudomonas, Ancylobacter,* and *Methylobacterium* (Keharia and Madamwar 2003). Yu and Mohn (2002) successfully used the *Zoogloea resiniphila* DhA-35 in the bioaugmentation treatment of resin acid containing pulp and paper mill wastewater. Similarly, Muttray et al. (2001) used *Pseudomonas abietaniphila* BKME-9 for the treatment of resin acid in the pulp and paper mill wastewater. Chauhan and Thakur (2002) treated pulp and paper mill wastewater in a fixed-film bioreactor by *P. fluorescens* and noted reductions of 45% lignin, 75% color, 79% COD, and 66% phenol within 15 days of incubation. Removal of organochlorine from bleached kraft pulp and paper mill wastewater by dehalogenating indigenously grown *Pseudomonas*, *Ancylobacter*, and *Methylobacterium* strains was reported by Fulthorpe and Allen (1995). Keharia and Madamwar (2003) compared the degradation potential of *Pseudomonas, Ancylobacter*, and *Methylobacterium* strains for organochlorine from bleached kraft pulp and paper mill wastewater. They observed that *Ancylobacter* showed the broad substrate range but could significantly reduce the AOXs from softwood wastewater only, whereas *Methylobacterium* with limited substrate range was capable of degrading AOXs from both hardwood and softwood effluents. Singhal and Thakur (2009a, b) reported the decolorization and detoxification of pulp paper mill wastewater under un-optimized and optimized conditions by *Cryptococcus* sp. This bacterial isolate reduced the 27% color and 24% lignin content of the wastewater in 15 days under un-optimized conditions. However, enhanced reduction in color (50–53%) and lignin (35–40%) was noted to occur after optimum treatment conditions were reached during the 24 h incubation: pH 5.0, temperature 35–40 °C, shaking speed 125 rpm, dextrose 1.0% w/v, tryptone 0.1% w/v, and inoculum size 7.5% v/v. Recently, *Halomonas* sp. and *Bacillus* sp. have been used for BL degradation and decolorization at high pollution load (Yang et al. 2008). Singh et al. (2011) reported bioremediation of pulp and paper mill wastewater by a tannic acid-degrading bacterium *Enterobacter* sp. Prior to the bioremediation of wastewater, authors optimized various parameters, viz., inoculum size, agitation, temperature, and treatment duration by using Qualitek-4 software. In batch culture experiment, the reduction of lignin up to 73% and color up to 82% along with COD and BOD with 16 h retention time was observed. Mishra and Thakur (2010) isolated *Bacillus* sp. from pulp and paper mill sludge and used this isolate in degradation and decolorization of BL. They noted that maximum color was removed at pH 8, temperature 35 °C, shaking speed 200 rpm, sucrose 2.5%, and inoculum size 5% (w/v) within 48 h from 10% BL. However, after optimization of various nutritional and environmental parameters by using the Taguchi approach, twofold increase in the removal of color and lignin from 25–69% and 28–53%, respectively, was noted. This study indicated the significance of Taguchi's approach in decolorization and delignification of lignin in pulp and paper mill wastewater. Chandra and Abhishek (2011) studied the decolorization of BL in axenic and mixed condition by isolated bacterial strains, i.e., *Citrobacter freundii* and *Citrobacter* sp., and characterized their metabolites. Under mixed culture condition, the aerobic treatment could reduce 79% AOX, 79% color, 82% COD, and 60% lignin after 144 h of the incubation period. It was also observed that mixed bacterial culture produced the optimum level of peroxidase enzyme compared to axenic bacterial strain. The comparative GC–MS analysis of control and degraded BL revealed that along with lignin fragment, some chlorophenolic compounds, 2,4,6-trichlorophenol, 2,3,4,5-tetrachlorophenol, and pentachlorophenol, were detected in BL degraded by axenic culture, whereas these chlorophenolic compounds were completely absent in BL degraded by mixed bacterial culture (Table 1.2). Similarly, the decolorization of BL by a potential bacterial consortium consisting of *S. marcescens*, *Citrobacter* sp., and *Klebsiella pneumoniae* under optimized environmental and nutritional conditions has been reported by Chandra et al. (2011a). The study has shown that bacterial growth and BL degradation were associated with ligninolytic enzyme production and numerous metabolites were also detected in bacterial degraded BL (Table 1.2; Chandra et al. 2011a, b). The pulp and paper mill wastewater decolorization and detoxification by using the different inoculums ratio in mixed bacterial culture have been evaluated at laboratory scale (Chandra et al. 2011b). This study deals with the degradation and detoxification of pulp paper mill wastewater by three bacterial strains, i.e., *S. marcescens*, *S. liquefaciens*, and *Bacillus cereus* in different ratios, and found that two ratios, 4:1:1 and 1:4:1, were effective for the degradation of pulp and paper mill wastewater. These ratios reduced the various pollution parameters from pulp and paper mill wastewater. HPLC and GC–MS analysis also showed that the mixed bacterial culture in 4:1:1 ratio degraded 95% of lignin and 98% of chlorophenols, and several other related compounds, whereas ratio 1:4:1 reduced lignin and chlorophenols up to 84% and 58%, respectively, after 7 days of incubation (Table 1.2). Chandra and Singh (2012) also studied the decolorization and detoxification of rayon grade pulp paper mill wastewater in different nutritional as well as environmental parameters by a developed bacterial consortium comprising *S. marcescens*, *Citrobacter* sp., and *K. pneumoniae* strains. The degradation study result showed that the ligninolytic activities were found to be growth associated and the developed bacterial consortium was efficient for the reduction of color, BOD, and COD up to 85%, 74%, and 83%, respectively. The GC–MS analysis also showed that most of the compounds detected in untreated wastewater were diminished after bacterial treatment, while formic acid hydrazide, 4-cyclohexane-1,2-dicarboxylic acid, carbamic acid, 1,2-benzenedicarboxylic acid, and erythro pentanoic acid were found as new metabolites. Simultaneously, Chandra and Singh (2012) also reported the decolorization and detoxification of rayon grade (RG) pulp paper mill effluent by mixed bacterial culture comprising *Pseudochrobactrum glaciale, Providencia rettgeri,* and *Pantoea* sp. The results showed that mixed culture effectively reduced color, COD, and BOD up to 96.02%, 91%, and 92.59%, respectively, from pulp paper mill effluent within 216 h of the incubation period. During degradation and decolorization, maximum enzyme activity for lignin peroxidase (LiP), manganese peroxidase (MnP), and laccase was recorded at 48, 72, and 144 h of the incubation period, respectively. Further, GC–MS analysis revealed that majority of the compounds present in the untreated sample were completely removed and only a few metabolites were generated after bacterial treatment (Table 1.2). A mammalian cell line-based toxicological evaluation of pulp and paper mill BL biodegraded in a soil microcosm by indigenous alkalotolerant *Bacillus* sp. was reported by Mishra et al. (2014). GC–MS analysis performed after biodegradation showed the formation of simpler compounds like *p*-hydroxyhydrocinnamic acid, homovanillic acid methyl ester, and 3,5-dimethoxy-*p*-coumaric alcohol. The methyltetrazolium assay for cytotoxicity, 7-ethoxyresorufin-O-deethylase assay for dioxin-like behavior, and alkaline comet assay for genotoxicity evaluation were carried out with the human hepatocarcinoma cell line HuH-7 before and after bacterial treatment. The result revealed that bioremediation for 15 days reduced toxicity, as shown by a 139-fold increase in BL LC_{50} value, a 343-fold reduction in benzo(a)pyrene equivalent value, and a fivefold reduction in the olive tail moment. Similarly, Haq et al. (2016, 2017) evaluated the bioremediation potentiality of ligninolytic enzyme producing *S. liquefaciens* for detoxification of wastewater discharged from pulp and paper industry after secondary treatment and characterized their metabolic products. The bacterium *S. liquefaciens* effectively reduced color, lignin, COD, and phenol of real

Table 1.2 Identified organic compounds present in pulp and paper industry wastewater and their degradation and characterized metabolic products after bacterial treatment (Chandra and Singh 2012; Chandra and Abhishek 2011; Chandra et al. 2011a, b; Haq et al. 2016, 2017)

Effluent	S. no.	Name of identified compound	UW	BTW
Rayon grade pulp paper mill wastewater	1.	4-Isopropoxy-butyric acid	+	–
	2.	3,7,11,15,18-pentaoxa-2,19-disilaneicosane	+	–
	3.	Butane-1-ol	+	–
	4.	Propane	+	–
	5.	2-methyl-2,4-dimethoxy butane	–	+
	6.	4,5-octanediol,3,6-dimethyl	–	+
	7.	Diphenylthiocarbazide	+	–
	8.	Propane,1-(1-Ethoxyethoxy)	+	–
	9.	Cyclohexanecarboxylic acid	–	+
	10.	6-Oxabicyclo9,3,1,0,0hexan-3-one	+	–
	11.	Pyrrolo(1,2A)pyrazine-1,4-dione, hexahydro	+	–
	12.	Pyrrolo(1,2A)pyrazine-1,4-dione, hexahydro	+	–
	13.	Trichloroacetyl isocyanate	+	–
	14.	1-Phenyl-1-nonyne	–	+
	15.	Tetradecanoic acid	+	–
	16.	6-Chlorohexanoic acid	+	–
	17.	2,5-Piperazinedione,3,6-bis(2-methyl propyl)	+	+
	18.	Pyrrolo(1,4-dione,hexahydro-3-(phenyl methyl)	+	–
	19.	1-Chloro Octadecane	+	–
	20.	1,2 Benzene carboxylic acid	+	–
	21.	4,8-Dimethyl undecane	+	–
	22.	3-Trifluoroacetoxydodecane	+	–
	23.	Benzeneacetic acid,3-tetradecyl ester	+	–
	24.	Cyclo-(L-leucyl-l-phenylalanyl)	+	–
	25.	Butanoic acid	+	–
Black liquor	1.	Propanoic acid	–	+
	2.	Acetic acid	–	+
	3.	Butanoic acid	–	–
	4.	Benzoic acid	–	+
	5.	2,4,6 trichloro phenol	–	–
	6.	2,3,4,5 tetrachloro phenol	–	–
	7.	Tetradecanoic acid	–	+
	8.	Pentachlorophenol	–	–
	9.	Dibutyl phthalate	–	+
	10.	Hexadecanoic acid	–	–
	11.	Octadecanoic acid	–	+
	12.	Bis(2-ethylhexyl) phthalate	+	+
Black liquor	1.	Propanoic acid	+	–
	2.	Formic acid hydrazide	–	
	3.	4-Cyclohexane-1,2-dicarboxylic acid	–	

(continued)

Table 1.2 (continued)

Effluent	S. no.	Name of identified compound	UW	BTW
	4.	1,2 Butanediol	+	–
	5.	Carbamic acid	–	
	6.	3-Cyclohexane 1-methanol	+	–
	7.	2-Methoxy phenol (Guaiacol)	+	–
	8.	4-Methyl benzaldehyde	+	–
	9.	Benzoic acid	+	–
	10.	Benzene acetic acid	+	–
	11.	Benzylemalonic acid	+	–
	12.	3-Hydroxy-4-methoxymandilic acid	+	–
	13.	Butylated hydroxytoluene	+	–
	14.	2,4-Bis (1,1-dietyl)-phenol	+	–
	15.	Heptadecanoic acid	+	–
	16.	2-Methoxy propanoyl chloride	+	–
	17.	4-Hydroxy-3,5-dimethoxy benzaldehyde	+	–
	18.	Tetradecanoic acid	+	–
	19.	1,2-benzenedicarboxylic acid	–	+
	20.	Dibutyle phthalate	+	–
	21.	Erythropentanoic acid	–	+
	22.	Ricinoleic acid	+	–
	23.	Phthalate	+	+
	24.	Cholesterol trimethylsilyl ether	+	+
	25.	1,1-(1,2-ethanediyl) bis[4-methoxy] benzene	+	–
	26.	2,4-Bis (1-phenylethyl)-pheno	+	–
	27.	Bis (2-ethylhexyl) phthalate	+	–
Pulp and paper mill wastewater	1.	Propanoic acid	+	+
	2.	Benzeneacetonitrile	–	–
	3.	Pyridine	–	–
	4.	Phosphoric acid	+	–
	5.	1[(Formyl)oxymethyl]benzene	–	+
	6.	(+)-5-Hydroxy-6-(1-hydroxyethyl)-2,7-dimethoxynapthoquinone	+	–
	7.	l-(+)-Tartaric acid, bis(trimethyl silyl) ether, bis(trimethyl silyl)ester	+	–
	8.	3-Octadecene, (E)-	+	–
	9.	Uric acid	–	+
	10.	D-Fructose, 1,3,4,5,6-pentakis-O-(trimethyl silyl)-O, methyloxime	+	–
	11.	(2 R,3 S)-2-[(E)-2-(Ethoxycarbonyl)ethenyl]-2, 3-dimethylaziridine	–	+
	12.	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)	–	+
	13.	1,4-Diazo-2,5-dioxo-3-isobutyl bicyclo (4.3.0) nonane	–	+
	14.	1-Octadecene	+	–

(continued)

Table 1.2 (continued)

Effluent	S. no.	Name of identified compound	UW	BTW
	15.	Hexadecanoic acid	+	–
	16.	1-Monolinoleoyl glycerol trimethyl silyl ether	+	–
	17.	1-Heneicosanol	+	–
	18.	Octadecanoic acid	+	–
	19.	Tetracosanic acid	+	–
	20.	A-D-Galactopyranoside, methyl 2,3-bis-o-(trimethyl silyl)-, cyclic methylbronate	+	–
	21.	2′-4′-6′-Trinitro-5′-phenyl-1,1′:3′,1″-terphenyl	+	–
	22.	N,N′-Dicyclohexyl-1-cyano-7-pyrrolidinylperylene-3,4:9,10-tetracarboxylic acid	+	–
Pulp paper mill wastewater	1.	1-O-Pentadecylglycerol	+	–
	2.	Glycerol	–	+
	3.	L-Glutamic acid	–	+
	4.	Iron,tricarbonyl(N-(phenyl-2-yridinylmethylene) benzenamine)	+	–
	5.	Butanal	–	+
	6.	Hexanedioic acid	+	–
	7.	D-galactofuranose	+	–
	8.	D-Fructose	–	+
	9.	D-Glucose	+	–
	10.	D-Gluconic acid	–	–
	11.	D-Mannitol	+	–
	12.	Glucopyranose	+	–
	13.	1,6,8-trihydroxy-2-isopropyl-3-methoxy-9,10-anthraquinone	–	+
	14.	2,4-dimethoxyphenyl	+	–
	15.	2,6-Dinitro-4,40-di-tert-butylbiphenyl	–	+
	16.	Diethyl 3,4-dihydro-2-nepthyl-phosphonate	+	–
	17.	4,6-dimethoxy-2,3-dimethyl	+	–
	18.	2,4,6-trinitro-5-phenyl	+	–
Pulp paper mill wastewater	1.	2-Ethoxyethoxy-Trimethylsilane	–	+
	2.	Propylene carbonate	–	+
	3.	Butanoic acid,2-oxo (acid)	–	+
	4.	Methanediamine,N,N,N,N-tetramethyl	–	+
	5.	2-Ethoxyethoxy-trimethylsilane	–	+
	6.	Butane,2Ethoxy-	–	+
	7.	Diphenylthiocarbazide	–	+
	8.	1-(2,4-Diethoxy-phenyl)Ethanone	–	+
	9.	1,4-Dimethoxy-2-Phenylbutane(phenol)	–	+
	10.	Oxalic acid,Cyclobutyl heptadecylester (cyclo)	–	+
	11.	8-Pentadecanone(ketone)	+	–

(continued)

Table 1.2 (continued)

Effluent	S. no.	Name of identified compound	UW	BTW
	12.	1,2Benzenedicarboxylic acid,Bis (2-Methylpropyl) Ester	+	–
	13.	1-Phenyl-1-nonyne(surfactant)	–	+
	14.	Sulphurousacid,Octadecyl 2-Propylester	+	–
	15.	Benzene,1,3-Bis(1-methylethenyl)	–	+
	16.	3-Ethenyl-6-Dimethylaminomethyleneaminobenzonitrile	–	+
	17.	N-(3-Bromo-1-Methyloxycarbonyl-1H-Indol-2-YLmethyl)-N-(1-Methoxycarbonyl-2-methybutyl	–	+
	18.	Proponoic acid,2-(Benzoylamino)-333 Trifluro-2-[(Trifluromethyl)phenyl]amino-ethyl	–	+
	19.	Butane,2-phenyl-3-(trimethylsilyloxy)	–	+
	20.	2-Propanoic acid,3(4-Methylphenyl)-, ethylester	–	+
	21.	2-Propanoic acid,3-(MethylPhenyl), Ethylester	–	+
	22.	Phthalicacid,Dodecyl 2-Ethylhexylester	–	+

+ present, – absent, *UE* untreated effluent, *BTE* bacterial treated effluent

wastewater after 144 h of treatment at 30 °C, pH 7.6, and 120 rpm. Further, the bacterium-treated effluent was evaluated for residual toxicity assessment by alkaline single-cell (comet) gel electrophoresis (SCGE) assay using *Saccharomyces cerevisiae* MTCC 36 as a model organism. The toxicity reduction to treated effluent was found up to 49.4%. They also characterized the major metabolic products during bacterial treatment of pulp paper mill wastewater as shown in Table 1.2. Tiku et al. (2010) also reported the holistic bioremediation of pulp mill wastewater using three autochthonous bacteria strains, *P. aeruginosa, and B. megaterium*, to reduce the BOD and COD level of such wastewater up to permissible level, i.e., 30 mg L^{-1} and 250 mg L^{-1}, respectively, within a retention time of 24 h in batch culture. However, the continuous mode of treatment may further decrease the retention time. A concomitant reduction in TDS, AOXs, and the color was also observed. The bacterial degradation of lignin is limited compared to fungi.

Fungal Bioaugmentation/Biostimulation

Fungi are the only microorganisms studied extensively for the degradation and decolorization of lignin and its related monomers (Hofrichter 2002). The use of fungi has a great potential for tertiary treatment and removal of residual organic compounds in wastewater discharged from pulp and paper industries (Wu et al. 2005; Apiwattanapiwat et al. 2006; Da Re and Papinutti 2011; Rajwar et al. 2017). White-rot fungi, such as *Phanerochaete chrysosporium* (Zouari et al. 2002; Mittar et al. 1992; Wu et al. 2005), *Trametes* (*Coriolus*) *versicolor*

(Martin and Manzanares 1994; Manzanares et al. 1995; Modi et al. 1998; Garg and Modi 1999; Bajpai et al. 19,993; Mehna et al. 1995; Archibald et al. 1990), *P. radiata* (Lankinen et al. 1991; Hatakka 2001), *Marulius tremellosus* (Lankinen et al. 1991), *Rhizomucor pusillus* (van Driessel and Christov 2001), *Lentinus edodes* (Esposito et al. 1991; Wu et al. 2005), *Pleurotus* spp., *P. sajor-caju*, *P. platypus*, *P. citrinopileatus* (Ragunathan and Swaminathan 2004), *Steccherinum* sp. (Da Re and Papinutti 2011), *Datronia* sp. (Chedchant et al. 2009), and *Trichaptum* (Apiwattanapiwat et al. 2006), have been reported to be effective in reducing the various pollution parameters of pulp and paper industry wastewater. Decolorization and detoxification of extraction-stage effluent from chlorine bleaching of kraft pulp by *Rhizopus oryzae* have been investigated by Nagarathnamma and Bajpai (1999). Table 1.3 shows the analytical results for the effluent sample. A total of 37 standards of chlorophenols and chloroaldehydes were run, and 13 types of chlorophenols and three types of chloroaldehydes were found in the extraction-stage effluent (Table 1.3). *R. oryzae* was found to decolorize, dechlorinate, and detoxify bleach plant effluent at lower co-substrate concentrations. With glucose at 1 g L^{-1}, this fungus removed 92–95% color, 50% COD, 72% AOXs, and 37% EOXs in 24 h at pH of 3–5 and temperatures of 25–45 °C, although the fungus removed up to 78% of the color without added co-substrate.

Bioremediation of pulp and paper industry wastewater by a novel fungal consortium, comprising two basidiomycetous fungi (*Merulius aureus* syn. *Phlebia* sp. and an unidentified genus) and a deuteromycetous fungus (*Fusarium sambucinum* Fuckel MTCC 3788), isolated from pulp and paper mill wastewater-affected soils in immobilized condition was assessed by Malaviya and Rathore (2007). First, these fungus isolates were immobilized on nylon mesh, and the developed consortium was further used for the treatment of pulp and paper mill wastewater in a continuously aerated benchtop bioreactor. The treatment resulted in the reduction of lignin, color, and COD of the wastewater in the order of 79.0%, 78.6%, and 89.4% in 4-day incubation period. A major part of reductions in lignin, color, and COD of the wastewater occurred within the first 24 h of the treatment, which was also characterized by a steep decline in the pH of the wastewater. Singhal and Thakur (2009a) evaluated the efficiency of the biological treatment process for the decolorization and detoxification of pulp and paper mill wastewater for its safe disposal in the environment. In this study, they used *Emericella nidulans* var. *nidulans* for the treatment process. The process parameters for optimum decolorization of pulp and paper wastewater were optimized by the Taguchi approach. Decolorization of wastewater was improved by 31% with reduction in 66.66% color and 37% lignin after treatment by *E. nidulans* var. *nidulans* in batch culture. Variation in pH from 6.0 to 5.0 had the most significant effect on decolorization (71%), while variation in temperature from 30 to 35 °C had no effect on the process. Later, treated effluent was evaluated for genotoxicity by alkaline single-cell gel electrophoresis assay using *Saccharomyces cerevisiae* MTCC 36 as a model organism, indicating a 60% reduction in toxicity. Rocha-Santos et al. (2010) also evaluated the effects of a tertiary treatment by fungi (*Pleurotus sajor-caju*, *T. versicolor*, *P. chrysosporium*, and *R. oryzae*) on individual organic compounds of a *Eucalyptus globulus* bleached

Table 1.3 Identified organic pollutants from pulp and paper industry wastewater and their degradation by fungi (Nagarathnamma and Bajpai 1999; Rajwar et al. 2017)

S. no.	Identified compounds	UW	TW	S. no.	Identified compounds	UW	TW
1.	1–3-Dimethyl benzene	–	+	1.	2-Chlorophenol	+	–
2.	Acetic acid	–	+	2.	4-Chlorophenol	+	+
3.	Phenol	–	–	3.	2,6-Dichlorophenol	+	–
4.	1-Methyl-4-(1-methylethenyl)-cyclohexene	+	–	4.	5-Chloroguaiacol	+	–
5.	Diethylene glycol monoacetate	–	–	5.	4-Chlorocatechol	+	–
6.	3,7-Dimethyl-1,6-octadien-3-ol	+	–	6.	4,6-Dichloroguaiacol	+	+
7.	4-Tert-butyl-2-methylphenol	–	–	7.	4,5-Dichloroguaiacol	+	–
8.	Diethylene glycol diacetate	–	–	8.	3,5-Dichlorocatechol	+	+
9.	(–)-β-Caryophyllene	+	–	9.	3,4,6-Trichloroguaiacol	+	–
10.	4-Hexen-2-one,5-phenyl	+	–	10.	4,5-Dichlorocatechol	+	–
11.	Hexadecane	–	+	11.	3,4,5-Trichloroguaiacol	+	–
12.	Nonadecane	–	–	12.	4,5,6-Trichloroguaiacol	+	+
13.	Phytane	–	+	13.	Tetrachloroguaiacol	+	+
14.	Diisobutyl phthalate	+	+	14.	2-Chlorosyringaldehyde	+	+
15.	Pentadecanoic acid	–	+	15.	Trichlorosyringaldehyde	+	–
16.	Butyl phthalyl butyl glycolate	+	–	16.	2,6-Dichlorosyringaldehyde	+	–
17.	Eicosane	–	+	17.			
18.	Benzene-1,2-dicarboxylic acid	+	–	18.			
19.	Octyl phthalate	+	–	19.			
20.	Butyl-octyl-diphenylamine	+	–	20.			
21.	Tetracontane	–	+	21.			

+ present, – absent, *UW* untreated wastewater, *TW* fungi treated wastewater kraft pulp and paper mill wastewater discharged after secondary treatment. A total of 38 compounds (carboxylic acids, fatty alcohols, phenolic compounds, and sterols) were detected and quantified in the *E. globulus* bleached kraft pulp mill final effluent discharged after secondary treatment. The four fungus species showed an adequate capacity to eradicate organic compounds and color from wastewater. Biodegradation of pulp and paper mill wastewater by co-culturing ascomycetous fungi in the repeated batch process has also been studied by Rajwar et al. (2017). A fungal consortium (consisting *Nigrospora* sp. and *Curvularia lunata*) exhibited enhanced biomass production under optimized medium conditions and significantly reduced color (82.3%), BOD (85.6%), COD (80%), and lignin concentration (76.1%) under catalytic enzyme activity; however, unutilized Lac, MnP, and LiP activities were observed to be 13.5, 11.4, and 9.4 U mL^{-1} after the third cycle of wastewater treatment in repeated batch process. The GC–MS analysis also showed the reduction of complex organic compounds and the formation of numerous low-molecular-weight metabolites. This indicated the massive potential of the novel fungal consortium to degrade recalcitrant organic pollutants. Biological treatment of pulp and paper industry wastewater by oleaginous yeast *Rhodosporidium kratochvilovae* was integrated with production of biodiesel as reported by Patel et al. (2017). *R. kratochvilovae* has the remarkable efficiency to reduce the toxicity of phenols (99.60%) and lignin (94.27%), respectively, from the wastewater with a high reduction in COD (94.22%), BOD (77.36%), and TDS (84.59%). The integrated process establishes toxic removal from pulp and paper industry wastewater along with sustainable biodiesel production for transportation fuels.

Algal Treatment (Phycoremediation)

Microalgal culture offers a cost-effective approach to remove nutrients from wastewater discharged from pulp and paper industry after secondary treatment (Saikia et al. 2010, 2011) . Microalgae have a high capacity for inorganic nutrient uptake, and they can be grown in mass culture in outdoor solar bioreactors. Dileká et al. (1999) reported the removal of color and AOXs from pulping effluent by mixed culture of algae obtained from the oxidation pond of the wastewater treatment plant. The mixed culture of algae was composed mainly of *Chlorella*, *Chlorococcum*, and *Chlamydomonas* species. Besides these, *Microcystis* and *Anabaena* species were present to a somewhat lesser extent, and a few species of *Euglena, Phacus, Nitzschia, Cyclotella, Pandorina, Eudorina, Gonium,* and *Prymnesium* were also observed. For the total mill effluent (composed of both pulping and bleaching effluents), AOX removal was found to be independent of initial color value and was around 70%. Up to 80% removal of color from pulping effluent was achieved within 30 days under continuous lighting conditions. It was found that algae reduced the color of pulping of relatively low initial color more efficiently than that of high initial color. Under simulated field lighting conditions, up to 60% color removal from pulping effluent was observed after 60 days of exposure, whereas for the total mill effluent, it was up to 64% after 45 days of incubation. Tarlan et al. (2002a) reported 58% of COD, 84% of color, and 80% of AOXs removal from pulp and paper industry wastewaters by using some green algae (*Chlorella*), and diatom species were dominant in the treatment. This study also showed that algae grew mixotrophically, and the main mechanism of color and organics removal from pulping effluents was partly metabolism and partly metabolic conversion of colored and chlorinated molecules to noncolored and non-chlorinated molecules. In a separate study, Tarlan et al. (2002b) treated highly polluted pulp and paper industry wastewaters in sequential batch reactors (SBR) by using algae and found up to 74% COD and 74% color removal in about 40 days of incubation batch studies. From the preliminary SBR experiments, filling period was found to be a critical step affecting the overall efficiency when mixing and aeration are applied during filling. For all filling periods, COD, color, and AOXs removal efficiencies increased with increasing filling time. Maximum removal efficiencies achieved were 60–85% for COD, 42–75% for color, and 82–93% for AOXs for the filling periods of 4–12 days. Authors stated that organics in the contaminated wastewater were both chlorinated and non-chlorinated; algae removed these contaminants mainly by metabolism, and chlorine cleavage from chlorinated organic molecules was more rapid than the degradation of non-chlorinated and colored organics. Adsorbed lignin on algal biomass was found to be varying between 10 and 20% depending on filling period applied. Most recently, removal of nutrients and organic pollution load from pulp and paper industry wastewater by microalgae in outdoor open pond has been reported by Usha et al. (2016). In this lab study, a mixed culture of microalgae, containing two *Scenedesmus* species, was used for pulp and paper mill wastewater treatment and microalgal cultivation, and result showed a maximum of 82% and 75% removal of BOD and COD, respectively. The author recommended that pulp and paper mill wastewater could be used effectively for cultivation of microalgae to minimize the freshwater and nutrient requirements.

1.5.2 Anaerobic Treatment

Many highly chlorinated compounds are known to be quite stable and difficult to degrade. However, anaerobes can sometimes catalyze biotransformation reactions in which chloride ions of the chlorinated compounds are displaced by protons (Chandra and Kumar 2015b). The more chloride ions are thus removed, the more reactive the resultant compounds become, thereby rendering them susceptible to conventional AS treatment. The anaerobic treatment provides advantages of pollution decreasing with energy production. Anaerobic digestion is a process frequently employed for the secondary treatment of industrial wastewater. It has many potential advantages in comparison with aerobic treatment such as lower sludge production, lower chemical consumption, smaller land requirements due to smaller reactors, and energy production in the form of methane. Anaerobic technologies provide good treatment efficiencies at low hydraulic retention times. However, it was reported that anaerobic microorganisms are more sensitive to toxic substances than aerobic microorganisms when anaerobic treatment is utilized for bleached kraft wastewaters (Johansson

2012; Lin et al. 2012). For this reason, several authors investigated aerobic membrane bioreactor (MBR) for pulp and paper mill wastewater treatment, and it was reported that the COD removal efficiencies were found to be between 86% and 99.5% (Bérubé and Hall 2000; Galil et al. 2003; Dias et al. 2005; Gommers et al. 2007; Lerner et al. 2007; Zhang et al. 2009; Savant et al. 2006). Lafond and Ferguson (1991) reported that anaerobic treatment in an upflow hybrid reactor removed 17–40% of AOXs. Similarly, Mishra et al. (2016) compared the effluent treatment efficiency of a hybrid unit of upflow fixed-bed anaerobic bioreactor (UFBAB) along with slow sand filter (SSF) with the single-unit UFBAB for paper and pulp mill wastewater. The hybrid system showed better treatment efficiency as the SSF provides a polishing effect to the effluent generated after the UFBAB treatment. Erkan and Engin (2017) used a submerged membrane bioreactor (sMBR) to eliminate dissolved substances present in paper mill wastewater. In this study, an sMBR was operated for the treatment of paper mill industry wastewater at 35 h of HRT and 40 days of SRT. The COD, ammonical nitrogen (NH_3–N), and total phosphorous (TP) removal efficiencies were found to be 98%, 92.99%, and 96.36%. The results demonstrated that sMBR was a suitable treatment for the removal of organic matter and nutrients for treating paper mill wastewater except for the problem of calcium accumulation.

1.6 Ligninolytic Enzymes in Degradation and Decolorization of Pulp and Paper Industry Wastewater

Lignin is difficult to biodegrade; white-rot fungi are the most widely unique organisms able to degrade lignin efficiently to complete mineralization (Chandra et al. 2015b; Glenn and Gold 1985; Kirk et al. 1984; Tien and Kirk 1984; Ahmad et al. 2010). However, several bacterial species recently reported as lignin degraders of genera *Bacillus pumilus* and *Bacillus atrophaeus* (Huang et al. 2013), *Aneurinibacillus aneurinilyticus* (Raj et al. 2007a), *Bacillus* sp., (Raj et al. 2007b), *Novosphingobium* sp. B-7 (Chen et al. 2012a, b, c), *Pandoraea* sp. B-6 (Shi et al. 2013), *Comamonas* sp. B-9 (Chen et al. 2012a), *Dysgonomonas* sp. WJDL-Y1 (Duan et al. 2016a), *Acetoanaerobium* sp. WJDL-Y2 (Duan et al. 2016b), *Xanthomonas* sp. (Archana and Mahadevan 2002), *Paenibacillus* sp., *A. aneurinilyticus* (Raj et al. 2007a, b), *Gordonia* strin JW8 (Chen et al. 2012b), *Citrobacter freundii*, and *Serratia marcescens* (Abhishek et al. 2017). The major extracellular ligninolytic enzymes involved in lignin biodegradation by fungi as well as bacteria are lignin peroxidase (LiP; EC 1.11.1.14) and manganese peroxidase (MnP; EC 1.11.1.13) and laccase (Lac; EC 1.10.3.2) (Ahmad et al. 2010; Abdelaziz et al. 2016; D'Souza et al. 2006; Chandra et al. 2017a). White-rot fungi produce various isoforms of extracellular enzymes that give these fungi the ability to degrade lignin and also allow them to grow in presence of a wide range of recalcitrant organic pollutants. In fact, these enzymes have demonstrated to be capable of degrading a vast number of environmental contaminants, including dyes, polychlorinated biphenyls, melanoidins, and pesticides, making ligninolytic enzymes as a potential efficient tools for biotechnological processes of wastewater pollutants (Kumar and Chandra 2018a; Kumari et al. 2002). MnP is an extracellular oxidoreductase enzyme that belongs to class II fungal haem-containing peroxidases produced by almost all wood-colonizing white root and several litter-decomposing basidiomycetes during secondary metabolism in response to nitrogen or carbon starvation (Hofrichter 2002; Chen and Wan 2017). It has also been produced by some indigenous bacterial strains (Kumar and Chandra 2018a; Xu et al. 2018; Huang et al. 2013). During the catalytic process, the MnP system generates highly reactive and nonspecific free radicals that cleave carbon–carbon and ether interunit bonds of various phenolics and non-phenolic compounds (Hofrichter 2002). Generally, MnP catalyzes the oxidation of Mn^{2+} to Mn^{3+} chelate Mn^{3+} to form stable complexes that diffuse freely and oxidized phenolic substrate (e.g., simple phenol, amines, dyes, phenolic lignin substructure, and dimers) by one-electron oxidation of the substrate, yielding phenoxy radical intermediate, which undergoes rearrangement, bond cleavage, and nonenzymatic degradation to yield several breakdown products. Figure 1.6 illustrates the catalytic cycle of MnP enzyme.

Similarly to MnP, LiP is also an extracellular H_2O_2-dependent heme-containing glycoprotein produced by white-rot fungi as well as some bacterial species (Kumari et al. 2002; Ahmad et al. 2010; Abdelaziz et al. 2016; Xu et al. 2018). Among them, LiP was first discovered in nitrogen and carbon-limited cultures of *P. chrysosporium* and since then has become one of the most studied peroxidases. It catalyzes the oxidative cleavage of C_α–C_β linkages, β-O-4 linkages, and other bonds present in lignin and its model compounds (Chandra et al. 2017a, b). The enzyme also catalyzes side-chain cleavages, benzyl alcohol oxidations, demethoxylation, ring-opening reactions, and oxidative dechlorination. The immobilization of LiP and MnP produced by *P. chrysosporium* on Amberlite IRA-400 resin and its utilization on the remediation of effluent from pulp and paper industry were evaluated by Peralta-Zamora et al. (1998). They reported that immobilized enzyme was very effective in removing color and phenolics species from kraft effluent with insignificant adsorption of colored species by the support. Decolorization of kraft effluent by free and immobilized lignin peroxidases and horseradish peroxidase was studied by Ferrer et al. (1991). The free lignin peroxidase and horseradish peroxidase removed color from kraft effluent. Laccases are multi-copper-containing polyphenol oxidases that are widely distributed in microorganisms, insects, and plants, showing a specific function in each of them. From this group, white-rot fungi are the most studied organism to produced laccases. Laccase catalyzes the oxidation of various aromatic compounds, particularly those with electron-donating groups such as phenols (-OH) and anilines (-NH_2), by using molecular oxygen as an electron acceptor. Laccases use molecular oxygen to oxidize a variety of aromatic and nonaromatic hydrogen donors via a mechanism involving radicals. These radicals can undergo further laccase catalyzation of the reaction and/or nonenzymatic reaction such as polymerization and hydrogen abstraction. Therefore, laccase has also the ability to oxidize a wide range of phenolic and non-phenolic substrates (Wong 2009). This enzyme has attracted wide attention because of their number of diverse applications, namely, delignification of lignocellulosic, cross-linking of polysaccharides, detoxification of

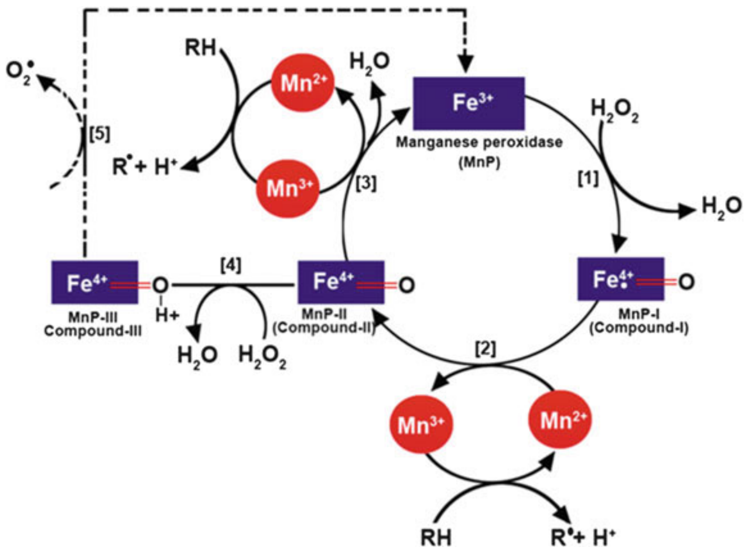

Fig. 1.6 Catalytic cycle of manganese peroxidase (Chandra et al. 2017a)

waste, and transformation of dye (Manzanares et al. 1995). A wide variety of microorganisms—bacteria, yeasts, molds, and algae—have been implicated in lignin biodegradation as well as decolorization of pulping effluents (Garg and Modi 1999). Lignin degradation by fungi is essentially a secondary metabolic process, as fungi and bacteria do not utilize lignin as a carbon source for their growth. This unique feature makes fungi suitable for their application in pulp pretreatment, which can reduce the energy requirement during the mechanical pulping and also will increase the efficiency of bioconversion (Kirk et al. 1992; Kang et al. 2007). Several fungus species such as *Aspergillus niger* (Kannan and Oblisami 1990), *Bjerkandera adusta*, *Phanerochaete chrysosporium* (Costa et al. 2017), *Fibrodontia* sp. (Kreetachat et al. 2016), *Cryptococcus* sp. (Singhal and Thakur 2009b), *Paecilomyces* sp. (Chuphal et al. 2005), *Phanerochaete chrysosporium*, *Pleurotus ostreatus*, *Lentinus edodes*, *Trametes versicolor* (Wu et al. 2005), and *Emericella nidulans* var. *nidulans* (Singhal and Thakur 2009a) have been reported to decolorize and detoxify the paper and pulp industry wastewater and remove lignin efficiently from the wastewater. Michel Jr et al. (1991) investigated the role of MnP and LiP of *P. chrysosporium* in the decolorization of kraft bleach plant effluent (KBPE). They observed when *P. chrysosporium* was grown in a medium with no Mn^{2+} and high levels of LiPs, but negligible levels of MnP were produced, and the rate and extent of KBPE decolorization by such cultures were quite low. This indicated that LiP plays a relatively minor role in KBPE decolorization. Further, high rates of KBPE decolorization were seen on 3 and 4 days of incubation, when the cultures exhibit high levels of MnP activity but little or no LiP activity. The results of this study indicated that MnP plays a relatively major role than LiPs in KBPE decolorization by *P. chrysosporium.* Yadav et al. (2010) treated the kraft pulp of mixed hardwood with lignin-degrading fungi *Ceriporiopsis subvermispora* during the bleaching pretreatment. They observed that the fungal treatment made the bleaching process energy efficient and reduced the chlorine consumption up to 4.8%, lignin content 4.7%, and pollution load in terms of COD and BOD by 32.6% and 41.5%, respectively. In bacterial bioremediation of pulp and paper industry wastewater, the role of lignin-degrading enzymes (Lac, LiP, and MnP) is already documented. A diverse spectrum of ligninolytic bacteria capable of degrading lignin and other organic pollutants present in pulp and paper industry wastewater has been isolated and identified over the years (Kumar et al. 2012; Ojha and Markandeya 2016; Raj et al. 2007a, b; Chandra et al. 2011a, b; Chandra and Singh 2012; Raj et al. 2007a, b). Arica et al. (2009) used immobilization of laccase onto nonporous poly(GMA/EGDMA) beads for degradation of industrial effluent. In addition, Sharma et al. (2008) immobilized the enzyme tannase (E.C.3.1.1.20) to possess desirable properties such as stability at extreme pH and temperature and board substrate specificity for industrial applications. The studies by Chandra and Singh (2012) showed induction of Lac, LiP, and MnP during bioremediation of rayon grade pulp and paper mill wastewater by a developed bacterial consortium of *Pseudochrobactrum glaciale*, *Providencia rettgeri*, and *Pantoea* sp. They reported a 90% reduction of lignin and chlorophenol within 216 h of treatment. The studies by Raj et al. (2014a, b) also confirmed the induction of laccase enzyme during bioremediation of paper mill wastewater by *Paenibacillus* sp. Hooda et al. (2015) conducted a study to explore the degradation of pulp and paper mill wastewater by *Brevibacillus agri* strain RJH-1, a rod-shaped gram-positive bacterium isolated from sludge, based on its efficiency to reduce COD, color, AOX, and lignin content under batch and semicontinuous reactor processes. In the batch study, the isolate reduced 47% color, 69% COD, 39% AOX, and 37% lignin after 5 days, whereas in control flask, 26% color, 40% COD, 22% AOX, and 19% lignin reduction were observed by the indigenous bacterial communities present in such wastewater. During semicontinuous reactor study, it reduced 62% COD, 37% color, 30% lignin, and 40% AOX of wastewater at a retention time of only 32 h, whereas the reduction in 21% color, 36% COD, 29% AOX, and 18% lignin was reported in control reactor. This study confirmed that the *B. agri* has the potential to degrade the lignin and reduce the color and COD of the pulp and paper mill wastewater. Lignin decolorization and degradation of pulp and paper mill effluent by ligninolytic bacteria *Bacillus subtilis*, *B. endophyticus*, and *Bacillus* sp. have been reported by Ojha and Markandeya (2016). A LiP-producing *Serratia liquefaciens* was used for bioremediation of pulp and paper mill effluent. The treatment led to toxicity as well as pollution parameter reduction (Haq et al. 2016). Gaur et al. (2018) also investigated that *Klebsiella pneumoniae* strain NITW715076_2 was capable of 74.5% decolorization of pulp and paper industry at the optimized condition. They observed that Lac and MnP activity was increased at the optimum value of pH 6.5, temperature 35 °C, agitation speed 130 rpm, inoculum size 4 mL, carbon source (1%), sucrose and nitrogen source (0.5%), and yeast extract. MnP, LiP, and laccase are the most important ligninolytic enzymes involved in biomechanical pulping and kraft pulp bleaching. In the laboratory scale, consumption of refining energy in mechanical pulping was reduced with MnP pretreatment. However, MnP degraded residual lignin of kraft pulp and enhanced the pulp bleaching effect. The laccases have also attracted considerable interest for pulp biobleaching. During lignin degradation, laccases are thought to act on small phenolic lignin fragments.

1.7 Emerging Approaches for Pulp and Paper Industry Waste Treatment

1.7.1 Phytoremediation Approaches

Phytoremediation is an emerging, cost-effective, eco-friendly, in situ technology that uses plants to remediate pollutants from the soil, sludge, sediments, and water contaminated with organic and inorganic contaminants (Garbisu and Alkorta 2001; Chandra et al. 2015a, 2018b, c, d; Chandra and Kumar 2017c, 2018). Phytoremediation utilizes plants and their associated microorganisms to reduce, remove, degrade, and/or immobilize harmful environmental pollutants (Chandra and Kumar 2015a). This can reduce risk from contaminated soil, sludges, sediments, and water through contaminant removal or degradation (Alkorta et al. 2004; Rajkumar and Freitas 2008; Chandra and Kumar 2017c). Generally, phytoremediation technology is focused on the ability of plants to accumulate higher concentrations of HMs (up to 100 times the normal concentration) in their shoot and leaves (i.e., they are hyperaccumulator plants as defined by Baker (1981)) (Chandra et al. 2018c, d). Plants have been found to remediate paper mill wastewater, containing multiple contaminants including HMs, viz., Fe, Zn, Cu, Ni, Mn, Hg, and Pb, with variable success (Kumar and Chopra 2016). Several potential native plants that grow on pulp and paper industry waste-contaminated sites under natural conditions have indicated the phytoremediation potential (Fig. 1.7; Chandra et al. 2018b, c, d).

Mishra et al. (2013) assessed the phytoremediation potentials for remediation of HMs by six aquatic macrophytes plants, including *Eichhornia crassipes, Hydrilla verticillata, Jussiaea repens, Lemna minor, Pistia stratiotes,* and *Trapa natans*, grown in paper mill effluent. They found that all the plants caused decreased levels of Cu and Hg in the effluent. Among the six tested plants, *L. minor* and *E. crassipes* were showed high tolerance to Cu and Hg with increased hyperaccumulation. Similarly, a study was conducted by Mazumdar and Das (2015) in Northeast India, to assess the phytoremediation potential of Pb, Zn, Fe, and Mg by 25 wetland plants grown on paper mill wastewater-contaminated sites. Out of 25 species, 10 species were excluders, and the rest were accumulators for different HMs. All the plant species thrived in high Fe, Mg, Pb, and Zn in soil and water, which indicated promise for phytoremediation. Further, the same authors conducted a separate study in 2016 to assess the potential of an aquatic fern, *Salvinia cucullata*, to remediate high BOD, COD, TS, TSS, TDS, P, hardness, and chloride and several HMs (Cd, Cu, Cr, Ni, Pb, Mg, Mn, Fe, and Zn) containing pulp and paper mill wastewater after treating it for 28 days (Das and Mazumdar 2016). They demonstrated that *S. cucullata* thrives in different concentrations of pulp and paper

Fig. 1.7 Some native plants grown on pulp and paper industry wastewater-discharged site showing in situ phytoremediation of hazardous pollutants. (**a**) *Commelina benghalensis*; (**b**) *Phragmites australis* L.; (**c**) *Argemone mexicana*; (**d**) *Alternanthera* sp.

mill wastewater and was capable of accumulation of HMs in different parts, beyond the permissible limits. The fact that this plant survived a wide range of wastewater concentrations and flourished well, particularly at 25% (v/v) treatment, shows better growth, augmentation of all the major antioxidant enzymes, and its capacity to resist membrane injury and attacks of H_2O_2 and O_2 reflected its potential as a phytoremediator. Nevertheless, from the biochemical and anatomical perspective, beyond 25% (v/v) wastewater, the plants suffered stress. Simultaneously, Kumar and Chopra (2016) conducted a laboratory experiment to investigate the reduction of pollution load of paper mill wastewater through phytoremediation technique using water caltrop (*Trapa natans*). *Trapa natans* significantly removed TDS, BOD, COD, TKN, PO_3^{-4}, Ca^{2+}, Mg^{2+}, K^{+}, Cd, Cu, Fe, Ni, Pb, and Zn of the paper mill wastewater. They recommended that *T. natans* can be used for the treatment of paper mill wastewater up to 50% concentration for 60 days using phytoremediation technique. Chandra et al. (2017b) investigated the HMs phytoextraction potential of native wetland plants growing on organic pollutant-rich pulp paper sludge. They selected 12 representative native plants based on their luxuriant growth on the pulp paper sludge and evaluated the plants for their phytoextraction potential of HM removal. The metal accumulation pattern revealed that all the native plants growing on sludge sediments have accumulated tested metals in root and shoot. Thus, it was observed that all the growing plants had HM phytoextraction efficiencies in the organic pollutant-rich environment. The HMs (Cd, Cu, Fe, Pb, Mn, and Zn) uptake by water lettuce (*Pistia stratiotes* L.) from paper mill effluent (PME) with its prediction modeling has been studied by Kumar et al. (2019). Lab-scale phytoremediation experiments were performed in glass aquariums to grow *P. stratiotes* in 0% (bore well water as a control), 25%, 50%, 75%, and 100% concentrations of PME. The results showed that *P. stratiotes* was capable of uptaking maximum contents of all heavy metals in its roots, leaves, and the whole plant when grown in 75% PME concentration. This work represents an effective method to model heavy metal uptake by *P. stratiotes* from PME. The author recommended that this methodology can also be adopted for predicting effective metal uptake by plant species being used for the phytoremediation of heavy metals from industrial effluents. The potential prospect of wetland plant for bioremediation of different pollutants from pulp paper mill effluent has also been reported through the constructed wetlands (CWs) treatment system (Kumar and Chopra 2016; Arivoli et al. 2015; Rani et al. 2011). Phytoremediation of HMs and organic pollutants using CWs offer effective, reliable treatment to pulp and paper industry wastewater in a simple and inexpensive manner. CWs are engineered systems that have been designed and constructed to utilize the natural processes, involving wetland vegetation, soils, and their associated microbial assemblages to assist in treating wastewater (Kadlec and Wallace 2009; Vymazal 2014). Macrophytes are the main biological component of wetland ecosystems; they contribute directly to pollution reduction through uptake and assimilation and indirectly by facilitating the growth of important pollutant-degrading microorganisms through complex interactions in the rhizosphere (Guan et al. 2015; Kumar and Chandra 2018b). They not only assimilate pollutants directly into their tissues but also act as catalysts for purification reactions by increasing the microbial diversity in the root zone through the release of oxygen and exudates and promotion of a variety of chemical and biochemical reactions that enhance purification (Stottmeister et al. 2003; Chandra et al. 2018e). Several experiments with the use of CWs to treat wastewaters discharged from pulp and paper industries were carried out by various workers (Knight et al. 1994; Tettleton et al. 1993; Hatano et al. 1994; Moore et al. 1994). Thut (1990, 1993) studied a 3750 m^2 horizontal flow-constructed wetlands (HF-CWs) planted with *P. australis* and *S. californicus* to treat pulp mill wastewater. The system was very effective in removing BOD with removal being consistently between 80% and 90%. Hammer et al. (1993) reported on the use of HF-CWs for removal of color from pulp mill wastewater. The early color removal results were encouraging despite the concomitant export of BOD_5. The authors suggested that a treatment system for tannins and lignins should be designed to optimize environmental conditions and retention times to enhance fungal decomposition of complex organics and incorporate similar components for further decomposition by bacterial populations. Since fungal populations require an attachment substrate, vegetated sand or porous soil substrate is likely to simulate natural soil conditions and provide an aerobic environment and hydraulic conductivity needed to enhance fungal growth. Knight et al. (1994) reported the use of free water surface (FWS)-CWs consisting of six cells receiving secondary-treated effluent indicated that the cells with the longest length/width ratio (10:1) performed better than cells with a lower aspect ratio (5:1 and 2.5:1). Removal of phenol from pulp and paper mill wastewaters was studied by Abira et al. (2005) in Webuye, Kenya. The HF-CWs with an area of 30.7 m^2 was filled with gravel to a depth of 0.3 m and planted with *Cyperus immensus*, *C. papyrus*, *P. mauritianus*, and *Typha domingensis*. The inflow phenol concentration varied between 0.43 and 1.7 mg L^{-1}, while the outflow phenol concentrations ranged from 0.18 to 0.23 mg L^{-1} and from 0.1 to 0.13 mg L^{-1} for the HRT of 5 and 3 days, respectively. In India, Choudhary et al. (2010) used an HF-CWs to remove chlorinated resin and fatty acids from a paper mill wastewater. The experimental wetlands with a total area of 5.25 m^2 were filled with gravel and planted with *Canna indica*. At an HRT of 5.9 days, the removal efficiency varied between 92% for 9,10,12,13-tetrachlorostearic acid and 96% for 9,10-dichlorostearic acid. The authors concluded that the most probable mechanisms for the removal of chlorinated resin and fatty acids were adsorption/absorption and microbial degradation in the root zone of the plants. Arivoli et al. (2015) demonstrated the feasibility of CWs to treat the heavy metals from pulp and paper industry wastewater by using vertical flow constructed wetlands (VF-CWs) planted with commonly available macrophytes such *as T. angustifolia, Erianthus arundinaceus,* and *Phragmites australis.* The results indicate that the removal efficiencies of VF-CWs for Fe, Cu, Mn, Zi, Ni, and Cd were 74, 80, 60, 70, 71, and 70%, respectively. On the contrary, the removal efficiency of the unplanted system was significantly lower ranging between 31% and 55%. Among the macrophytes, *T. angustifolia* and *E. arundinaceus* exhibited comparatively higher bioconcentration factor (102–103) than *P. australis.* Rani et al. (2011) carried out a pilot-scale study to examine the feasibility of a CWs system for treatment of pulp and paper mill wastewater during summers as well as winters at different HRT, viz., 1.5, 3.5, and 6.5 day. Wetland beds were prepared with easily available plants such as *T. angustifolia* and *Canna indica*. Comparison of mean inlet and outlet concentrations showed that the CWs system could effectively reduce the output of color (89.4%), BOD_5 (80.01%), COD (86.6%), and TS (87.6%) during summer and color (74.90%), BOD_5 (72.07%), COD (70.94%), and TS (72.15%) during winter at 3.5 day HRT.

1.7.2 Vermiremediation

Vermitechnology is an appropriate technique to reduce the level of hazardous substances from wastewater sludge solids. Vermicomposting involves combined interaction between earthworms and microbes for faster mineralization of organic wastes to produce a mature and stable final product known as vermicompost (Sonowal et al. 2013; Bhat et al. 2017). Earthworms carry out toxicity reduction of industrial wastes very efficiently during vermicomposting process (Bhat et al. 2018).

The chlorogocyte cells and the intestinal microorganisms in earthworms can detoxify most of the wastes/sludges (Srivastava et al. 2005). Co-composting with and without *Eisenia fetida* for the conversion of toxic paper mill sludge to a soil conditioner was studied by Kaur et al. (2010). It was observed that mixing cattle dung with the sludge improved physicochemical characteristics (with transition metals in the permissible range for manures) of the products of both the processes and enhanced its acceptability for worms. A higher decline in organic carbon and higher content of nitrogen and phosphorous along with lower electrical conductivity and higher pH of the products of vermicomposting indicated that *E. fetida* helped in the fast conversion of toxic paper mill sludge into a soil conditioner in 100 day. Vermistabilization of paper mill wastewater sludge using *E. fetida* has been carried out by several researchers (Sutharn et al. 2014). Gupta and Garg (2009) reported the vermiremediation and nutrient recovery of nonrecyclable paper waste employing *E. fetida.* In this study, an attempt has been made to vermicompost nonrecyclable postconsumer paper waste amended with cow dung (CD), employing *E. fetida* earthworm in order to transform it into a value-added product, i.e., vermicompost. Vermicomposting of paper waste resulted in a net reduction in ash content and total organic carbon (42.5–56.8%), but increment in total Kjeldahl nitrogen (2.0–2.4-fold), total potassium (2.0-fold), and total phosphorous (1.4–1.8-fold) was achieved after 91 day of worms' activity. The C/N ratio decreased with time in all the worm-worked vermireactors in the range of 71.9–82.0%, depicting an advanced degree of organic matter stabilization.

1.8 Two-Stage Sequential/Phase Separation/Sequential/ Combined Approaches for Pulp and Paper Industry Wastewater Treatment

The establishment of sequential anaerobic–aerobic/two-step wastewater treatment facilities is a promising approach to reduce color and toxic contaminants from pulp and paper industry wastewater. The sequential anaerobic and aerobic treatment in two-step bioreactor was evaluated for removal of color in the pulp and paper mill wastewater (Singh and Thakur 2006). In anaerobic treatment, lignin (25%), color (70%), AOX (15%), COD (42%), and phenol (39%) were reduced in 15 days of incubation. Further, the anaerobically treated wastewater was separately applied in a bioreactor in the presence of fungal strain (*Paecilomyces* sp.) and bacterial strain (*Microbrevis luteum*). This study showed reduction in lignin (86%), color (95%), AOX (67%), COD (88%), and phenol (63%) by *Paecilomyces* sp., whereas *M. luteum* showed reduction in lignin (69%), color (76%), COD (75%), AOX (82%), and phenol (93%) by day third when 7-day anaerobically treated wastewater was further treated by aerobic microorganisms. The two or more types of microbes may be attempted sequentially, in which one organism may transform the original organic pollutant by initial catabolic reactions to products that are then mineralized by another organism(s). The potential fungal and bacterial strains (*Paecilomyces* sp. and *Pseudomonas syringae* PV myricae) isolated from pulp and paper mill wastewater were applied for the treatment of pulp and paper industry wastewater in a two-step and three-step fixed-film sequential bioreactor containing sand and gravel at the bottom of the reactor for immobilization of microbial cells. The result revealed that microbes exhibited significant reduction in lignin (79.5%), color (88.5%), phenol (87.7%), and COD (87.2%) in two-step aerobic sequential bioreactor and lignin (76.5%), color (87.7%), phenol (87.2%), and COD (83.9%) in three-step anaerobic–aerobic sequential bioreactor. The concept of sequential treatment is very important because both anaerobic and aerobic fungi and bacteria can be used to treat effluent at different stages in the bioreactor (Chuphal et al. 2005). Similarly, two-step sequential treatment of pulp and paper industry wastewater by *C. albidus* and *E. nidulans* var. *nidulans* in a sequential manner in 2 L bioreactor was reported by Singhal and Thakur (2012). In treatment (I), the wastewater was first treated by *C. albidus* (stage A), and this treated wastewater was further treated by *E. nidulans* var. *nidulans* (stage B). In treatment (II), wastewater was first treated by *E. nidulans* var. *nidulans* (stage C), and this treated wastewater was further treated by *C. albidus* (stage D). Treatment (I) was more efficient than treatment (II) with 71%, 51%, 44%, and 70% reduction in color, lignin, COD, and genotoxicity, respectively. Class distribution of comets also showed that treatment (I) was more efficient than treatment (II). The author recommended that the effluent treatment process (I) can be scaled up for industrial use.

1.9 Challenges and Future Prospects

The detoxification of pulp and paper wastewater after secondary treatment, prior to discharge in the environment, is a thrust need of the country for sustainable development of industry and the environment. During the papermaking process, pulping is the most important polluting step. Pulping technologies have undergone constant improvements due to market demands and new developments in research. Enzymatic processes are being developed to increase pulp brightness, to reduce troublesome pith, to improve paper quality, and to purify the effluent. Efforts have been made to improve the pulp-producing process by using isolated enzymes. These efforts have limited success as lignin, which is the major problem, and lack the regular and ordered repeating units found in other natural polymers.

Several techno-economic analyses have been carried out recently in order to optimize the production processes to have less environmental drawbacks while providing more quality for the products from an economic perspective. However, the industry is not yet able enough to minimize the pollution load in final wastewater, and it is expected for wastewater from pulp and paper industry to remain as one of the most polluted industrial wastewaters through the world containing recalcitrant and complex organic compounds. The conventional biological treatments have shown a limited efficiency for the treatment of recalcitrant and complex pollutants such as AOXs which can remain in the treated wastewater, causing several environmental and health problems. Hence, there is also a need to perform further life cycle assessment studies for the conventional treatment methods applied to this type of wastewater. Certain biological treatments offer opportunities to reduce cost (both capital and operating), reduce energy consumption, and minimize environmental impact. The application of such versatile biological agents for the treatment of industrial wastewater on large scale is still limited due to several factors, such as limited amount and sources of biocatalysts, lack of optimum substrate specificities, environmental and cultural conditions required for the growth of microorganisms, competition from native microbes, lack of efficient microbial expression, and appropriate treatment reactor vessels, that make the biological treatment processes slow compared to the conventional processes. However, the necessity of allocating a relatively large area for biological treatments, relatively long-time treatment requirements as well as uncompleted treatment, and local issues such as the bad smell resulting from the bacterial activities are the main drawbacks of such systems. Further, it appears that enzymes such as laccase and peroxidase also have great potential for decolorization of phenolic effluents. However, the activities of the bacterial and fungal enzyme system can be enhanced by the utilization of innovative advanced techniques such as cell/enzyme immobilization and nanotechnology. Protein engineering can be exploited to improve enzyme stability, substrate specificity, and kinetic properties. However, further detailed studies are required to be carried out for selected conditions, which allow more efficient decolorization process from technical and economic viewpoints suitable for commercialization.

A large amount of enzymes required for the effluent treatment and presence of all the enzymes in a single microorganism is difficult, thus becoming a bottleneck for industrial application of microbes and their enzyme system in paper and pulp mill wastewater treatment. However, the application of two or more microbes in combinations can solve the problem of limited resource availability of enzymes. The biodegradation efficiency can further be enhanced by exploring the microbial expression for a specific enzyme. Furthermore, isolation, characterization of new microbial strains, immobilization, and genetics of lignin-degrading microorganisms are the area of future research required to make the direct use of biological agents in wastewater treatment processes.

1.10 Conclusion

Safe disposal of wastewater from pulp and paper industry is a matter of debate which is continuously tainting the environment as treated or raw wastewater is discharged back into the receiving ecosystem, resulting in negative environmental impacts. Several physicochemical methods have been attempted for the removal of color and toxicity from discharged wastewater, but often are not implemented, because of the high costs involved. More recently, the paper and pulp industry has been investigating the use of biological remediation steps to replace or augment current treatment strategies. Although, biological treatments offer opportunities to reduce cost (both capital and operating), reduce energy consumption, and minimize environmental impact, these methods are comparatively slow, and available natural enzyme sources (microorganisms) cannot meet the market demand due to low yields and their incompatibility toward standard industrial processes. Therefore, to achieve the desired standard norms for discharging of wastewater, successful implementation of microbes in biological treatment processes of paper and pulp mill effluent requires the identification of optimum application conditions such as pH, temperature, substrate specificities, and reaction media. However, pulp and paper industry wastewater containing different types of pollutants does not easily degrade by the single-step treatment process. Therefore, treatment of wastewater by a novel two-step treatment/phase separation method might be a novel and more promising approach for the bioremediation of pulp and paper industry wastewater. The use of hybrid systems, a combination of either biological and physicochemical processes or two biological processes, for wastewater treatment under optimized operating conditions is the most appropriate option for pulp and paper industry to obtain a satisfactory contaminant removal performance with higher efficiencies, especially for color removal; reduce GHG emission and energy costs; and meet environmental regulations.

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