

# Wastewater Treatment and Reclamation: A Review of Pulp and Paper Industry Practices and Opportunities

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The pulp and paper (P&P) industry worldwide has achieved substantial progress in treating both process water and wastewater, thus limiting the discharge of pollutants to receiving waters. This review covers a variety of wastewater treatment methods, which provide P&P companies with cost-effective ways to limit the release of biological or chemical oxygen demand, toxicity, solids, color, and other indicators of pollutant load. Conventional wastewater treatment systems, often comprising primary clarification followed by activated sludge processes, have been widely implemented in the P&P industry. Higher levels of pollutant removal can be achieved by supplementary treatments, which can include anaerobic biological stages, advanced oxidation processes, bioreactors, and membrane filtration technologies. Improvements in the performance of wastewater treatment operations often can be achieved by effective measurement technologies and by strategic addition of agents including coagulants, flocculants, filter aids, and optimized fungal or bacterial cultures. In addition, P&P mills can implement upstream process changes, including dissolved-air-flotation (DAF) systems, filtration save-alls, and kidney-like operations to purify process waters, thus reducing the load of pollutants and the volume of effluent being discharged to end-of-pipe wastewater treatment plants.

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Nomenclature			
AOPs	Advanced Oxidative Processes	PANS	Poly Aluminum Nitrate Sulfate
AOXs	Adsorbable Organic Halides	PCBs	Coplanar Polychlorinated Biphenyls
BAS	Biofilm Activated Sludge	PCDD	Polychlorinated Dibenzo- <i>p</i> -Dioxins
BCTMP	Bleached ChemiThermoMechanical Pulp	PCDF	Polychlorinated Dibenzofurans
BOD	Biochemical Oxygen Demand	PCDTs	Polychlorinated Dibenzothiophenes
COD	Chemical Oxygen Demand	PCNs	Polychlorinated Naphthalenes
DADMAC	Di Allyl Di Methyl Ammonium Chloride	PHA	Polyhydroxyalkanoates
DAF	Dissolved Air Flotation	POPs	Persistent Organic Pollutants
ECF	Elemental Chlorine Free	P&P	Pulp and Paper
GHG	Greenhouse Gas	PPI	Pulp and Paper Industry
GAC	Granulated Activated Carbon	PVDF	Polyvinylidene Fluoride
LCFA	Long Chain Fatty Acids	RAS	Return Activated Sludge
LMEs	Lignin Modifying Enzymes	RO	Reverse Osmosis
LSP	Low Sludge Production	SRT	Solids Retention Time
MBR	Membrane Bioreactors	TCF	Total Chlorine Free
MF	Microfiltration	TOC	Total Organic Carbon
MSG	Monosodium Glutamate	TSS	Total Suspended Solids
NCASI	National Council for Air and Stream Improvement	TMP	Thermomechanical Pulping
NF	Nanofiltration	TMP	Trans-Membrane Pressure
OLR	Organic Loading Rate	UF	Ultrafiltration
PAC	Poly Aluminum Chloride		

## INTRODUCTION

The pulp and paper (P&P) industry occupies a challenging position with respect to the natural environment. On the positive side, the industry is based on the usage of renewable, photosynthetic resources. On the other hand, the industry discharges huge quantities of aqueous effluents. Large volumes (up to 70 m<sup>3</sup>) of wastewater are generated for each metric ton of paper produced, depending on the nature of raw material, the type of finished product, and the extent of water reuse (Rintala and Puhakka 1994; Latorre *et al.* 2007). The P&P industry uses about 70% of its massive water intake as process water. Reducing water consumption, by increasing internal water recirculation after the implementation of internal cleaning processes, saves money and also decreases the use of scarce environmental resources. The industry has reduced water consumption over the past 20 years by nearly a half and over the past 30 years by an impressive 95% per tonne of paper (Blanco *et al.* 2004). Since the main unit operations associated with pulping and papermaking are carried out in aqueous media, the application of various chemical additives can considerably alter the properties of the produced effluents, making it harmful for the receiving environments. The total closure of the water circuits is limited by the accumulation of contaminants in the process water, which can give rise to corrosion, deposits, and odors and alter the runnability of the paper machine and the quality of the final product. If further closure is required, then the effluent has to be extensively treated so that it can be used again in the process.

The main pollutants discharged to water streams nowadays are solids and organic matter. In general, pulp and paper mill effluents contain a complex mixture of various classes of organic compounds, such as degradation products of carbohydrates, lignin, and extractives (Uğurlu *et al.* 2008; Uğurlu and Karaoğlu 2009). Polluting effluents are formed in wood preparation, pulping, pulp washing, screening, paper machine, and coating operations, and especially in bleaching operations (Ali and Shreekrishnan 2001; Pokhrel

and Viraraghavan 2004; Savant *et al.* 2006). Clearly, the properties of wastewater from various process stages depend on the type of process and raw material, the recirculation of the effluent, and the amount of water used (Pokhrel and Viraraghavan 2004). The effluents contain high values of biochemical oxygen demand (BOD), chemical oxygen demand (COD), and chlorinated chemicals that are collectively termed as absorbable organic halides (AOX). While AOX content is generally proportional to the chlorine consumption in bleaching (Savant *et al.* 2006), this emission has been reduced by over 80% since 1990 (Friere *et al.* 2003). The ratio of BOD to COD is a particularly useful quantity because it represents the fraction of organic compounds in the effluent that are easy to degrade (McCubbin and Folke 1993). Chemical pulping processes have been reported to generate more than 40% of poorly biodegradable organics within the total organic matter of the effluent (Dahlman *et al.* 1995).

If the wastewater were to be discharged without treatment, then the adverse effects would include depletion of dissolved oxygen, toxic effects on fish and other aquatic organisms, and unacceptable changes to color, turbidity, temperature, and solids content of the receiving waters. Issues related to toxicity have been the focus of much attention (Walden and Howard 1981; Owens 1991; Kamali and Khodaparst 2015). For the protection of the environment, and also to satisfy legal requirements, it is necessary for the industry to remove harmful materials from wastewater before it is discharged to the environment. For example, in the US the establishment of “cluster rules” for regulation of discharges from P&P facilities (Vice *et al.* 1996; Swann 1998; Vice and Carroll 1998) provided major incentive for reductions in discharged pollutants. In China part of the solution to the same issues has been to replace older manufacturing facilities with new capacity that is better suited to the minimization of wastewater impacts (Zhang *et al.* 2012).

In Canada, the discharge of wastewaters from pulp and paper mills into water frequented by fish is controlled by the Pulp and Paper Effluent Regulations (PPER). These regulations aim at protecting water quality that sustains fish, fish habitat and the use of fisheries resources. The PPER set limits on the amounts of total suspended solids (TSS) and biochemical oxygen demand (BOD), and prohibit the discharge of effluents that display acute lethality to fish (Environment and Climate Change Canada 2016). Secondary treatment for the biological break down of biodegradable material and toxic components, resulting in reductions in biochemical oxygen demand, toxicity and total suspended solids, became common by 1996 following the establishment of current regulatory limits in 1992. Environmental regulation of pulp and paper mills also includes the Pulp and Paper Mill Effluent Chlorinated Dioxins and Furans Regulations, issued under the Canadian Environmental Protection Act (CEPA), to control the level of dioxin and furan in the effluent of mills using a chlorine bleaching process. Additionally, Pulp and Paper Mill Defoamer and Wood Chip Regulations, also issued under the CEPA, govern the use of defoamers containing dibenzofuran or dibenzo-para-dioxin and wood chips from wood that was treated with polychlorinated phenols (Environmental Compliance Insider 2010).

In Europe, the Integrated Pollution Prevention and Control Directive sets permit conditions based on the use of best available technologies published in the BREF documents (BREF 2015), and voluntary agreements through the Confederation of European Paper Industries (CEPI) further enhanced the sustainability behavior.

Although the focus of this article is on the treatment of wastewater, it is important to keep in mind that purification of the effluent water is not the only goal. A wider goal is to achieve a sustainable P&P production in which environmental performance and competitiveness go hand in hand to supply a wide range of useful products. For efficient

water use and treatment, a sustainable integrated water management is motivated by multiple drivers including: legislation; protection against water-related risks in water stress regions; limits in sensitive water bodies; cost of water; business opportunities; general expectation; proudness of the company; and corporate image, *etc.* Within this approach the concept of water-fit-for-use is becoming increasingly important; therefore attention will be paid in this review to which approaches tend to be cost-effective and sufficient to meet the different water quality demands.

Much of the content of the present article can be regarded as an overview of “best practices” in terms of wastewater and process water treatment technologies that have been implemented in the P&P industry. The article aims to provide explanations not only of practices that have become widely used in the industry, but also of practices that hold the potential of greater effectiveness of wastewater treatment in the future within the P&P industry. Ideally, wastewater treatment operations ought to be regarded as highly reliable, highly effective, cost-competitive, and evidence of good stewardship on the part of industry leaders.

The subject of treating the effluent and process water from P&P manufacturing facilities has been considered earlier, with emphasis in a number of key areas. The toxicity of such wastewater and its potential effects on the environment have been reviewed by Ali and Sreekrishnan (2001). Review articles by Pokhrel and Viraraghavan (2004), Zhao *et al.* (2014), and Kamali and Khodaparast (2015) provide background for different types of treatment facilities. Bajpai and Bajpai (1994) reviewed strategies for the removal of color from P&P mill wastewater. Various articles have focused on the performance and “best available technology” for treating P&P mill wastewater in different regions (Lescot and Jappinen 1994; Hammar and Rydholm 1972; Gehm 1973; Rajvaidya and Markandey 1998; European Commission 2001; Demel *et al.* 2003; Tiku *et al.* 2007; Menezes *et al.* 2010; Zhu *et al.* 2012; BREF 2015). Regarding advanced oxidation systems applicable as a primary or a tertiary treatment, the review by Bautista *et al.* (2008) gives excellent descriptions of Fenton (iron/ hydrogen peroxide) wastewater treatment systems, though P&P applications are not considered. Hermosilla *et al.* (2015) reviewed the implementation and development of advanced oxidation systems implemented for P&P mill effluents. Buyukkamaci and Koken (2010) focus on the economic aspects of different wastewater treatment options available for P&P mill effluent. Various authors have considered options of treating the process water so that it can be reused within the normal operations of papermaking (Tenno and Paulapuro 1999; Verenich *et al.* 2000; Webb 2002; Nuortila-Jokinen *et al.* 2004; Hubbe 2007c; Ordóñez *et al.* 2010; Mauchauffee *et al.* 2012; Saif *et al.* 2013). Wider review articles and books dealing with general aspects of wastewater treatment have appeared (Scott and Ollis 1995; Thompson *et al.* 2001; Pokhrel and Viraraghavan 2004; Singh *et al.* 2012; Riffat 2013; Ranade 2014; Spellman 2014; Zhao *et al.* 2014; Hopcroft 2015; Blanco *et al.* 2016; Fatta-Kassinos *et al.* 2016). Finally, Ince *et al.* (2011) reviewed strategies that can be implemented in the P&P industry to prevent pollution.

### Criteria of Successful Treatment

Those who set out to remove pollutants from the wastewater of P&P manufacturing facilities face a variety of challenges, the difficulty of which will depend a lot on the nature of the wastewater that needs to be treated. The challenge also will depend on the required purity to be achieved in the treated water. To begin with, any successful wastewater management system needs to clearly define water demands and water qualities for different

uses in order to optimize water reuse based on the principle of water-fit-for-use, where water is treated only to the required quality. Second, the final effluent must be treated to accomplish the discharge limits. Table A in the appendix of this article lists the percentage removal values reported in a wide range of studies devoted to the treatment of P&P wastewater. In addition, it is important to achieve stable and reliable operations of both the pulp/papermaking process and the wastewater treatment system.

#### *Settling or flotation rate, speed of processing*

The rate of separation of wastewater solids in a waste treatment plant can limit the throughput of settling or flotation units. On the other hand, if methods can be developed and optimized to accelerate separation, then the size and capital costs of the plant might be reduced. Various researchers have shown that separation rates can be sped up by chemical treatments (Leitz 1993; Al-Jasser 2009). Furthermore, the use of some hybrid chemicals can promote the removal of a higher percentage of organic matter or specific inorganic material (*e.g.* silica) with the solids (Miranda *et al.* 2015). The operating conditions of the biological treatment plant can affect settling rates (Avella *et al.* 2011). Elliott and Mahmood (2012) found that biological sludge digestion could be optimized to speed up the process of handling the sludge.

#### *Quantity of sludge*

In recent years there has been increasing realization that, in addition to removing pollutants from the wastewater, it is important to minimize the amount of solid waste sludge that is generated as a byproduct of the treatment operations (Leitz 1993; Tripathi and Allen 1999; Alvares *et al.* 2001; Mahmood and Elliott 2006; Chanworrawoot and Hunsom 2012). One way to reduce sludge is to place increased emphasis on anaerobic biological treatment as an early step in the treatment program (Ashrafi *et al.* 2015; Kamali and Khodaparast 2015; Ordóñez *et al.* 2010). Alternatively, researchers have shown that thermophilic (higher temperature) biological treatment systems can achieve better efficiency and lower sludge amounts even under aerated conditions (LaPara and Alleman 1999; Skouteris *et al.* 2012). Also, by carrying out the treatment in stages, much of the initial sludge volume can be consumed by other types of organisms living within different zones within wastewater treatment operations (Lee and Welander 1996). Optimum sludge dewatering is also important, as well as the maximum removal of dissolved and colloidal material to keep the water circuit relatively clean. In conjunction with the development of technologies to minimize sludge production, avenues have been explored to utilize the generated sludge for beneficial purposes as opposed to just bearing expenses for treatment and removal of waste (Elliott and Mahmood 2005).

#### *Greenhouse gas emissions*

While the main goal of wastewater treatment is to remove pollutants from wastewater, one of the secondary goals, as we look to the future, is to minimize the production of other pollutants, such as gaseous emissions. Ashrafi *et al.* (2015) emphasized impacts of different wastewater-treatment options on greenhouse gas (GHG) emissions. In addition to the evolution of CO<sub>2</sub>, methane, and other GHG components from the waste materials, one also needs to be concerned about GHGs associated with the usage of electrical energy during the treatment of wastewater (Baig and Liechti 2001; Ashrafi *et al.* 2015). For instance, though improved efficiencies and treatment rates often can be achieved with modern reactors designed for biological wastewater treatment, such

operations sometimes may require more electrical energy in comparison to conventional treatment systems (Castillo and Vivas 1996; Buzzini and Pires 2002; El-Ashtoukhy *et al.* 2009). According to Kamali and Khodaparast (2015), a goal of saving electrical energy costs may be responsible for a more widespread use of mesophilic (medium temperature) rather than thermophilic (higher temperature) conditions in biological treatment plants, even though the latter have been reported to achieve higher performance in many cases. In fact, some of the generated effluents already have a relatively high temperature, so they can already be handled in the thermophilic range without further chilling the effluent. Anaerobic wastewater treatment operations are often regarded favorably by environmental advocates because they actively generate methane that can be retrieved and used in place of other combustible fuels (Maat and Habets 1987; Tabatabaei *et al.* 2010; Saha *et al.* 2011; Meyer and Edwards 2014; Sanusi and Menzes 2014).

GHG emissions by on-site and off-site processes in a typical industrial wastewater treatment plant that used aerobic, anaerobic, and hybrid anaerobic/aerobic treatment processes were studied by Bani Shahabadi *et al.* (2009, 2010) and Yerushalmi *et al.* (2011). Yerushalmi *et al.* (2013) and Ashrafi *et al.* (2013, 2014, 2015) estimated GHG emission and energy consumption by wastewater treatment plants of the P&P industry and determined the contribution of individual processes to the on-site and off-site GHG emissions. On-site GHG emissions are due to liquid and solid treatment processes as well as biogas and fossil fuel combustion for energy generation. Off-site GHG emissions are related to the production of electricity for plant, production, and transportation of fuel and chemicals for on-site use, degradation of remaining constituents in the effluent of wastewater treatment plant, as well as transportation and disposal of solids. The on-site biological treatment processes were shown to make the highest contribution to GHG emissions in the aerobic treatment system, while the higher usage of chemicals in anaerobic and hybrid treatment systems resulted in higher GHG emission from material production and transportation in those treatment systems. The recovery of biogas, generated during anaerobic treatment processes or anaerobic sludge digestion, and its reuse as fuel were shown to have a remarkable impact on GHG emissions and reduction of the overall emissions. Biogas recovery and reuse as fuel can cover the total energy needs of the treatment plants for aeration, heating, and electricity, considerably reducing the net GHG emissions in the treatment plants. Heating of an anaerobic digester was identified as a major energy-demanding process, suggesting that solid digestion at lower temperatures should be exercised to reduce the associated GHG emissions.

Based on the results of studies published by the above investigators, the manufacturing of material for on-site consumption should use methods that generate lower amounts of GHGs, thus reducing upstream GHG emissions attributed to the wastewater treatment plant. Electricity and fossil fuels should also be generated and handled by more efficient methods in order to decrease the overall GHG emissions of treatment plants.

Another strategy for GHG emissions reduction is to use alternative nutrient removal processes such as the anaerobic Anammox process (Greenfield and Batstone 2005), which removes nitrogen with a lower consumption of energy and lower carbon use. In this process, the reduced aeration energy consumption reduces GHG production related to energy demands of the treatment plant, while the extra available carbon can be converted to methane via anaerobic processes and be used as a source of energy for on-site consumption, further reducing GHG emissions. The use of hybrid anaerobic/aerobic systems for wastewater treatment under optimized operating conditions was shown to be

the most appropriate option for pulp-and-paper industry to obtain a satisfactory treatment performance, reduce GHG emission and energy costs, and meet environmental regulations.

#### *Operating costs justified*

Closely related to the topic of energy usage is the topic of operating costs. Hammar and Rydholm (1972), when reviewing the state of the art of wastewater treatment in the 1970s, complained about the relatively high cost of treatments capable of removing biodegradable organic pollutants. Although aerated biological treatment has long been regarded as a highly reliable and predominant approach utilized within the P&P industry, the pumping of the air represents one of the major operating costs of such systems (Maat and Habets 1987). Advanced oxidation systems, which have the potential to remove some of the most challenging toxic or highly colored components from P&P mill effluents, also have been criticized for their high operating costs (Heinzle *et al.* 1992; Byukkamaci and Koken 2010). Membrane treatments are also very efficient, and they are becoming more popular due to substantial reductions in membrane prices.

#### **Quantification of Wastewater Load**

Before considering different approaches used for the minimization or removal of contaminants from wastewater, the subsections below address some of the most common criteria for assessing the quality of treated water (McKeown and Gellman 1976; Owens 1991). Standard methods for the most widely used tests have been established in the US by the American Public Health Association (APHA 2001, 2005). In Europe, the corresponding standards are in the EU Directive 91/271/EEC of the Environmental Protection Agency.

#### *Oxygen demand*

From an environmental standpoint, biodegradable substances, which are quantified in terms of the biological oxygen demand (BOD) test, are generally regarded with favor. However, if such materials were to be discharged into rivers, lakes, and estuaries at excessive levels, the resulting biological metabolism would sometimes be sufficient to consume all or most of the available dissolved oxygen, leading to the death of fish and other aquatic life (Taylor *et al.* 1996; Chhonkar *et al.* 2000). Such impacts are often quantified by measuring the BOD. This quantity is evaluated by sealing a volume of water to be tested with a known amount of gaseous oxygen; the level of oxygen gas in the container is measured five days later (BOD<sub>5</sub> test), after microbes have had a chance to reproduce and to consume the decomposable organic materials (APHA 2016, Standard Method 5210). As can become evident from inspection of the contents of Table A (see Appendix), the BOD test is among the most frequently used methods to characterize untreated and treated wastewaters.

It has been recently shown that microbial consortia that have become acclimated to the degradation of lignin-related compounds can reduce the BOD levels in the pulp-and-paper wastewaters below levels that are normally achievable by using indigenous microorganisms (Ordaz-Diaz *et al.* 2014). BOD levels also have been found to correlate with the pulping yield and with the color in the treated wastewater from P&P mill facilities (Bajpai and Bajpai 1994).

The oxidizable matter in a wastewater also can be measured by the chemical oxygen demand (COD) test (APHA 2001). The COD test takes advantage of the relatively rapid reaction of potassium dichromate with the oxidizable materials in the water sample. The

results from BOD and COD tests will be different if the wastewater sample contains difficult-to-biodegrade oxidizable compounds or toxic materials that inhibit biological activities. Thus the ratio of BOD to COD is often reported as a way to quantify the relative recalcitrance of organic compounds in wastewater (Yeber *et al.* 1999b; Baig and Liechi 2001; Kreetachat *et al.* 2007; Ghaly *et al.* 2011). This value, which is often in a range between about 0.05 and 0.5 for P&P wastewaters, will help to determine what treatment strategy is appropriate.

### *Color*

The color of an organic chemical compound, *i.e.* its ability to absorb visible light, generally requires a sufficiently long sequence of single and double carbon-carbon bonds, *i.e.* a conjugated structure (Adachi and Nagao 2001). The lignin component of wood is highly susceptible to becoming strongly colored due to its high content of aromatic rings, in addition to other unsaturated structures (Sarkanen 1971). Thus, although natural lignin present in native wood generally has a light color, deep coloration develops during kraft pulping. Indeed, the appearance of “black liquor,” the spent alkaline solution left over after kraft pulping, can be attributed to such compounds. As noted by Bajpai and Bajpai (1994), highly colored compounds in typical pulping and bleaching wastewaters often are resistant to biodegradation and removal during treatment operations. The sources and types of colored compounds that develop during pulping and papermaking have been reviewed (NCASI 2011). Measures to remove color from the effluent of P&P mills have been reviewed and reported (Bajpai and Bajpai 1994; Garg and Tripathi 2011; Garg *et al.* 2012). Langergraber *et al.* (2004) discussed the evaluation of color in such wastewater by instrumental methods.

### *Total suspended solids (TSS) and turbidity*

Suspended matter in wastewater has the potential to obstruct the passage of light and interfere with the respiration of aquatic organisms. These contaminants are commonly quantified as the total suspended solids (TSS) and turbidity. The TSS values are determined by weighing the solid matter filtered from a water sample onto a tared piece of standard filter paper composed of glass fibers (APHA 2016, Standard Method 2540). Some of the most effective measures for reducing TSS are separation of solids by sedimentation, flotation, or membrane techniques. Treatment of the raw wastewater with coagulants and flocculants, at optimized dosages, can promote the speed and completeness of such separations.

### *Toxicity*

Toxic compounds may be present in wastewaters of pulping facilities, but they are not common in papermaking processes. They are a matter of concern (Lugowski 1991; Owens 1991; Ali and Srekrishnan 2001) not only because of their toxic effects on the environment (Mahmood-Khan *et al.* 2013), but also they may disrupt the beneficial biological activities during wastewater treatment operations (Freire *et al.* 2000; Liu *et al.* 2011). Discharged effluents having toxic content can damage the reproductivity of aquatic species (Costigan *et al.* 2012; Waye *et al.* 2014). According to Magnus *et al.* (2000) long-chain fatty acids, generated during pulping operations, constitute one of the primary sources of toxicity coming from pulping operations. Chlorinated organic compounds, and dioxin in particular, have been noted for their toxic and often carcinogenic effects (Safe 1990; Wiegand *et al.* 2006). The presence of toxic substances (mainly AOX and dioxins)

in effluents from pulp bleaching has been reduced by 95% down to a level of  $\leq 0.1$  KgAOX $\cdot$ t<sup>-1</sup> of pulp since 1990, mainly thanks to the replacement of chlorine gas by elemental-chlorine-free and total-chlorine-free chemicals in bleaching processes (Aspapel 2011; CEPI 2013). Kostamo and Kukkonen (2003) reported that secondary wastewater treatment with activated sludge can be effective for the removal of toxicity.

#### *Recalcitrant, persistent compounds*

Organic compounds that resist biodegradation are of great concern because they can remain in the wastewater even after it has been treated by widely used aerobic biological processes that employ activated sludge (Gergov 1988; Scott and Ollis 1995; Magnus *et al.* 2000; Contreras Lopez 2003) or with anaerobic biological wastewater treatment (Korcak *et al.* 1991; Sierraalvarez *et al.* 1991). Eriksson and Kolar (1985) employed isotopic labeling to explore the mechanisms involved in the biodegradation of such compounds. Efforts to eliminate such compounds by alternative treatment methods such as advanced oxidation processes (AOPs) have been widely reported (Rodriguez *et al.* 1999; Pokhrel and Viraraghavan 2004; Eskelinen *et al.* 2010; Merayo *et al.* 2013; Lindholm-Lehto *et al.* 2015). AOPs can be employed either as pretreatment to increase the biodegradability of the organic solids or as post-treatment to remove the remaining organic content. Inoculation of wastewater treatment systems with lignin-degrading fungal species has shown promise in breaking down the recalcitrant compounds and reducing the toxicity levels (Pellinen and Joyce 1990; Thakur 2004), in spite of the inherent issues arising from such methods such as low tolerance of the fungal strains for variations in pH.

#### *Sulfur content*

Sulfur-containing compounds in aqueous wastewaters are considered a problem because of possible action of sulfate-reducing bacteria in the environment. Anaerobic conditions can lead to the generation of toxic H<sub>2</sub>S gas, as well as other sulfur-containing compounds that contribute to unpleasant odors (Smet *et al.* 1998; Devai and DeLaune 1999; Goyer and Lavoie 2001). The removal of sulfur from pulp-and-paper wastewaters will be discussed in a later section (Lens *et al.* 1998; Janssen *et al.* 2009).

#### *Salt, electrical conductivity*

Inorganic salts and ionic compounds such as sodium chloride in industrial wastewaters can significantly increase the salinity and electrical conductivity of the receiving waters (Gehm 1973; Achoka 2002). Upset conditions in a P&P mill, causing the release of alkaline pulping liquors, can be detected by conductivity measurements (Kemeny and Banerjee 1997). Sulfates may also be limited by regulation or contract when treated effluents are discharged.

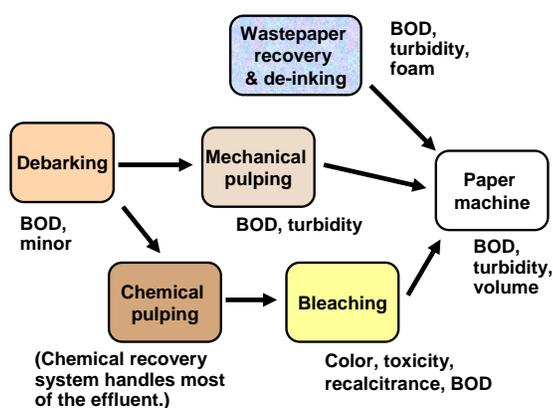
## **PULP AND PAPER WASTEWATER**

The closure degree of P&P mill water circuits depends on the type of product. While water circuits can be highly closed for brown grades (Pietschker 1996; Gubelt *et al.* 2000), a total closure without the application of advanced treatment processes is not practical for chemical pulping processes and for manufacturing of white paper grades. Because the nature of different waste streams from P&P operations has been reviewed in

other publications (Gehm 1973; Costa *et al.* 1979; Ashafi *et al.* 2015; Kamali and Khodaparast 2015; Blanco *et al.* 2016), such subjects will be treated only briefly here.

### Sources and Characteristics of P&P Wastewater

The first point worth emphasizing is that wastewater characteristics are highly variable, especially when comparing one pulp or papermaking operation to another. Much of the observed variation can be attributed to the different characteristics of wastewater streams emerging from specific kinds of pulping, bleaching, or papermaking processes (Gehm 1973; Hubbe 2007b; Hossain and Ismail 2015; Kamali and Khodaparast 2015). Also, the nature of the effluent will be dependent on how much fresh water is being utilized in the process. Figure 1 provides a snapshot of the categories or “streams” of wastewater mentioned in subsequent paragraphs.



**Fig. 1.** Main categories of contaminated water within a typical pulp and paper manufacturing facility, with an indication of important potential environmental impacts

#### Debarking

Following the sequence of the manufacturing process, one of the first streams of contaminated water is associated with soaking of logs and removal of bark (Gehm 1973; Vepsäläinen *et al.* 2011). Because mainly mechanical processes are involved in bark removal, the levels of contamination resulting from debarking tend to be relatively low in comparison to other wastewater streams. For example, Vepsäläinen *et al.* (2011) showed that such wastewater could be effectively treated by electro-coagulation. Furthermore, dry debarking allows reducing wastewater production and potentially making it possible to obtain more energy from the bark in a power boiler (BREF 2015).

#### Mechanical pulping

The type of virgin pulp most often used in the production of newsprint and high-circulation magazine papers is obtained by mechanically separating the fibers in wood. Though this is another mainly mechanical process, the amount of energy expended per unit mass of generated pulp is high, and that may explain why there is significant release of soluble and particulate materials into the water phase (Stephenson and Duff 1996). Mechanical pulping is often carried out at elevated temperatures, *i.e.* thermomechanical pulping (TMP), which enables softening of the lignin between the fibers, making it possible to preserve a much greater proportion of full-length fibers during the separation process. The heating is probably responsible for increased release of material into the water phase

(Rintala and Puhakka 1994; Stephenson and Duff 1996; Kortekaas *et al.* 1998; Willfor *et al.* 2003), though the literature search did not reveal data to support such an expectation. The peroxide-bleaching of thermomechanical pulp (BCTMP) is known to convert hemicellulose components of TMP into negatively charged carboxylate species, which readily enter into solution and can contribute to the pollutant load (Sundberg *et al.* 2000; Puro *et al.* 2010; Hubbe *et al.* 2012b; Miao *et al.* 2013). In general, however, high-yield pulps contribute relatively low levels of COD to the effluent.

### *Kraft pulping*

Because kraft pulping and optional subsequent bleaching of wood-based and non-wood cellulosic pulps can involve solubilization of about 30 to 60% of the solid mass, depending on the manufacturer's objectives (Biermann 1996), it is easy to understand why such operations have the potential to produce highly contaminated wastewaters. The leftover liquid after a kraft cooking process (the black liquor) is rich in lignin byproducts, as well as alkali, sodium sulfate, and the soaps of resin acids and fatty acids, among other contaminants (Vishtal and Kraslawski 2011; Lehto and Alén 2015).

Under ideal circumstances a very high percentage of the solubilized matter from alkaline pulping is circulated back to the chemical recovery system, diverting the potential contaminants away from the wastewater treatment system (Biermann 1996). But when the fiber source contains a high content of silica, as is the case for many annual plant types of biomass, the chemical recovery can be very difficult due to the deposition of inorganic scale on the equipment (Deniz *et al.* 2004). In addition, conventional bleaching technologies, based on chlorine dioxide, sodium hypochlorite, and related chemicals, yield wastewaters that would be excessively corrosive to the equipment used for chemical recovery, hence discouraging the recovery of pulping chemicals from such wastewater streams. The condensate collected during evaporative concentration of spent pulping liquor is a notable source of toxicity and odor, which needs to be treated (Wagner and Nicell 2001; Tielbaard *et al.* 2002).

Pollutants from various stages of bleaching of kraft pulps are among the most difficult to remove from wastewater (Prat *et al.* 1988; Kemeny and Banerjee 1997; Vidal *et al.* 1997; Yeber *et al.* 1999b; Kansal *et al.* 2008; Uğurlu and Karaoğlu 2009; Quezada *et al.* 2014; Larsson *et al.* 2015). Many of these compounds may have some adverse effects on the receiving media, such as formation of slime and scum, toxic effects to the exposed living organisms, and thermal impacts (Ali and Sreekrishnan 2001; Catalkaya and Kargi 2008; Garg and Tripathi 2011) or they are highly colored (Bajpai and Bajpai 1994).

### *Sulfite pulping process*

The production of sulfite pulp is presently much smaller than the production of kraft pulp because of generally worse strength properties. However, sulfite pulp does provide better properties in terms of some specialty pulp applications. Different sulfite processes, such as acid (bi)sulfite, magnefite, or neutral sulfite, may mainly be applied by just changing the pH and the type of base that is used in the process. The sulfite cooking process uses aqueous sulfur dioxide (SO<sub>2</sub>) and a base of magnesium, calcium, sodium or ammonium. Chemical and energy recovery, as well as water use, will be affected by the selected base type. Magnesium sulfite pulping is the dominating process in Europe (≈11 mills), and there is another mill using sodium base, because both types allow chemical recovery. Lignosulfonates, sugars, and other substances that are generated within the cooking liquor might further be used as raw materials for the production of different

chemical products. As noted by Rintala and Puhakka (1994), it is a high priority to remove toxicity from the evaporator condensate in a sulfite plant's recovery cycle. Most of these sulfite pulp mills operate biological treatment plants to purify wastewater generated in different processes (washing losses, effluents from the bleach plant, and condensate from the evaporation plant, mainly) (BREF 2015).

#### *Paper recycling operations*

When fibers are recovered from recycled papers, a wider spectrum of contaminants will be present due to the variability in the nature of the used paper materials, their contamination during paper's use and recovery, and the additives that are used for dispersing the fibers, removing ink, and bleaching (Muhamad *et al.* 2012a). Such waters are characterized by a high organic dissolved load, which typically has an anionic character (Miranda *et al.* 2009a).

In the past, deinking wastes were regarded as posing challenges during their clarification (Gehm 1973). Difficulties in gravitational separation of solids from deinking operations might be attributable to the dispersants that are widely used to separate the ink particles from the fibers. In this case, adequate coagulants and flocculants are required to destabilize the colloidal material and promote the aggregation of particles for their removal by sedimentation or dissolved air flotation (DAF). The past challenges during the clarification of de-inking waters generally have been solved, and these days it is possible to treat and reuse the effluents by membrane procedures, although silicic ions have to be removed to increase the recovery in reverse osmosis (RO) units (Ordóñez *et al.* 2011). Though the focus here is on the water-borne pollutants, it is important to bear in mind that a deinking process can result in the generation of large amounts of solid wastes; it has been estimated that about 70% of solid wastes, mainly in the form of sludge, are generated by de-inking operations (Monte *et al.* 2009).

#### *Papermaking operations*

The paper machine itself, in some respects, can be regarded as having the cleanest process water circuit in the plant. Excess water from the forming and press sections of the paper machine is clarified by filtration (*i.e.* a save-all operation) or by DAF and reused in the papermaking process. When high quality water is required, for example in high-pressure showers, a further treatment such as ultrafiltration (UF) can be used.

On the other hand, the process water in a paper machine system, *i.e.* the "white water", can contain a variety of additives, including mineral filler products such as calcium carbonate, clays, and titanium dioxide. Sizing agents, such as rosin products, alkenylsuccinic anhydride, or alkylketene dimer, are typically added to the fiber slurry in the form of emulsions, and not all of this is retained in the paper product. In the case of colored papers, though they are usually present at low amounts, dyes are important in terms of wastewater treatment on account of their high visibility.

Substantial pollutant loads can be expected whenever certain additives to the paper machine wet end are poorly retained in the product (Bilitewski *et al.* 2012). Starch products, which are rendered soluble in water by cooking operations, are commonly added to paper furnish at levels as high as 1% of the product mass (Howard and Jowsey 1989; Formento *et al.* 1994). Most of that wet-end-added starch is of the cationic form, and its positive charge favors a relatively high efficiency of retention onto the negatively charged fibers (Roberts *et al.* 1987; Howard and Jowsey 1989). By contrast, the surface-applied starch ("size-press starch") is typically uncharged "pearl" starch, which does not have any

electrostatic attraction to the fiber surfaces. The size press starch can be routinely added at amounts several times larger than what is practical at the wet end of the paper machine. Thus, when defective paper, *i.e.* “dry-end broke”, is repulped and sent back to the paper machine, a high proportion of the surface-applied starch may end up in the aqueous phase, such that it later can be discharged to the wastewater treatment plant.

### Recalcitrant Organic Compounds in Pulp and Paper Mill Wastewaters

Pulp and paper mill effluents contain a variety of recalcitrant materials, such as lignosulfonic acids, chlorinated resin acids, chlorinated phenols, dioxins, and chlorinated hydrocarbons (Kumara Swamy *et al.* 2012; Singh and Srivastava 2014). Although in most cases the toxicity is low, effluents from pulp bleaching are characterized by high strength of COD (1000 to 7000 mg L<sup>-1</sup>), low biodegradability ratio (BOD<sub>5</sub>/ COD) ranging from 0.02 to 0.07, and a moderate strength of suspended solids (500 to 2000 mg L<sup>-1</sup>) (Ramos *et al.* 2009; Eskelinen *et al.* 2012). Compounds, especially those containing chlorine (measured by the parameter AOX) are recalcitrant because they contain chemical structures uncommon in nature, such as the carbon-chlorine bond (Jokela *et al.* 1993; Mounteer *et al.* 2007a). It is widely reported that high molecular weight (HMW > 1 kDa) organic matter in bleaching effluents is more recalcitrant to biological treatment than low molecular weight (LMW < 1 kDa) organic matter (Dahlman *et al.* 1995; Savant *et al.* 2006). Dissolved lignin and its degradation products, hemicelluloses, resin acids, fatty acids, diterpene alcohols, juvaniones, tannins, and phenols (Pokhrel and Viraraghavan 2004) are responsible for the dark color and toxicity of the effluent (Malaviya and Rathore 2007; Chopra and Singh 2012).

#### *Lignin and its derivatives*

Among the main biomass components, lignin is the most difficult to degrade by biological means (Kumar *et al.* 2010; Pu *et al.* 2015). It is a three-dimensional amorphous polyphenolic polymer that is primarily biosynthesized from three typical types of phenylpropanoid precursors: coniferyl, sinapyl, and *p*-coumaryl alcohol (Thakur 2004). Once incorporated into the lignin polymer, these monomers form guaiacyl, syringyl, and *p*-hydroxyphenyl lignin subunits. The lignin macromolecule is primarily linked via ether bonds and carbon-carbon bonds among phenylpropanoid units (Samuel *et al.* 2014).

Lignin is degraded during pulp and paper production to a variety of high, medium, and low molecular weight chlorinated and non-chlorinated fractions (McKague 1981). In particular, the HMW lignin compounds are not effectively degraded during conventional effluent treatment, and the majority of such compounds in wastewater may be discharged into receiving waters (Hyötyläinen and Knuutinen 1993). Lignin and its derivatives are recalcitrant and highly toxic compounds responsible for the high BOD and COD values of effluents as well as the dark brown color of pulp effluents formed during pulping (Wong *et al.* 2006). In pulp bleaching, chlorine reacts with lignin, its derivatives, and other organic matter present in the pulp, forming highly toxic and recalcitrant compounds, such as chlorinated lignosulfonic acids, chlorinated resin acids, chlorinated phenols, guaiacols, catechols, benzaldehydes, vanillins, syringo-vanillins, and chloropropioguaiacols (Knuutinen 1982; Kringstad and Lindström 1984; Thakur 2004). Especially in acidic media, lignin molecules tend to undergo self-condensation, and they subsequently show resistance to degradation (Ali and Sreekrishnan 2001). Chlorolignins mostly end up in the effluent of the alkaline extraction stage, which is a major source of AOX, COD, BOD, and color (Sun *et al.* 1989; Ali and Shreekrishnan 2001).

### *Chlorinated organic compounds*

In pulp and paper mill effluents, hundreds of chlorinated organic compounds have been identified, including chlorinated hydrocarbons, phenols, catechols, guaiacols, furans, dioxins, syringyl lignin, and vanillins (Suntio *et al.* 1988; Freire *et al.* 2003). Organochlorine compounds are usually biologically persistent, recalcitrant, and highly toxic to the environment (Baig and Liechti 2001; Thompson *et al.* 2001). They have been detected especially in water and sediments in the vicinity of pulp and paper mill effluents (Virkki *et al.* 1994; Munawar *et al.* 2000; Lacorte *et al.* 2003). Organochlorine compounds are widespread and are found even in relatively pristine environments (Abrahamsson and Klick 1991). The recalcitrance of an individual compound towards biological processes is related to the number and position of the halogen substituents (Naumann 1999). Additionally, enantioselectivity and chiral discrimination of optically active compounds can have an influence on the degree of their accumulation (Reich *et al.* 1999; Vetter and Maruya 2000). Isomers, diastereomers, and enantiomers can have varying toxicity (Willett *et al.* 1998; Carr *et al.* 1999).

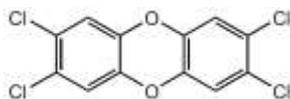
Chlorinated phenols are synthetic compounds, typically formed by hydrolysis of chlorobenzenes and in pulp bleaching (Kringstad and Lindström 1984). Chlorophenols may also be formed as by-products in paper production, cooking processes, or distillation of wood (Paasivirta *et al.* 1983, 1988; Öberg *et al.* 1989). Monomeric chlorophenols include 19 compounds of mono-, di-, tri-, and tetrachloroisomers and pentachlorophenol. Generally, they are crystalline solids at room temperature, excluding the liquid orthochlorophenol (Ahlborg 1977).

In the bleaching operations following kraft wood pulping, HMW and LMW chlorinated organic compounds are formed, the latter comprising of about 250 smaller chlorinated compounds (Rantio 1997). In pulp bleaching, chlorophenolics are present both in free (hexane extractable) and bound (extractable with strong alkali) forms and bound to dissolved organic matter and particles (Paasivirta *et al.* 1992). For example, chlorophenols, guaiacols, and catechols are formed in high quantities (Suntio *et al.* 1988; Koistinen *et al.* 1990), guaiacols and catechols being chemically bound to chlorolignin (Schechter *et al.* 1990). They can be methylated by microorganisms to more persistent and lipophilic forms as chloroanisoles, veratroles, or aromatic chloroethers, which are persistent derivatives of chlorophenolics. In addition, during the cooking and chlorine bleaching, chlorinated cymenes, (methyl-(methylethyl)benzenes, CYMS) and cymenenes (methyl-(methylethenyl)-benzenes, CYMD) are formed (Kuokkanen 1989; Rantio 1997). Chlorinated cymenes were first identified in the effluents of kraft pulp and sulfite mills in the late 70s, and dechlorinated cymene compounds have been found both from kraft and sulfite mills and chlorinated compounds from kraft pulp mills (Bjørseth *et al.* 1977). Residues of CYMS and CYMD have been found in fish and mussels in the recipient water bodies (Paasivirta *et al.* 1984; Herve 1991), and they can be employed as indicators of the exposure of biota to effluents from pulp bleaching (Rantio 1997).

Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are two classes of tricyclic, aromatic, and lipophilic compounds that contain some of the most toxic chemical substances ever known (Kringstad and Lindström 1984). PCDD and PCDF are formed as side products in chlorophenol production and in thermic reactions, such as combustions and chlorinations but also in pulp and paper production (Alcock and Jones 1996; Kim *et al.* 2002). In pulp production, the PCDD and PCDF are mostly formed by condensation of polychlorinated phenoxyphenols in pulping and by chlorination of

dibenzofuran and dibenzo-*p*-dioxin in pulp bleaching (Hrutfiord and Negri 1992; Luthe and Berry 1996; Yunker *et al.* 2002).

Generally, a mixture of different PCDD and PCDF is formed, but isomers with chlorine atoms in the 2, 3, 7, and 8 positions (7 PCDD and 10 PCDF) are the most toxic to organisms, with 2,3,7,8 tetrachlorodibenzo-*p*-dioxin, as shown in Fig. 2, being the most toxic (Malisch 2000; Fueno *et al.* 2002). PCDD and PCDF are acute or chronic toxins, recalcitrant and persistent in nature due to their lipophilic properties and resistance to biological and chemical degradation (Vallejo *et al.* 2015). This leads to biomagnification along food chains and various degrees of toxic effects (Van den Berg *et al.* 2006). They have been classified as priority pollutants by the United States Environmental Protection Agency (USEPA 1998) and ‘dirty dozen’ group of persistent organic pollutants (POPs) identified by United Nations Environment Program (UNEP 1995). Dioxins are named as ‘known human carcinogens’ by the World Health Organization (WHO 1997).



**Fig. 2.** Chemical structure of 2,3,7,8 tetrachlorodibenzo-*p*-dioxin

PCDD and PCDF have been detected, *e.g.* in bleach plant effluents, bleached paper products, sediments of the receiving waters, and fish living in the recipient water bodies (Rappe *et al.* 1989; Clement *et al.* 1989; Lacorte *et al.* 2003). The elimination of dibenzofuran and dibenzo-*p*-dioxin from defoamer products, the exclusion of chlorophenol-contaminated wood chips, and the introduction of chlorine dioxide bleaching have dramatically decreased the production of PCDD and PCDF in the P&P effluents (Hagen *et al.* 1997; Yunker *et al.* 2002).

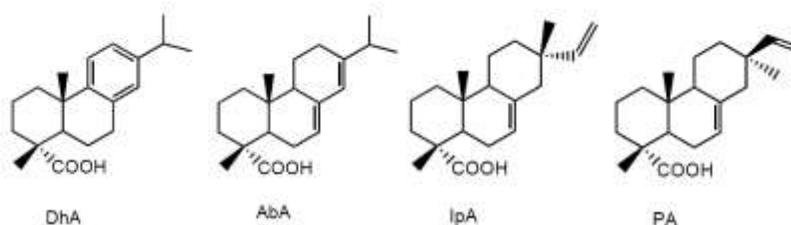
Other chlorinated and non-chlorinated substances that are released from pulp mills include planar aromatic compounds, which can be characterized as alkylated polychlorodibenzofurans, alkyl polychlorobiphenyls, and alkyl polychlorophenanthrenes (Paasivirta 1988; Wiberg *et al.* 1989). Their levels are orders of magnitude higher than those of dioxins and furans in pulp mill effluents, several nanograms per gram in dry weight (Paasivirta 1991). Polychlorinated dibenzothiophenes (PCDTs) are sulfur analogues of polychlorinated dibenzofurans (PCDFs) and have structural resemblance to PCDDs and PCDFs (Sinkkonen 1997; Koivisto 2001). In addition, other compounds may have dioxin-like toxicity, including the non-chlorinated ones, such as indocarbazoles, benzantracenes, and benzoflavones (Paasivirta 1988).

During the last decades, there has been a drastic decrease in the use of molecular chlorine as a bleaching agent, and it has been replaced with chlorine dioxide (Elementary Chlorine Free, ECF), molecular oxygen, peroxide, or ozone (Totally Chlorine Free, TCF), which has led to a drastic decrease in AOX, PCDD, and PCDF (Shimp and Owens 1993; Rantio 1997). There are several modifications made to reduce the generation of chlorinated organic compounds from bleach plant effluents by employing modified strategies. A key strategy involves removing more lignin *i.e.*, by extended delignification, reducing the kappa number of unbleached pulp. Further strategies involve modifying the conventional bleaching process to ECF and TCF bleaching (Kinstrey 1993). This reduction of chlorine content in the effluents has made it possible to improve the closure of the water circuits system of the mill and to recycle the bleach plant effluent back to the mill's chemical recovery system. The reduction of the generation of organic substances in bleaching stages

has been possible thanks to previously increasing delignification efficiency, modifying cooking, additional oxygen stages, spill collection systems, a more efficient washing, and stripping and reusing condensates. The installation of external treatment plants of different designs has been another successful contributing factor to decreasing AOX and unchlorinated toxic organic compounds emissions to receiving water (BREF 2015). In Canada as a result of federal regulations, the quality of pulp and paper effluent released directly to the environment has progressively improved. In 2013, 96.2%, 99.9%, and 99.8% of effluent samples met regulatory requirements for toxicity tests on fish, BOD, and TSS, respectively (Environment and Climate Change Canada, 2016).

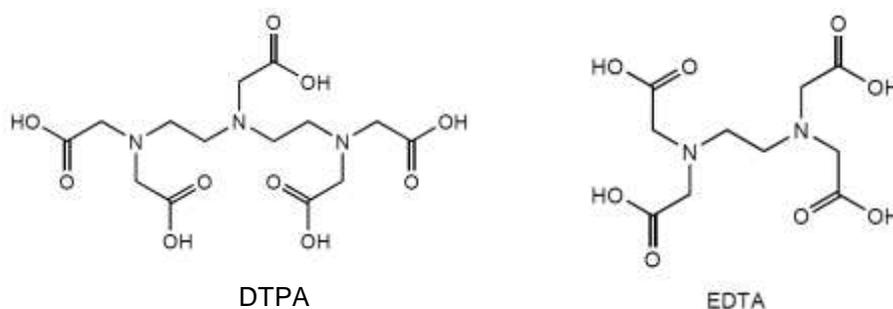
#### *Non-chlorinated recalcitrant compounds*

Wood extractives are hydrophobic components that are soluble in neutral solvents. They are composed of *e.g.* resin acids, fatty acids, sterols, diterpene alcohols, and tannins (Holmbom 1999; Lacorte *et al.* 2003). Resin acids, as shown in Fig. 3, are tricyclic diterpenoids and natural constituents of conifer wood. Fatty acids exist as free fatty acids and neutral esterified fatty acids in triglycerides and steryl esters (Ekman and Holmbom 2000; Björklund Jansson and Nilvebrant 2009). Generally, fatty acids include palmitic, linolenic, linoleic, and oleic acids, while resin acids include abietic, neoabietic, levopimaric, palustic, and dehydroabietic acids (Back and Ekman 2000). Resin acids are released in high amounts during pulping and paper production, especially in mechanical pulp production (Johnsen *et al.* 1993). Resin acids are very resistant to chemical degradation due to their stable tricyclic structure (Dethlefs and Stan 1996). They are thought to be the main contributors to the toxicity of the pulp mill effluents (Makris and Banerjee 2002; Rigol *et al.* 2004) and have been reported to end up in sediments of the receiving water bodies (Dethlefs and Stan 1996; Rämänen *et al.* 2010).



**Fig. 3.** Chemical structures of typical resin acids that may be released from softwood species during pulping (DhA = dehydroabietic acid; AbA = abietic acid; IpA = isopimaric acid; PA = pimaric acid)

In addition to substances originating in the wood, there may be situations in which P&P wastewater contains toxins from other sources. Many of the organic substances produced by the chemical industry are toxic or resistant to biological treatment (Lapertot *et al.* 2006; Muñoz and Guieysee 2006). Chelating agents, such as DTPA and EDTA (Fig. 4), are relatively large organic molecules that are able to bind metals (Tana and Lehtinen 1996). They are increasingly used with peroxide and ozone bleaching of wood pulp and discharged with spent bleach liquors. Chelating agents have been reported to either totally resist degradation or to undergo slow biodegradation (Hinck *et al.* 1997). They have been found *e.g.* in marine sediment, but so far no direct harmful effects in the environment have been reported (Sprague *et al.* 1991; Puustinen and Uotila 1994). However, it has been suggested that chelating agents can prevent the sedimentation of metals close to the point of discharge, leading to the spread of metals over a large area in low concentrations (Tana and Lehtinen 1996).



**Fig. 4.** Molecular structures of two widely-used chelating agents (DTPA = diethylenetriaminepentaacetic acid; EDTA = ethylenediaminetetraacetic acid)

### Toxicity of Recalcitrant Compounds

The discharged pollutants of the pulp and paper mill effluents affect both aquatic and terrestrial organisms (Pokhrel and Viraraghavan 2004). Several studies have reported toxic effects on fish species due to pulp mill effluents, including respiratory stress, liver damage, mutagenic, and genotoxic effects (Owens *et al.* 1994; Johnsen *et al.* 1998; Leppänen and Oikari 1999; Schnell *et al.* 2000b; Rana *et al.* 2004). Sublethal effects and changes in plankton population have been reported (Yen *et al.* 1996; Baruah 1997), but also delayed sexual maturity, changes in reproduction, smaller gonads, and altered productivity of aquatic invertebrates and fish (Munkittrick *et al.* 1997; Karels *et al.* 1999). Additionally, decreased number of juveniles, physiological and skin diseases, and changes in communities, population structure, and in growth rates of fish have been observed (Sepúlveda *et al.* 2002). Furthermore, effluents from pulp bleaching impair the quality of fish and fish flesh in the receiving waters (Herve 1991; Redenbach 1997).

Increase in the amount of toxic substances in water kills zooplankton and fish, affecting the terrestrial ecosystem (Burton *et al.* 1983). Other problems may occur due to failure of the treatment processes employed to treat the pulp and paper mill effluent. This can result in the release of suspended solids and nutrients, such as nitrogen and phosphorus, which can lead to eutrophication of the receiving water bodies and oxygen depletion (Thompson *et al.* 2001). Endocrine disruptors may be also present in the wastewater (Balabanic *et al.* 2012), though relatively little is known about potential endocrine disruption effects of paper mill effluents on aquatic organisms. For example, plant sterols (phytosterols) may act as disruptors of the hormonal and biochemical systems of aquatic organisms (Kostamo and Kukkonen 2003). Pulp mill effluents are known to contain varying amounts of phytosterols, which have the structure similar to that of the steroid hormones of vertebrates (Lehtinen *et al.* 1999). In addition, transformation products of sterols can have androgenic (Stahlschmidt-Allner *et al.* 1997) and hermaphroditic effects on fish near sewage treatment plants (Zachrazewski *et al.* 1995; Lacorte *et al.* 2003).

#### *Chlorinated compounds*

Chlorinated phenolics and chlorinated lignin derivatives are a group of chemicals contributing greatly to the toxicity of pulp and paper mill effluents (Walden and Howard 1981). Multiple adverse health effects have been linked to organochlorine compounds, such as endocrine disruption (growth retardation, thyroid dysfunction, decreased fertility and feminization or masculinization of biota) and impaired liver function in fish exposed to these effluents (Oikari and Nakari 1982; Munkittrick *et al.* 1998; Lacorte *et al.* 2003).

Chlorinated phenols, catechols, and guaiacols are known to cause mutagenesis in mammalian cells (Hattula and Knuutinen 1985). Two examples of such molecules are shown in Fig. 5. Additionally, lignin and its derivatives are toxic to aquatic organisms and animals (Priha and Talka 1986).

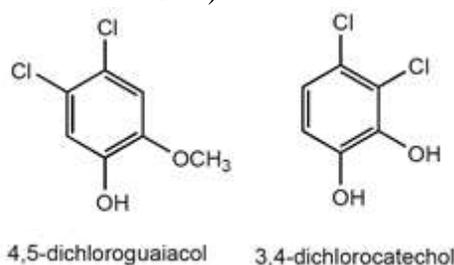


Fig. 5. Molecular structures of two chlorinated phenols

Even though chlorinated phenolics represent less than 2% of the organically bound chlorine in bleaching effluents, they are large contributors to effluent toxicity, carcinogenicity, and mutagenicity (Savant *et al.* 2006; Kukkola *et al.* 2011). The majority of organochlorinated compounds present in pulp and paper mill effluents are HMW chlorolignins (>1 kDa). These compounds are likely to be biologically inactive and have a small contribution to the toxicity, mutagenicity, and BOD of pulp mill effluents (Hileman 1993; Ali and Shreekrishnan 2001). On the other hand, LMW compounds (<1 kDa) are the main contributors to mutagenicity and bioaccumulation because they can penetrate cell membranes (Heimberger *et al.* 1988; Sun *et al.* 1989). They can bioaccumulate in the aquatic food chain in the body fat of animals in higher trophic levels (Renberg *et al.* 1980; Ali and Shreekrishnan 2001). However, there are indications that also derivatives of HMW lignin exhibit toxicity (Pessala *et al.* 2010).

Acute toxicity of chlorinated phenolics increases with the degree of chlorination, the more distant position of chlorine atom relative to the phenolic hydroxyl group, and with chlorophenol lipophilicity (Loehr and Krishnamoorthy 1988; Sierra-Alvarez *et al.* 1994). Chlorinated phenolics with the chlorine at position 2 are less toxic than the other chlorophenols, while toxicity increases as a chlorine atom is substituted at 3, 4, and 5 positions (Saito *et al.* 1991; Czaplicka 2004). The bioaccumulation potential increases with the number of chlorine substituents on the phenolic ring. Phenol and most of the chlorophenolic compounds can induce mutations in certain bacteria and yeasts (Smith and Novak 1987). Chlorophenols are less readily biodegradable than phenol, and their rate of biodegradation decreases with increasing number of chlorine substituents on the aromatic ring (Banerjee *et al.* 1984). It has been suggested that position of the substituent has an effect on the degradability; the order for chlorophenols was found to be ortho > meta > para during anaerobic conditions in aquifer sediments and in digested sludge (Boyd and Shelton 1984; Genthner *et al.* 1989; Annachhatre and Gheewala 1996).

Dioxins are found to bioaccumulate in fish downstream of pulp and paper mills, while chlorophenolic compounds, coplanar polychlorinated biphenyls (PCBs) isomers, polychlorinated naphthalenes (PCNs), polychloroanthracenes, tetrachloroazo- and azoxybenzenes, and PCDEs are acutely toxic but not very prone to bioaccumulation (Paasivirta 1988; Howie *et al.* 1990; Frakes *et al.* 1993). However, chlorinated hydrocarbons (*e.g.* hexachlorocyclohexanes, residues of DDT (dichlorodiphenyl-trichloroethane), chlordanes, PCNs, and PCBs) have shown high bioaccumulation rates

and biomagnification at higher trophic levels (Paasivirta 1988; Herve *et al.* 1988; Paasivirta and Rantio 1991; Koistinen 1992).

### *Extractives*

Wood extractives, *e.g.* resin and fatty acids, sterols, and diterpene alcohols account for a large part of toxicity in various paper mill effluent streams (Lacorte *et al.* 2003). In particular, the toxicity of resin acids has been studied extensively for decades (*e.g.* Oikari *et al.* 1984; Meriläinen *et al.* 2007). The most commonly monitored resin acids in aqueous pulping effluents include abietic acid, dehydroabietic acid, neoabietic acid, pimaric acid, isopimaric acid, sandaracopimaric acid, levopimaric acid, and palustric acid, among which isopimaric acid is the most toxic (Wilson *et al.* 1996). Additionally, retene (7-isopropyl-1-methylphenanthrene) is a naturally formed polycyclic aromatic hydrocarbon causing teratogenicity in fish larvae. Retene is formed in surface sediments contaminated by resin acids from pulp mill effluents (Oikari *et al.* 2002).

The toxicity of tannins to several enzymes has been well established (Korczak *et al.* 1991; Sierra-Alvarez *et al.* 1994). Methanogenic toxicity of tannins depends on the degree of polymerization (Field *et al.* 1988). HMW tannin polymers and humic acids exhibit low toxicity because their size limits their ability to penetrate into the bacterial cells. The highest toxicity is found in oligomeric tannins due to their ability to form strong hydrogen bonds with proteins (Field *et al.* 1989; Sierra-Alvarez *et al.* 1994). Condensed tannins from spruce bark are toxic, not only to methanogens at concentrations present in the paper mill wastewaters, but also to aquatic organisms, such as fish (Field *et al.* 1988; Temmink *et al.* 1989). In addition, unsaturated fatty acids (16-C and 18-C) of softwood, such as oleic acids, linoleic acid, and linolenic acid are also a source of toxicity to fish, especially salmonoids (Voss and Rapsomatotis 1985). Long chain fatty acids (LCFA) have been shown to inhibit methanogenic bacteria (Koster and Cramer 1987). This makes the anaerobic treatment of wastewaters relatively troublesome since methanogenic bacteria play a crucial role in the anaerobic wastewater treatment.

### **Biological Processes – Susceptibility to Enzymatic Breakdown**

Microorganisms with lignolytic properties can degrade contaminants in pulp and paper mill effluents containing toxic and recalcitrant compounds (Thakur 2004). Lignolytic microorganisms include fungi, actinomycetes, yeast, bacteria, and algae, all of which can produce enzymes responsible for lignocellulose degradation (Bajpai and Bajpai 1994; Annachatre and Gheewala 1996). Enzymatic treatment can be applied as a single step or with other physical and chemical methods, as extensively reviewed by Chen *et al.* (2010), Saritha *et al.* (2012), and Barakat *et al.* (2014).

Fungal enzymes, collectively termed as ligninases or lignin-modifying enzymes (LMEs), can degrade lignin into simple sugars and starch (Bocchini *et al.* 2005; Dashtban *et al.* 2010; Chopra and Singh 2012). Ligninases can be classified as phenol oxidases (laccase) or heme peroxidases (Martínez *et al.* 2005). The latter is further subdivided as lignin peroxidases, manganese peroxidases, and versatile peroxidases (Singh and Shrivastava 2014). Depending on the species of fungi, one or more of the lignin-modifying enzymes can be secreted. For example, white-rot fungi (*e.g.* *P. chrysosporium*) are able to degrade lignin efficiently using a combination of extracellular ligninolytic enzymes, organic acids, mediators, and accessory enzymes (Singh and Shrivastava 2014). Even though lignin peroxidase is able to oxidize the non-phenolic part of lignin (which forms 80 to 90% of the lignin composition), it is absent from many lignin-degrading fungi (Wang *et*

*al.* 2008a). Enzymes able to perform dechlorination are generally termed as dehalogenases (Savant *et al.* 2006). These enzymes are able to degrade a variety of environmentally persistent pollutants, such as chlorinated aromatic compounds, heterocyclic aromatic hydrocarbon, and various dyes (Singh and Shrivastava 2014).

A broad range of fungi degrade lignin to varying degree (Pokhrel and Viraraghavan 2004). They include soil fungi (*Fusarium* sp.), soft rot fungi (*Populaspora*, *Chaetomium* sp.), pseudo soft rot fungi (*Hyoxylon*, *Xylaria*), lignin degrading fungi (*Callybia*, *Mycena*), white rot fungi (*Trametes*, *Phanerochaete*), and brown rot fungi (*Gleophyllum*, *Poria*). They can also degrade modified lignin and their derivatives found in effluent but also COD, AOX, and color from pulp mill effluents (Pokhrel and Viraraghavan 2004). White-rot fungi, particularly *P. chrysosporium* and *C. versicolor*, can degrade refractory material efficiently and reduce color, lignin, and COD (Bajpai and Bajpai 1994). However, only a few strains of fungi can reduce chlorinated aromatic compounds (Bajpai and Bajpai 1997; Singh 2007). White-rot basidiomycetes, such as *Coriolus versicolor* (Wang *et al.* 2008a), *P. chrysosporium*, and *T. versicolor* (Moreno *et al.* 2003) have been found to be the most efficient lignin-degrading microorganisms.

In nature, lignin is degraded during wood decay mainly by basidiomycetes white-rot fungi, of which many attack lignin, hemicellulose, and cellulose simultaneously, *e.g.* *Trametes versicolor* (Tanaka *et al.* 1999) or *Heterobasidium annosum* (Daniel *et al.* 1998), whereas some other white-rot fungi preferentially work on lignin in a selective manner, *e.g.* *Physisporinus rivulosus* (Hilden *et al.* 2007) and *Dichomitus squalens* (Fackler *et al.* 2006).

Enzymatic treatment is a safe and ecofriendly process (Kim *et al.* 2002), but a long residence time is required (up to 10-14 days), and high costs of enzymes limit its commercial applications (Pu *et al.* 2015). Furthermore, selectivity of enzymes can be low and also carbohydrates are partially consumed by microorganisms. So far, enzymatic treatment of pulp and paper mill effluent generally has not been successful due to a lack of suitable organisms, various recalcitrant compounds, and poor process optimization for industrial-scale treatment.

#### *Recalcitrant compounds and their treatment*

Approximately half of the organic matter in typical pulp and paper mill effluent is recalcitrant to biodegradation by both anaerobic and aerobic bacteria (Ortega-Clemente *et al.* 2009). For example, wood resin, tannins, and chlorinated phenolics are toxic to methanogenic bacteria (Rintala and Puhakka 1994; Vidal *et al.* 2001). However, certain bacterial strains are quite effective in breaking down recalcitrant organic phenolic compounds and their derivatives and can also reduce the color of pulp mill effluent to some extent (Bajpai and Bajpai 1997). Anaerobic bacteria able to degrade chlorinated organics are classified as alkyl dehalogenators and aryl dehalogenators (Mohn and Tiedje 1992). The alkyl dehalogenators include physiologically diverse groups of strict anaerobes and facultative anaerobes, such as methanogens, species of *Clostridium*, *Acetobacterium woodii*, and *Shewanella* (Savant *et al.* 2006). These organisms mainly dechlorinate LMW compounds, such as chloroform, tetrachloroethene, dichloromethane, trichloroethane, and trichloroethene. Aryl dehalogenators mainly belong to proteobacteria and genera, such as *Desulfitobacterium* and *Desulfobacter*.

Anaerobic bacteria are believed to use chlorinated organic compounds as a source of carbon and energy, as a cometabolite, or as an electron acceptor depending on the strain of bacteria (Holliger *et al.* 1998). Thus they are better suited to reductively dehalogenate

highly chlorinated phenolics, while aerobic biological systems are suitable for less halogenated phenolics (Neilson 1990; Latorre *et al.* 2007). A sequence of anaerobic treatment followed by aerobic treatment permits the degradation of compounds that are non-degradable anaerobically (Rintala and Puhakka 1994).

Mixed microbial communities can overcome the problems faced by monocultures in the environment, such as nutritional limitations and toxic substrates (Thakur 1995; Kim *et al.* 2002). For example, a mixture of various bacteria can degrade phenolic compounds due to their varying structures and toxicity. In addition, two or more microorganisms can be applied sequentially, one carrying out the initial catabolic reactions and another completing the rest of the metabolic pathway to mineralize the organic compounds. Bicyclic aromatics such as chlorinated biphenyls, chlorinated dibenzofurans, and naphthalene sulfonates have been treated sequentially, resulting a reduction in color, lignin, COD, and phenol (Pokhrel and Viraraghavan 2004; Singh and Thakur 2006).

#### *Susceptibility to oxidation*

In the natural environment, many organic refractory compounds can be degraded, either biologically or by photochemical reactions, and further transformed by evaporation or adsorption (Czaplicka 2004). Photochemical processes include photodissociation, photosubstitution, photooxidation, and photoreduction. In the aquatic environment, photodegradation occurs only in the surface layer and is faster in summer than in winter, especially in the northern latitudes (Kawaguchi 1992a). The properties of chlorophenols are favorable to sorption and accumulation, especially into bottom sediment and suspended matter (Brusseu and Rao 1991; Peuravuori *et al.* 2002; Czaplicka 2004). Chlorophenols can undergo reactions of auto-oxidation and catalysis, especially on surfaces made of clay and silica. They can evaporate, with the rate depending on vapour pressure and water solubility, but under typical environmental conditions evaporation plays an insignificant role (Piwoni *et al.* 1989; Czaplicka 2004).

## OVERVIEW OF WASTEWATER TREATMENT OPTIONS

Before reviewing advances in wastewater treatment technologies related to the P&P industry, an overview is presented of conventional approaches. These approaches address not only the treatment of such effluent, but also reducing its amount by implementing strategic changes to the operations within P&P mills. Wastewater treatment systems have commonly been understood to function as “end-of-pipe” solutions to environmental issues, whereas the least expensive way to treat polluted water may be to produce less of it in the first place (Stratton *et al.* 2004; Hossain and Ismail 2015). Unit operations within P&P mill water treatment systems have been reported before and can be mentioned here (European Commission 2001; Demel *et al.* 2003). Blanco *et al.* (2016) have recently reviewed the state of the art on water reuse.

### **Pulp Mill Operations and Wastewater**

A process known as counter-current washing has been widely used within the P&P industry to effectively separate used cooking liquors from the cellulose fibers while minimizing the volume of rinse water (Hammar and Rydholm 1972; Ala-Kaila *et al.* 2005). Such systems are set up with a series of washing operations, such that the cleanest water is

used to wash the cleanest pulp. The rinse water is directed backwards through the series of washers until the most contaminated rinse water enters the chemical recovery system.

In modern pulp and paper making facilities it is still common to employ screen cylinders (*i.e.* “deckers”) which rotate slowly while partially submerged in a vat filled with pulp suspension (Fig. 6). A mat of pulp collects on the outer surface of the cylinder, as filtrate is removed by gravity from the space within the cylinder. Wash water is applied above the wet mat of fibers to displace the contaminated water with cleaner water. Lindau *et al.* (2007) demonstrated that higher efficiency can be achieved in such systems by improving the uniformity of the pulp pad. The counter-current principle can easily be applied to such systems by employing the filtrate from the final stage of washing as the rinse water for the next preceding stage, and so-on for the whole series of deckers. Such systems have been considered theoretically (Potucek 2003, 2005). Counter-current washing is also used in recovered paper mills. In such mills, water is used for cleaning operations and separated from the pulp through disk filters and pressed in such a way as to segregate filtrate streams having different levels of contamination. The separated waters then can be recirculated in different process loops, such as showers. The most contaminated water is circulated back to the pulper.

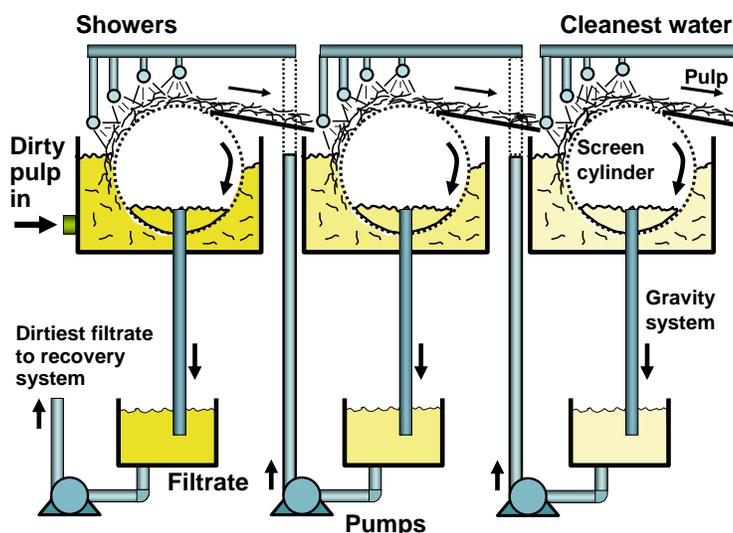


Fig. 6. Schematic of a series of three decker-type pulp washers, with counter-current washing

Continuous washing equipment has been installed in many modern pulp mills, especially those that employ continuous kraft digesting equipment, as a means to achieve more favorable washing efficiency and to minimize the amount of concentrated liquor that needs to be evaporated during the chemical recovery process (Richter 1966; Edwards and Rydin 1976; Lee 1979, 1984; Gullichsen 1999). In addition to incorporating the principle of counter-current washing, some additional gains in displacement efficiency have been achieved in such installations by avoiding the dense compaction of pulp within the pulp washing tower. Because the rinse water flows quite slowly from where it is injected towards a cylindrical screen in the tower, there is sufficient time for contaminants to diffuse from the fibers and become almost equilibrated with the rinse water at each point. Thus, higher overall efficiency can be achieved in comparison to systems that rapidly displace the contaminated water from a wet mat of pulp (Richter 1966; Potucek 2005; Lindau *et al.*

2007). By operating under pressure, some such designs make it possible to utilize very hot rinse water, while at the same time avoiding the generation of foam bubbles (Gullichsen 1999).

#### *Oxygen delignification*

Oxygen bleaching (often called extended delignification) does not involve corrosive chloride ions. Therefore, the wash water can be combined with the brown-stock wash liquor and directed back towards the chemical recovery system. This process reduces the emission of organic substances to the wastewater and the amount of chemicals to be added, which makes such an operation suitable for systems with high levels of water reuse (BREF 2015). In addition, research suggests that effluent from oxygen bleaching stages is highly biodegradable (Vidal *et al.* 1997). Furthermore, this stage will reduce the load of bleaching plant pollutants entering the biological wastewater treatment system. Hence, such a process can reduce the loading of organic material that otherwise would be released from the pulp during bleaching of a kraft pulp (Hammar and Rydholm 1972; Stratton *et al.* 2004). Oxygen delignification tends to be less selective than some other options, such as using chlorine dioxide. As a consequence, extensive oxygen delignification tends to break down the cellulose macromolecules, lowering the average molecular mass, and eventually weakening the material. Therefore, magnesium salts (typically  $\text{MgSO}_4$ ) are usually added, with the aim of preserving the strength of pulp.

#### **Paper Mill Operations and Wastewater**

Paper machine systems use large volumes of water. Nevertheless, there are many opportunities either to limit the amounts of substances dissolved in the water or to reuse the process water multiple times in the mill.

#### *Separation of loops*

A good strategy for sustainable water use is the separation of process water in several loops (1 to 4) to keep the water around the paper machine as clean as possible. Stock from a more contaminated process loop is transferred to the following one at high consistency to minimize the transfer of contaminant. Kappen and Wildered (2002) have developed a method to determine the efficiency of this approach based on the COD content at different stages of the process.

#### *Increased retention of fines and polymeric materials*

The basic strategy for efficiently retaining polymeric and fine particulate matter in the fiber web during the manufacturing of paper can be summarized in the two words *coagulation* and *flocculation* (Bratby 2006; Hubbe and Rojas 2008; Nawaz *et al.* 2014). It is well known that the negative charge associated with cellulosic materials, especially the hemicellulose and extractives components, tends to favor a well-dispersed system. The colloidal matter from the natural plant materials tends to coat the free surfaces with a layer of negative charges (Jaycock and Pearson 1976). So one of the first steps towards getting the finely divided and polymeric materials to be retained in the wet web of paper often involves a partial or almost complete neutralization of the net surface charges in the system (Strazdins 1989; Hubbe and Rojas 2008). This can be done by adding such agents as aluminum sulfate, polyaluminum chloride, or highly charged cationic polymers. With the advent and greater usage of streaming current devices in paper mills, it is possible to carry out the (partial) neutralization with greater repeatability, leading to more predictable

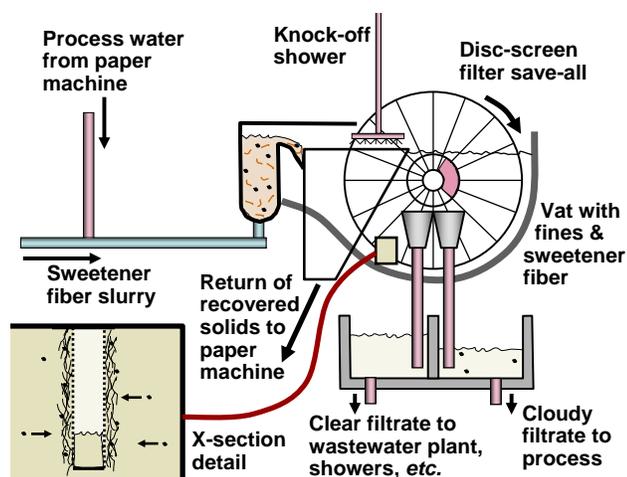
outcomes in terms of fine-particle retention, dewatering rates, and paper properties. Such equipment also can be applied in wastewater treatment (Dentel and Kingery 1989; Dentel 1995).

The reason that partial neutralization of net surface charges is often preferred, rather than aiming for a fully neutralized system (*i.e.* zero zeta potential) is to allow for the efficient action of another charged additive, the flocculant, which is called a “retention aid” by papermakers. By leaving a small proportion of the original negative charge at the surfaces of the fibers, a cationic acrylamide copolymer of very high molecular mass is able to find suitable points of adsorption in order to be effective (Hubbe *et al.* 2012b). Retention aids have been shown to function by a bridging mechanism, such that the polyelectrolyte is able to join the solids together efficiently, especially in the presence of agitation (Gregory 1973; Hubbe *et al.* 2009). The mechanisms of coagulation and flocculation are worth emphasizing here, since essentially the same steps are also often involved in the primary or secondary clarification of P&P effluents. On the paper machine an effective combined usage of coagulation and flocculation will tend to gather most of the polymeric and finely divided matter onto the fiber surfaces, such that relatively little solid material leaves the system with the excess water from the process. Also, it has been shown that any retention aid polymer that enters the wastewater treatment system is likely to end up in the sludge rather than remaining dissolved in the treated water (Pelzer 2008).

#### *Save-all systems*

The volumetric flow rate of effluent can have a major effect on the retention time of a wastewater treatment system; therefore it is very important to review the systems that papermakers employ to reduce the volume of wastewater. In the early days of mechanized papermaking using a continuous mesh screen, any excess water was sent directly to the sewer (Hunter 1947; Hills 1988). Fine particles that had not been retained in the wet web of paper ended up in the outfall from the mill. To improve process yield and to maintain better community relationships, unit operations called save-alls were developed and implemented (Stevens 1975; Perrault 1993). As noted by Milliken (2006), a well-operating save-all system can save both energy and water costs.

Two types of save-all systems are common. The most prominent system, especially in recent installations, is based on screening. Disk screen systems generally work by collecting fine matter on a mat of “sweetener fibers” that initially collect on the screen surfaces, while the clarified process water flows through (Stevens 1975; Perrault 1993; Milliken 2006). As shown in Fig. 7 (redrawn based on the design described by Milliken 2006), such equipment employs pairs of filter disks arranged in a sandwich form, such that the solids collect on the outside of the pair, and filtrate is collected from the interior space. By careful design and operation of such a system, operators are able to collect filtered process water having two levels of clarity. Only the clearest water, having the lowest content of solid particles, is discharged to the wastewater treatment plant. Such filtered water also may be further cleaned and then used in such applications as showers within the papermaking process. Karvonen *et al.* (1999) showed that the performance of a save-all system can be enhanced by the use of retention aid treatment of the incoming process water and sweetener fiber. Recent developments in save-all design and operation have been reported (Shukla 2012). The other common type of save-all device is the flotation save-all (Rebarber 1998; Teerikangas 2001; Nasser 2003).



**Fig. 7.** Schematic drawing of a disk filter save-all system (redrawn based on illustrations by Milliken 2006)

### *Water circuit closure*

Process water reuse is limited by the accumulation of dissolved matter that may affect the process and the final product quality. The optimum closure mainly depends on the nature of the final product. Various paper mills and operators of pilot paper machine systems have either evaluated or implemented the complete elimination of wastewater (Alexander and Dobbins 1977; Heller *et al.* 1979; Pietschker 1996). Wastewater-free operation is common in systems in which recycled paperboard products are produced, while generally it is not feasible in pulping operations and white grades. Alternatively, wastewater treatment schemes closely related to those that will be featured in later sections of this review article can, in principle, be implemented within the paper mill's water cycle (Tenno and Paulapuro 1999; Verenich *et al.* 2000; Webb 2002; Nuortila-Jokinen 2004; Hubbe 2007c; Mauchauffee *et al.* 2012; Singh *et al.* 2012; Saif *et al.* 2013). Another approach, which ends up as having the same net effect, has been to employ the final effluent from wastewater treatment as the intake for the papermaking system (Ordóñez *et al.* 2010). A water reduction monograph was prepared detailing many in-mill strategies to minimize the demand for fresh water for many areas of the papermaking process (PAPRICAN 2001).

## **Basic Wastewater Treatment Operations**

All wastewater treatment systems need to accomplish three objectives: They need to remove suspended particles from the wastewater, they need to remove solubilized pollutants, and they need to eliminate acute toxicity. Conventionally this is done in two steps, starting with gravity separation, *i.e.* primary treatment, with the use of a clarifier or a set of clarifiers. Flotation may be used in place of gravity separation in some cases. The second step is biological wastewater treatment, *i.e.* "secondary treatment". The general principles and operations of conventional and state of the art wastewater treatment technologies, with emphasis on P&P mill applications, have been reviewed (Gehm 1973; Scott and Ollis 1995; Kamali and Khodaparast 2015).

### *Primary treatment: Clarification by settling*

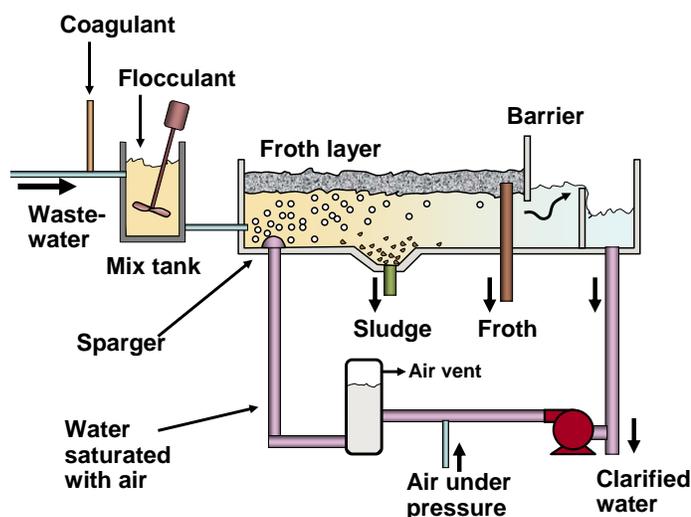
Gravity-based separation systems are dependent not only on a difference in density between the contaminant and the liquid medium, but they also require that the solid particles be large enough to settle at a fast enough rate. The latter objective is typically

achieved by agglomerating the particles together, noting that larger particles of the same general type generally settle more rapidly (Leitz 1993; Matko *et al.* 1996; Fernandes *et al.* 2014).

Although settling can be achieved in a simple unagitated “pond” or “stabilization basin” (Gehm 1973), it is generally preferred to employ a circular-shaped clarification basin, equipped with a slowly-rotating skimmer and raking device (Lugowski 1991; Grijspeerdt *et al.* 1996; Albertson and Wilson 1997). The skimmer picks up foam and any lighter-than-water material that has floated to the surface. The raking device, operating at the floor of the basin, pushes settled sludge into a collection system. Hynninen (1998) describes common designs of clarifier equipment, some of which employ baffles to regulate the direction of flow or create laminar conditions as wastewater moves through the unit. As might be expected, primary sludge from papermaking facilities tends to have a high content of fine cellulosic matter and minerals such as calcium carbonate or clays (Mahmood and Elliott 2006).

#### *Dissolved air flotation units*

In addition to settling, flotation can be found as an alternative for some P&P facilities to clarify mill effluent. This method is commonly referred to as a dissolved air flotation (DAF) system. As illustrated in Fig. 8, such devices inject a pressurized stream of air-saturated water at the base of a shallow chest containing the process water from the paper mill. Upon reduction of pressure, as the injected water is released into the chest, tiny bubbles of air come out of solution and begin to rise. The rising bubbles tend to carry along any solid particles to which they adhere. The solids then are able to be skimmed from the surface of the water.



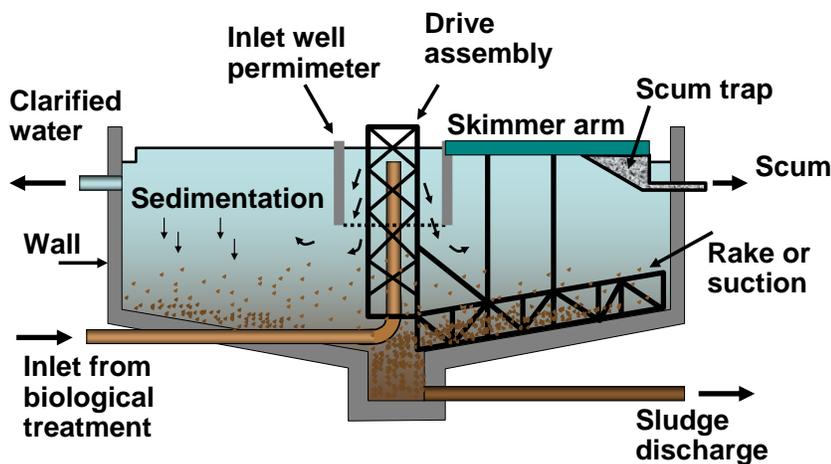
**Fig. 8.** Schematic diagram of a dissolved air flotation clarifier unit in operation

DAF units have been found to be cost effective for treatment of large water flows transporting a wide range of solids content (300 to 5000 mg·L<sup>-1</sup>) (Ackermann *et al.* 2000). In fact, it is possible to implement up to five DAF units (first loop, second loop, paper machine loop, sludge treatment, and effluent treatment) in recycled paper mills; which may efficiently remove 80 to 98% of the suspended solids, as well as a wide variety of contaminants such as ink particles and lipophilic extractives. Furthermore, it is possible to

remove finely dispersed and colloidal organic particles ( $>0.2 \mu\text{m}$ ) using appropriate coagulant and flocculant aids. On the other hand, there is a limit of about 20%, based on the COD, for the reduction of organics by use of traditional coagulants (Miranda *et al.* 2009b), but greater reductions can be achieved with hybrid coagulants (Miranda *et al.* 2015). Finally, sludge from DAF units may be jointly treated in some mills with the sludge coming out from the biological wastewater treatment plant.

#### Secondary treatment: Activated Sludge

The most common system to remove organic material from wastewater, with 100 years of tradition, involves aeration and the recirculation of a portion of the sludge back to the intake of the system, *i.e.* an activated sludge system (Liver *et al.* 1993; Pere *et al.* 1993; Scott and Ollis 1995; Nakamura *et al.* 1997; Novak *et al.* 1998; Sarlin *et al.* 1999; Thompson *et al.* 2001; Diez *et al.* 2002; Kostamo and Kukkonen 2003; Mahmood and Elliott 2006; Agridiotis *et al.* 2007; Chakrabari *et al.* 2008; Elliott and Mahmood 2012; Kaluža *et al.* 2014). Figure 9 provides a schematic illustration of a clarifier unit that would follow such treatment.



**Fig. 9.** Schematic illustration of a clarifier, as usually employed after a typical aerated biological system

When further efficiency is needed or there is not sufficient space for a gravity-based clarifier, a membrane bioreactor (MBR) or other type of bioreactor with a mixed or moving bed can be used. MBRs are able to operate in a submerged design, thus requiring low transmembrane pressure (TMP) working values, which minimize fouling effects. Moreover, as microfiltration (MF) or ultrafiltration (UF) membranes are installed to separate sludge, MBR technology will not experience problems associated with filamentous bulking. Furthermore, incorporating membrane treatment into biological processing can allow the reactors to run with a higher dried solid concentration (8 to 15  $\text{g}\cdot\text{L}^{-1}$ ) than conventional activated sludge (3-5  $\text{g}\cdot\text{L}^{-1}$ ), therefore producing less biological sludge and improving the degradation of organics. These properties can make it possible to reduce hydraulic retention times and/or volumes needed to carry out effective biological treatment (Judd 2006).

### *Sludge thickening*

Secondary sludge, generated during biological treatment operations, is primarily composed of biological cells and their decomposition products. As a consequence, such sludge is notoriously difficult to extract water from. Each biological cell can be regarded as being like a little water balloon. To compensate for the poor dewaterability, it is common practice to blend the secondary sludge with primary sludge, which is composed of fibrous materials, achieving a mixture that is more amenable to dewatering (Elliott and Mahmood 2005). A variety of methods have been employed to raise the solids content of secondary sludge, rendering it more suitable for transportation and beneficial use or landfilling (Gehm 1973; McKeown 1979; Mahmood and Elliott 2006). These include the effect of the raking or scraping of sludge at the floor of a clarifier, various pressing devices, and centrifugation. One of the most popular and effective devices for decreasing the water content of sludge is the belt press (Nichols *et al.* 2003). Screw presses also can be found at many P&P facilities and generally provide a dryer final sludge cake (Dorica *et al.* 1999).

### *Polishing treatments*

To reach the discharge requirements, a wide variety of treatment options have been listed as possible polishing or “tertiary” treatments (Gehm 1973; Chen and Horan 1998; Rajvaidya and Markandey 1998; Kamali and Khodaparast 2015). In particular, the colored, hard-to-biodegrade compounds resulting from delignification and bleaching processes in P&P mills often survive the first two stages of wastewater treatment. As tertiary treatments for such water, authors have described approaches such as coagulation, adsorption onto activated carbon (Chen and Horan 1998; Rajvaidya and Markandey 1998), advanced oxidation systems (Helbe 1999; Lucas *et al.* 2012), membrane technologies (Quezada *et al.* 2014), and electrocoagulation (Zodi *et al.* 2011). Such options will be discussed in more detail in later sections of this article.

## ADVANCES IN PRIMARY CLARIFICATION

Although much of the following section deals with primary treatment, several of the key principles, such as the fundamentals of settling, also can be applied to enhance the secondary clarification of biological treated effluent in secondary clarifiers.

### **Stokes Settling**

Rates of sedimentation in a gravity field can be estimated based on the simplifying assumption that the suspended particles or agglomerates of particles can be modeled as perfect spheres, making it possible to employ the Stokes equation (Lamb 1994),

$$V = \frac{2(\rho_p - \rho_f)}{9\mu} g R^2 \quad (1)$$

where  $V$  is the terminal velocity of settling,  $\rho_p$  is the density of the particulate matter (which needs to account for any fluid within agglomerated solids),  $\rho_f$  is the density of the fluid,  $\mu$  is the dynamic viscosity of the fluid,  $g$  is the gravitational acceleration, and  $R$  is the particle radius (modeled as a sphere). As shown by Eq. 1, if one models suspended matter as a variety of spheres or spherical clusters, then the rate of settling can be expected to depend on two factors – the average equivalent diameter and the effective density. One of the challenges in clarification of wastewater is the fact that the agglomerated matter is likely

to have a lower effective density than that of the component particles that make up a cluster of particles. That is because the agglomerate is likely to function as an assembly of the solid matter plus pockets of water. This implies that an ideal coagulating agent or process ought not only to increase the effective size of the units of suspended matter, but it also ought to produce relatively dense clusters.

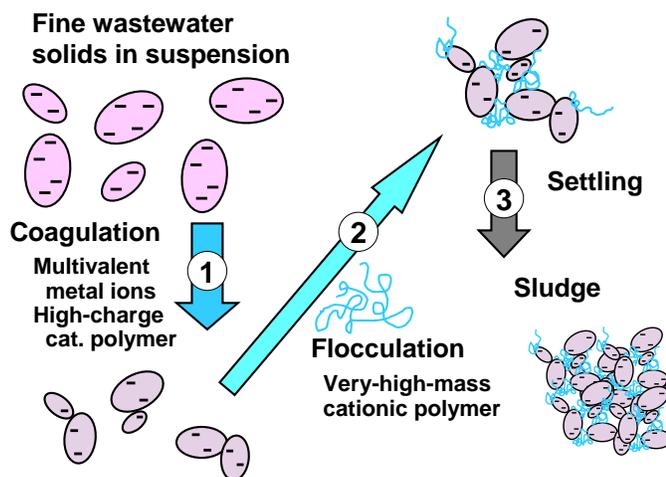
### Colloidal Mechanisms

The use of gravity settling systems or DAF units as a first step in the treatment of water is highly dependent on whether or not the suspended particles in the mixture have a tendency to stick together during random collisions. The ability of particles to remain suspended without forming agglomerates is called colloidal stability. Factors affecting colloidal stability have been discussed in several articles dealing with the treatment of wastewater from P&P facilities (Leitz 1993; Novak *et al.* 1998; Wang and Pan 1999; Huang and Pan 2002; Opedal *et al.* 2011; Nawaz *et al.* 2014). Mikkelsen *et al.* (1996) showed that the colloidal stability of activated sludge solids had large effects on the floc size of sludge particles.

#### Colloidal destabilization

One of the key factors affecting the colloidal stability in wastewater is the surface charge of particles. Most biological materials bear a negative electrical charge, which can be attributed to the dissociation of carboxylic acid groups (Herrington and Petzold 1992; Stenius and Laine 1994; Laine 1997). Repulsive forces develop as these like-charged surfaces approach each other at distances less than a few nanometers (Hiemenz and Rajagopalan 1997). The most common strategy for destabilization of colloidal suspensions involves the addition of ionic materials having an opposite charge and high valence. The dosage of such additives is important; an overdose of a strongly positively charged additive may reverse the charge of the suspended solids, leading to a restabilized system (Agridiotis *et al.* 2007).

As illustrated in Fig. 10, chemical-based clarification may be regarded as a three-step process.



**Fig. 10.** Schematic representation of three key steps (coagulation, flocculation, and settling or flotation) in a chemical program to enhance separation of finely-suspended solids in either primary clarification or in clarification following a biological wastewater treatment stage

In the first step, as recommended by the downward arrow, the system is treated with a coagulant, such as aluminum sulfate (papermaker's alum) or a high-charge cationic polymer (e.g. poly-dimethylamine-epichlorohydrin). As suggested in the figure, such treatment decreases the negative character of the surfaces of the suspended particles, allowing them to come together and stick, due mainly to the London dispersion component of van der Waals forces (Hiemenz and Rajagopalan 1997).

### Inorganic Coagulants

Positively charged multivalent ions are widely used to neutralize negatively charged particles of cellulosic matter. According to an empirically-based relationship known as the Schulze-Hardy rule (Schulze 1882; Hardy 1900), the ability of an oppositely charged ion to bring about coagulation is related to the inverse sixth power of its valence. In other words, the concentrations of different cations to bring about coagulation are according to the following relationship (Eq. 2),

$$C_{\text{Na}^+} = 2^6 * C_{\text{Ca}^{2+}} = 3^6 * C_{\text{Al}^{3+}} \quad (2)$$

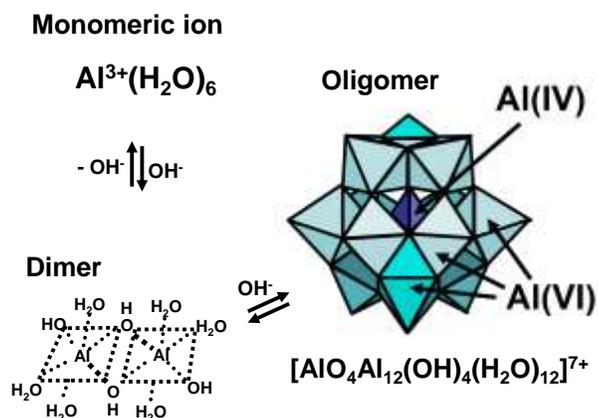
where the  $C$  terms represent the relative concentration of the different ions to bring about the same degree of coagulation of a given suspension. The ratio of concentrations represented by the series shown in Eq. 2 is 1 : 1/64 : 1/729. It follows that more highly charged cations can be hugely more effective in coagulation than lower-charged ions such as  $\text{Na}^+$  and  $\text{Ca}^{2+}$ .

#### Aluminum sulfate

Aluminum sulfate, which is often called "alum," is a widely used coagulant for wastewater treatment. The use of alum for coagulation and settling of suspended solids in the wastewater from P&P facilities has been frequently reported (Rudolfs and Amberg 1953; Carter and Sigler 1981; Stephenson and Duff 1996; Ganjidoust *et al.* 1997; Chen and Horan 1998; Rohella *et al.* 2001; Mahesh *et al.* 2006; Agridiotis *et al.* 2007; Ahmad *et al.* 2007, 2008; Žarković *et al.* 2011; Simonič and Vnučec 2012; Nawaz *et al.* 2014).

Although the hydrated  $\text{Al}^{3+}$  ion almost certainly is prominent in highly acidic solutions of aluminum sulfate, research has shown that alum's remarkable ability to coagulate suspensions of negatively charged particles can be attributed to oligomeric species comprised of several aluminums in combination with  $\text{OH}^-$  ligands (Akitt *et al.* 1972a,b; Arnson and Stratton 1983; Bottero and Fiessinger 1989; Exall and vanLoon 2003; Bi *et al.* 2004; Zhao *et al.* 2008). The ratio between the amounts of Al and  $\text{OH}^-$  in the system has been found to be critical in the performance of the coagulant species (Strazdins 1986, 1989; Öhman *et al.* 1997). An especially stable and well-studied aluminum oligomer has the formula  $\text{Al}^{\text{VI}}_{12}(\text{H}_2\text{O})_{24}\text{Al}^{\text{IV}}\text{O}_4(\text{H}_2\text{O})_{12}^{7+}$  (Akitt *et al.* 1972a; Bottero and Fiessinger 1989).

Figure 11 represents the partial hydroxylation process by which trivalent aluminum ions, present in highly acidic aqueous solution, can be transformed to this advantageous species under suitable conditions of hydroxylation. This ion has been shown to be remarkably effective for the destabilization of colloidal suspensions, including wastewater (Exall and vanLoon 2003; Zhao *et al.* 2008).



**Fig. 11.** Representation of the monomeric ionic species of aluminum, in contrast with the highly symmetric, high-valence oligomeric species that appears to play a key role in effective coagulation processes

### *Polyaluminum chloride (PAC)*

The coagulating agent poly-aluminum chloride (PAC), which contains partially hydroxylated aluminum, can be regarded as a ready-to-deliver recipe containing some of the most effective ionic species for coagulation (Jiang and Graham 1997; Lartiges *et al.* 1997). Usage of PAC and related products for the treatment of P&P wastewater has been reported (Stephenson and Duff 1996; Wang and Pan 1999; Nandy *et al.* 2002; Agridiotis *et al.* 2007; Ahmad *et al.* 2008; Renault 2009; Wang *et al.* 2011; Bennani *et al.* 2012; Dhakhwa *et al.* 2012; Simonič and Vnučec 2012). Alternative products such as polyaluminum nitrate sulfate (PANS) are also being used (Latour *et al.* 2013; Miranda *et al.* 2015). An advantage of PANS is that it minimizes the input of chloride, which can be corrosive to equipment.

### *Iron products*

Iron salts such as ferric chloride and ferrous sulfate are often used as coagulants for wastewater treatment (Nandy *et al.* 2002; Agridiotis *et al.* 2007; Dhakhwa *et al.* 2012). The ion  $\text{Fe}^{3+}$  ion is similar to  $\text{Al}^{3+}$  in terms of valence and its strong tendency to complex with  $\text{OH}^-$  ions. The fact that iron compounds are highly colored generally precludes their usage in papermaking applications, but for water treatment they can offer a less expensive alternative compared to aluminum salts in some cases.

### *Massive lime (CaO)*

The so-called “massive lime” strategy for the treatment of wastewater from P&P mills takes advantage of the fact that large amounts of calcium oxide are routinely combined with water (*i.e.* “slaked”) and then converted to calcium carbonate during the process of regenerating the pulping chemicals that are used for kraft cooking of the fibers (Gehm 1973; Rajvaidya and Markandey 1998; Eskelinen *et al.* 2010). The following recipe for this process is provided by Rajvaidya and Markandey (1998): The CaO generated in the calcining operation of a kraft pulp mill needs to be mixed with water (slaked) to yield  $\text{Ca}(\text{OH})_2$ . Instead of mixing the CaO with fresh water, in the massive lime process it is instead combined with wastewater, and the resulting  $\text{Ca}(\text{OH})_2$  is allowed to settle. The sludge then is used in the causticizing process to prepare the kraft pulping liquor (white liquor). Because the organic solids are returned to the chemical recovery system for kraft

pulping, most of them eventually become incinerated, with the production of steam, which is used in the manufacturing process.

### *pH*

It is also technically possible to neutralize the surface charge of biological materials by lowering the pH of the solution. By reducing the pH to about 2, essentially all of the carboxyl groups present will be protonated, giving a neutral charge and encouraging coagulation. However, such an approach is generally regarded as impractical in full-scale operations, and there are few mentions of this strategy in the literature (Pere *et al.* 1993; de los Santos Ramos *et al.* 2009). For example, de los Santos Ramos *et al.* (2009) lowered the pH to 1 or 3 in order to precipitate lignin from the solution before ozone treatment.

### **Organic Coagulants**

Highly cationic organic polymers are often preferred over inorganic coagulants because of the potential for forming denser or larger agglomerates that settle more rapidly (Ghosh *et al.* 1985; Leitz 1993; Aguilar *et al.* 2003; Al-Jasser 2009; Ariffin *et al.* 2012). Several investigators have described the usage of such agents in the treatment of wastewater from P&P facilities (Ganjidoust *et al.* 1997; Pere *et al.* 1993; Rohella *et al.* 2001; Al-Jasser 2009; Razali *et al.* 2011). Ariffin *et al.* (2012) found that polydiallyldimethylammonium chloride (poly-DADMAC) was effective for coagulation of suspended matter into small flocs. Razali *et al.* (2011) found that the effectiveness of poly-DADMAC as a coagulant for P&P mill wastewater increased with molecular mass. It seems likely that the observed effect of molecular mass was related to a “charged patch” mechanism in which the polyelectrolyte adsorption created a contrast between covered areas having positive charge and uncovered areas having a negative charge. Such conditions have been shown to bring about more effective coagulation at low dosage than mere charge neutralization, especially if the generated charged patches are large enough (Sandell and Luner 1974; Goossens and Luner 1976; Pfau *et al.* 1999; Horn 2001).

There has been much interest in the use chitosan as a coagulating agent, in light of the fact that it is the only cationic polymer that can be easily isolated from a natural product. Chitosan is made from chitin, which is found in the shells of shrimp and crabs. The chitin is deacetylated to form chitosan by treatment with NaOH. The following authors have demonstrated its effectiveness for coagulating P&P wastewater (Ganjidoust *et al.* 1997; Rodrigues *et al.* 2008; Renault *et al.* 2009; Wang *et al.* 2009). Rodrigues *et al.* (2008) reported that the chitosan treatment favored settling and the formation of a dense sludge. Miranda *et al.* (2013) showed the efficiency of chitosans for the treatment of process water by DAF.

### **Hybrid Coagulants**

Polyaluminum chlorides (PACs), as well as polyaluminum nitrate sulfate (PANS), have been extensively used in the last decades for wastewater treatment in the paper industry (Pernitsky and Edzwald 2006; Miranda *et al.* 2009b, 2015). These products can be modified with organic polymers to create inorganic-organic hybrids or composite coagulants, which improve the coagulation performance of the inorganic salts alone due to the synergy between the individual components (Lee *et al.* 2012; Latour *et al.* 2015). The organic coagulants offer the advantage of lower dosages, broader pH operating ranges, and smaller sludge production (de Nardi *et al.* 2008; Miranda *et al.* 2009b). Although these organic polymers are more expensive, considerable savings on coagulant dosage can be

made when they are combined with inorganic salts for the same removal performance (Bolto and Gregory 2007; Miranda *et al.* 2009b; Latour *et al.* 2013).

## Flocculants

The main function of flocculants, which consist of very-high-mass polyelectrolytes, usually having a cationic charge, is to collect small agglomerates into large agglomerates.

According to Ghosh *et al.* (1985), the agglomerates formed by means of flocculants tend to be stronger and more shear-resistant than agglomerates brought about just by charge neutralization. Early researchers studying how such polyelectrolytes work in bringing about agglomeration coined the term “bridging,” since it was possible to destabilize suspensions even when there was a net surface charge preventing the particles from coming close to each other (La Mer and Healy 1963). With their very long chains, flocculants are able to overcome such barriers by adsorbing on two particles simultaneously. Such polyelectrolytes have become widely used in clarification of wastewater from P&P mills (Wang and Pan 1999; Wong *et al.* 2006; Ahmad *et al.* 2007, 2008; Žarković *et al.* 2011; Ariffin *et al.* 2012; Simonič and Vnučec 2012).

Wastewater treatment operations commonly use sequential combinations of treatment with a coagulant, then with a cationic flocculant of very high mass but low charge density (Ghosh *et al.* 1985; Ahmad *et al.* 2007, 2008; Wang *et al.* 2011; Žarković *et al.* 2011; Ariffin *et al.* 2012; Simonič and Vnučec 2012). The idea is to employ a suitable amount of a relatively inexpensive coagulant to reduce the surface charge of the suspended matter. The flocculants, which are more expensive, would be wasted if they came into contact with an excess of negative charges in the system. In some systems it can be very effective to “sensitize” the suspension with the addition of a sufficient amount of cationic coagulant, then use an anionic flocculant to bring about precipitation of large agglomerates (Wang and Pan 1999). Miranda *et al.* (2008, 2009c) investigated the effect of flocculant charge density and of new chemicals on the removal of contaminants by DAF. By contrast, nonionic polyacrylamide, which does not have any electrostatic attraction to either type of charged sites on wastewater solids, has been found to be ineffective for the treatment of wastewater from a P&P mill (Ganjidoust *et al.* 1997).

## Enhanced Clarification

### *Dosage optimization*

Because the composition of wastewater tends to be highly variable, it follows that the optimum treatment level of a coagulant is likely to change over time. One common way to deal with such a situation is to equip the plant operator with a laboratory and a set of matched stirrers in a matched set of beakers. The operator then treats the contents of several beakers with a different level of coagulant and finds out which of the treatment levels bring about the most effective coagulation and settling. Follow-up tests might be done if the best treatment level appeared to be outside of the tested range. A further challenge faced by operators of wastewater treatment plants is that the coagulant by itself sometimes is insufficient to bring about a distinct change in the appearance of the mixture; rather, the desired rapid settling and large flocs might occur only upon addition of the flocculant, and then only if the coagulant had been added within a narrow optimum window of treatment level.

The situation just described can be addressed by use of a charge demand titration (Hubbe *et al.* 2012b). The charge demand corresponds to the amount of a strongly charged polyelectrolyte that needs to be added to reach a charge-neutral condition of the surfaces

of the suspended matter. One of the most popular ways to sense the neutralized conditions, thus facilitating the needed titrations with polyelectrolytes, is by means of a streaming current detector (Gerdes 1966; Barron *et al.* 1994; Chen *et al.* 2003). The use of streaming current instruments to enable the addition of optimal amounts of flocculant to wastewater, thus ensuring reliable removal of solids, has been considered in various articles (Dentel and Kingery 1989; Dentel 1995; Mahmood and Elliot 2007; Yap *et al.* 2012; Al Momani and Ormeci 2014; Ratnaweera and Fettig 2015).

Focused beam reflectance probe measurements have also been demonstrated as being very useful to monitor and optimize flocculation processes. Flocculation performance can be monitored on-line, allowing a continuous assessment and insights into flocculation mechanisms (Rasteiro *et al.* 2008; Blanco *et al.* 2002a,b). This approach has been used to optimize dissolved air flotation systems for pulp and paper mills (Negro *et al.* 2005; Saarimaa *et al.* 2006a,b; Miranda *et al.* 2008, 2009b, 2013).

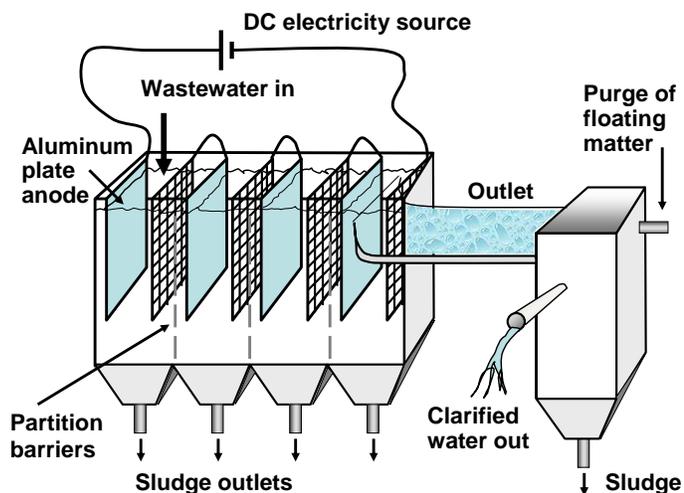
#### *Particulate coagulation aids*

Minerals such as clay and calcium carbonate, which are much denser than water, have been considered as a way to increase the rate of settling in a wastewater treatment operation. For example, Carter and Sigler (1981) employed clay in combination with poly-DADMAC as a coagulant to treat paper mill wastewater. The “massive lime” treatment mentioned earlier might be regarded as essentially the same kind of approach. Diatomite and other solid materials are often added as “filter aids” during the clarification of wastewater with the goal of increasing the rate of press dewatering of the resulting sludge (Zhao *et al.* 1995; El-Safey *et al.* 2005). Any of these mineral products can be expected to increase the density of agglomerated matter in the suspension, thus increasing the rate of settling.

In addition to mineral products, modified lignin has been found to be effective in promoting the settling of proteins in wastewater (Wang *et al.* 2014). Kraft lignin that had been irradiated with gamma rays was found to be somewhat more effective in wastewater from an enzyme production facility. The benefit was correlated with a drop in phenolic hydroxyl content and an increased water solubility of the lignin.

### **Electrocoagulation**

As an alternative to the direct addition of coagulating chemicals, similar effects can be obtained by an electrochemical method (Mollah *et al.* 2001; Chen 2004). Electrocoagulation uses the oxidation of either an aluminum or an iron electrode, which functions as the anode in contact with the water to be treated (Mollah *et al.* 2001; Emamjomeh and Sivakumar 2009). Figure 12, based on a system studied by Pérez-Sicairos *et al.* (2011), illustrates an example of such a system. Several authors have described experiments in which electrocoagulation was used to clarify wastewater from P&P mills (Ugurlu *et al.* 2008; Khansorthong and Hunsom 2009; Behrooz *et al.* 2011; Katal and Pahlavanzadeh 2011; Vepsäläinen *et al.* 2011a,b; Zodi *et al.* 2011; Al-Shannag *et al.* 2012; Antony and Natesan 2012; Bellebia *et al.* 2012; Chanworrawoot and Hunsom 2012; Lewis *et al.* 2013; Shankar *et al.* 2013). All of the cited studies reported positive results. There was no clear indication of markedly different results relative to conventional coagulation by means of chemical additives.



**Fig. 12.** Schematic illustration of an electrocoagulation system in which an aluminum electrode serves as the anode, releasing soluble ionic species of aluminum (redrawn based on a system studied by Pérez-Sicairos *et al.* (2011))

Because the end result of electrocoagulation is very similar what can be achieved by the direct addition of inorganic coagulants such as alum or iron salts, it is worth considering whether there are any potential advantages of employing a system that requires the installation of electrodes, which need frequent replacement, in addition to a system for supplying a controlled voltage between the electrodes. According to Mollah *et al.* (2001), electrocoagulation can avoid the introduction of excess ions to the treated water. In a well-designed system, the metal ions produced at the anode eventually associate with  $\text{OH}^-$  ions, leading to the generation of charge-neutral sediment. Moreover, unlike the use of alum or ferric chloride, there is no addition of chloride or sulfate ions to the water. Avoidance of sulfate ions can be important, both to avoid problems related to sulfate reducing bacteria (Roest *et al.* 2005; Janssen *et al.* 2009) and because sulfate ions have been shown to suppress the availability of coagulating species such as  $\text{Al}^{3+}$  (Akitt *et al.* 1972). There is also a possibility that by in-situ generation of the metal cations, within the medium that is being treated, the metal ionic species might be different initially from what can be achieved during addition of an inorganic coagulant. According to Mollah *et al.* (2001), another key reason why some operators prefer electrocoagulation is because it has a reputation of yielding lower amounts of sludge.

A key limitation of the electrocoagulation method is that the solution to be treated needs to have a relatively high electrical conductivity. Chen (2004) described the optimization of conditions for electrocoagulation of a variety of wastewaters and noted that an optimum range of current density may minimize the wastage of energy, the heating of the wastewater, and the fouling of the cathode surfaces. Best results can be expected with relatively salty effluents or solutions with pH values several units away from the neutral point (such as those from ECF bleaching effluents).

#### *Electrode type*

Several studies have considered the use of iron electrodes, aluminum electrodes, or a comparison of both to bring about destabilization of P&P mill wastewater. The following authors considered only the use of iron electrodes: Khansorthong and Hunsom 2009; Vepsalainen *et al.* 2011b; Al-Shannag *et al.* 2012. Al-Shannag *et al.* (2012) found that the

results could be enhanced by carrying out the treatment in the presence of iron sulfate or calcium carbonate additives. Vepsalainen *et al.* (2011b) found that the ferrous ions produced by such treatment were very effective for the removal of sulfide ions from pulp mill effluent.

Iron and aluminum electrodes have been compared in several studies involving wastewater from P&P mills. Boroski *et al.* (2008) and Uğurlu *et al.* (2008) found fairly similar performance, whereas Zodi *et al.* (2011) obtained more favorable results with the iron electrodes. Katal and Pahlavanzadeh (2011) found positive results with either kind of electrode over a wide range of pH (5 to 7), making it feasible to treat the paper mill wastewater without the adjustment of pH. Bellebia *et al.* (2012) found that an aluminum electrode system had a lower optimum pH (5.3) compared to an iron system (pH=7.2).

#### *Coagulants used with electrocoagulation systems*

A few studies have shown benefits of combined treatments with electrocoagulation in the presence of conventional coagulating agents such as alum or iron compounds (Mahesh *et al.* 2006; Al-Shanning *et al.* 2012). For instance, Mahesh *et al.* (2006) found that treatment with aluminum sulfate after electrochemical degradation of paper mill wastewater contributed to further reduction in oxygen demand and improved settlability. Al-Shanning *et al.* (2012) employed either iron sulfate or calcium carbonate, both of which substantially increased the efficiency of removal of chemical oxygen demand (COD) components from the water. By contrast, Khansorthong and Hunsom (2009) did not find any benefit of polyelectrolyte addition during an electrocoagulation process, with wastewater from a P&P facility.

#### *Dissolved air flotation used with electrocoagulation systems*

Dissolved air flotation (DAF) often has been incorporated into electrocoagulation (Boroski *et al.* 2008; Emamjomeh and Sivakumar 2009). According to Mollah *et al.* (2001), microbubbles, presumably hydrogen gas (Chen 2004) formed at the cathode of an electrocoagulation system, can contribute to the flotation of suspended particles. According to Chen (2009) the hydrogen bubbles formed in a typical electrocoagulation unit are smaller (usually 15 to 45  $\mu\text{m}$ ) in comparison to a typical DAF unit (usually 50 to 70  $\mu\text{m}$  bubble size).

Conventional DAF units have a variety of applications in separating solids from water. Such equipment also is widely used, in combination with surfactants, to remove hydrophobic ink particles from aqueous mixtures during the deinking of recycled printing papers (Ashley and Heindel 1999; Heindel 1999).

DAF systems rely upon the fact that increasing amounts of gas can be made to become solubilized in water by the application of pressure (Thompson *et al.* 2001; Edzwald 2010). Then, if the pressure is suddenly reduced, the dissolved gas quickly forms itself into small bubbles, just as it does when a shaken soda can is opened. When this takes place in the presence of suspended particles, the rising bubbles collide with particles, which then can be lifted to the water surface and collected there. Such separations have been shown to be enhanced by addition of coagulants (Meysami and Kasaeian 2005). Furthermore, Han *et al.* (2006) observed the highest flotation efficiency following treatment with coagulant, resulted in an opposite sign of effective charge of the surfaces of bubbles and solid particles.

## ADVANCED OXIDATION SYSTEMS

An inherent difficulty in the treatment of wastewater from kraft pulping and the bleaching of kraft pulps, is the resistance of lignin-related species to biodegradation (Lindholm-Lehto *et al.* 2015). This problem has been often addressed by advanced oxidation processes (AOPs) (Esplugas *et al.* 1994; Masten and Davies 1994; Hörsch *et al.* 2003; Oller *et al.* 2011; Merayo *et al.* 2013; Hermosilla *et al.* 2015). AOPs can be regarded as an enabling step before biological treatment of wastewater from P&P facilities because they may increase biodegradability as well as decompose bio-refractory organic substances (Oller *et al.* 2011; Merayo *et al.* 2013). The efficiency of subsequent biological treatment stages can be increased (Kamali and Khodaparast 2015). Whether they are used as a pretreatment or for the polishing of water after biological treatment, AOPs can reduce organic refractory and toxic compounds from pulp and paper mill effluents (Catalkaya *et al.* 2003; Hsueh *et al.* 2005). AOPs include ozone, various oxidizing species used in combination with catalysts or UV light, and the Fenton method, which is a catalytic oxidation method based on electron transfer between H<sub>2</sub>O<sub>2</sub> and metal ions (Fe<sup>2+</sup>) serving as homogeneous catalysts (Ince *et al.* 1997; Catalkaya and Kargi 2007).

### Ozonation

Ozone is a powerful oxidant and has been studied since the 1970s (Bauman and Lutz 1974; Rodríguez *et al.* 1998). It is a highly energetic form of oxygen that has the capability of breaking down many hard-to-biodegrade organic compounds found in pulping and bleaching wastewaters in two ways, directly reacting with dissolved substances, and indirectly producing hydroxyl radicals; the reaction is improved under basic pH conditions, without the need to apply ultraviolet light, use a catalyst, or add iron compounds (Rice 1997; Alvares *et al.* 2001; Pokhrel and Viraraghavan 2004; Tripathi *et al.* 2011; Hermosilla *et al.* 2015). There have been many investigations devoted to the treatment of P&P wastewater using ozone by itself (Prat *et al.* 1988; Heinzle *et al.* 1992; Chen and Horan 1998; Rodríguez *et al.* 1988; Heble *et al.* 1999; Yeber *et al.* 1999b; Freire *et al.* 2000; Amat 2005b; Kreetachat *et al.* 2007; Wang *et al.* 2008b; de los Santos Ramos 2009; Kishimoto *et al.* 2010; Merayo *et al.* 2013; Cheng *et al.* 2015; Hermosilla *et al.* 2015). Enhanced biodegradation of contaminants owing to the inclusion of an ozone pretreatment of industrial wastewaters has been reported (Yeber *et al.* 1999b; Heinzle *et al.* 1992; Wang *et al.* 2008b; de los Santos Ramos 2009; Tripathi *et al.* 2011).

Ozone use as a post-treatment after biodegradation was found to be favorable by Merayo *et al.* (2013). The review article by Alvares *et al.* (2001) advocates the “partial” treatment with ozone as a pretreatment for biological wastewater treatment; such an approach has the potential to minimize the high costs generally associated with ozone use. Heble *et al.* (1999) found best results when using two stages of ozonation and an intermediate biodegradation stage. Baig and Liechti (2001) reported that the alternate combination of bio-filters after ozonation stages (O<sub>3</sub>+bio-filter+O<sub>3</sub>+bio-filter) improved the removal of the COD and reduced the overall cost of the treatment. One of the successes of ozonation for the treatment of real wastewater from pulp and paper mills, whether biologically pre-treated or not, is their capability to produce an effective degradation of toxic lignin products and chlorophenolic compounds and the reduction of color (Hermosilla *et al.* 2015).

Ozone reacts with colored and halogenated organic compounds; it improves biodegradability of recalcitrant compounds by degrading and transforming HMW compounds into smaller and more harmless fractions (Masten and Davies 1994; Zhou and Smith 1997). However, it is still an emerging method for wastewater treatment, even though it is widely used in drinking water preparation (Zhou and Smith 1997; Freire *et al.* 2001). By ozonation, even 80 to 90% reductions in color have been reported (Catalkaya and Kargi 2007; Meza *et al.* 2011). The efficiency of ozonation depends on the process operating conditions and the quality of wastewater. Furthermore, it is a rather expensive process and has been shown to be more efficient in decoloration than in COD removal (Pokhrel and Viraraghavan 2004; Lei and Li 2014). Ozonation has successfully been used to oxidize chemicals in pulp and paper mill effluents, such as eugenol, catechol, vanillin, guaiacol, syringaldehyde, phenol, chlorinated phenols, and cinnamic acid derivatives (Amat *et al.* 2005b; Fontanier *et al.* 2005a). In addition, ozone oxidation of resin acids has been shown to be relatively effective (Korhonen and Tuhkanen 2000; Ledakowicz *et al.* 2006).

The combination of ozone and hydrogen peroxide ( $O_3/H_2O_2$ ) has also been proposed to remove refractory organic chemicals, but hydrogen peroxide leads to faster ozone degradation and higher  $O_3$  consumption (Masten and Davies 1994; Gogate and Pandit 2004a,b; Amat *et al.* 2005b; Mounteer *et al.* 2007b).

Although ozone treatments generally have been carried out without the assistance of a catalyst, a recent study by Cheng *et al.* (2015) showed a benefit of using a heterogeneous Fe-Mn sepiolite catalyst in combination with the ozone treatment of wastewater from papermaking processes. By enhancing decomposition of organic matter, catalytic ozonation has been found to lower the amount of ozone required (Fontanier *et al.* 2005b). The almost complete mineralization of compounds, including phenol, chlorinated phenols, guaiacol, vanillin, catechol, and syringaldehyde, has been achieved by using cobalt as the active metal deposited on a mineral catalytic support (Fontanier *et al.* 2005b). Other combinations, *e.g.* peroxymonosulfate salt ( $2KHSO_5:KHSO_4:K_2SO_4$ ) and ozone led to a reduction of color and COD (79 % and 14 %) but a negligible TOC removal (Joss *et al.* 2007). The  $CO_3^{2-}$  ion negatively affected the ozone oxidation, manifesting a radical scavenging effect under neutral and basic conditions (Barndöck *et al.* 2012).

Balcioglu *et al.* (2007) proposed the treatment of bleaching effluents from a pulp mill by ozone assisted by granulated activated carbon (GAC) as catalyst. COD removal improvement was 23% relative to direct ozonation and 15% in comparison to standalone GAC. Ko *et al.* (2009) also found similar results. In addition, the reduction of COD of a bleaching wastewater from a kraft pulp and paper mill was increased by more than 25% by the addition of 5 mM  $Fe^{2+}$  or  $Mn^{2+}$  in comparison to its ozone treatment (Balcioglu and Moral 2008).

Ozonation is the most frequently employed AOP in combination with biological treatment processes (Bijan and Mohseni 2005; Balcioglu *et al.* 2006). Pre-ozonation before biological treatment can prevent process failure and improve the purification efficiency by decreasing BOD and COD load (Tuhkanen *et al.* 1997; Thompson *et al.* 2001). Another option is to use ozone after biological treatment (Hostachy *et al.* 1997; Chow *et al.* 1999). Secondary reactions of ozone with the by-products are in some cases unwanted, creating new compounds, such as ketones, organic acids, and aldehydes of differing toxicity (Hostachy *et al.* 1997; Latorre *et al.* 2007).

*Fenton and photo-Fenton processes*

The Fenton method and its variants are discussed by Bautista *et al.* (2008). Such processes make use of the catalytic reaction between hydrogen peroxide and ferric or ferrous ions in solution, giving rise to the HO• species with high oxidation potential, *i.e.* the hydroxyl radical. The latter is believed to be the key reagent in breaking down hard-to-biodegrade compounds related to lignin. The main reactions involved in a typical Fenton treatment are as shown below (Hermosilla *et al.* 2009).

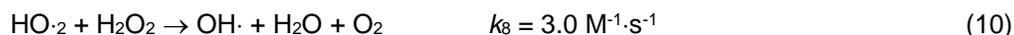
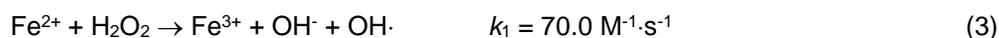
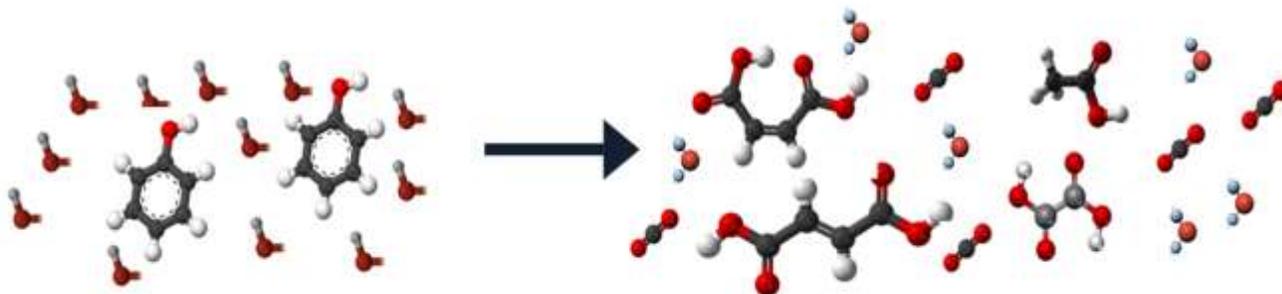
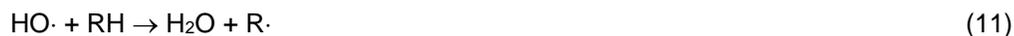


Figure 13 provides a molecular view of one of the key reactions, which is a subsequent step in which Fenton species take part in degradation of an aromatic compound.



**Fig. 13.** Fenton reaction sequence leading to decomposition of phenol, as an example

Reactions taking place between biomass components (shown as “R”) and the Fenton reagents include the following:



The conventional Fenton process has been tested in the pulp and paper industry at laboratory scale to polish different mill effluents (from kraft pulp to recovered paper mills) reporting good oxidation removal efficiencies (COD removal > 60%; Hermosilla *et al.* 2015), although the partially-oxidized composition of the treated wastewater did not show a reduction of toxicity to *Artemia salina* in comparison with the untreated effluent (Tambosi *et al.* 2006).

Figure 14 outlines the process sequence in a conventional Fenton system for wastewater treatment.

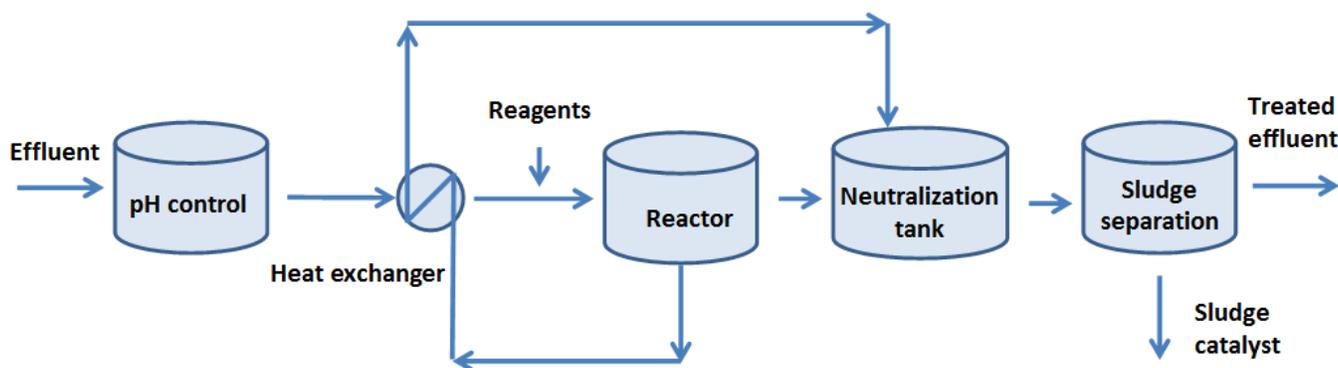


Fig. 14. Schematic of a conventional Fenton wastewater treatment system

Torrades *et al.* (2003) and Hermosilla *et al.* (2012a) showed that the Fenton reaction was more efficient when combined with ultraviolet irradiation (*i.e.* “photo-Fenton”) when used for the treatment of pollutants in the retentate from a reverse osmosis membrane separation of contaminated water in a recovered paper mill. Similar results were reported by Jamil *et al.* (2011). Moreover, Merayo *et al.* (2016) reported good efficiency for the heterogeneous photo-Fenton treatment of lignin using zero valent iron microspheres as catalyst instead of ferrous iron.

Lucas *et al.* (2012) and Fernandes *et al.* (2014) reported effective treatment of pulp mill wastewater with a solar-Fenton process. In such systems daylight illumination is used to assist the process, significantly reducing the energy cost associated to UV-light application. Rodriguez *et al.* (1999) found that the decomposition of chlorophenols (which are often present in pulp bleaching wastewaters) was promoted by the addition of various dihydroxybenzoic acid or benzene species in combination with Fenton treatment.

Parilti and Akten (2011) showed the effectiveness of a hybrid system for the treatment of pulp mill wastewaters; they combined a Fenton system (ferric ions) with TiO<sub>2</sub> as a catalyst. The main mechanism involving the application of such a catalyst is the formation of reactive oxygen barriers under which superoxide ( $\cdot\text{O}_2^-$ ) is produced as a result of the reduction of molecular oxygen (O<sub>2</sub>) (Turrens 2003). Such species are very reactive towards the pollutants in P&P mill wastewater.

According to Hermosilla *et al.* (2015), although Fenton processes seem to perform well under laboratory settings, they are not often implemented at industrial scale in comparison to ozone treatment, probably due to there being much more experience in the implementation of ozone processes. Other factors include the more frequent availability of ozone treatments for bleaching stages in paper mills, as well as some disadvantages of Fenton processes application, such as the production of iron sludge and the requirement of acidic conditions for optimal performance. These drawbacks may be overcome by using heterogeneous catalysts or by applying these treatments at neutral pH (Merayo *et al.* 2016; Hermosilla *et al.* 2012a). Beltrán-Heredia *et al.* (2001) tested the use of sequential treatments with Fenton reagents and ozone.

Biodegradability improvement is generally difficult to demonstrate after the application of these highly oxidizing processes, since they are not selective and also remove biodegradable material. On the other hand, their use after a biological treatment, where almost all the biodegradable fraction has already been removed, has been reported

to be very efficient, achieving over 90% removal of the COD present in the effluent after the biological treatment (Hermosilla *et al.* 2015).

#### *UV-catalysis (with TiO<sub>2</sub> or peroxide)*

Ultraviolet radiation alone is, in general, less effective than other AOPs, but its efficiency may be increased greatly when it is used in combination with other AOPs (*e.g.* UV-ozone) or in combination with H<sub>2</sub>O<sub>2</sub> or certain catalysts (metal salts and semiconductors) (Hermosilla *et al.* 2015). Due to its strong absorption in the short wavelength range, UV irradiation has the potential to break down aromatic-based compounds such as lignin byproducts. This has been demonstrated, for instance, by Amat *et al.* (2005b), who used model compounds to represent the recalcitrant components of pulp mill wastewater. In that study the UV irradiation increased the breakdown of the model compounds under fixed conditions of ozonation. Similar results were reported earlier by Yeber *et al.* (1999b) in a study of bleachery wastewater and in the review article by Rice (1997). Dahm and Lucia (2004) demonstrated the breakdown of lignin and showed that the catalyst (TiO<sub>2</sub>) had to be present to ensure effectiveness of the process. Prat *et al.* (1988) found that combinations of UV light and H<sub>2</sub>O<sub>2</sub>, in the absence of catalyst, necessitated long treatment times and had low efficiency for the treatment of bleachery waters. Jamil *et al.* (2011) studied the treatment of effluent from a board paper mill by different photocatalytic processes, achieving a COD removal efficiency of  $\approx 80\%$  by the photo-Fenton treatment; as well as the  $\approx 11$  and  $33\%$  respectively when applying UV and UV/H<sub>2</sub>O<sub>2</sub>. In fact, 4-chlorophenol and phenol have been reported to be efficiently degraded by UV/H<sub>2</sub>O<sub>2</sub> (Rueda-Márquez *et al.* 2015). In addition, Ahmed *et al.* (2009) found good efficiencies in the UV/H<sub>2</sub>O<sub>2</sub> treatment of a Tunisian pulp and paper mill effluent, suggesting that the degradation of lignin derivatives and tannins leads to generation of aromatic intermediates that further undergo oxidative ring opening, producing aliphatic carboxylic acids, just as it has previously been discussed for other AOPs application. In final treatment steps, carboxylic acids may mineralize into CO<sub>2</sub> and H<sub>2</sub>O.

The efficacy of ultraviolet light in the presence of catalysts had been demonstrated (Rodrigues *et al.* 2008; Bu *et al.* 2014). The catalyst is usually a semiconductor material, of which TiO<sub>2</sub> particles are the most commonly applied. These methods have been shown to be effective in breaking down organic compounds derived from lignin in the wastewater from pulping and papermaking processes (Catalkaya and Kargi 2008; Merayo *et al.* 2013, 2016). However, Hermosilla *et al.* (2012a) found such a system to be less effective than photo-Fenton treatment in the case considered. Various authors have shown that such systems can be made even more effective by the addition of hydrogen peroxide (Boroski *et al.* 2008; Catalkaya and Kargi 2008; Ugurlu and Karaoglu 2009; Ghaly *et al.* 2011; Kumar *et al.* 2011).

Botia *et al.* (2012) compared TiO<sub>2</sub> and ZnO catalysts in the presence of UV light for the treatment of pulp bleachery wastewater. The photocatalytic system resulted in very efficient removal of chemical oxygen demand (COD) with either kind of catalyst after the biological treatment with an aerated film reactor. The photocatalytic system by itself, without the biological treatment, gave rise to a high level of oxygen demand, however. Kansal *et al.* (2008), who studied the treatment of bleach plant effluents, found better results when using a TiO<sub>2</sub> system rather than a ZnO system. In particular, it has been reported that photocatalytic treatments developed with a supported catalyst showed similar results as when added in suspension, but the supported type required a longer reaction time to produce the same results (Yeber *et al.* 1999a, 2000); although the supported system

avoids the need for a recovery step. In addition, Yuan *et al.* (2007) showed that it was possible to attach TiO<sub>2</sub> particles securely to activated carbon fibers; such particles were found to be effective, while loaded onto such a support, in the treatment of paper mill wastewater under UV irradiation.

As a pretreatment *before* biological treatment, Duran *et al.* (1994) showed that irradiation in the presence of ZnO markedly enhanced the effectiveness of a specific type of fungus in decolorization of the first alkaline extraction stage (E1) of kraft pulp bleaching effluent. Likewise, Goel *et al.* (2010) showed that such an integrated treatment was very effective for the treatment of 4-chlorophenol in water. Ruas *et al.* (2012) reported that the combination of H<sub>2</sub>O<sub>2</sub> with UV irradiation was helpful as a pretreatment before anaerobic digestion to remove chlorinated organics from bleached kraft mill wastewater effluent. Jamil *et al.* (2011) reported 0.25, 0.45, and 0.7 increases of the BOD<sub>5</sub>/COD ratio for the treatment of an effluent from a board paper mill by UV, UV/H<sub>2</sub>O<sub>2</sub>, and photoFenton processes, respectively; as well as a significant destruction of aromatic chlorinated compounds in all the trialed photocatalytic processes. Moraes *et al.* (2006) achieved good efficiencies (75% color removal and an increase of mineralization of the 140% with respect to the previous biological treatment) in the application of photocatalysis as post-biological treatment of black liquor. In addition, a mineralization increase of the 45% was obtained for the pre-biological treatment of kraft effluent by photocatalysis (Moraes *et al.* 2006). Notably, Merayo *et al.* (2013) did not find any significant benefit of photocatalysis either before or after biological treatment, whereas ozone was found to be quite effective as a post-treatment.

The use of solar light instead of UV radiation has also been tested, leading to good results. Amat *et al.* (2005a) assessed its application to the treatment of effluents from the board industry, achieving about a 40% COD removal at the pre-industrial level and a 50% in laboratory trials.

#### *Wet oxidation with O<sub>2</sub>*

Oxygen is a much less reactive oxidant than ozone, but it can be made to react with organic compounds in wastewater by application of heat and pressure, *i.e.* by implementation of wet oxidation conditions (Bhargava *et al.* 2006). The effectiveness of such systems in treating wastewater from P&P mills has been reported (Verenich *et al.* 2000, 2001; Pintar *et al.* 2001; Akolekar *et al.* 2002; Garg *et al.* 2005, 2007; Dhakhwa *et al.* 2012). Verenich *et al.* (2000, 2001) showed that wet oxidation improved the effectiveness of a subsequent biodegradation stage of treatment. Others have demonstrated the ability of catalysts to promote wet oxidation (Verenich *et al.* 2000; Pintar *et al.* 2001; Akolekar *et al.* 2002; Garg *et al.* 2005). Bhargava *et al.* (2006) noted that wet oxidation treatments without the use of a catalyst can yield recalcitrant compounds having carboxylic acid functions. Pintar *et al.* (2001) found a good correlation between the catalytic effects and the surface areas of the solid catalysts used. Garg *et al.* (2005) showed that a variety of catalysts were able to promote removal of color and oxygen demand from P&P effluent at temperatures between 20 and 95 °C. By contrast, Dhakhwa *et al.* (2012) found the best results when using a non-catalyzed wet oxidation treatment.

Insights into the mechanism were revealed by Garg *et al.* (2007), who found that the pH of the solution decreased initially and then decreased in the course of wet oxidation of synthetic P&P mill effluent. This sequence was attributed to the initial formation of carboxylic acids, presumably through breakage of ester bonds, followed by the decomposition of those acids.

Herney-Ramirez *et al.* (2011) investigated the degradation of Acid Orange 7, which is a typical dye used in the paper industry, by a heterogeneous catalytic wet hydrogen peroxide process that used a pillared saponite as support for the impregnation with Fe (16% w:w). This catalytic process completely degraded the dye in less than 4 h of treatment. On the other hand, Baurotian *et al.* (2013) assessed the use of wet oxidation as pre-treatment of anaerobic biological treatment of sludge from paper mills, achieving more than a 90% destruction of extractive compounds after 20 min of wet oxidation performance. The 95.7% of phenolics, 98.6% fatty acids, 99.8% resin acids, and the 100% of phytosterols were degraded in 120 min. Moreover, acetic acid concentration significantly increased after this pre-treatment, thus making the pre-treated sludge more suitable for anaerobic digestion.

### *Electro-oxidation*

The term “electro-oxidation” is used when voltages and other factors in an electrode system are optimized for *in-situ* production of reactive, oxidizing species (El-Ashtoukhy *et al.* 2009), in contrast to the generation of  $Al^{3+}$ ,  $Fe^{3+}$ , or  $Fe^{2+}$  in the case of electrocoagulation (Mollah *et al.* 2001; Chen 2004). Organic compounds will therefore directly be degraded on the electrodes, and different oxidative radicals will be produced by electrolysis, including the hydroxyl radical, sulfate, and chlorine. The main factors affecting this process are: current density, electrode material, reaction time, and the characteristics of the wastewater (Hermosilla *et al.* 2015). According to Chen (2009), such direct oxidation takes place by a surface interaction between the organic compound and an adsorbed hydroxyl radical species. Alternatively, metal ions having a higher oxidation state, *e.g.*  $Fe^{3+}$ , may serve as mediators for the transformation of the organic compounds.

Electro-oxidation has been examined by several research groups in the treatment of wastewater from P&P facilities (Mahesh *et al.* 2006; Wang *et al.* 2007; El-Ashtoukhy *et al.* 2009; Särkkä *et al.* 2009; Soloman *et al.* 2009; Kishimoto *et al.* 2010; Antony and Natesan 2012; Qu *et al.* 2012; Krishna *et al.* 2014; Lindholm-Lehto *et al.* 2015) even using rice straw as raw material to produce paper pulp (El-Ashtoukhy *et al.* 2009). Patel *et al.* (2008) evaluated the removal of pentachlorophenol, as well as the treatment of pulp bleaching effluent from a bamboo-based mill, by an electrochemical process, reporting the removal of  $10 \text{ mg L}^{-1}$  of pentachlorophenol in less than 10 minutes when performing such treatment. Eskelinen *et al.* (2010) aimed the treatment of some wood extractives and achieving 51%, 76%, and 83% concentration removals of 12 mg/L abietic acid, 11.8 mg/L oleic acid, and 0.6 mg/L  $\beta$ -sitosterol, respectively. Particular value-added products, such as vanillin and syringaldehyde, were identified in the electro-oxidized reaction media of acid bisulfite pulping effluents (Moodley *et al.* 2011). Dominguez-Ramos *et al.* (2008) obtained positive results for the treatment of lignosulfonate, which may be regarded as a component of effluent from sulfite pulping. Särkkä *et al.* (2009) used an electrochemical treatment to oxidize sulfides present in paper mill wastewater. Krishna *et al.* (2014) used the term “bioelectrochemical treatment” to describe a system in which wastewater was treated within a reactor that was set up to generate electrical current. The electrode that was identified as the cathode was at the air-water interface, and that part of the cell was separated from the rest of the aqueous system with a selectively permeable membrane. The authors reported that not only did the system outperform parallel systems carried out under anaerobic conditions without an electrochemical set-up, but also the decomposition of organic matter was greater. Loraine and Huchler (2006) reviewed the use of a variety of electrochemical approaches that have been used in Holland for treatment of P&P mill

waters. Wang *et al.* (2007) presented evidence that a modified kaolin additive had a catalytic effect on the electro-oxidation process.

Other authors have reported the enhancement of biodegradability in the solution after its electro-oxidation treatment (Soloman *et al.* 2009; Antony and Natesan 2012). Particularly, anodic oxidation enhanced the biodegradability of 2,4-dichlorophenol solutions and it is a promising alternative for the degradation of chlorophenols (Chu *et al.* 2010). Qu *et al.* (2012) reported the improvement of COD removal efficiency after an anaerobic membrane bioreactor stage, suggesting that this integrated technology may produce a more suitable effluent for subsequent reuse and ultimate systems closure.

Finally, the electro-Fenton treatment, *i.e.* the combination of Fenton process with electrochemical oxidation, might also be an interesting alternative to improve treatment efficiency. Selvabharathi and Kanmani (2010) reported a 90% COD removal during the application of electro-Fenton to a biologically-treated newsprint paper industry effluent.

### Reduction

Since the colored nature of many organic compounds can be attributed to conjugated carbon-carbon double bonds (repeated double-single-double, *etc.* sequences), it is logical that decolorization of pulp mill wastewater might be achieved by chemical reduction. Such an approach has been demonstrated (Calvo *et al.* 2007; Ghoreishi and Haghghi 2007). For instance, Calvo *et al.* (2007) used catalytic hydrogenation to detoxify and decolorize kraft bleaching effluents. Ghoreishi and Haghghi (2007) used the strong reducing agent sodium borohydride to decolorize P&P mill wastewater. This was followed by aerated biodegradation in a second reactor. Given the rarity of studies of this nature, this would seem to be a prime field for future research.

## FILTRATION, PACKED BED, AND BIOREACTOR SYSTEMS

Various kinds of filtration procedures are used at different stages of wastewater treatment, but there has been particular interest in their usage in connection with so-called “bioreactors,” as internal or external configurations (Kamali *et al.* 2016). Such systems are designed to speed up biological decomposition processes in an efficient way. A later section will consider some further applications of filtration technologies when they are employed as a final polishing step before discharge of treated water.

### Filtration Options

When paper mill operators are looking for ways to save money and increase the overall yield, much attention can be paid to save-all systems. The final effluent leaving from a paper machine system may be carrying away solid material that could become part of the product, rather than part of the sludge from water treatment. The most commonly used save-all systems are essentially screen systems, and they might be regarded as a first step in wastewater treatment. There is potential to minimize solids losses at that point in the paper machine system by such steps as proper maintenance of the save-all equipment, attention to providing a steady amount of suitable sweetener fiber, and the use of an effective retention aid system (Hubbe *et al.* 2009). Though it has been shown that retention aid can be fed directly to the intake of the save-all itself (Milliken 2006), it is often regarded as more practical just to apply such chemicals before forming the paper sheet in an effort to achieve a suitably high first-pass retention, leading to less load on the save-all operation.

### Membrane filtration

When the goal is to mechanically separate contaminants smaller than about 100  $\mu\text{m}$  in diameter from a suspension, then membrane technology can be a promising approach. In particular, membrane systems tend to use less energy relative to evaporation of water or centrifugation. Various authors have provided overviews of membrane-related treatments of wastewater from the P&P industry (Gehm 1973; Nuortila-Jokinen 2004; Hubbe 2007c). Different membrane products are rated according to their pore sizes, which also determine what entities (particles, molecules, *etc.*) they are able to effectively exclude. Membrane systems have been used by some P&P facilities to meet government regulations regarding effluent discharge. The Irving Pulp and Paper in New Brunswick, which is a 950 t/d facility, has been in operation for 15 years without the need for a biological wastewater treatment system (Hodgson *et al.* 1998) due to membrane usage.

Some of the most commonly mentioned types of membrane filtration are indicated in Table 1 (Khulbe *et al.* 2008).

**Table 1.** Classification of Membrane Filtrations Systems

Membrane filtration type	Typical pore sizes	Selected references
Microfiltration	0.1 to 2 $\mu\text{m}$	Pizzichini <i>et al.</i> 2005; Hong <i>et al.</i> 2007; Leiviska <i>et al.</i> 2008, 2009
Ultrafiltration	2 to 100 nm	Minami <i>et al.</i> 1991; Tavares <i>et al.</i> 2002; Gönder <i>et al.</i> 2011, 2012
Nanofiltration, dialysis	1 to 5 nm	Ahn <i>et al.</i> 1998; Lastra <i>et al.</i> 2004; Kaya <i>et al.</i> 2010
Reverse osmosis	< 1 nm	Sierka <i>et al.</i> 1997; Khosravi <i>et al.</i> 2011; Ordóñez <i>et al.</i> 2011

Starting from the top of Table 1, the coarsest membranes, *i.e.* microfiltration membranes, appear to have been mainly considered as pre-filtration membranes upstream of membranes having finer pores for wastewater applications (Le-Clech *et al.* 2006). Another usage has been as a means to separate and analyze different size classes of solids within P&P mill wastewaters (Hong *et al.* 2007; Nataraj *et al.* 2007; Leiviska *et al.* 2008, 2009). Nataraj *et al.* (2007) combined microfiltration with electro dialysis to purify paper industry wastewater. Sierka *et al.* (1997) and Ordóñez *et al.* (2011) showed that microfiltration or ultrafiltration steps could serve as useful pretreatments before reverse osmosis membrane separations.

Ultrafiltration (UF) membranes have been more widely used for the treatment of P&P industry wastewaters. One of the key considerations is to employ a membrane having sufficiently fine pore distribution to exclude the passage of biological cells and viruses. The following studies have employed ultrafiltration to separate clarified water from the solids in P&P mill process waters or effluent (Minami *et al.* 1991; Zaidi *et al.* 1992; Ragona and Hall 1998; Huuhilo *et al.* 2002; Tavares *et al.* 2002; Komesvarakul *et al.* 2003; Nuortila-Jokinen *et al.* 2004; Mänttari *et al.* 2008; Ordóñez *et al.* 2010; Puro *et al.* 2010; Gönder *et al.* 2011, 2012; Simonič and Vnučec 2012; Singh *et al.* 2012; Quezada *et al.* 2014). Notably, Tavares *et al.* (2002) were able to demonstrate the removal of metals from such effluent. Iron, magnesium, and calcium compounds were complexed by addition of polyelectrolytes and then retained during membrane clarification of the water. Ragona and Hall (1998) ran an ultrafiltration system in parallel with a bioreactor (see page 8000) and obtained good results with both systems.

Nanofiltration (NF) can be considered when the goal is to exclude large molecules from the permeate. For example, Lastra *et al.* (2004) were able to separate metal complexes from pulp mill wastewater by nanofiltration. Other researchers have found nanofiltration to be effective for the removal of color and hard-to-degrade organic compounds in such effluents (Ahn *et al.* 1998; Huukilo *et al.* 2002; Mänttari and Nyström 2007; Gönder *et al.* 2011; Khosravi *et al.* 2011; Sheldon *et al.* 2012). Laitinen *et al.* (2001) found that the performance of membrane processes could be improved by an optimized program of backflushing.

Reverse osmosis (RO) membranes, which are the “tightest” membranes available, are designed to allow the passage of water but to exclude most other molecules, including salt ions. High pressures are required to force water molecules through such membranes, often in opposition to what would be expected from salt concentration gradients and the resulting osmotic pressure. They have been used in some P&P industry applications where the goal is to desalinate the water, in addition to removing other contaminants (Zhang *et al.* 2009; Khosravi *et al.* 2011; Li and Zhang 2011; Sheldon *et al.* 2012; Saif *et al.* 2013; Ordóñez *et al.* 2013). For instance, Khosravi *et al.* (2011) demonstrated the use of an RO system in removing color and oxygen demand from P&P mill effluent. The permeate flux was low, but the resulting water quality was distinctly higher than what was achieved in parallel tests involving nanofiltration. Li and Zhang (2011) found that the RO process was facilitated by pretreating the raw wastewater with a flocculant blend. Ordóñez *et al.* (2010) found the possibility of reusing the effluent of a recovered newsprint paper mill as fresh water (*i.e.* in high pressure showers) by reverse osmosis. Recovery, and therefore efficiency were limited by the presence of silica. As a consequence, several studies have been devoted to achieving the successful removal of silica as a necessary pre-treatment of membrane operation within the pulp and paper industry (Hermosilla *et al.* 2012b; Latour *et al.* 2013, 2014a-c, 2015). Results showed that the level of silica can be lowered by water softening treatment or by flocculation and separation.

When choosing among the options just presented, a compromise often needs to be reached between the ability to exclude passage of substances and the rate of flux (Quezada *et al.* 2014). The main drawback is that membrane filters tend to become fouled (see next subsection), as indicated by a decrease in the flux at a constant pressure. For instance, Kallioinen *et al.* (2005, 2006) found that the ratio of decrease in membrane permeability was related in complex ways to the chemical nature of the process water from P&P facilities. Filtration technologies merely separate, but do not change any of the components of the mixture. This is important especially in the case of highly polluted effluents. Other steps are often necessary to degrade the solid matter concentrates after being separated from the effluents.

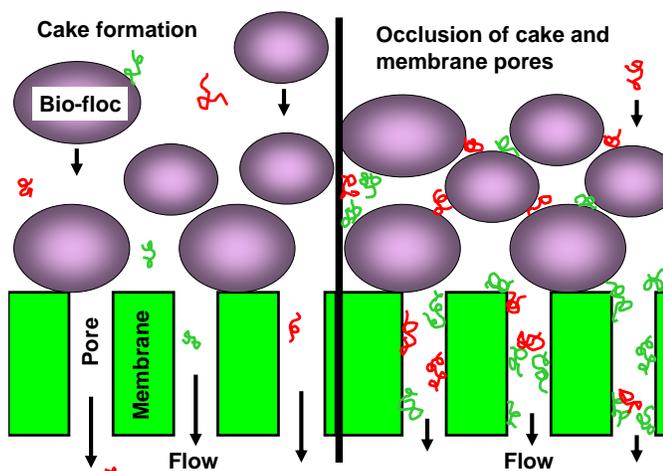
## Membrane Operational Issues

### *Clogging, fouling*

The plugging or blocking of pores, *i.e.* fouling, has been a main preoccupation of those who have considered or used membrane technologies for the treatment of various types of wastewater (Puro *et al.* 2010). Some review articles have focused on strategies to minimize or delay fouling (Le-Clech *et al.* 2006; Meng *et al.* 2009).

Studies conducted under constant applied pressure have found an initial rapid decrease in membrane flux, followed by a more gradual decrease (Le-Clech *et al.* 2006). These findings suggest an initial rapid build-up of a “cake” at the membrane surfaces, followed by more gradual changes, such as either filling in of the cake structure or gradual

occlusion of pores within the membrane itself. These features are illustrated in Fig. 15, which is based on concepts presented by Meng *et al.* (2009).



**Fig. 15.** Concepts of cake formation on membranes (left) and progressive occlusion of membranes (right) that are used for the filtration of wastewater. In this schematic illustration the green coiled lines represent colloidal organic matter having a generally hydrophobic nature; the red coiled lines represent negatively charged colloidal matter.

#### Flow strategies

Studies have shown that fouling and reduced permeability of membranes may develop more rapidly with the increase of applied pressure or flow rate (Le-Clech *et al.* 2006). In particular, particulate matter appears to get trapped at membrane surfaces when the flow rates are too high, whereas polymeric substances can accumulate onto membrane surfaces even in the absence of flow. Such results have suggested that membrane filtration operations ought to be conducted with optimized flow rates that are less than a critical flux value. Also, a two-phase “bubbly” flow has been found to minimize or slow the rate of fouling in some cases (Le-Clech *et al.* 2006). Strategies such as surface functionalization (*e.g.*, attachment of some other materials to the surface of the membranes) are increasingly under development to resist the fouling of the membranes. Electrical treatment of the membrane is another possible way to minimize fouling (Kamali *et al.* 2016).

#### Pretreatments

The fouling of membranes often can be substantially reduced by pre-treating the contaminated water upstream of the membrane units. Nuortila-Jokinen *et al.* (2004) listed the following pretreatment strategies as being promising for maintaining the flux through membranes when treating P&P mill wastewaters: chemical treatment (*i.e.* coagulation), ozonation, and biological treatment. Such strategies may prevent fine suspended matter from clogging the membrane pores or eroding the active membrane layer. However, few authors have reported favorable results regarding membrane performance after such treatments of P&P mill effluent (Li and Zhang 2011). Even Simonič and Vnuceč (2012) and Bennani *et al.* (2012), who compared the performance of coagulation and ultrafiltration systems in parallel, did not run any tests of the two approaches in sequence.

A variety of other pretreatment strategies have been employed in an attempt to minimize the fouling of membranes. For instance, Gönder *et al.* (2011) optimized the pH, temperature, applied pressures, and a volume reduction factor in order to minimize flux

reduction through a nanofiltration membrane. The pH of the treated wastewater was found to have the biggest effect, and a pH of 10 resulted in the minimum rate of loss of flux. Related work by Kallioinen *et al.* (2006) showed that although it may be possible to correlate permeability reduction to the values of adjustable variables, such relationships can be completely changed in the course of biological treatment of the wastewater. Thus, those authors were surprised to observe a case in which biological treatment failed to follow their predictions of improved membrane permeability behavior. A possible explanation is that there was flux loss due to silica deposition (Ordóñez *et al.* 2011). Kamali and Khodaparast (2015) cited various studies in which enzymatic treatments tended to improve the flux through membranes used for treating the effluent from P&P mills.

An alternative approach for the prevention of fouling and clogging of membranes is the generation and use of microbubbles, as discussed by Takahashi *et al.* (2003), Agarwal *et al.* (2012), and Yerushalmi (2014). Microbubbles are produced when gas-saturated water passes through the membranes. In this approach, the water is mixed with a gas, *e.g.* air or ozone, and will go through a de-gassing stage for the removal of non-dissolved gases before passing through the membranes. During the passage of gas-saturated water through the membranes, the transmembrane pressure gradient transforms the dissolved gases into microbubbles. The microbubbles contribute to the prevention of fouling and continuous cleaning of membranes by several mechanisms including scrubbing and self-collapse. Microbubbles benefit from a large surface area, high gas-dissolving capability, and enhanced mass transfer efficiency. In addition, they have the tendency of shrinking under water due to the surface tension and dissolution of gas in the surrounding water. According to the Young-Laplace equation (Takahashi *et al.* 2003; Agarwal *et al.* 2012), the shrinking of microbubbles leads to the progressive increase in their internal pressure until they collapse. The high pressure spot created at the final stage of microbubbles collapse produces pressure waves that will be distributed in the vicinity of a collapsing bubble and will promote the detachment of deposits from the membranes. As reported by Agarwal *et al.* (2012), microbubbling is more efficient than chemical cleaning with NaOCl solution for the removal of extracellular polymeric matrix of biofilms. Furthermore, collapsing microbubbles have been shown to generate free radicals (Takahashi *et al.* 2003; Agarwal *et al.* 2012), which react rapidly and non-selectively with the chemicals in the water and cause their rapid degradation. The strong oxidation effects of free radicals will further degrade the recalcitrant compounds and will remove them from the water.

## Bioreactor Designs Incorporating Filters

### *Membrane bioreactor concept*

A membrane bioreactor (MBR) can replace an independent settling-clarification stage with a membrane separation stage (Le-Clech *et al.* 2006). Yamamoto *et al.* (1989) were apparently the first to submerge a membrane filter assembly right within the reaction vessel where biodegradation of pollutants in wastewater was taking place. Both hollow fiber and flat sheet membrane assemblies have been used in bioreactors for wastewater treatment (Le-Clech *et al.* 2006). However, for the treatment of P&P mill effluents, polyvinylidene fluoride (PVDF) is the dominant polymer used so far (Kamali *et al.* 2016). Membrane bioreactors have become commonly used in the treatment of P&P mill effluents (Pellinen and Joyce 1990).

Figure 16 illustrates two simplified designs of MBR systems based on the textbook by Park *et al.* (2015). Figure 16A corresponds generally to the approach used by Yamamoto *et al.* (1989), which has been widely applied. Figure 16B shows a general

design that offers more active recirculation of activated sludge within the bioreactor system. According to Le-Clech *et al.* (2006) typical membrane pore sizes employed in membrane bioreactors are in the range 50 to 400 nm (corresponding to the upper end of UF up to the midrange of MF).

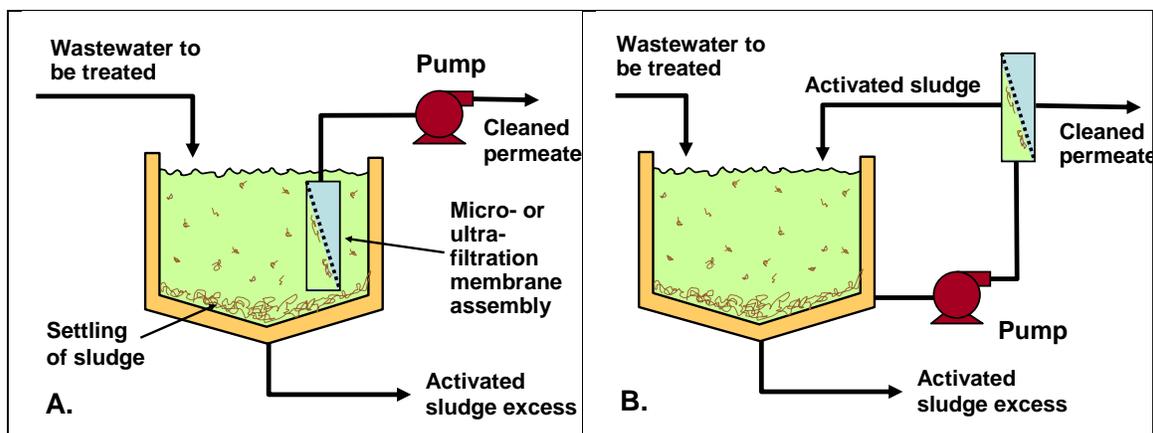


Fig. 16. Conceptual views of two types of bioreactor

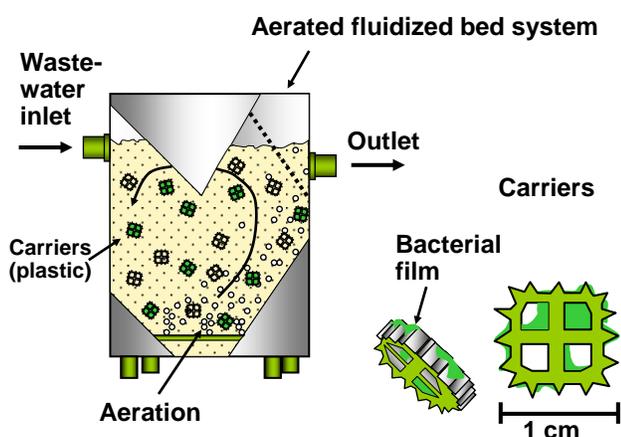
The attachment of bacterial or fungal cells to solids surfaces or sludge particles within a bioreactor appears to play an important role in enabling such a system to metabolize various organic chemicals. In other words, a bio-film composed of living cells is present within the reactor (Rusten *et al.* 1994; Lee and Welander 1996; Helble *et al.* 1999; Baig and Liechti 2001; Huuhilo *et al.* 2002; Wu *et al.* 2005; Muhamad *et al.* 2012a,b, 2013; Osman *et al.* 2013; Kamali and Khodaparast 2015). Biofilms anchored to suitable support surfaces or activated sludge within biological treatment systems allow the microorganisms to become acclimated to the wastewater and to diversify their populations in such a way as to be more capable of degrading the diverse organic compounds present in that source of wastewater. According to Kamali and Khodaparast (2015), the biofilm surfaces provide a combination of adsorption and biodegradation; thus, hard-to-degrade compounds can be removed from the water phase, and the enzymatic breakdown may take place at least partly within the immobilized biofilm. There are a number of such processes currently in operation at P&P mills (Malmqvist *et al.* 2004; Rankin *et al.* 2007). At these facilities the biofilm/activated sludge (BAS) system is used. Benefits of the system include reduced nutrient demand, less excess secondary sludge generated, and a reduced footprint for the operating equipment.

#### *Fixed bed (film) reactor*

In fixed bed systems for wastewater treatment, the bioreactor is packed with a porous material, often granulated solids (Minami *et al.* 1991; Welander *et al.* 1997; Marwaha *et al.* 1998; Helble *et al.* 1999; Baig and Liechti 2001; Tziotziou *et al.* 2005). For example, Nakamura *et al.* (1997) used polyurethane foam as the support medium for immobilization of activated sludge. Osman *et al.* (2013) studied the use of activated carbon as a support. Rajeshwari *et al.* (2000), in their review article, mention the use of polyvinyl chloride particles, ground rock, and ceramic rings as supports for biofilm in reactors used for wastewater treatment. In other wastewater applications, Apilániz *et al.* (1998) compared diatomite, sand, and activated carbon surfaces; they reported the best results with the activated carbon.

### Fluidized bed

Bioreactor designs that rely on packed bed systems often suffer from clogging or channeling problems (Maat and Habets 1987; Rusten *et al.* 1994). Such problems can be overcome by the use of fluidized bed systems in which the upward flow of wastewater and/or recirculated treated water causes support particles to remain suspended in the fluid phase (Rajeshwari *et al.* 2000; Hubbe 2007c). The flow system can be optimized to provide continual mixing of the suspended media. For instance, as suggested in Fig. 17, the circulation may be achieved as part of the aeration system. Applications of fluidized bed bioreactors have been reported for P&P effluent treatment (Haggblom and Salkinojasalonen 1991; Heinzle *et al.* 1992; Rusten *et al.* 1994). According to Maat and Habets (1987) the energy required to maintain fluidization of such systems probably accounts for why they are not more widely used.



**Fig. 17.** Schematic view of a fluidized bed system that employs plastic carriers, with agitation provided by aeration

### Upflow sludge blanket

Upflow sludge blanket systems operate similarly to the fluidized bed concept just discussed, except that no support media are used, other than the sludge itself, and the material has a tendency to form itself into a contiguous blanket rather than being continually mixed. Although mixing sounds like a great concept, from a design standpoint, the sludge blanket concept has the potential to allow different organisms to thrive in different layers of the sludge, thus achieving a better overall effect (Roest *et al.* 2005). Upflow sludge blanket reactors have been reported for the treatment of P&P mill effluent (Lettinga *et al.* 1980; Maat and Habets 1987; Kortekaas *et al.* 1998; Rajeshwari *et al.* 2000; Ahn and Forester 2002; Buzzini and Pires 2002, 2007; Roest *et al.* 2005; Bhunia and Ghangrekar 2008; Buyukkamaci and Koken 2010). Carter and Sigler (1981) describe a system in which a blanket of sludge helps to filter the effluent water from an otherwise conventional biological treatment. Rajeshwari *et al.* (2000) noted that upflow sludge blanket systems may have a relatively long start-up time due to the need for formation of a new sludge blanket after any long interruption in the operation.

### Bio-disk systems

By utilization of a slowly rotating disc it is possible to achieve a more active control of biological interactions during wastewater treatment (Apilánez *et al.* 1998). Such

systems only rarely have been reported for treating P&P industry effluents (Castillo and Vivas 1996; Hynninen 1998).

## ADVANCES IN AEROBIC TREATMENT WITH ACTIVATED SLUDGE

### Mechanism of Action

Aerobic biological treatment of wastewater is widely practiced in P&P mills (Ghem 1973; Costa *et al.* 1974; Gergov *et al.* 1988; LaPara and Alleman 1999; Schnell *et al.* 2000a; Thompson *et al.* 2001; Kostamo and Kukkonen 2003; Chakrabarti *et al.* 2008; Kamali and Khodaparast 2015). One of the main objectives of aerated biological treatment is to reduce the BOD levels of the treated wastewater. As has been noted (Ghem 1973), such treatments are typically less effective for the removal of color, which would require the breakdown of recalcitrant compounds (Graves and Joyce 1994).

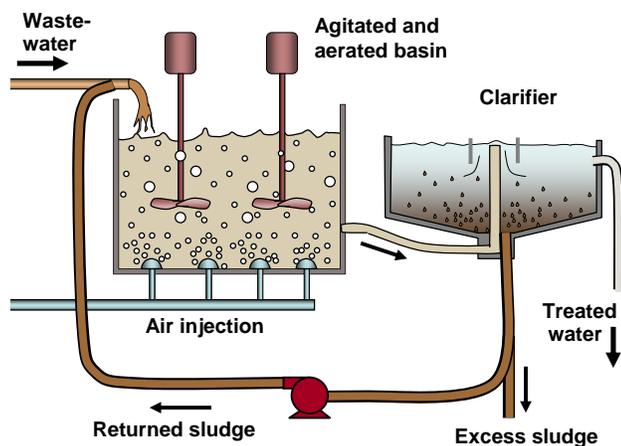
The mechanism of aerobic biological treatment of wastewater can be understood in terms of the key steps of biosorption, metabolism, and bioflocculation. Adsorption means that compounds present in the wastewater can come into contact with either the living microbes or with the enzymes that they produce. Metabolism involves a series of biochemical reactions by which microorganisms, through use of their enzymes and organelles, transform the contaminants into smaller molecules or completely mineralize them to carbon dioxide and water (Dilek *et al.* 1999; Tarlan *et al.* 2002a,b; Park *et al.* 2015). The term bioflocculation implies that the extracellular exudates from the microbes may play an important role in the agglomeration of the biological material, with the formation of settleable sludge. Avella *et al.* (2011) characterized such extracellular matter in a wastewater treatment system by means of gel permeation chromatography.

Aerobic treatment of P&P industry wastewater can be limited by the presence of inhibitory or toxic matter in the wastewater. Achoka (2002) found that the amounts of various metal ions in treatment wastewater could be increased in the process of aerated treatment. As can be seen from various published data summarized in Table A, it is common for aerated biological treatment to remove far less than 100% of BOD from effluent.

### Recirculation

The concept of returning a portion of the sludge from aerated biological treatment back to the intake of the process has been utilized for a long time (Rudolfs and Amberg 1953). Such a system is illustrated schematically in Fig. 18. The recirculation process increases the solids retention time (SRT), which plays an important role in improving the stability of operation and the overall removal efficiency of contaminants. Moreover, the return activated sludge (RAS) provides diversity in the microorganisms. The incoming effluent is continually inoculated with microbes that have become acclimatized with the prevailing conditions; thus activated sludge tends to speed up the process of biodegradation and to allow the process to proceed in a more stable manner. Also, the recirculation of microbes can allow for the development of a more optimized community of bacteria and other organisms, resulting in a system that is better able to endure the shocks inherent in changing processing conditions. It has been shown that a consortium of different organisms may provide for a more comprehensive decomposition (Chakrabarti *et al.* 2008; Chandra and Singh 2012; Ordaz- Díaz *et al.* 2014). Hynninen (1998) provides a discussion of how operators of activated sludge treatment plants can optimize their systems by

monitoring and controlling such factors as the sludge load, the sludge's dry weight per unit volume, the settling properties of the sludge, the ratio of COD to activated sludge amount, the dissolved oxygen concentration, the number of times biosludge is recirculated on average, the sludge age, and other such factors.



**Fig. 18.** Schematic illustration of an activated sludge wastewater treatment system, equipped with an aerated basin, a clarifier, and return of a portion of the settled sludge from the clarifier

### *Sludge activation treatment*

Researchers have reported that activated sludge systems can benefit from various treatments of the sludge before it is returned to an aeration basin. For example, Mahmood and Elliott (2006) describe how ozone treatment of returned sludge has the potential to render the organic compounds in it more susceptible to biodegradation; such treatment can lower the overall production of sludge from the process. Chu *et al.* (2009) provided a comprehensive review of the status of ozonation of activated sludge including its addition via the sludge recirculation line. This well proven technology can reduce the sludge yield of an activated sludge system between 45 and 100% depending on the point of application and the dosage applied. Additional benefits of ozonation of recirculated activated sludge include improved settleability and denitrification. A dosage range of 0.03 to 0.05 gO<sub>3</sub>/g TSS is suggested. Drawbacks of the technology include its high capital and operational costs. The technology has come to market and is being implemented in full-scale facilities. Praxair has patented the Lyso™ Process, which is their marketed technology.

### **Aeration**

The addition of air (or oxygen) is an essential step in the aerobic treatment of wastewater. Aeration is commonly implemented by fountains of spray or by use of diffusers to create bubbles of air in lagoons or more formally constructed wastewater containment basins. Such systems have been widely studied for the treatment of P&P industry effluents (Costa *et al.* 1974; Graves and Joyce 1994; Welander *et al.* 1997; Schnell *et al.* 2000a; Ordaz-Díaz *et al.* 2016).

According to Mahmood and Elliott (2006), a venturi system can be employed in order to more efficiently disperse air into the wastewater and to increase its dissolution rate. Garcia-Ochoa and Gomez (2009) reviewed oxygen transfer rates in bioreactors, showing the importance of flow conditions, surface areas, and other aspects of reactor design and running conditions. Based on the literature review, there appears to be a need

for more study of ways to ensure an adequate degree of aeration to avoid anaerobic conditions and to optimize the process in P&P effluent treatment.

### Temperature

Because different bacterial populations need different temperatures for optimal growth and proliferation, the adjustment of temperature can be very important relative to the results of biological treatment. Thus, Chakrabarti *et al.* (2008) cautioned that P&P mill effluent often needs to be allowed to cool down before being subjected to biological treatment. On the other hand, it can be advantageous to maintain conditions that favor the proliferation of thermophilic microbes, those that can thrive at temperature levels between 45 and 60 °C (Tripathi and Allen 1999; Suvilampi *et al.* 2001). LaPara and Alleman (1999) reported that substrate utilization rates can be three to ten times higher when using thermophilic, compared to mesophilic temperatures. Tripathi and Allen (1999) found that thermophilic conditions were more favorable for the decomposition of long-chain fatty acids, which otherwise can be hard to break down. Aerated biotreatment under thermophilic conditions has been shown to be well suited to the use of fixed bed bioreactors (Huuhiilo *et al.* 2002; Simstich *et al.* 2012).

According to Suvilampi *et al.* (2001) the P&P industry has been slow to adopt thermophilic conditions of biological treatment, perhaps due to a perception that the high temperatures will suppress the performance of activated sludge processing. Also, it has been reported that thermophilic bacteria do not aggregate readily (LaPara and Alleman 1999), which can be unfavorable in terms of sludge clarification. However, it has been shown that the sludge from a mesophilic process can be relatively rapidly re-acclimated to thermophilic conditions, leading to efficiencies that are at least as high as those achieved under mesophilic conditions (Suvilampi *et al.* 2001).

### Retention Time

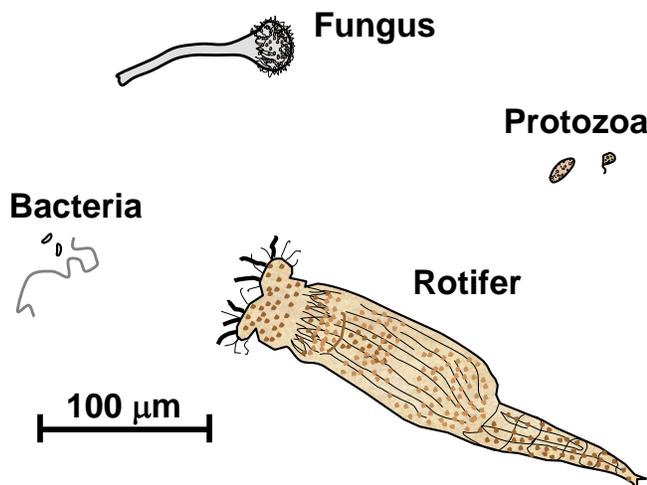
The residence time of bacterial matter in a reactor is clearly a key variable. Time is required for such processes as cell division, enzyme production, and metabolism. The following studies have considered the effects of the retention time of solids on the outcome of treating P&P mill wastewaters (Diez *et al.* 2002; Pougatch *et al.* 2007). By extending the aeration time, a greater degree of biodegradation can be achieved (Buyukkamaci and Koken 2010). Extending the time of aeration also can be expected to reduce the final amount of sludge produced, which can be attributed to a greater completion of the metabolic processes (Mahmood and Elliot 2006). The same authors noted that a longer aeration time also promotes the development of a broader range of organisms, including protozoa and rotifers, which consume the bacterial matter in the sludge.

Figure 19 compares the relative sizes of some typical organisms involved with biodegradation. Ordaz-Díaz *et al.* (2016) studied the acclimation of bacterial populations during long-term treatment in an aerated lagoon. Such populations were found to adapt to changes in aeration and other operating parameters.

### Operational Issues of Aerobic Stages

#### *Filamentous bacteria*

Various practical issues confront the operators of aerated wastewater treatment systems. Depending on the design and operational conditions in a wastewater treatment plant, the bacterial culture may develop either as singly dispersed, attached, or filamentous forms.



**Fig. 19.** Relative sizes of typical kinds of organisms involved in the biodegradation of pulp and paper mill effluents

Filamentous bacteria can be regarded as an integral component within a biological waste treatment system (Richard 2003). From a qualitative perspective, it is desirable to maintain a controlled balance of filamentous bacteria within a biological system. Operational issues become apparent when proportional amounts of filamentous bacteria are either too great, or deficient. A lack thereof can create issues with turbidity in effluent streams (Sezgin *et al.* 1978) due to less desirable ‘pin-floc’ formations. At increased proportions within the biomass, filamentous bacteria give rise to what is known as bulking sludge. This type of unfavorable sludge condition decreases settling velocities and reduces compaction of sludge in sedimentation tanks (Thompson *et al.* 2001), though such effects can be at least partly addressed by the use of coagulants (Agridiotis *et al.* 2007). Factors that contribute to the occurrence of bulking sludge development can be linked to poor aeration, extended periods of lower food/mass ratios (Cingolani *et al.* 1994), as well as deficient nutrient concentrations of nitrogen and phosphorous (Richard and Cummins 1997). In a multi-site microbial survey, research found the development of *Thiorix* bacteria to be the most predominant form of filamentous existing in bulk settling circumstances (Bergeron and Pelletier 2004). This operational concern is warranted by the elevated risk of increased COD in final effluent streams (Wanner 1994), or potential loss in treatment capacity due to reductions in recirculation volumes (Thompson *et al.* 2001).

### *pH*

Favorable pH conditions are critical to the optimization of a successful secondary wastewater treatment system. Typically, a permit requirement holds operations accountable to specific pH conditions in both pre- and post-treatment of wastewater. In aerobic systems, pH adjustments are made in order to reach maximal process efficiency. This is due, in part, to the adaptive preference of floc-forming species of bacteria and their ability to flourish in these conditions. Ghanizadeh and Sarrafpour (2001) demonstrated that enhanced settling can be brought forth by increases in pH from 5 to 9 in sludge treatment systems. Alkalinity also serves as a buffer to resist abrupt swings in pH, therefore allowing for a greater degree of process stability with regards to influent and effluent pH.

## Bio-augmentation

The term bio-augmentation refers to the addition of selected populations of viable bacterial, algal, or fungal cells to enhance the performance of biological processes. Various researchers have reported improvements in biological treatment owing to the addition of selected bacterial cultures (Chandra and Singh 2012; Chen *et al.* 2012; Garg *et al.* 2012; Hossain and Ismail 2015). For instance, Garg *et al.* (2012) showed that dechlorination and detoxification of bleach plant effluent components could be enhanced by the addition of *Pseudomonas putida*, which is a Gram-negative bacterium. Matafonova *et al.* (2006) isolated and cultured a bacterium from an aeration pond at a P&P mill and demonstrated that the pure strain was effective for the degradation of 2,4-dichlorophenol, which may serve as a model compound for pulp bleaching effluents. Tiku *et al.* (2010) found favorable results with three kinds of bacteria for the reduction of BOD, toxicity, color, and related factors of pulp mill wastewaters.

Others researchers showed favorable results when using mixed cultures of bacteria (Chakrabarti *et al.* 2008; Chandra and Singh 2012; Ordaz-Díaz *et al.* 2014). The consortia of bacteria present in a properly operating wastewater treatment plant may be accompanied by protozoa, fungi, and rotifers (Chakrabarti *et al.* 2008). Such a combination can be expected to allow the system to deal effectively with a wide variety of pollutants, which are likely to shift from hour to hour.

Various authors have found favorable effects when using white-rot fungal species to treat pulp mill wastewater and bleach plant effluents (Eriksson and Kolar 1985; Pellinen and Joyce 1990; Duran *et al.* 1994; Gökçay and Dilek 1994; Wolfaardt 1994; Marwaha *et al.* 1998; Saxena and Gupta 1998; Taseli and Gökçay 1999; Sakurai *et al.* 2001; Pokhrel and Viraraghavan 2004; Thakur 2004; Wu *et al.* 2005; Malaviya and Rathore 2007; Freitas *et al.* 2009; Singhal and Thakur 2009; Garg and Tripathi 2011; Kakahi *et al.* 2011; Liu *et al.* 2011; Souza *et al.* 2014; Hossain and Ismail 2015; Kamali and Khodaparast 2015). Eriksson and Kolar (1985) observed much more favorable effects from the addition of a white-rot fungal strain, in comparison to two bacterial mixtures; the fungus promoted more rapid degradation of chlorolignins. Thakur (2004) evaluated eight fungal species and three bacterial isolates and found all of them capable of degrading absorbable organic halides (AOX) in P&P mill effluent. Kakahi *et al.* (2011) reviewed the use of fungal treatments to augment wastewater treatment in the P&P industry and noted that fungal treatment has been effective for color removal. The strong enhancements in biodegradation, decolorization, and removal of toxicity observed generally in the studies cited above are consistent with the role of white-rot fungi in degrading the lignin component of wood by the release of specialized enzymes such as laccase and peroxidases (Duran *et al.* 1994; Freitas *et al.* 2009; Souza *et al.* 2014).

Algae can be defined as a diverse primitive group of eukaryotes that receive energy by photosynthesis. Since many wastewater treatment operations are exposed to sunlight, the use of algal treatment has been considered for wastewater from P&P mills. A number of researchers have shown encouraging results for such treatment (Dilek *et al.* 1999; Tarlan *et al.* 2002a,b; Hossain and Ismail 2015). Dilek *et al.* (1999) demonstrated that color removal was mainly a result of metabolism, rather than biosorption. On the other hand, Tarlan *et al.* (2002a) found that decolorization of P&P mill effluent was attributable to a combination of metabolism and conversion of chromophoric compounds to colorless compounds.

Mahmood and Elliott (2006) consider that bioaugmentation is a promising approach for the reduction of sludge amounts resulting from aerobic treatment of

wastewaters. Presumably, some of these favorable results can be attributed to the release of enzymes capable of breaking down some of the hard-to-biodegrade and possibly toxic organic compounds present in the wastewater (Chandra and Singh 2012; Chen *et al.* 2012).

### Nutrient Supplementation

Because biodegradation is dependent on life processes, certain nutrients are required to be present (Simstich *et al.* 2012). Depending on the inputs to a pulp and paper process, from which the wastewater is derived, it may be necessary to supply some macro- (mainly phosphorous) and micronutrients to properly operate biological treatment systems. Nutrient limitations can hinder effective waste treatment within biological systems. This may be countered by the addition or reduction of nitrogen and phosphorous to the system, yet issues can arise if supplementation is not managed correctly (Cingolani *et al.* 1994). Similar to the necessary presence and operational control of filamentous bacteria, a homeostatic balance is needed for nutrient supplementation. Insufficient nutrient addition can promote performance decline in the treatment. This is indicative in the decline of metabolic function, which can be symptomatic of increased dissolved oxygen concentrations in aerobic monitoring systems. Just as nutrient deficiency can be troublesome to operations, a nutrient surplus can also be unfavorable. Nutrient overabundance can create issues such as excessive foam, secondary scum, increased BOD and TSS load within the outgoing effluent, and the potential for eutrophication (Ekholm *et al.* 2007; Kenny 2010). The optimization of nutrient addition not only serves as effective quality control; it also offers the important benefit of operational cost reduction. Thus, Wu *et al.* (2005) found benefits of treating the system with ammonium tartrate. Likewise, Garg *et al.* (2012) found that supplementation of the wastewater with yeast extract, a source of nitrogen, promoted microbial decolorization of P&P mill wastewater.

The addition of glucose, used as an alternative energy source by microorganisms, has been shown to increase the rate and extent of biodegradation (Gökçay and Dilek 1994; Wu *et al.* 2005; Garg *et al.* 2012). However, such treatment may not always be advantageous in terms of the overall results of treatment. According to Mahmood and Elliott (2006) it can be advantageous to keep the nutrient level low. Such an approach can favor the production of polysaccharide-producing bacteria, which then can be consumed by higher level organisms, leading to less final sludge in specially designed treatment systems.

### Enzyme Treatment

The specific enzymes responsible for observed degradation of pollutants have been isolated or identified in some studies (Owens 1991; Duran *et al.* 1994; Freitas *et al.* 2009; Chandra and Singh 2012; Chen *et al.* 2012; Souza *et al.* 2014). It has been shown that direct addition of those enzymes to P&P mill effluent can facilitate the degradation of lignin species (Hakulinen 1988; Wagner and Nicell 2001; Fernandez-Fernandez *et al.* 2013; Hossain and Ismail 2015; Kurnik *et al.* 2015). Ko and Fan (2010) showed the feasibility of a two-step process in which laccase enzyme was used to polymerize lignin-based compounds and then the mixture was separated using membranes with a range of different pores sizes.

#### *Immobilization*

The use of pure enzymes in the treatment of wastewaters requires their extraction and purification. The costs of such extraction and purification often prohibits the use of

isolated enzymes in full-scale applications. Hence, it is generally preferred to use bacterial or fungal cells to grow and to release the enzymes *in situ*. One possible motivation for isolation and use of pure enzymes might be related to the possibility of immobilization (Duran and Esposito 2000). As noted by Fernandez-Fernandez *et al.* (2013), immobilization of enzymes can improve their storage stability and prolong their effectiveness during wastewater treatment. On the other hand, it is also possible to immobilize the fungal organisms on a suitable support and generate the needed enzymes *in-situ* (Marwaha *et al.* 1998; Taseli and Gökçay 1999; Wesenberg *et al.* 2003; Wu *et al.* 2005; Malaviya and Rathore 2007). Given the relatively low number of studies in this area, further work of this type seems warranted.

### Aerobic Bioreactors

The use of bioreactor equipment, including MBRs, may be justified for aerobic treatment of P&P mill effluents for various reasons, such as avoiding the space and capital expense of building conventional settling basins or clarifier equipment or making it possible to process wastewater in a smaller space (Kamali and Khodaparast 2015). The feasibility of such systems has been evaluated, with generally favorable results reported (Helbe *et al.* 1999; Taseli and Gökçay 1999; Magnus *et al.* 2000; Tziotziou *et al.* 2005; Muhamad *et al.* 2012a,b, 2013; Mahmood-Khan and Hall 2013).

#### *Aerobic trickling filter*

In an effort to enhance the performance and stability of bioreactors for the treatment of P&P mill wastewaters, various authors have introduced solid support media onto which bacterial or fungal cells can attach themselves (Hagglom and Salkinojasalonen 1991; Wang *et al.* 2008b; Muhamad *et al.* 2012a,b, 2013). Hagglom and Salkinojasalonen (1991) demonstrated the effectiveness of a “trickling filter” for degradation of chlorinated organic compounds from kraft pulp bleaching. Taseli and Gökçay (1999) showed that a system with packed glass wool could be used for over a year in the treatment of pulp mill effluents. Huuhilo *et al.* (2002) demonstrated the effectiveness of a “suspended carrier” concept for internal treatment of P&P mill wastewaters, which were then returned to the mill process streams. Rusten *et al.* (1994) employed freely-suspended plastic elements that provided surfaces for biofilms to form, while the system was kept well mixed in an agitated tank. Wang *et al.* (2008b) employed clay beds in a packed column “biofilter” system for evaluation of the effect of ozonation on subsequent biodegradation. Muhamad *et al.* (2012a,b, 2013) and Osman *et al.* (2013) evaluated systems in which granulated activated carbon was used as the support medium.

Noting that a solid support can enhance biodegradation, various authors have employed the activated sludge itself as a kind of bio-filter for treatment of P&P mill wastewater (Tziotziou *et al.* 2005; Souza *et al.* 2014). Tziotziou *et al.* (2005) found that a packed bed system with gravel was more tolerant of high phenol concentrations and achieved higher removal rates in comparison to a stirred, aerated reactor without packing materials.

Although the use of support material for the formation of biofilms mainly has been implemented in compact bioreactor installations and lab-scale studies, Welander *et al.* (1997) showed that a similar approach can be applied in an aerated lagoon. The use of support materials encourages the establishment of biofilms. Much better results, using the support materials, were obtained in a pilot-scale implementation, in comparison to parallel

evaluations in an industrial-scale wastewater treatment plant, indicating that further study may be needed.

The use of a rotating solid support medium within a biodegradation vat reactor was reported by Pellinen and Joyce (1990), Rovel *et al.* (1994), and Hynninen (1998). According to Pellinen and Joyce (1990) such a system appeared to provide inadequate contact time, and the system needed to be cleaned out every three to four weeks when treating concentrated effluent from P&P mills.

#### *Aerobic membrane reactor*

As was discussed earlier, the incorporation of a membrane into the equipment design, immersed into or following the biological treatment stage, makes it possible to remove purified water from the mixture while concentrating the sludge and permitting adequate residence time of the decomposing biomaterials within a relatively small space (Smith *et al.* 1969; Gander *et al.* 2000). Such designs have been evaluated for treatment of P&P mill wastes (Helbe *et al.* 1999; Tenno and Paulapuro 1999; Magnus *et al.* 2000; Huuhilo *et al.* 2002; Mahmood and Elliott 2006; Zhang *et al.* 2009; Qu *et al.* 2012; Simstich *et al.* 2012; Mahmood-Khan and Hall 2013). Tenno and Paulapuro (1999) developed a mathematical model for their bioreactor and showed that the throughput could be increased by increasing the solids level. Qu *et al.* (2012) reported that cake formation on the membrane surfaces was the primary mode of membrane fouling during the aerobic treatment of P&P mill wastewater.

#### *Staged biological treatment*

Because attached-growth bioreactors are designed to occupy considerably less space than a conventional wastewater treatment operation of similar capacity, it sometimes can make sense to think about using two or more stages of treatment sequentially. Thakur (2004), who studied biodegradation by immobilized bacterial or fungal cells in packed columns, found superior results when the wastewater was passed sequentially through two columns. Mahmood and Elliott (2006), in their review article, noted that sequential treatment often results in less sludge production in comparison with a conventional aerated wastewater treatment operation.

Several authors have noted that the inclusion of higher-level organisms such as protozoa and rotifers, along with the bacterial and fungal cells in a biological treatment operation, will reduce the amount of final generated sludge (Lee and Welander 1996; Chakrabarti *et al.* 2008). Provision of a second stage of treatment, where the sludge is at a later stage of maturity, has been found to favor the action of predator species that feed upon the bacterial material in the sludge (Lee and Welander 1996; Mahmood and Elliott 2006). It is also likely that different trophic levels of organisms may inhabit the suspended sludge growth *vs.* the attached growth in the same reactor system (Mahmood and Elliott 2006). The process is termed the low sludge production (LSP) process.

### **Sludge Post-treatment**

Before leaving the subject of aerated biological wastewater treatment, it is important to note a key area of developing technologies related to post-treatment of biological sludge (Pere *et al.* 1993; Mahmood and Elliott 2006). Key concerns are to minimize the amount of sludge and to increase its solids content, thus reducing the cost and various problems associated with its transportation and disposal. Thus, Pere *et al.* (1993) showed that the amount of sludge could be reduced by oxidative conditioning

(Fenton's reagent), which facilitated dewatering in a filter press. Pervaiz and Sain (2011) employed a different approach and used sludge from a paper mill wastewater treatment plant as a source of proteins, which were successfully demonstrated as a potential wood adhesive. In many countries such biological sludge can be used in agriculture. In recovered paper mills, sludge from biological treatment stages can be combined with deinking sludge and treated by gravity tables and presses (Hermosilla *et al.* 2010). This dried sludge can be revalorized, for example within the ceramic and cement industries.

A bottleneck of many aerobic treatment systems involves the time, effort, and expense of dewatering biological sludge. The conventional method is to combine the difficult-to-dewater biological sludge with the relatively easy to dewater primary sludge. Specifically designed polymers are then added and mixed with the combined sludge, and the mixture is thickened prior to pressing using either a centrifuge, a belt press, or a screw press. An in-depth review of the dewatering practices can be found in the work of Dorica *et al.* (1999). Up 50% of the operating costs of a wastewater treatment system can be associated with sludge management (Mahmood and Elliott 2007). As much as 70% of the cost can be attributed to the demand for dewatering chemicals. Mahmood and Elliott (2007) provided a novel method for reducing the demand for expensive dewatering chemicals by applying a low-cost acid to the secondary sludge prior to dewatering.

## ADVANCES IN ANAEROBIC TREATMENT

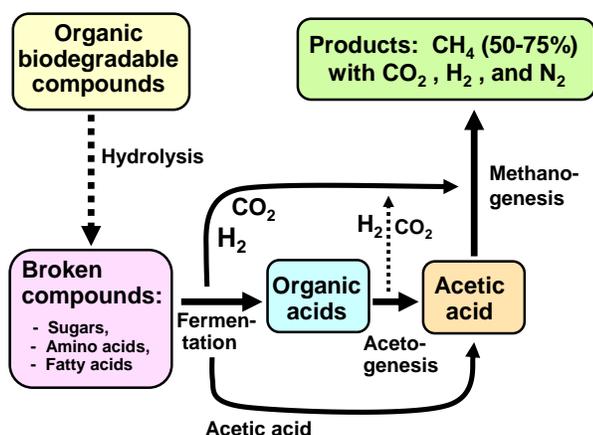
The term anaerobic implies a process of biodegradation in which no air or oxygen is supplied. The ensuing biological processes are analogous to fermentation. Rajeshwari *et al.* (2000) provided a general review of anaerobic digestion as a stage in wastewater treatment operations. Also there have been review articles devoted to the treatment of P&P mill effluents using anaerobic conditions (Graves and Joyce 1994; Rintala and Puhakka 1994; Savant *et al.* 2006; Meyer and Edwards 2014; Kamali and Khodaparast 2015). Many other authors have reported evaluations of factors affecting the anaerobic treatment of P&P mill wastewaters (Sierraalvarez *et al.* 1991; Korczak *et al.* 1991; Vidal *et al.* 1997; Kortekaas *et al.* 1998; Bengtsson *et al.* 2008a; Ruas *et al.* 2012; Krishna *et al.* 2014; Larsson *et al.* 2015).

A plus side of anaerobic treatment is that one does not need to pay for the pumping of air into the system (Maat and Habets 1987), and, according to many reports, the amounts of sludge produced are generally less than in conventional aerated biological treatment systems (Ashrafi *et al.* 2015; Kamali and Khodaparast 2015). Anaerobic processes produce gases such as methane, requiring their collection and safe disposal. Nevertheless, the retrieving and reuse of biogases such as methane and hydrogen as a source of energy during full-scale treatment operations can provide substantial economic benefits to the treatment plants. Such methane and hydrogen either can be sold or they can be burnt for the generation of heat (Tabatabaei *et al.* 2010).

### Principles of Anaerobic Treatment

In chemical terms, the process of anaerobic digestion in a typical wastewater treatment operation can be broken down into the steps of hydrolysis, acid formation, acetogenesis (with the production of hydrogen and carbon dioxide), and methanogenesis (Maat and Habets 1987; Kamali *et al.* 2016). These terms are diagrammed as a process schematic in Fig. 20. Due to the value of methane as a fuel, and perhaps also the

importance of avoiding its release into the atmosphere (Weiland 2010), much research has been devoted to its generation during anaerobic treatment of P&P mill wastewater (Maat and Habets 1987; Korczak *et al.* 1991; Minami *et al.* 1991; Sierraalvarez *et al.* 1991; Vidal *et al.* 1997; Kortekaas *et al.* 1998; Ahn and Forster 2002; Buzzini and Pires 2007; Yilmaz *et al.* 2008; Tabatabaei *et al.* 2010; Lin *et al.* 2011; Saha *et al.* 2011; Elliott and Mahmood 2012; Bayr *et al.* 2013; Ekstrand *et al.* 2013; Hagelqvist 2013; Hassan *et al.* 2014; Meyer and Edwards 2014; Larsson *et al.* 2015).



**Fig. 20.** Schematic diagram of main chemical and metabolic steps involved in the anaerobic decomposition of biodegradable organic compounds

#### Other byproducts

In addition to fuel-type products such as methane, some researchers have explored the feasibility of generating more complex and potentially more valuable byproducts (Laycock *et al.* 2014). For instance, Bengtsson *et al.* (2008a,b) isolated polyhydroxyalkanoates (PHA), which were attributed to the biotransformation of fatty acids in P&P mill effluents. Acetate, propionate, and butyrate compounds also were obtained in that study.

Bioethanol production from cellulosic materials has been widely studied (Alvira *et al.* 2010). Because the cellulosic material in the wastewater from a P&P facility may already have been delignified and otherwise broken down, such wastewater has been considered as a raw material source for ethanol production (Lin *et al.* 2012; Liu and Shonnard 2014). Two inherent problems that would need to be faced, to make such production viable, involve the expected variability of the effluent water to be treated and the relatively dilute nature of cellulosic matter in typical wastewater.

#### Sulfur reducing bacteria

An inherent problem associated with anaerobic processes is the likelihood of reducing sulfate ions to other compounds such as sulfides or  $\text{H}_2\text{S}$  (Lens 1998; Janssen *et al.* 2009). Such compounds are generated through the action of sulfate-reducing bacteria (Roest *et al.* 2005; Janssen *et al.* 2009). The reduced sulfur compounds can interfere with the generation of methane (Minami *et al.* 1991).  $\text{H}_2\text{S}$  is regarded as the most toxic form of the sulfide species towards microbial communities responsible for the production of methane. In addition, the concrete corrosion in full-scale reactors is another drawback of the activity of the sulfate reducing bacteria (Barton and Fauque 2009). One practical way

to deal with the problem is to process the water or sludge through further aerated stages of treatment (Lens 1998; Janssen *et al.* 2009). Combination treatments aimed at the removal of sulfur-containing compounds from the system will be considered later in this article.

## Operating Conditions of Anaerobic Treatment

### *Temperature*

The temperature of the mixture has a big influence on anaerobic treatment. In particular, various studies have shown the potential for higher rates of biodegradation at higher temperatures, favoring the growth and activity of thermophilic rather than mesophilic organisms (Ahn and Forster 2002; Tartakovsky *et al.* 2003; Yilmaz *et al.* 2008). Tartakovsky *et al.* (2003) found that thermophilic conditions were more effective in the breakdown of lignin-related compounds in the mixture. Yilmaz *et al.* (2008) found more effective removal of the soluble components of biological oxygen demand while operating an anaerobic system in the higher temperature range. Ahn and Forster (2002) found that lowering of the biological oxygen demand took place progressively under thermophilic conditions, whereas lower temperature treatment did not show any reduction in oxygen demand with increasing hydraulic retention time. Jeison *et al.* (2008) showed that thermophilic anaerobic reactors may treat higher contents of organic substances than mesophilic ones. Moreover, reactors working in the thermophilic range managed to work at higher volumetric loading rates than AnMBRs operating within the mesophilic range. Saha *et al.* (2011) found that when thermophilic conditions were employed during anaerobic treatment, there was little benefit of pretreating the sludge by any of the methods that they considered.

### *Supplementation*

The term “supplementation” will be used here to mean that something is being added to wastewater before subjecting it to anaerobic treatment. Savant *et al.* (2006) reviewed the action of specific micro-organisms in the degradation of absorbable organic halides, which are a product of the bleaching of kraft pulps. The cited authors make the point that such micro-organisms need nutrients to be in certain ranges in order to thrive and be effective in breaking down the organic matter.

Deshmukh *et al.* (2009) found that the addition of glucose or acetate before anaerobic treatment of P&P mill wastewater has potential to promote the breakdown of absorbable organic halides (AOXs). The observed effects were attributed to the additives serving as electron donors in an enzymatic process.

Because anaerobic digestion is a biological process, it is critical that the mixture contains a sufficient level of biologically available nitrogen. Kamali and Khodaparast (2015) in their review emphasized the importance of this variable and the need to optimize the ratio of nitrogen to carbon in anaerobic treatment of P&P mill effluents. However, there appears to be a lack of published research in this area.

Meyer and Edwards (2014) recommended co-digestion of different wastewater streams from paper mills as a way to avoid disruptions and to diminish toxic effects. Co-digestion also can be considered for the further treatment of sludge generated from the treatment of P&P mill wastewaters. Such an approach can achieve a favorable balance between nitrogen and carbon, as required for biological growth. Hagelqvist (2013) co-digested secondary sludge from a P&P mill together with municipal sludge. The forest-industry sludge was able to replace up to 50% of the municipal sludge while maintaining the same level of methane production. Lin *et al.* (2011, 2012) co-digested P&P sludge

with monosodium glutamate (MSG) waste liquor. A high efficiency of methane generation was observed.

### Reactor Systems for Anaerobic Treatment

Anaerobic baffled reactors, anaerobic filters, upflow anaerobic sludge bed reactors, and anaerobic membrane bioreactors are the main anaerobic reactors applied so far for the treatment of P&P mill wastewaters (Kamali *et al.* 2016). The main idea for the development of such high-rate reactors has been to decrease the hydraulic retention time, making it possible to treat higher amounts of wastewater in a given time.

As in the case of aerobic systems, a variety of reactor designs have been considered in efforts to promote anaerobic biodegradation and to reduce the footprint of the treatment plant. One of the underlying principles is to enhance the convective contact between water and films of biomass. For instance, Minami *et al.* (1991) employed a fixed bed of pumice stone so that the wastewater would pass over the surfaces of adsorbed biofilms under anaerobic conditions.

Jackson-Moss *et al.* (1992) employed activated carbon as a substrate for a bioreactor for bleach plant effluent and anaerobic conditions. Rajeshwari *et al.* (2000), in their review article, mention the use of activated carbon, polyvinyl chloride, crushed rock, and ceramic rings as packing materials that can be used for microbial immobilization during anaerobic treatment of wastewater. In addition to the formation of biofilm on the support medium, sludge aggregates become trapped between the packing elements of such systems, which may be beneficial to the overall process. Ruas *et al.* (2012) employed an immobilized biomass system for pretreatment of bleached kraft mill wastewater before an advanced oxidation system. Zain *et al.* (2013) and Hassan *et al.* (2014) employed a baffled reactor in which the wastewater was forced to flow up and down repeatedly as it passed through the system.

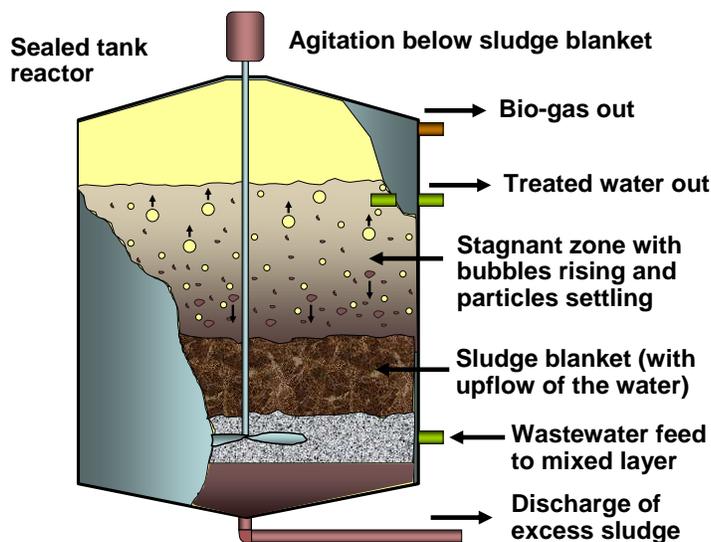
#### *Anaerobic upflow filters*

Upflow filter systems have been reported for anaerobic treatment of P&P mill wastewaters (Ahn and Forster 2002; Deshmukh *et al.* 2009). For instance, Deshmukh *et al.* (2009) employed a column in which the effluent was slowly pumped up through a column filled with plastic pall rings (38 mm x 38 mm) of skeletal form. The main disadvantage of systems using attached biomass growth appears to be an increased occasion for clogging (Maat and Habets 1987). Additional measures may be required to minimize clogging, thus increasing the cost of the treatment process.

As was mentioned earlier in the context of aerobic treatment, a blanket of sludge in principle can serve as a support medium for microbial immobilization. Such an arrangement is illustrated in Fig. 21. In such systems the wastewater to be treated is introduced below a layer of sludge and allowed to percolate up through that layer (Maat and Habets 1987; Hynninen 1998). The flow velocity can be as high as 2 to 3 m/h in some high velocity upflow systems (Rajeshwari *et al.* 2000).

Under anaerobic conditions, where the production of sludge is expected to be less (Ashrafi *et al.* 2015; Kamali and Khodaparast 2015), the same approach nevertheless has been evaluated (Lettinga *et al.* 1980; Habets and Knelissen 1985; Maat and Habets 1987; Rajeshwari *et al.* 2000; Buzzini and Pires 2002; Roest *et al.* 2005; Bhunia and Ghangrekar 2008; Buyukkamaci and Koken 2010; Sheldon *et al.* 2012). For instance, Bhunia and Ghangrekar (2008) found that such a system could be optimized by controlling the organic loading rate (OLR) to the system and by inoculating the system with thick sludge. Buzzini

and Pires (2002) reported stable operation of an anaerobic reactor, with low maintenance and operational costs. Later work by the same group showed advantages of recirculating some of the sludge from treatment of P&P mill wastewater (Buzzini and Pires 2007).



**Fig. 21.** Schematic of an anaerobic wastewater treatment with a sealed reactor, agitation at the level where wastewater is fed to the system, an upflow sludge blanket, and a stagnant liquid zone in which sludge particles settle and the generated bio-gas rises to the gaseous headspace

#### *Anaerobic fluidized bed*

Fluidized bed systems operating under anaerobic conditions have been used for wastewater treatment. The support media in such systems, if present, are sized such that they can be suspended by agitation and the rising of pumped wastewater that is being treated. The bed is generally composed of granular anaerobic sludge. Rajeshwari (2002) pointed out that the firm attachment of the biological matter to the support surfaces also can be critical to the operation. Various researchers have evaluated such systems for the treatment of P&P mill wastewaters (Hagglblom and Salkinojasalonen 1991; Rusten *et al.* 1994; Huang *et al.* 2015). Huang *et al.* (2015) fluidized the sludge particles themselves as a relatively uniform mixture.

Unlike aerobic systems, in which aeration serves as a means to mix the liquid by the rise of bubbles, anaerobic systems use mechanical agitation, *e.g.* an impeller, to provide adequate mixing of liquid. Rusten *et al.* (1994) considered using such a system for P&P industry wastewaters. Maat and Habets (1987) criticized such systems as having relatively large energy demands to maintain fluidized conditions.

#### *Anaerobic membrane bioreactor*

Several researchers have evaluated the use of membrane bioreactors operating under anaerobic conditions in which ultrafiltration or nanofiltration is used to extract clarified water, while pollutants are concentrated in the sludge, which is digested under anaerobic conditions (Liao *et al.* 2006; Skouteris *et al.* 2012; Lin *et al.* 2013; Ashrafi *et al.* 2015). However, a search of the literature did not reveal publications of such equipment being used for anaerobic treatment of P&P industry wastes. This could be due to the

relatively low accumulation of sludge often observed under anaerobic conditions. Alternatively, this could be due to the efficient results achieved by other anaerobic reactors in the pulp and paper industry, such as UASB and EGSB (Ordóñez *et al.* 2010), which do not need the use of energy for the separation of the sludge.

### **Pretreatments of Sludge before Anaerobic Digestion**

The pre-treatment of sludge, generated during the treatment of pulp-and-paper wastewaters, has often been applied in an effort to increase the efficiency of subsequent digestion process (Saha *et al.* 2011; Elliott and Mahmood 2012; Bayr *et al.* 2013; Meyer and Edwards 2014). The anaerobic digestion of sludge is discussed by the following authors (Mahmood and Elliott 2006; Elliott and Mahmood 2012; Hagelqvist 2013; Kaluža *et al.* 2014; Meyer and Edwards 2014). The rupturing of P&P secondary sludge by a rapid release in pressure was found to be an effective method to render the sludge more amendable for subsequent anaerobic treatment (Stephenson *et al.* 2007). A drawback of many of these systems is the energy costs of operation.

Ultrasonic treatment of secondary sludge was considered by Saha *et al.* (2011) and Bayr *et al.* (2013). Saha *et al.* (2011) found ultrasonication to be effective for dispersing the sludge and breaking down the solids. However, the quantity of soluble compounds that resisted subsequent anaerobic treatment actually increased. Bayr *et al.* (2013) observed only a minor increase in methane yield during subsequent anaerobic treatment following ultrasonication. The ultrasonic treatment is generally expected to disrupt biological cells in the sludge by lysis, which might have enabled more effective degradation. Shaw and Lee (2008) showed that ultrasonication was able to decrease the color and turbidity of final effluent from a kraft pulp and paper mill.

Hydrothermal treatment, consisting of either 70 °C heating for 40 min or 150 °C heating for 10 min, was evaluated by Bayr *et al.* (2013). The higher temperature pretreatment was found to be among the most effective strategies that they considered. The amount of sludge was reduced and methane yield was increased. Enzymatic treatment with a cellulose-decomposing cocktail was found to be effective, especially in combination with the hydrothermal treatment (Bayr *et al.* 2013).

Saha *et al.* (2011) found microwave pretreatment to be effective for secondary sludge from a pulp mill, enabling more effective action of an anaerobic treatment stage. Specific methane yields were increased by 90% compared to controls. Ozone has also been tested for the pre-treatment of sludge, increasing its biodegradation rate (Mahmood and Elliott 2006).

One of the systems considered by the Japan Sewage Works Agency for sludge reduction involves the ozonation of return sludge before it enters the aeration basin solubilizing bacterial cells (Murakami 1998). Chu *et al.* (1999) reported a process called BIOLEADER, which uses these principles, and it was applied to pulp and paper wastewater treatment systems. Degremont Inc. has also developed a process called the Biolysis, which has been shown to reduce sludge yield by as much as the 80% (Rewcastle *et al.* 2004).

Considering that both sonochemical treatment and microwave irradiation have the potential to provide a considerable output energy to the system, for instance through the phenomenon of ultrasonic cavitation in the case of ultrasonic irradiation, more studies are required to identify the optimum conditions for such methods and to maximize their efficiency when used for the (pre-) treatment of pulp and paper mill sludge.

## COMBINATION TREATMENTS

### Sequences that Make Sense

With the goal of achieving more efficient and more comprehensive treatment of P&P mill effluents in the coming years, one of the most effective approaches can be expected to be the combining of more than one treatment stage, taking advantage of positive features of each step. As noted by Kamali and Khodaparast (2015), such approaches have the potential to achieve better overall environmental benefits and/or lower overall costs of operation. Mauchauffee *et al.* (2012) reviewed such approaches relative to treatment of effluents from a broad range of industries.

The selection of appropriate treatment processes and the sequence of operation is a challenging issue that confronts the engineers during the design of future wastewater treatment systems. Ordóñez *et al.* (2010) investigated a sequence involving gravity-based clarification, anaerobic biological treatment, aerobic biological treatment, ultrafiltration, and finally reverse osmosis. Such a sequence makes sense because the gravity-based clarification removes a lot of solids at low cost, avoiding the need to subject the removed solid matter to further stages of treatment. The anaerobic stage can be justified because it reduces the amount of BOD, without generating a lot of sludge byproduct. The follow-up aerobic treatment will degrade the byproducts of anaerobic treatment and will further decrease the BOD and undesirable byproducts of anaerobic treatment, such as sulfides and the final treatment of organic matter. The ultrafiltration ensures that there is no significant carry-over of biological cells from the biotreatment stages, while avoiding the cost of building a clarifier to begin the thickening process of the final sludge, ensuring adequate water quality for reverse osmosis. And finally, the reverse osmosis stage can be regarded as an option in cases where a high purity, desalinated water might be required for a specific usage. Such options will be considered in somewhat more detail in the subsections that follow.

### Coagulation Followed by Other Processes

#### *Coagulant followed by flocculant*

As was noted earlier in this article, the settling of solids during gravity-based clarification can be enhanced by the addition of highly cationic agents that neutralize the predominantly negative surface charge of typical wastewater solids (Stephenson and Duff 1996; Ariffin *et al.* 2012; Simonič and Vnučec 2012). Some published strategies will be discussed in which such coagulation was used as an initial stage in two-stage treatments.

The combination treatment in which a high-charge or high-valence cationic agent (the coagulant) is followed by a very-high-mass polyelectrolyte (the flocculant) is worth mentioning again at this point due to its central role in many treatment plant operations. Ahmad *et al.* (2008) described a typical example in which either aluminum sulfate (alum) or poly-aluminum chloride (PAC) served as the coagulant, and then they added either a positively or negatively charged acrylamide copolymer as the flocculant. Highly efficient removal of suspended solids and reduction in oxygen demand were observed, and a low settling time was achieved.

#### *Coagulation, then flotation*

Coagulation also can be used in combination with a subsequent flotation stage. This is essentially what happens in an electrocoagulation-flotation system (Chen 2004; Han *et al.* 2006; Boroski *et al.* 2008; Emamjomeh and Sivakumar 2009). In the cited work by

Boroski *et al.* (2008),  $\text{Al}^{3+}$  or iron (ferric or ferrous ions) were formed at an anode, and bubbles of hydrogen gas, formed at the cathode, caused agglomerated materials to rise and to form a froth. In principle, uncharged substances in water tend to be less hydrophilic in comparison with substances bearing an ionic charge. Thus, the neutralization of charges, brought about by addition of a coagulant, can be favorable for the attachment of air bubbles (which can be regarded as hydrophobic) with the agglomerated matter. The effectiveness of such electrocoagulation-flotation systems for the treatment of P&P mill effluents has been demonstrated (Chen and Horan 1998; Boroski *et al.* 2008).

The same benefits also can be achieved, in principle, by the direct addition of coagulating agents, followed by dissolved air flotation (DAF). Meyssami and Kasaeian (2005) showed that the addition of coagulants such as chitosan, alum, and ferric chloride, followed by flotation, could achieve high levels of water clarification. Yap *et al.* (2012) found that it was possible to optimize the surface charge of a system before DAF clarification by means of streaming current tests; in the cited work the neutralization was achieved either by the addition of alum or by lowering the pH with acid.

#### *Electrocoagulation, then adsorption or photodegradation*

Bellebia *et al.* (2012) showed that electrocoagulation could be used in combination with adsorption of the precipitated matter onto granular activated carbon. The combination was found to be effective for the removal of oxygen demand from paper mill wastewaters. Laboratory work showed that electrocoagulation also can be used as a precursor to photocatalytic degradation (Boroski *et al.* 2008). P&P mill effluent was coagulated using iron electrodes and subsequently treated with UV light in the presence of  $\text{TiO}_2$ . The combined treatment was more effective for reducing the color of the treated wastewater.

#### *Coagulation, then membrane separation*

There are several logical explanations by which to justify the idea of using a sequence of coagulation followed by membrane filtration. On the one hand, membranes achieve separation by preventing the passage of particles above a specified size. Coagulation gathers colloidal or dissolved matter together into particles and tends to increase their size by means of continued agglomeration. A further issue is that membrane separation methods continually face difficulties related to the occlusion of their pores; by coagulating the solids into larger particulates, it is then less likely that the solids will be able to get into the fine pores or to form a dense, impermeable cake layer on the membrane surface. Hong *et al.* (2007) showed that the ultrafiltration flux could be enhanced by pretreating pulp mill wastewater with alum or ferric chloride. The flux decline rates were greatly reduced, in addition to reducing the oxygen demand and color in the permeate. Li and Zhang (2011) showed good results when using a composite flocculant ahead of a reverse osmosis membrane.

Bennani *et al.* (2012) demonstrated a further refinement of the approach just described by coagulating the wastewater solids, using aluminum chloride, so that it adsorbed onto the surface of clinoptilolite tuff, which is a natural zeolite having a high absorptive capacity. The treatment enhanced the performance of a subsequent filtration process with a reverse osmosis membrane.

### **Advanced Oxidation followed by Other Processes**

Although advanced oxidation processes such as ozonation, Fenton oxidation systems, or UV irradiation in the presence of a catalyst have exhibited quite effective

degradation of various aromatic organic compounds, they do not offer a full treatment option because the associated cost may be too high. Sometimes costs can be reduced by the combination of AOPs with conventional treatment processes, which are often less expensive. However, some advanced oxidation processes are not yet sufficiently mature to be applied in full-scale applications. Eskelinen *et al.* (2010) suggested integrating advanced oxidation with physico-chemical and biological treatments in order to maximize the treatment efficiency (Merayo *et al.* 2013). The hypothesis here is that one can break down the non-biodegradable compounds in the content of P&P mill wastewater (*e.g.*, AOXs from bleaching sequences) and make these compounds ready for the subsequent biological treatments.

#### *Biological treatment after AOP*

The combination of advanced oxidation followed by biological treatment has received attention from many research teams (Heinzle *et al.* 1992; Pere *et al.* 1993; Nakamura *et al.* 1997; Rice 1997; Helble *et al.* 1999; Yeber *et al.* 1999b; Alvares *et al.* 2001; Baig and Liechti 2001; Bijan and Mohseni 2005; Balcioglu *et al.* 2007; Wang *et al.* 2008b; Soloman *et al.* 2009; Buyukkamci and Koken 2010; Goel *et al.* 2010; Oller *et al.* 2011; Tripathi *et al.* 2011; Antony and Natesan 2012; Hermosilla *et al.* 2012a; Lucas *et al.* 2012; Merayo *et al.* 2013). Essentially all of these researchers presented evidence, either direct or collected from other sources, of more complete or more rapid biodegradation following the oxidative treatment. The overall finding supports the view that those compounds in pulp and bleaching effluents that are recalcitrant to enzymatic degradation by micro-organisms are nevertheless susceptible to degradation by sufficiently strong oxidizing species such as the OH• radical, which has been shown to play a central role in such systems (Bautisa *et al.* 2008). However, the need for the catalysts that can be activated without illumination (*e.g.*, UV irradiation) is also an urgent need to reduce the treatment cost and to enhance the application of such systems in full-scale treatment plants. Duran *et al.* (1994) reported good results from UV irradiation in the presence of a catalyst followed by fungal treatment.

The concept of partial oxidation before biological treatment was reviewed by Alvares *et al.* (2001). According to the concept, a sufficient and effective overall treatment can be achieved without fully oxidizing the organic substances during the initial treatment. Based on results presented in the cited work, it was concluded that over 90% transformation to oxidized species was needed in order to ensure the best overall results following the biological treatment.

Various studies, involving a sequence of advanced oxidative treatment followed by biological treatment, have helped to shed light on the mechanisms. Bijan and Mohseni (2005) showed that ozonation decreased the molecular mass of recalcitrant organic matter in pulp mill effluent, and it was suggested that the smaller molecules would be more biodegradable. Goel *et al.* (2010) reported that although chlorophenol could be broken down eventually by extended biotreatment, the time required could be decreased by almost a factor of three by photo-oxidation pretreatment. Because the combined treatments often remove toxicity effects (Yeber *et al.* 1999b; Rodriguez *et al.* 1999; Freire *et al.* 2000; Balcioglu *et al.* 2007; Catalkaya and Kargi 2008), it seems likely that some of the benefit of pretreatment could be related to higher viability of microorganisms during a subsequent biological phase of treatment. On the other hand, Alvares *et al.* (2001), in their review article, cited evidence of the development of toxic species following certain advanced oxidation treatments.

### Reduction followed by Aeration

As mentioned earlier, there has been scant attention to the possibility of reductively treating paper mill wastes, even though such treatment has been shown to be very effective for decreasing the color of lignin-derived chromophores in wastewater (Ghoreichi and Haghghi 2007). The cited authors employed an aerated biological treatment as a follow-up stage to reductive treatment. The oxidative conditions of the biological treatment substantially reduced the oxygen demand, and also a low level of suspended solids was achieved by the combined treatment.

### Anaerobic followed by Aerobic Treatment

Many researchers have evaluated the use of an anaerobic biological treatment stage followed by an aerobic stage for the treatment of P&P mill effluents (Hagglblom and Salkinojasalonen 1991; Graves and Joyce 1994; Rusten *et al.* 1994; Demel *et al.* 2003; Zhang *et al.* 2009; Ordóñez *et al.* 2010; Sheldon *et al.* 2012). Marwaha *et al.* (1998) showed the feasibility of aerobic treatment of the sludge obtained from anaerobic digestion of black liquor. Review articles considering sequential anaerobic and aerobic biological wastewater treatment technology have been presented (Maat and Habets 1987; Suvilampi *et al.* 2001; Pokhrel and Viraraghavan 2004; Buyukkamaci and Koken 2010; Katahi *et al.* 2011; Ashrafi *et al.* 2015). In many instances, the primary reason for the aerobic stage is to remove residual organic matter from the anaerobically treated mill effluent. This sequential combination has some other important advantages. The anaerobic treatment reduces the total production of sludge, and also it produces biogas that could be used for energy production in the mill. On the other hand, anaerobic treatment cannot remove all the organic substances, and some inorganic compounds will be decreased. This means that, after an anaerobic stage, the final aerobic stage may be more effective in the removal of organics. Such an approach may be helpful in meeting legislated discharge levels. In other cases, the combination of these treatments with membrane filtration may be used to further polish the effluent for a possible reuse as a replacement for fresh water in the mill. However, Kortekaas *et al.* (1998) reported some undesirable effects of sequential anaerobic and aerobic treatment of hemp thermomechanical pulping wastewater; the aerobic stage resulted in increases in both color and the molecular weight of residual lignin.

The combination of both anaerobic and aerobic treatments can reduce the organic load and toxicity of a paper mill whitewater (Latorre *et al.* 2007). Singh and Thakur (2006) employed anaerobic treatment and subsequently fungus (*Paecilomyces* sp.) and bacterial strain (*Microbrevis luteum*) separately in two steps (Singh and Thakur 2006). Reduction of AOX during anaerobic treatment indicated the slow degradation of toxic compounds and elimination of chlorinated compounds present in the effluent. On the other hand, batch post-treatment of anaerobically-treated wastewater using *L. edodes* was able to remove COD, color, and ligninoids from the anaerobic effluent (Estrada-Vázquez *et al.* 1998). An aerobic reactor packed with *T. versicolor* immobilized on wood cubes fed with the anaerobic effluent is one of the few applications with extended performance (3 months) with no need of glucose supplement or other expensive carbohydrate, leading to the reduction of color, ligninoids, and COD by 68%, 52%, and 32% in 30 days (Ortega-Clemente *et al.* 2009).

### *Sulfur conversion*

Several researchers have investigated a combined treatment, starting with anaerobic treatment of P&P mill wastewater, as a means to remove sulfur. This is important because sulfur compounds may be at high concentrations in effluents from paper mills, and it may be necessary to remove them from the effluent before their discharge. Sulfur compounds have the potential to be transformed into hydrogen sulfide if the discharged water subsequently encounters anaerobic conditions (Lens *et al.* 1998). According to Minami *et al.* (1991), sulfur compounds can inhibit anaerobic biological treatment, so it is advisable to strip the H<sub>2</sub>S gas and purge it from the system. According to Janssen *et al.* (2009), sulfur was substantially removed from the biogas after an anaerobic stage of treatment. To avoid the corrosive conditions inherent in a conventional gas sweetening process with NaOH scrubbing, the hydrogen sulfide gas was first dissolved into water in the form of hydrogen sulfite and then it was oxidized to elemental sulfur under a controlled level of aeration in a biological treatment stage. Residual reduced sulfur compounds still present in the water after the anaerobic stage were oxidized by a subsequent conventional aerobic biological wastewater treatment. Another alternative proposed by researchers is to convert sulfide to elemental sulfur at short hydraulic retention times by applying a biological post-treatment to anaerobic effluents (Buisman *et al.* 1988, 1990). In addition, Särkkä *et al.* (2009) demonstrated the electrochemical oxidation of sulfides from anaerobic wastewater treatment. Alternatively, Vepsäläinen *et al.* (2011b) showed that ferrous ions could be used to precipitate iron sulfide from such solutions, which is currently the most common method for sulfide precipitation (Bajpai 2000). The drawbacks of this method are the cost of iron salts and the accumulation of FeS in the reactor, which may be responsible for low contents of active biomass in the suspended solids fraction, and may also increase total sludge production.

Another option is a two-stage anaerobic process, where sulfur is reduced to hydrogen sulfide and removed in a first stage (Bajpai 2000); this creates better conditions for the activity of sulfate reducing bacteria, so that sulfate removal will be improved. In a second stage, better conditions for the activity of methanogenic bacteria activity are set, which improves the removal of the organic load. Furthermore, another alternative to remove sulfurous compounds based on the same process consists of using an anaerobic filter reactor functioning with downflow conditions. Such a system enables the physical separation of sulfur-reducing bacteria in the upper portion of the reactor's fixed media; whereas methanogenic bacteria will grow in the lower section. The produced biogas in the lower section of the reactor tends to strip out hydrogen sulfide, so it can work as a two-stage reactor (Bajpai 2000).

### *Anaerobic treatment followed by UV H<sub>2</sub>O<sub>2</sub>*

The treated water after an anaerobic biological treatment stage commonly benefits from an oxidative treatment. Hence, as an alternative to aerobic biological treatment, chemical oxidants can be considered. Such a post-treatment process for treatment of kraft pulp bleaching effluent after anaerobic biotreatment was demonstrated by Ruas *et al.* (2012).

### **Aerobic Treatment Combinations**

Combined treatment processes can address some problems often encountered during aerobic biological treatment processes such as the presence of recalcitrant compounds in the solution, difficulties in the settling of sludge, and the generation of a large volume of sludge.

### *Staged biotreatment with bacterial, predator steps*

It may be counterintuitive to think that a promising way to address some of the issues just mentioned may be to follow aerobic treatment with another stage of aerobic treatment, but several researchers have proposed just such an approach. As was mentioned earlier, in another context, this can be called “staged” treatment (Lee and Welander 1996; Chakrabarti *et al.* 2008). As noted in the cited work, the system needs to be designed in such a way that active biological organisms are allowed to establish themselves on suitable support surfaces within the second stage of treatment. Predator species (protozoa and metazoa, including rotifers) in the second stage of treatment can proliferate under such conditions and feed upon the bacterial matter that is allowed to proliferate in the absence of predation in the first stage of treatment. Lee and Welander (1996) showed substantial reductions in both suspended solids and sludge solids after the second stage.

### *Aerobic treatment followed by coagulation*

Given the widespread use of coagulants and flocculants in wastewater treatment, it is surprising that few publications have addressed the impact of using such additives in conjunction with aerobic wastewater treatment of P&P mill effluents. Aerobic treatment of effluent is generally regarded as a necessary step to achieve cost-effective compliance with local government regulations, but chemical additives may be needed to achieve adequate clarification after the aerobic stage. Hodgson *et al.* (1998) documented the use of aluminum sulfate as the coagulant to remove residual contaminants before its discharge into environmentally sensitive receiving waters. Agridiotis *et al.* (2007) showed that the addition of ferrous sulfate during secondary treatment of paper mill wastewater changed the bacterial matter from a filamentous form to a compact, more rapidly settling form. Aluminum chloride initially showed some promising results, but the sludge quality deteriorated; a likely explanation for the latter observations is that the system may have become overdosed with cationic charge, causing redispersal of the solid matter (Strazdins 1989).

For the treatment of secondary sludge, Pere *et al.* (1993) studied the effect of the residual iron in the content of wastewater when Fenton oxidation was applied as a pre-treatment method. They found that the dewatering was improved after advanced oxidation, using Fenton’s reagent. Though it is likely that some of the improvement in dewatering was due to the oxidation itself, the cited authors also noted a partial neutralization of the negative charge of the flocs, consistent with the presence of the iron ions. Finally, Newis *et al.* (2013) found that electrocoagulation was effective either as a pretreatment or as a post-treatment for aerobic biological treatment of sulfite pulping wastewater.

### *Ultrasonic treatments to enhance biodegradation*

Ultrasonication has been applied to facilitate the removal of chlorine-based organic compounds from effluents (Pham *et al.* 2009). Efforts have been made to use not only sonication, but also hybrid technologies that couple ultrasound with hydrogen peroxide or ozone towards the destruction of pollutants associated with industrial waste water (Mason 2007; Gogate 2008). Acoustic cavitation produces hydroxyl radicals that are expected to oxidize organic species, lowering COD, and bleaching organic chromophores (Eskelinen *et al.* 2010). Sonication of pulp and paper effluent can bleach chromophores and reduce turbidity (Shaw and Lee 2009). However, the decrease of COD remains low, possibly due to scavenging of hydroxyl radicals by bicarbonate and sulfate ions present in the effluent. Additionally, Fenton-like oxidation has been used in combination with ultrasonic

irradiation to breakdown refractory compounds from bleaching effluents (Vilve *et al.* 2009). Ultrasonic treatment as a pre- or post-oxidation combined with biodegradation of paper mill effluent has been reported to decrease toxicity and enhance biodegradability (Gonze *et al.* 2003).

## POLISHING TREATMENTS

The term “polishing” implies a step to finish up a wastewater treatment process, ideally helping to assure that the discharged water will reliably meet the specifications and to comply with stringent environmental regulations. In earlier publications the term “tertiary treatment” often has been applied as a general label for all such treatment operations (Chen and Horan 1998). One of the priorities is that such a treatment must not add anything objectionable, such as a precipitate, and it ought not result in extremes of pH, which would remain in the outfall. One is aiming to end up with water that would be clear, odorless, and compatible with aquatic life.

### Membrane Polishing Filtration

Many researchers have evaluated membrane filtration as a final step before discharge of the treated effluent from P&P making facilities (Huuhiilo *et al.* 2002; Pokhrel and Viraraghavan 2004; Mänttari *et al.* 2008; Gönder *et al.* 2011), or using that water in place of fresh water in mill operations (Ciputra *et al.* 2010; Ordóñez *et al.* 2010; Benani *et al.* 2012). Ciputra *et al.* (2010) described nanofiltration as a “broad spectrum” purification method, meaning that it is able to remove a very wide range of contaminants, all in one shot.

Among the various available membrane types, ultrafiltration membranes having pores in the range of about 2 to 100 nm (see Table 1) have been mentioned the most often for the final step in cleaning of paper industry wastewaters (Huuhiilo *et al.* 2002; Pokhrel and Viraraghavan 2004; Mänttari *et al.* 2008; Ordóñez *et al.* 2010). Such membranes have sufficiently fine porosity to exclude not only biological cells but also large molecules, such as some of the lignin decomposition products. At the same time, the flux through an ultrafiltration membrane will tend to be much higher than that of the next finer classes of membrane, the nanofiltration and reverse osmosis membranes, at a given transmembrane pressure.

Nanofiltration membranes, having a pore size range of about 1 to 5 nm, have been reported to outperform ultrafiltration membranes for the exclusion of organic contaminants (Huuhiilo *et al.* 2002). Furthermore, Ciputra *et al.* (2010) found that nanofiltration was generally superior to the use of an ion exchange resin or activated carbon adsorption for comprehensive polishing of recycling paper mill effluent.

Going one step further, reverse osmosis membranes, which have pore sizes generally less than 1 nm, have shown good capability in cases where there is a need to exclude even small ions (Ordóñez *et al.* 2010, 2011; Li and Zhang 2011). Thus, the permeate can be used as intake water for a paper mill, making it possible to run the operation with close to zero liquid effluent (Pizzichini *et al.* 2005; Khosravi *et al.* 2011; Hermosilla *et al.* 2012a; Saif *et al.* 2013). Sierka *et al.* (1997), Zhang *et al.* (2009), and Bennani *et al.* (2012) evaluated systems in which nanofiltration was used as a preliminary step before reverse osmosis separation of paper industry wastewater, reporting almost complete removal of solutes. Mattari and Nystrom (2007) found that a nanofiltration

membrane offered higher flux than a reverse osmosis membrane, but it was not as effective for the exclusion of monovalent ions such as chloride.

## Treatment of Retentate from Membrane Filtration

### *Organic content of membrane retentate*

The treatment and disposal of the retentate is an important problem in membrane filtration processes. As most treatment systems for P&P mill wastewaters will include at least one biological treatment stage; the retentate from membrane filtration can be recycled back to the intake of such a stage (Mahmood and Elliott 2006), but the presence of salts may inhibit the biological stage. Recognizing the recalcitrant nature of the organic compounds likely to be present in such retentate, Mänttärý *et al.* (2008) showed the effectiveness of ozone treatment before returning the stream to biological treatment. Hermosilla *et al.* (2012a) treated the membrane retentate with advanced oxidation systems including Fenton oxidation and UV-assisted oxidation, achieving the reduction of the concentration of organics to values meeting legislation requirements. It is possible to remove essentially all of the organics when performing the photo-Fenton process.

### *Salt removal from membrane retentate*

Even after removal of most of the organic matter from retentate, high concentrations of inorganic ions may render the water unsuitable for re-use or for discharge to the environment. Ways to overcome such problems have been reviewed (Curcio and Drioli 2005; Kim 2011; Pérez-González *et al.* 2012). For instance, solar evaporation and deep-well injection of brines are often regarded as low-cost options for their disposal (Kim 2011). Evaporation technology to recover fresh water from salty or brackish water has become quite advanced (Woldai 2016). Alternatively, it may be advantageous to remove inorganic matter by crystallization, which traditionally has been carried out by evaporation and cooling. Membrane technology is providing opportunities to carry out such evaporation and crystallization with less use of space and energy (Lawson and Lloyd 1997; Kim 2011; Pérez-González *et al.* 2012). In addition, by suitable feeding of chemical agents, there are opportunities to selectively precipitate such compounds as CaSO<sub>4</sub> (gypsum) or CaCO<sub>3</sub> (Curcio and Drioli 2005). However, because of the complex and variable nature of waste streams from pulp and paper facilities, there will be challenges to overcome in order to adopt methods that have become established in the desalination industry.

## Adsorption

The need for high applied pressures generally can be avoided by use of a media filtration process that takes advantage of adsorption of the contaminant on solids having a suitably high surface area and affinity (Chen and Horan 1998; Pokhrel and Viraraghavan 2004; Ciputra *et al.* 2010). Due to their very high surface area and generally hydrophobic nature, activated carbon products would be expected to be quite effective for removal of colored or hard-to-decompose aromatic compounds still present in water after other treatment stages. Several studies have shown the effectiveness of activated carbon for polishing of P&P mill wastewaters (Chen and Horan 1998; Ciputra *et al.* 2010). Activated carbons, as well as other adsorbent products derived from cellulosic materials, have been found to be effective for removal of metal ions, dyes, and other organic compounds from waters (Hubbe *et al.* 2011; 2012a; 2014). Ciputra *et al.* (2010) found that both ion exchange resins and activated carbon were effective for adsorptive removal of higher-mass

fractions of dissolved organic matter present in paper mill wastewaters. One likely complication of such approaches is that, depending on the level of organic matter still present in the water, the surfaces might yet again become coated with biofilms; in other words what was intended as a final adsorption step might morph into another aerobic bioreactor stage at the end of the treatment cycle.

### Ozone as a Polishing Treatment

Ozone treatment has a number of features that tend to recommend it as a final polishing treatment. Consisting of only a reactive form of oxygen, it is not expected to produce any objectionable residue having long-term stability. It generally does not induce the formation of precipitates or sludge. It can disinfect water and remove color (Hermosilla *et al.* 2015). Also it can convert any remnant substance from anaerobic treatment into suitable oxidized forms that are less likely to contribute to smells or depletion of oxygen in the receiving waters; or to contribute to the final polishing of the effluent after biological treatment. Moreover, its implementation is easy, and its presence is usual in the bleaching operations of pulp and paper mills. Thus, several authors have specifically recommended ozonation as a polishing treatment for P&P industry effluents before their discharge (Chen and Horan 1998; Baig and Liechti 2001; Pokhrel and Viraraghavan 2004; de los Santos Ramos *et al.* 2009). Oxidation by ozone as a stand-alone technology could be considered as uneconomical (Bijan and Mohseni 2008) due to the usual high volume of effluents in pulp and paper mills. Also, there may be a high content of organics and biodegradable compounds in the solution that can be removed cost-effectively from the effluent by biological technologies before a final treatment by ozone.

The efficiency of ozonation has mainly been attributed to the effective degradation of non-biodegradable compounds, such as toxic lignin by-products and chlorophenolic compounds (Hermosilla *et al.* 2015). A previous pre-treatment of easily biodegradable organic compounds can increase the efficiency of the treatment because the oxidants are then used for the oxidation of non-biodegradable compounds, and not for the treatment of organics that can be more inexpensively treated by biological treatment. Furthermore, if ozone is applied to increase biodegradability by breaking down the biorefractory compounds that are remaining in the effluent, a final bio-treatment (*e.g.* biofilters) may increase the overall treatment efficiency up to an 80% of COD reduction (Mobius and Helble 2004), as well as it may consequently reduce the overall treatment cost. An average of 20 to 25% COD removal enhancement has been reported for the ozone post-treatment of biologically-treated effluents in comparison to performing such an AOP as a pre-treatment step (Hermosilla *et al.* 2015). In fact, the implementation of on-line control systems for the treatment of biologically treated effluents by ozone provided a 20% cost saving per year (Bierbaum and Oeller 2009). This technology has also been included in the BREF document as a post-biological treatment alternative for bio-recalcitrant organic load persisting in effluents of pulp and paper mills aiming to meet the quality standards for discharge (BREF 2015).

Another very interesting treatment alternative is the application of membrane treatments instead of biological processes, or the combination of both, as in MBRs, avoiding the unnecessary oxidation of low molecular weight or biodegradable compounds (Bijan and Mohseni 2008; Mänttari *et al.* 2008). Complementarily, and as it has previously been described, a second bio-treatment stage may be developed to remove turbidity, color, and further COD (Schlichter *et al.* 2003; Bijan and Mohseni 2008; Mänttari *et al.* 2008). In addition, Balcioglu *et al.* (2007) considered improving algal treatment with ozone pre-

treatment. This approach mainly enhanced color removal, but it also significantly reduced COD and UV280. Furthermore, the residence time of algal treatment was reduced from 8 to 5 days. Beneventi *et al.* (2009), reported the increase of efficiency of an ozone flotation system, achieving more than 20% COD removal in the flotation stage. Moreover, the use of pectinases, hemicellulases, cellulases, and lignolytic enzymes may be an option for the removal of persistent compounds after this treatment, being also an effective solution for deinking (Pala *et al.* 2004; Kamali *et al.* 2015). Finally, other different synergic options combining ozone with other treatments have been studied for increasing the overall treatment efficiency of ozonation as a polishing stage, such as the combined application with electrolysis (Kishimoto *et al.* 2010; Kamali *et al.* 2015).

Although ozone is probably the most applied AOP at the industrial scale for the final treatment of pulp and paper effluents, as well as being the reference technology in the BREF document (BREF 2015), there are other AOPs that have been tested, mainly at laboratory scale, for the final treatment of pulp and paper mills effluents. These are conventional Fenton (Hermosilla *et al.* 2015; Lucas *et al.* 2012; Balabaniç *et al.* 2012; Sevimli 2005; Catalkaya and Kargi 2007; Kazmi and Thul 2007), photo-Fenton (Catalkaya and Kargi 2007; Balabaniç *et al.* 2012), solar photo-Fenton (Gomathi and Kanmani 2006; Lucas *et al.* 2012; Hermosilla *et al.* 2015), electro-Fenton (Selvabharathi and Kanmani 2010), photocatalysis (Balabaniç *et al.* 2012), solar TiO<sub>2</sub> photocatalysis (Merayo *et al.* 2013; Gomathi and Kanmani 2006), or photocatalysis + H<sub>2</sub>O<sub>2</sub> (Catalkaya and Kargi 2008). In short, the pretreatment of the effluents by a biological stage can lead to an approximate 20% increase in the COD removal efficiency of the AOP treatment (Hermosilla *et al.* 2015).

In addition, information about the wastewater composition is not sufficient to establish the optimum operating conditions for these treatment processes. Rather, it is recommended to perform laboratory trials to determine specific operating conditions and the expected efficiencies of these treatments for each effluent (Hermosilla *et al.* 2015).

## Bioaccumulation

### *Final lagoons and constructed wetlands*

Once the final treated effluent is discharged from the wastewater treatment plant, it can be expected to mingle with the waters already present in the environment. That being the case, it makes logical sense to wonder whether there might be an advantage to letting such mingling to an ecosystem take place for a while before the final discharge beyond the property of the P&P mill facility. In other words, is there value of establishing or maintaining a wetland through which the treated effluent passes before joining the receiving waters?

In principle, as water flows through a marsh or other plant-filled wetland, various chemical components can be taken up by the plants, *i.e.* a process of bio-accumulation (Sakurai *et al.* 2001). Choudhary *et al.* (2013) found evidence of such bioaccumulation in the case of chlorinated organics as P&P mill wastewater flowed through a constructed wetland. There was substantial removal of absorbable organic halides from the water. On the other hand, the same organic matter may have the potential to persist in the environment and to become passed up the food chain (Contreras Lopez 2003). Thus, bioaccumulation can be regarded as a less favorable outcome than biodegradation of the organic compounds from P&P mill effluents.

In a constructed wetland one can envision the flow gradually moving horizontally below the water surface, *i.e.* sub-surface flow (Vymazal 2009; Choudhary *et al.* 2013).

Vymazal (2009) describes the use of such designed lagoon systems for treatment of wastewaters from a wide variety of sources. Knight (2004) reported on a comprehensive study of the use of constructed wetlands for treatment of P&P mill wastewaters on behalf of the National Council for Air and Stream Improvement (NCASI). Although the study found many benefits of wetland strategies, there was no indication of reductions in the concentrations of dissolved solids, conductivity, or color. Hence, constructed wetlands were not regarded as being cost-effective relative to other means of treating P&P mill wastewaters.

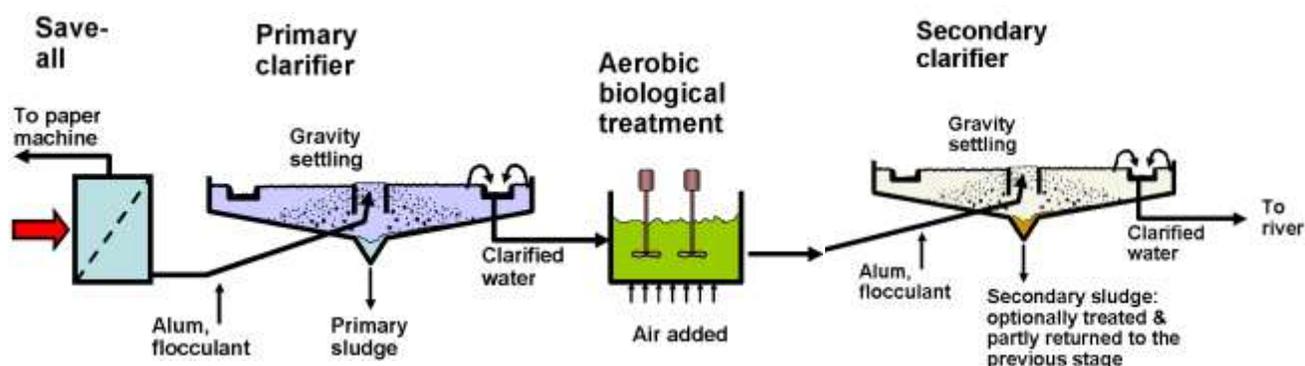
## SUMMARY COMMENTS

### Use Nature as a Guide

An important benchmark against which to compare the quality of treated water, after a P&P operation, consists of assessing the quality of water upstream of that operation. Such intake water can be expected to contain a variety of contaminants including humic acids (Hubbe 2007a). In principle the discharged water ought to be clean, in important respects, relative to the quality of the water that was borrowed from the environment.

### Visions for Future Implementations

To envision what might be good options for future green-field implementations or retrofitting of existing systems for P&P mills, a series of two figures will be considered. The first of these figures will show just the “bare bones” of a very traditional system entailing a save-all operation, primary clarification, and secondary aerobic biological treatment. The second figure will introduce a number of additional optional stages that seem to follow from findings that have been discussed in the course of this article.



**Fig. 22.** Schematic diagram of a traditional, simple wastewater treatment plant for the pulp and paper industry

The traditional system, as shown in Fig. 22, may in fact be an ideal design in cases where it can consistently meet the effluent quality requirements at a suitably low cost of operations. This is particularly the case when the costs of construction of clarifiers and other equipment already have been incurred.

In Fig. 22, some factors that are especially important for primary treatment are coagulant dosage, flocculant dosage, and pH. Likewise, some factors that are especially

important for aerobic treatment include aeration rate, temperature, retention time, nutrients, pH, active sludge recycling, and sludge age.

The cost of building and operating save-all systems for paper machines can be justified by improvements in the yield of a papermaking operation (Milliken 2006). The fine, solid matter present in excess process water discharged from papermaking ought to be returned efficiently to the process so that most of it becomes incorporated into the paper product. Furthermore, the fines fraction of a papermaking furnish can be expected to contain a disproportionate amount of the adsorbed additives, such as sizing agents and strength agents (Marton 1980a,b). Thus, if fines are allowed to pass into the wastewater treatment system, then the company is losing the potential value of those additives.

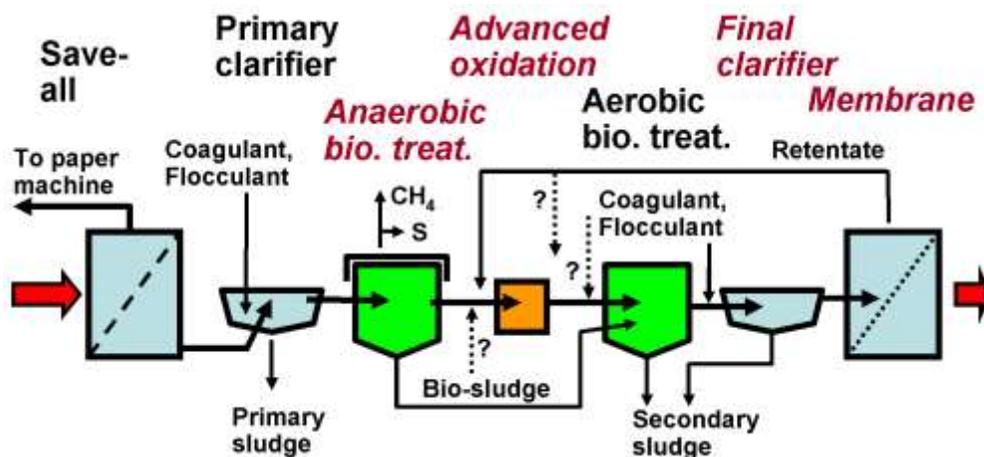
One might think that in some cases it can be reasonable to simply skip the primary clarification of paper machine effluent and immediately commence with biological treatment. But the problem with that option is that the sludge from primary treatment is usually much easier to handle. It tends to be dense and compact, especially if the source is a paper mill that employs a mineral filler such as calcium carbonate or clay (Mahmood and Elliott 2006). It might be a mistake to wait and have to handle such solids as part of the secondary sludge, which is characteristically much more difficult to dewater. Still, given the cost and space requirements of primary clarification, there is no assurance that this treatment stage will be included in future wastewater treatment plants for P&P mills.

None of the work cited in this review questioned the need for at least one biological treatment stage to treat wastewaters from pulp or paper mills. The large quantity of biodegradable material, such as hemicellulose, extractives, starches, and their decomposition products present in these wastewaters dictates the need for the inclusion of a biological process during the treatment operation. Biodegradation processes tend to be cost-effective relative to the available alternatives, especially for dealing with the most easily degradable compounds present.

Though Fig. 22 does not explicitly show a separate clarification stage after the biological treatment stage, the use of a separate clarifier can be regarded as a standard practice in most facilities at present.

One might argue that Fig. 22 really ought to include a “tertiary treatment” stage, since such stages have been widely mentioned in the literature for many years (Chen and Horan 1998; Rajvaidya and Markandey 1998; Helbe 1999; Gragnon and 2002). However, there has been no widespread consensus regarding the necessity to employ such a tertiary stage, nor has there been any widespread consensus of one system that is best for most P&P mill facilities.

Figure 23 portrays a hypothetical treatment plant that incorporates a number of optional steps, consistent with findings discussed in the course of this article. In Fig. 23, the save-all options would include disk screen systems and dissolved air flotation (DAF). The oxidation options would include ozone, Fenton processes, UV illumination with or without catalysts such as  $\text{TiO}_2$  and possibly supplemented by  $\text{H}_2\text{O}_2$ , as well as electro-oxidation. The membrane options would include ultrafiltration, nanofiltration, and reverse osmosis.



**Fig. 23.** Schematic diagram showing options for enhancements of wastewater treatment plants for the pulp and paper industry

A key item that appears in Fig. 23 but not in Fig. 22 is an anaerobic treatment stage. The reasons for suggesting the inclusion of such stages in future implementations and improvements of wastewater treatment plants for P&P mills can be summarized as follows: low operating costs, relatively low sludge production, production of valuable methane gas, and substantial reductions of biological oxygen demand. But the capital cost of a new anaerobic treatment plant requires careful consideration, in light of the fact that the operation needs to be covered, and there must be a system for collection of methane and other reduced gases produced. Note also that Fig. 23 depicts the use of a scrubber system and associated sub-processes to extract sulfur-containing gases.

An advanced oxidation stage has been drawn into Fig. 23 as a further option to consider, if it is needed. In Fig. 23 such a stage is placed after the anaerobic stage, where the strategy would be to avoid using up valuable chemicals in the treatment of either easily biodegradable materials or that portion of such compounds that would be carried away as sludge. One of the open questions, however, is whether to target the soluble portion or to oxidize the entire discharge from the anaerobic biological treatment, thereby facilitating an overall reduction in the amount of sludge as a byproduct from the treatment operations. Additionally, an advanced oxidation system could be placed after the aerobic biological treatment as a polishing step. The answer is likely to depend on what option is most cost-effective. Other open questions are whether increasing the biodegradability of the organic matter, by means of a further biological stage (*e.g.* biofilters) or performing further wastewater treatment, will allow a production facility to meet their legislated limits.

Aerobic treatment is still included in Fig. 23, despite the option of using anaerobic treatment, due to the expected need to oxidize the biodegradable compounds that the anaerobic stage is not able to polish. The aerobic treatment also will oxidize any sulfides and sulfur-containing compounds remaining in the water phase. In some cases it might make sense to consider an ozonation or high-pressure oxygen stage, instead, but even in such cases, an aerated biological treatment stage would ordinarily be regarded as needed to economically cut down the release of biological oxygen demand.

As a final treatment stage, though Fig. 23 depicts the symbol of a membrane filter, it also can make sense to employ coagulative and flocculative settling of final water, or to ozonate the final water. Alternatively, as also shown in the figure, flocculation can be added as a feature during the settling of the sludge during clarification after the aerated

biological treatment stage. Thus, many options present themselves, depending on specific needs.

Although Fig. 23 can be regarded as a scheme that follows from the concepts discussed in this review article, there are many alternative designs that can be considered for the effective treatment of pulp-and-paper wastewaters. Much research is needed in a variety of disciplines including biology, microbiology, chemistry, and chemical and mechanical engineering to ensure the removal of recalcitrant pollutants that exist at very low concentrations in wastewaters emerging from P&P mills, especially those that resist removal by traditional treatment processes. These efforts will ensure minimal impact of the effluents on the quality of downstream waters and will contribute to the protection of the environment and aquatic life.

#### *Degradation products and legislative requirements*

In Europe, “The Best Available Techniques (BAT) Reference Document for the Production of Pulp, Paper, and Board,” which is included in the Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control), is the reference document determining BAT-associated emission levels for direct wastewater discharge from the different types of pulp and paper mills to receiving water (BREF 2015). In short, the yearly average emissions reported in this document go up to 30 kg/ADt of COD, 1.5 kg/ADt of total suspended solids, 0.3 kg/ADt of total nitrogen, 0.11 kg/ADt of total phosphorus, and 0.2 kg/ADt of adsorbable organically bound halogens. The higher values listed in the document generally are associated with bleached kraft and sulfite pulp mills.

Directive 2008/105/EC, on environmental quality standards in the field of water policy, includes a list of priority substances in its Annex I. According to the BREF (2015), none of these listed priority substances are used within pulp and papermaking processes in Europe. Some of these substances (*e.g.* dichloromethane, hexachlorocyclohexane, di(2-ethylhexyl)phthalate, nonylphenols, octylphenols, pentachlorophenol, or some other polyaromatic hydrocarbons) can be found in the emissions from waste water treatment plants, as it has previously been described in the “Pulp and Paper Wastewater” section of this review, or they can be introduced in the production process included in imported pulps or contained in upstream abstracted surface water that will be used in the papermaking process itself. Also, some of these compounds of concern can be produced in unit processes in pulp and paper manufacture, especially in bleaching operations. Further research related to such releases and their treatment will be required in the future.

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**Table A.** Wastewater Treatment Systems and their Performance for Pulp and Paper Mill Effluents

Type of effluent	Type of operation	Treatment specifics	Performance metric & % reduction	Notes	Citation
Kraft pulp & p	Biological	Aeration ponds & settling	Metal ions: ~0%	No consistent decreases in divalent or monovalent metals.	Achoka 2002
Paper mill	Chemical	Ferrous sulfate addition Aluminum chloride	Sludge vol.: 70% “ : Unstable	Filamentous bacteria became compact	Agridiotis <i>et al.</i> 2007
Pulp & paper	Chemical	Alum & cationic PAM flocculant	TSS: 99% Sludge vol: 37 mL/g	Optimization of clarifier settling treatment	Ahmad <i>et al.</i> 2007
Pulp & paper	Chemical	Alum & cationic PAM flocculant; PAC & anionic PAM flocculant	Turbidity: 99.8-99.9% TSS: 99.4-99.5% COD: 91-91%	Optimization of clarifier settling treatment; Best results with alum & cationic PAM	Ahmad <i>et al.</i> 2008
Pulp & paper	Biological	Anaerobic upflow, comparing mesophilic & thermophilic temps	COD:	Thermophilic condition were much more promising.	Ahn & Forster 2002
Recyc. paper	Mechanical	Nanofiltration membranes	TOC: 98.5% Color: 99.5%	Flux decline was due to fouling and concentration polarization.	Ahn <i>et al.</i> 1998
Pulp & paper	Chemical	Catalytic wet oxidation	TOC: 84%	Different catalysts showed strong differences.	Akolekar <i>et al.</i> 2002
Paper mill	Chemical	Electrocoagulation with Fe electrode & coagulants	TSS: 80-97% COD: 80-97%	Supplementary coagulants, FeSO <sub>4</sub> & CaCO <sub>3</sub> very effective	Al-Shannag <i>et al.</i> 2012
Cardboard	Chemical	Ozone or UV exposure of mill water & model compounds	COD: 18-99% BOD: 37-65%	Mild oxidation actually increased the BOD.	Amat <i>et al.</i> 2005
Bleaching	Electrobio	Electrocoagulation & electro-oxidation, then bio treatment	Cost: 41% vs. usual coagulation/biological	Electrocoagulation as a first step outperformed oxidation.	Antony & Natesan 2012
Pulp & paper	Chemical	Poly-DADMAC & polyacrylamide	Turbidity: 50-95% COD: 68-98% TSS: 60-94%	The coagulant destabilized the particles, and the subsequent flocculant made them bigger.	Ariffin <i>et al.</i> 2012
Paper mill	Ozone/bio	Combined ozone & fixed bed biological post-treatment of effluents after activated sludge	COD: 88	The BOD/COD ratio could be optimized by varying the ozone dosage.	Baig & Liechti 2001
CEH bleach	Chemical	Oxidation vs. catalytic oxidation as pretreatments for algal treatment	COD: 86-90% Color: 96-99%	Algal treatment without the oxidation decreased COD by 76% & COD by 53%.	Balcioglu <i>et al.</i> 2007

Kraft bleach	Chemical	Ozone, catalytic ozonation, Ozone + activated carbon	COD: 25-63%	Biodegradability enhancement	Balcioglu <i>et al.</i> 2008
Pulp & paper	Various	Hydrothermal, enzymatic, ultrasound, nitric acid, & NaOH pretreatments for anaerobic	Methane: Up 31%	Hydrothermal treatment at 150 C had the most positive effect.	Bayr <i>et al.</i> 2013
Recyc. Paper	Chemical	Electrocoagulation	Turbidity: 99.7% BOD: 96.1%	Optimization.	Behrooz <i>et al.</i> 2011
Cardboard	Chemical	Electrocoagulation with Al and Fe electrodes followed by granular activated carbon	COD: 75% - 79% BOD: 99.9%	The combination treatment was effective for highly concentrated organics.	Bellebia <i>et al.</i> 2012
Paper recycle mill	Chemical	Ozone	COD: 51%	Biotreated effluent: On-line ozone control production provided a 20% cost savings.	Bierbaum and Oeller 2009
Wood & pulp	Chemical	Coagulation with aluminum chloride and adsorption on tuff, then nanofiltration membrane	Total carbon: 67% TOC: 77% Inorganic C: 49%	The treated water could be recycled into the process.	Bennani <i>et al.</i> 2012
Pulp mill	Chem/bio	Integrated ozonation with bio treatment; focus on recalcitrant organic matter	High MW degradation increased from 5% to 50%	Integrated treatment showed 30% greater TOC mineralization.	Bijan & Mohseni 2005
Kraft ECF	Chemical	Ozone; Ozone & biological; Biological, ozline, & biological; NF & ozline & biological	COD: 17-65% TOC: 5-50% Color: 80%	Biodegradability improvement	Bijan & Mohseni 2008
Pulp & paper	Chemical	Electrocoagulation (Fe)-flotation followed by photocatalysis with UV and TiO <sub>2</sub>	COD: 88% BOD/COD: 0.15-0.89 Color:	Toxicity was reduced.	Boroski <i>et al.</i> 2008
Bleaching	Chemical	UV/TiO <sub>2</sub> & UV/ZnO on Al foil or luffa followed by biological	TOC: 96% Cl-phenols: 90-99%	Synergistic coupling of oxidation and bio-treatment.	Botia <i>et al.</i> 2012
Pulp mill	Biological	Upflow anaerobic sludge blanket reactor used to treat black liquor for 635 continuous days	COD: 80%	It was not necessary to removal any sludge.	Buzzini & Pires 2002
Pulp & paper	Biological	Upflow anaerobic sludge blanket reactor	COD: 78%	Hydraulic retention time could be reduced by recirculation.	Buzzini & Pires 2007

ECF bleach	Chemical	Catalytic hydrogenation in a trickle bed reactor using Pd/AC reactor.	Ecotoxicity: 70-98% AOX: 85%E1, 23%D COD: 12% BOD: Went up 47% Color: 61%	A home-made catalyst outperformed a commercial type.	Calvo <i>et al.</i> 2007
Pulp & paper	Chemical	Clay and polymer was used in place of alum in an up-flow solids contact clarifier	Turbidity: 90-99%	Sludge blanket issues were considered.	Carter & Sigler 1981
Pulp mill	Chemical	Advanced oxidation with UV, UV-H <sub>2</sub> O <sub>2</sub> , and UV-TiO <sub>2</sub>	TOC: 80% Toxicity: 94%	The UV-TiO <sub>2</sub> system resulted in the largest reduction in TOC.	Cataalkaya & Kargi 2008
Pulp mill	Biological	Aerobic biological treatment	COD: 65-71% AOX: 38-43%	The performance was best at a pH of 5 to 9.5 and 30-40 °C.	Chakrabarti <i>et al.</i> 2008
Pulp mill	Biological	Mixed culture of three bacterial strains	Color: 96% COD: 91% BOD: 93%	Peroxidase activity was evaluated, explaining the breakdown of chlorophenols.	Chandra & Singh 2012
Pulp & paper	Chem/bio	Electrochemical treatment with a membrane bioreactor	Color: 98% BOD: 98% COD: 97%	Optimized conditions were compared to steady-state operating conditions.	Chanworrawoot & Hunsom 2012
Pulp & paper	Tertiary	Chemical coagulation (alum), ozonation, activated carbon adsorption	COD: 70% Color: 90%	Chemical coagulation followed by dissolved air flotation was the most effective.	Chen & Horan 1998
Kraft lignin	Biological	Unicellular bacteria;	COD: 32%	The treatment effectively degraded the kraft lignin to low-mW compounds.	Chen <i>et al.</i> 2012
Pulp & paper	Chemical	Ozonation with catalysts (Fe-Mn/sepiolite)	pCP: 98% COD: 58%	Degradation of p-chlorophenol (pCP) was observed.	Cheng <i>et al.</i> 2015
Pulp & paper	Biological	Constructed wetland treatment with subsurface flow	AOX: 89% Cl-phenols: 67-100%	Some bioaccumulation of Cl-phenols in the biomass obsd.	Choudhary <i>et al.</i> 2013
Paper mill	Mechanical	Ion exchange resin, granular activated carbon, nanofiltration	DOC: 72, 76, 91%	Nanofiltration was most effect for removal all MW fractions.	Ciputra <i>et al.</i> 2010
Pulp mill	Chemical	UV photodegradation with or without TiO <sub>2</sub> catalyst	Lignin: 30-70%	Irradiation in the presence of catalyst was effective.	Dahm & Lucia 2004
Pulp & paper	Chemical	Sulfuric acid treatment (pH 1 or 3) followed by ozonation at pH 1-12	COD: 77% Color: 96%	Ozonation increased the biodegradability.	De los Santos Ramos <i>et al.</i> 2009
Pulp & paper	Biological	Upflow anaerobic filter treatment of bleachery effluent	AOX: 28-88% Enhanced to 90-93%	AOX removal was favored by adding acetate and glucose.	Deshmukh <i>et al.</i> 2009

Pulp mill	Chemical	Wet oxidation (with or without CuO/CeO <sub>2</sub> catalyst), then coagulation with FeCl <sub>3</sub> or PAC	COD: 51-77% Color: 71-87%	Biodegradability was increased to 0.6 and 0.96 after catalytic wet oxidation & combined.	Dhakhwa <i>et al.</i> 2012
Pulp mill	Biological	Activated sludge treatment was observed over 280 days.	BOD: 95% COD: 60%	Optimization of hydraulic retention time is important.	Diez <i>et al.</i> 2002
Pulp mill	Biological	Mixed culture algae	Color: 80% AOX: 70%	Total organic carbon and lignin were also removed by algae.	Dilek <i>et al.</i> 1999
Lignosulfonate	Chemical	Electrochemical oxidation	TOC: 80%	Kinetics were studied and conditions were optimized.	Dominguez-Ramos <i>et al.</i> 2008
E1 bleaching	Biological	<i>Lentinus edodes</i> fungi were used to decolorize phenolics.	Color: 73%	Combined photo-biological decolorization was effective.	Duran <i>et al.</i> 1994
Paper mill	Chemical	Electrochemical treatment (anodic oxidation)	COD: 97% Color: 53-100%	Results could be adjusted by varying the energy input.	El-Ashtoukhy <i>et al.</i> 2009
Sludge	Biological	Anaerobic digestion of sludge from pulp & paper mills was enhanced by pre-shearing the sludge.	Sludge amount: 85%	Preshearing the sludge before returning it to biotreatment reduced the amount by 85%	Elliott & Mahmood 2012
Pulp mill	Biological	Bacterial mixtures were used to treat spent bleaching effluent	Carbon: 35-45%	Fungal treatment was effective; Bacteria were slow to act.	Eriksson & Kolar 1985
Pulp & paper	Chemical	Ultrasonic treatment & Fenton-like oxidation, electrochemical, and or chemical precipitation	COD: 90%	Chemical precipitation with CaO at pH=12 was the most effective option tried.	Eskelinen <i>et al.</i> 2010
Pulp mill	Biological, chemical	Yeast isolates in combination with dark Fenton & solar Fenton	COD: 68% Polyphenols: 27% TOC: 90% (Fenton)	The best results were with yeast, followed by solar Fenton (Fe <sup>2+</sup> H <sub>2</sub> O <sub>2</sub> ).	Fernandes <i>et al.</i> 2014
E1 bleaching	Chemical	Ozonation of kraft E1 bleach effluent	TOC: 12% Phenols: 70% Color: 35%	Molecular mass of the effluent contents was reduced.	Freire <i>et al.</i> 2000
Bleaching	Biological	Fungal treatments (white rot and soft rot)	Color: 72-74% Lignin: 25-46% COD: 74-81%	Various enzymes were expressed.	Freitas <i>et al.</i> 2009
Pulp & paper	Chemical	Coagulation with alum, PEI, chitosan, or quat nitrogen polym.	TOC: 10-55% Color: 15-82%	The coagulants all reduced settling times.	Ganjidoust <i>et al.</i> 1997
Pulp & paper	Chemical	Thermochemical precipitation with CuSO <sub>4</sub> catalyst and others	COD: 63% Color: 92%	The residual copper acted as a catalyst for wet oxidation.	Garg <i>et al.</i> 2005

Pulp & paper	Chemical	Catalytic wet oxidation under moderate conditions	COD: 61-89%	Best results with CuO/activated carbon catalyst	Garg <i>et al.</i> 2007
Pulp & paper	Biological	Bacterial treatment	Color: 27-30% Dechlorination: 59%	Supplementation with glucose or yeast extract is needed.	Garg <i>et al.</i> 2012
Pulp & paper	Various	State of the art treatments compared	BOD: 67-90%	Systems with secondary (bio) treatment are effective.	Gehm 1973
Paper mill	Chemical	Solar catalytic treatment with TiO <sub>2</sub>	COD: 75% TSS: 80%	Biodegradability could be improved after long treatment.	Ghaly <i>et al.</i> 2011
Pulp & paper	Chemical, biological	Sodium borohydride was used to reduce the chromophores, then aerobic bio-treatment.	Color: 97% COD: 35-92% BOD: to 99% TSS: to 97%	The borohydride treatment alone actually increased the BOD level.	Ghoreishi & Haghghi 2007
Pulp mill	Chemical, biological	Integrated photo-catalytic (TiO <sub>2</sub> ) and biological treatment	Treatment time: 64%	The photo-oxidation decreased the time of bio treatment.	Goel <i>et al.</i> 2010
Pulp & paper	Biological	White-rot fungus	Color: 75%	High glucose conc. Needed.	Gökçay & Dilek 1994
Bio-treated effluent	Chemical	TiO <sub>2</sub> / solar UV	COD: 83%	Oxidation more efficient in pollutants that are more biorecalcitrant	Gomathi & Kanmani 2006
Pulp & paper	Biological, Mechanical	Biotreatment, followed by nanofiltration	COD: 91% Hardness: 92% Sulfate: 98%	Conditions optimized to minimize fouling.	Gönder <i>et al.</i> 2011
Pulp & paper	Mechanical	Ultrafiltration.	Hardness: 83% Sulfate: 97% Color: 95% COD: 89% Conductivity: 50%	The variable pH had the biggest influence on the results.	Gönder <i>et al.</i> 2012
Pulp & paper	Biological	Anaerobic co-digestion of secondary sludge with sewage	50% replacement of the sewage sludge	Methane production was kept constant with less sewage.	Hagelqvist 2013
Bleaching	Biological	Sequential anaerobic and aerobic trickling bed filter	AOX: 65% C—phenols: 75%	The combination treatment was effective.	Haggblom & Salkino-jasalonen 1991
Recyc. Paper	Biological	Anaerobic baffled reactor	COD: 85%	Methane production successful	Hassan <i>et al.</i> 2014
Bleaching	Chemical, biological	Integrated ozonation and bio-treatment.	COD: 50-70% TOC: 15-50% AOX: 70%	The amount of ozone consumed was markedly higher in a combined treatment	Heinzle <i>et al.</i> 1992
Pulp & paper	Chemical, biological	Combined ozone and fixed bed biofilm reactor	BOD:	The “hard” BOD was converted to biodegradable BOD.	Helble <i>et al.</i> 1999

Newsprint paper mill	Chemical	Conventional Fenton and UV Fenton oxidation of retentate from reverse osmosis system	COD: 80 to 100%	The UV-TiO <sub>2</sub> system was not effective on its own, but very beneficial to biodegradation.	Hermosilla <i>et al.</i> 2012a
Newsprint paper mill	Chemical	Coagulation and flocculation	SiO <sub>2</sub> removal: up to 100% COD: 50%	Pre-treatment for reverse osmosis membrane filtration	Hermosilla <i>et al.</i> 2012b
Pulp mill	Chemical, mechanical	Coagulation with ferric chloride or alum, followed by ultrafiltration	Color: COD:	The coagulants were both very effective in reducing the rate of flux decline.	Hong <i>et al.</i> 2007
Pulp & paper	Biological, mechanical	Anaerobic thermophilic suspended carrier biofilm or ultrafiltration & nanofiltration	COD: Sugar: TSS: Lignin:	Biological treatment improved filtration performance. Nanofiltration was much more effective than ultrafiltration.	Huuhilo <i>et al.</i> 2002
Bleach plant	Biological	Granular activated carbon reactor with anaerobic biofilm	COD: 50%	The biofilm extended the adsorption capacity of the activated carbon.	Jackson-Moss <i>et al.</i> 1992
Paper mill	Chemical, biological	Advanced oxidation systems were compared related to subsequent biodegradability	COD: 80% TSS: 97%	Biodegradability was greatly increased by the photo-Fenton oxidative treatment.	Jamil <i>et al.</i> 2011
Paper mill	Biological	Sulfur removal by bacterial treatment, biogas generation, H <sub>2</sub> S removal from the gas.	Sulfur: 95% Organics: 70-90%	Sulfur was removed from the biogas and also from the sludge.	Janssen <i>et al.</i> 2009
Pulp & paper	Biological	Membrane filtration unit	DOC: 54% Color: Went up.	Most organics were reduced, but turbidity went up.	Kallioinen <i>et al.</i> 2006
Pulp & paper	Mechanical	Membrane filtration using pilot-scale treatment system	–	Focus was on membrane flux performance.	Kallioinen <i>et al.</i> 2005
Pulp & paper	Chemical	Thermo-alkali hydrolysis of waste activated sludge followed by anaerobic digestion	COD: 76 to 80%	The treatment increased biogas production, but slightly decreased BOD reduction.	Kaluža <i>et al.</i> 2014
Pulp & paper	Chemical	Photocatalytic treatment with UV and TiO <sub>2</sub> or ZnO	COD: 66-90% BOD: 78-84%	Solar photocatalytic process was judged to be satisfactory.	Kansal <i>et al.</i> 2008
Paper mill	Chemical	Electrocoagulation with either Al or Fe electrodes	Color: 50-90% Phenol: 75-90% COD: 70-90%	Optimum pH was 5-7.	Katal & Pahlavanzadeh 2011

Paper mill	Mechanical	Nanofiltration, with pH adjustment	COD: 65-98% Color: 90-98% TSS: 66-100%	The fouling kinetics were examined. Nanofiltration gave the best results.	Kaya <i>et al.</i> 2010
Pulp & paper	Chemical	Electrocoagulation with iron electrodes.	Color: 91% COD: 77%	Polyelectrolytes had no effect on the results.	Khansorhong & Hunsom 2009
Pulp & paper	Mechanical	Nanofiltration and reverse osmosis membranes		The nanofiltration membrane gave the best results.	Khosravi <i>et al.</i> 2011
Pulp & paper	Chemical	Ozonation with electrolysis	COD: ~45%	The combination of ozone & electrolytes was better than either treatment alone.	Kishimoto <i>et al.</i> 2010
Pulp & paper	Biological	Constructed wetland systems	BOD, TSS, N, P - yes Salts, color - no	The poor results for color were of concern to the author.	Knight 2004
Pulp & paper	Biological, mechanical	Laccase polymerization was followed by membrane filtration	COD: 60%	Laccase treatment increased molecular weight in effluent.	Ko & Fan 2010
Pulp & paper	Mechanical	Colloid-enhanced ultrafiltration with surfactant-polymer complexes	Cl-phenols: 90-99%		Komesvarakul <i>et al.</i> 2003
Pulp mill	Biological	Anaerobic lab-scale treatment	COD: 80%	There was high methane but poor COD reduction from bleach wash effluent.	Korczak <i>et al.</i> 1991
TMP pulp	Biological	Anaerobic treatment of hemp TMP water (stem and bark)	COD: 63-72%	Low-mass lignin fractions were removed effectively.	Kortekaas <i>et al.</i> 1998
Pulp mill	Biological	Activated sludge system	Extractives: 97% Resin acids: 94% Sterols: 41%	Most of the extractives became attached to particles and removed with the solids.	Kostamo & Kukkonen 2003
Pulp & paper	Chemical	Ozonation and its effect on biodegradability	Color: 90% BOD/COD: 0.32	Biodegradability was increased moderately by the ozone.	Kreetachat <i>et al.</i> 2007
Pulp & paper	Biological, chemical	An anaerobic bioelectrochemical system	COD: 51-55% Color: 68-100%	There was simultaneous recovery of methane.	Krishna <i>et al.</i> 2014
Paper mill	Chemical	Photocatalytic treatment with UV & TiO <sub>2</sub> and optional peroxide	COD: 54-65% Color: 82-89%	Peroxide enhanced the system performance. The UV lamp had to be kept close.	Kumar <i>et al.</i> 2011
Phenolic	Biological	Peroxidases from potato pulp	Phenols: 90-95%	Stable in pH range 4 to 8.	Kurnik <i>et al.</i> 2015
Paper mill	Mechanical	Ultrafiltration membranes (ceramic)	COD: 36-50%	Backflushing conditions were optimized.	Laitinen <i>et al.</i> 2001

Pulp & paper	Biological	Anaerobic digestion of TCF bleaching effluent		Biogas yield was optimized.	Larsson <i>et al.</i> 2015
Pulp mill	Mechanical	Nanofiltration was used to remove metal complex from TCF effluent.	Fe, Mn: 99-100%		Lastra <i>et al.</i> 2004
Pulp & paper	Biological	Activated sludge treatment		Most of the contents were of medium molecular mass	Leiviska <i>et al.</i> 2008
Pulp & paper	Biological	Activated sludge treatment		Size fractionation before and after aerobic treatment	Leiviska <i>et al.</i> 2009
Sulfite pulp	Chemical	Electrocoagulation		Treatment was effective for high molecular mass fraction.	Lewis <i>et al.</i> 2013
Pulp & paper	Chemical, mechanical	Composite flocculant followed by reverse osmosis filtration	COD: 75%	The composite flocculant aided the reverse osmosis process.	Li and Zhang 2011
Pulp & paper	Biological	Anaerobic co-digestion with MSG and sludge from pulp & paper	COD: 48%	Good methane production was achieved.	Lin <i>et al.</i> 2011
Pulp & paper	Biological	Simultaneous saccharification & fermentation of the sludge	-	Co-digestion with the MSG sludge was helpful.	Lin <i>et al.</i> 2012
APMP pulp	Biological	<i>Aspergillus niger</i> treatment	MTBE: 97% COD: 60% Turbidity: 77% Color: 43%	These results were achieved without a preflocculation step.	Liu <i>et al.</i> 2011
TMP pulp	Biological	Activated sludge treatment	BOD:	Suggested to use an anaerobic stage & nutrient addition.	Liver <i>et al.</i> 1993
Pulp mill	Chemical	Solar Fenton treatment and dark Fenton	COD: 90% Polyphenols: 90%	Solar Fenton was effective before biological treatment	Lucas <i>et al.</i> 2012
Pulp & paper	Biological	Upflow anaerobic biological treatment	COD: 54-70%	Cost-effective, produces CH <sub>4</sub> ; best followed by aerobic treat.	Maat & Habets 1987
NSSC	Biological	High-efficiency compact reactor	COD: 65-70% BOD: 93-97% Extractives: 99% Acetates: 96% Carbohydrates: 80% Lignin-like: 15% Toxicity: 93-99%	The main contributor to the toxicity was the C <sub>18</sub> fatty acids.	Magnus <i>et al.</i> 2000

Pulp & paper	Chemical	Electrochemical degradation with Fe electrode	COD: 80% Color: 90%	Increased salinity reduced treatment time needed. Alum yielded further reductions.	Mahesh <i>et al.</i> 2006
Pulp mill	Biological	Aerated biological treatment	Phyto-sterols: 90%	Both biosorption & degradation were important.	Mahmood-Khan & Hall 2013
Pulp & paper	Biological	Fungi isolated from polluted soil were used as an immobilized fungal consortium.	Color: 79% Lignin: 79% COD: 89%	Most of the reductions were obtained during the first 24 hours of treatment.	Malaviya & Rathore 2007
Pulp & paper	Mechanical	Membrane filtration (nano- and reverse osmosis) of biologically treated effluents	Color: 97-100 COD: 66-100% BOD: 53-94% Monovalent: 95%	The main difference between NF and RO membrane was that RO regained monovalent ions.	Mänttari & Nyström 2007
Pulp & paper	Chemical, mechanical	Membrane filtration and ozone treatment of the concentrate	Turbidity: 50% Color: 96-99% COD: 83-97% Lignin: 50% Sulfate: 88-98% Salts: 76-92%		Mänttari <i>et al.</i> 2008
Pulp mill	Biological	Aerobic immobilized fungal treatment of black liquor	Color: COD:	The treatment was called bio-bleaching.	Marwaha <i>et al.</i> 1998
Pulp & paper	Biological	Bacterial degradation of chlorophenols	Cl-phenol: 20-83%	High concentrations of the Cl-phenols inhibited growth.	Matafonova <i>et al.</i> 2006
Pulp & paper	Chemical	Advanced oxidation with ozone or TiO <sub>2</sub> and irradiation	COD: 35-60% COD: 90% as post	Ozone was the more effective, especially as post-treatment.	Merayo <i>et al.</i> 2013
Lignin	Chemical	Heterogeneous photo-Fenton and photocatalysis	COD: 20-80%	Influence of alkalinity in AOPs heterogeneous processes	Merayo <i>et al.</i> 2016
Pulp & paper	Biological	Anaerobic digestion of wastewater or sludge	COD: 30-90% Vol. solids: 21%-55%	Co-digestion of streams can even out variations.	Meyer & Edwards 2014
Kraft pulp	Biological	Continuous anaerobic bioreactor with ultrafiltration	Sulfur: 80% BOD: 93%	Sulfur was stripped from the bio-gas and removed.	Minami <i>et al.</i> 1991
Paper industry	Chemical, Biological	Ozone & biofilter	COD: 60-85%	O <sub>3</sub> +bio-filter+O <sub>3</sub> +bio-filter improved COD removal >10% reducing the need of ozone.	Mobius and Helble 2004
Kraft pulp	Chemical	Heterogeneous photocatalysis ZnO/UV	TOC: 0-15% Color: 5-54%	The pre-biological treatment by photocatalysis enhanced 45% the biodegradability	Moraes <i>et al.</i> 2006

Recyc. paper	Biological	Aerated granulated carbon sequencing batch biofilm reactor	COD: 34-80%	The system failed to deliver stable performance.	Muhamad <i>et al.</i> 2012a
Recyc. paper	Biological	Aerated granulated carbon sequencing batch biofilm reactor	COD: 90% Cl-phenols: 90% Nitrogen (NH <sub>3</sub> ): 90%	The system was sensitive to aeration rates.	Muhamad <i>et al.</i> 2012b
Recyc. paper	Biological	Aerated granulated carbon sequencing batch biofilm reactor	COD: 95% Cl-phenols: 81% Nitrogen (NH <sub>3</sub> ): 100%	Optimization using RSM	Muhamad <i>et al.</i> 2013
Kraft pulp	Chemical, biological	A combination of ozone and immobilized activated sludge.		Strongly alkaline conditions enhanced lignin degradation.	Nakamura <i>et al.</i> 1997
Paper mill	Mechanical Chemical	A flotation save-all & coagulation with alum, ferric chloride, <i>etc.</i>	Solids: 80%-90%	Also discussed hypochlorite oxidation before discharge.	Nassar 2003
Pulp & paper	Mechanical chemical	Microfiltration & electro dialysis with ion exchange pairs	Salts: 95% Lignin: 90%	90% of the water could be returned clean to the system.	Nataraj <i>et al.</i> 2007
Pulp & paper	Mechanical chemical	Nanofiltration and ultrafiltration using shear-enhanced modules	Salts: 1-78% TOC: 25-88% Sugar: 36-97% Lignin: 17-97% Color: 86-98%	Chemical treatment, ozone, & biological to help membrane. Nanofiltration was much more effective than ultrafiltration.	Nuortila-Jokinen <i>et al.</i> 2004
Pulp & paper	Biological	Microbial consortium for the BOD test.	-	An acclimated consortium gave higher BOD numbers.	Ordaz-Díaz <i>et al.</i> 2014
Paper mill	Biological	Pilot-scale aerobic lagoon treatment	BOD: 73-93% Color: Increased	Bacteria were able to adapt to changing conditions.	Ordaz-Díaz <i>et al.</i> 2016
Recyc. paper	Biological, mechanical	Anaerobic, aerobic, ultrafiltration, reverse osmosis sequence.	COD: 53-81% BOD: 68-98% Sulfate: 30-96%	The multi-stage treatment enable reuse of the water.	Ordóñez <i>et al.</i> 2010
Paper mill	Mechanical	Micro- & nano-filtration, followed by reverse osmosis	Salt: 99%	Disinfecting agents were used to minimize fouling.	Ordóñez <i>et al.</i> 2011
Recyc. paper	Biological	Granulated activated carbon sequencing batch biofilm reactor	COD: 53-92% AOX: 26-99%	High hydraulic retention time increased performance.	Osman <i>et al.</i> 2013
Pulp mill	Chemical	TiO <sub>2</sub> /Fe(III)/solar UV oxidation	Color: 78% TOC: 64% AOX: 68%	Conditions were optimized.	Parilti & Akten 2011
Paper mill	Mechanical	Drum % disk save-alls compared	Solids:	Cloudy & clear filtrates made.	Perrault 1993
Bleach plant	Chemical	Catalytic wet air oxidation with TiO <sub>2</sub> or ZrO <sub>2</sub> or with ruthenium	TOC: 79-99.7%	Outstanding results when using ruthenium on oxide.	Pintar <i>et al.</i> 2001

Pulp & paper	Mechanical	Membranes (MF, UF, NF, RO)	COD: TOC:	Ceramic MF judged to be best.	Pizzichini <i>et al.</i> 2005
Bleachery	Chemical	Hydrogen peroxide and UV light	Color: 30-70%	Long treatment times needed, & incomplete decolorization	Prat <i>et al.</i> 1988
Pulp mill	Mechanical	Ultrafiltration membranes (regen. cellulose or polysulfone)	TOC: 80-92% Carbohyd.: 80-92%	Cellulose-based membranes exhibited less fouling.	Puro <i>et al.</i> 2010
Pulp & paper	Biological, chemical	Thermophilic submerged aerobic membrane bioreactor	COD: 87%-96% Color: Up to 100%	Cake formation was the dominant fouling mechanism.	Qu <i>et al.</i> 2012
Bleachery	Mechanical	Membranes (UF, UF/NF, NF)	COD: 79% Color: 86%	A "tight" UF membrane was judged to be the best.	Quezada <i>et al.</i> 2014
Paper mill	Mechanical	Ultrafiltration		Less effective than the membrane bioreactor (next).	Ragona & Hall 1998
Paper mill	Mechanical biological	Membrane biological reactor	COD: 48-58% Solids: 25-35% Salts: 20-30%	Water was recovered suitable for reuse in papermaking.	Ragona & Hall 1998
Pulp & paper	Chemical	Coagulation with poly-DADMAC of various molecular mass	Turbidity: 70-92% COD: 90-99%	Higher mass was more efficient	Razali <i>et al.</i> 2011
Recyc. paper	Chemical	Coagulation of water after bio-treatment using chitosan, PAC	COD: 40-80% Turbidity: 55-85%	Chitosan out-performed the poly-aluminum chloride (PAC).	Renault <i>et al.</i> 2009
Pulp & paper	Chemical	Coagulation-flocculation, using FeCl <sub>3</sub> & chitosan	Turbidity: 89% Color: 90% Lignins: 70-80%		Rodrigues <i>et al.</i> 2008
Pulp & paper	Chemical	Coagulation-flocculation, using FeCl <sub>3</sub> & chitosan, then UV/TiO <sub>2</sub> /H <sub>2</sub> O <sub>2</sub> with mercury lamps	Color: 98-100% BOD/COD: 0.71	Sulfur was mineralized to sulfate. Toxicity & odor were removed.	Rodrigues <i>et al.</i> 2008
Pulp mill	Chemical	Fenton with Fe complexes (DBHA, etc.)	AOX: Toxicity:	DBHA seemed to act as a mediator.	Rodriguez <i>et al.</i> 1999
Pulp & paper	Chemical	Polyelectrolyte treatment	Color: Turbidity: COD:	Polyelectrolyte treatment was compared with conventional alum treatment.	Rohella <i>et al.</i> 2001
Paper mill	Biological	Biofiltration using the Biofor process		Four paper mill effluents were evaluated.	Rovel <i>et al.</i> 1994
Kraft pulp	Biological	Anaerobic biological treatment alone	COD: 61% TOC: 69% BOD:90% AOX: 55%	This series was run as a default condition.	Ruas <i>et al.</i> 2012

Kraft pulp	Chemical, biological	Advanced oxidation with H <sub>2</sub> O <sub>2</sub> /UV as post-treatment after anaerobic treatment	COD: 0%-11% Lignin: 16-35% AOX: 23-54%	Peroxide increased the BOD/COD ratio. Post-treatment was effective.	Ruas <i>et al.</i> 2012
Paper mill	Biological, chemical	Aerobic thermophilic treatment with nutrient added, then alum	BOD: 81-97%	Thermophilic conditions yield dispersed cells that need to be agglomerated.	Rudolfs & Amberg 1953
Pulp & paper	Biological	Fluidized bed biofilm reactor, anaerobic, aerobic, then flotation.	COD: 35-50% BOD: 85% AOX: 50%	For challenging effluents, an anaerobic stage was followed by two aerobic stages	Rusten <i>et al.</i> 1994
Pulp & paper	Mechanical	Reverse osmosis membrane	-	The filtrate is suitable for reuse in papermaking.	Saif <i>et al.</i> 2013
Lignin	Biological	Fungal strain	Color: 80%	Adsorption & bioaccumulation were the main mechanisms.	Sakurai <i>et al.</i> 2001
Paper mill	Chemical	Electrochemical oxidation to convert sulfides		Sulfide removal was successful.	Särkkä <i>et al.</i> 2009
Pulp & paper	Biological	White-rot fungal treatment	Color: 34% COD: 41% Lignin: 16%	<i>Phanerochaete chrysosporium</i> with other fungi.	Saxena & Gupta 1998
Pulp & paper	Biological	Surfactants	Color: 81% COD: 75% Lignin: 66%	Best results with Tween-80	Saxena & Gupta 1998
Bleachery	Biological	Activated sludge & options with stabilization basins	Cl-phenolics: 85-93% AOX: 43-58% Toxicity: Removed	Lab-scale tests supported ways to enhance activated sludge treatment.	Schnell <i>et al.</i> 2000a
Newsprint paper	Chemical	Electro-Fenton	COD: 90% Color: 95%	Biologically treated effluent	Selvabharathi & Kanmani 2010
Bleachery	Mechanical	Ultrafiltration & reverse osmosis			Sierka <i>et al.</i> 1997
Paper mill	Biological, mechanical	Anaerobic/aerobic membrane bioreactor with NF or RO filtration	COD: 96-98%	The system performed stably with varying inputs.	Sheldon <i>et al.</i> 2012
Pulp mill	Biological	Anaerobic treatment of TMP and soda pulping effluents	Acidification: 50%	Wood resins inhibited methane production.	Sierraalvarez <i>et al.</i> 1991
Pulp & paper	Chemical	Coagulation with alum or PAC and a flocculant	Turbidity: 98% TSS: 92% COD: 60%	Optimized at pH=9.	Simonič & Vnucec 2012
Pulp & paper	Mechanical	Ultrafiltration	Turbidity: 99% TSS: 99%	Multi-channel membrane with Al <sub>2</sub> O <sub>3</sub> & ZrO <sub>2</sub>	Simonič & Vnucec 2012

Deinking	Biological	Submerged membrane bioreactor - thermophilic aerobic	COD: 83% BOD: 99% Ca: 20%-50%	Low sludge yield; diverse consortium of organisms.	Simstich <i>et al.</i> 2012
Pulp & paper	Mechanical	Ultrafiltration, comparing pretreatment with NaOH & SDS	-	The combination treatment decreased fouling.	Singh <i>et al.</i> 2012
Pulp & paper	Biological	Four fungi were compared	Color: 67% Lignin: 37% Toxicity: 60%	Conditions were optimized.	Singhal & Thakur 2009
Pulp & paper	Chemical, biological	Electrochemical pretreatment to improve biodegradability	COD: 55% Color: 87%	The pretreatment aided the biological treatment.	Soloman <i>et al.</i> 2009
Bleachery	Biological	White-rot fungal treatment with air-lift bioreactor	Color: 40-44% Phenol: 30-51% COD: 37-43%	Enzyme activity was detected.	Souza <i>et al.</i> 2014
TMP, BCTMP	Chemical	Coagulation with Fe & Al compounds	Carbon: 88% Color: 90% Turbidity: 98%	The pH had to be optimized to get clear & colorless treated water.	Stephenson & Duff 1996
Paper mill	Chemical	Fenton-like	COD: 50% Color: 100%	Treatment also at pilot scale	Tambosi <i>et al.</i> 2006
Pulp & paper	Biological	Algae batch reactor	COD: 84% AOX: 80%	Some <i>Chlorella</i> and diatom species were dominant.	Tarlan <i>et al.</i> 2002a
Pulp & paper	Biological	Sequential batch reactors with algae	COD: 60-85% Color 42-75% AOX: 82-93%	Algal treatment metabolized chlorinated organics. Some lignin was adsorbed.	Tarlan <i>et al.</i> 2002b
Pulp mill	Biological	Thermophilic anaerobic bio-treatment	COD: 80%	Thermophilic conditions were promising.	Tartakovsky <i>et al.</i> 2003
Pulp mill	Biological	Fungal upflow reactor with glass wool packing	AOX: 50-70% Color: Dechlorination:	No dissolved oxygen was needed by the fungus.	Taseli & Gokcay 1999
Pulp & paper	Mechanical chemical	Ultrafiltration with polymer complexation by PEI, PVOH	Metals: 35-92% COD: 45-57% Color: 88-98% Turbidity: 99%	The polymer treatments helped the ultrafiltration performance.	Tavares <i>et al.</i> 2002
Paper mill	Biological	Membrane bioreactors compared	DOC: 50-90%	Performance was modeled.	Tenno & Paulapuro 1999

Pulp & paper	Biological	Screening of microbial strains, both fungal & bacterial	Color: 25-82% Lignin: 24-50% AOX: Often went up.	Wide variations amount the different species.	Thakur 2004
Pulp & paper	Biological	Three selected bacteria	BOD: 50-90% COD: 50-70% AOX: 76%	Bacterial cultures were shown to be effective.	Tiku <i>et al.</i> 2010
Kraft pulp bleaching	Chemical	Fenton and photo-Fenton treatments	TOC: 90%	Elimination of chlorinated components by photo-Fenton.	Torrades <i>et al.</i> 2003
Kraft pulp	Biological	Mesophilic & thermophilic aerobic sequencing batch reactor	COD: 40-76% AOX: 20-75%	Thermophilic conditions were promising except for AOX.	Tripathi & Allen 1999
Paper mill	Chemical	Electrocoagulation with Al and Fe electrodes	Lignin:80-92% Phenol: 93-98% BOD: 70-80% COD: 55-75%	Removal increased with current density applied.	Ugurlu <i>et al.</i> 2008
Bleachery	Chemical	UV oxidation with TiO <sub>2</sub> & H <sub>2</sub> O <sub>2</sub>	AOX: 80-90% Lignin: 22-88%	Conditions were optimized.	Ugurlu & Karaoglu 2009
Pulp mill	Chemical	Electrocoagulation and then filtration	Toxicity: 100% Resins: 63-97% Copper: 80-100%	Synthetic wastewater with resin acids and copper; also debarking wastewater tested.	Vepsäläinen <i>et al.</i> 2011a
Pulp & paper	Chemical	Electrocoagulation with Fe electrodes	Sulfides: 88% Phosphorus: 40%	Electrocoagulation was promising for sulfur removal.	Vepsäläinen <i>et al.</i> 2011b
Paper mill	Chemical	Wet oxidation of membrane concentrates	COD: 50-80% TOC: 50-80%	The overall cost was lower with air than with oxygen.	Verenich <i>et al.</i> 2000
Pulp & paper	Chemical	Coagulation & wet air oxidation of TMP & membrane concentrate	COD: 50-100%	The combined treatment gave completely clean water.	Verenich <i>et al.</i> 2001
Kraft pulp	Biological, chemical	Horseradish peroxidase and H <sub>2</sub> O <sub>2</sub> treatment of foul condensate	Phenols: 90-100% Toxicity: 40-50% COD: marginal		Wagner & Nicell 2001
Pulp & paper	Chemical	Electrochemical oxidation with Co/Cu-modified kaolin	COD: 97%	Optimization at pH=3.	Wang <i>et al.</i> 2007
Paper mill	Chemical	Coagulation of wastewater, interferences by PEO, a-PAM	COD: increased Turbidity: increased TSS: increased	The polyelectrolytes appeared to stabilize the suspension.	Wang & Pan 1999
Pulp mill	Chemical	Aluminum chloride coagulation with a starch-based flocculant	Turbidity: 99.6% Lignins: 88%	Conditions were optimized.	Wang <i>et al.</i> 2011

Pulp mill	Chemical	Irradiation	Phenolic OH: 40%	Irradiation destroyed lignin's benzene ring skeleton.	Wang <i>et al.</i> 2014
Pulp & paper	Biological	Aerated lagoons with support material added at pilot scale	COD: 60-70% Phosphorus: 60-70%	In the full-scale system only 30-40% COD reduction seen.	Welander <i>et al.</i> 1997
Bleachery	Biological	White-rot fungal treatment	AOX: COD:	Such treatment was suggested for closed-water-system.	Wolfaardt 1994
Pulp & paper	Chemical	Flocculation using polyacrylamide of various charge	Turbidity: 95% TSS: 98% COD: 93%	Single-polymer treatment with cationic PAM was judged to be cost-effective.	Wong <i>et al.</i> 2006
Pulp mill	Biological	White-rot fungi on biofilm on porous plastic support to treat black liquor	Lignin: 71% COD: 48%	The pH was best to 9-10, and nutrients were needed (glucose or ammon. tartrate)	Wu <i>et al.</i> 2005
Bleachery	Chemical	Advanced oxidation with ozone, UV, TiO <sub>2</sub> , ZnO combinations	COD: 58-70% TOC: 75-80% Biodegrad.: 0.4-1	The ozone UV system was most efficient.	Yeber <i>et al.</i> 1999b
Kraft	Chemical	TiO <sub>2</sub> /UV supported	COD: 58% TOC: 55% AOX: 90%		Yeber <i>et al.</i> 12000
Paper mill	Biological	Mesophilic & thermophilic filters were compared.	COD: 80%	Methane generation was ~ the same for each temperature.	Yilmaz <i>et al.</i> 2008
Paper mill	Chemical	Photocatalytic treatment with TiO <sub>2</sub> on activated carbon support	COD: 62%	The catalyst could be used repeatedly.	Yuan <i>et al.</i> 2007
Pulp & paper	Mechanical	Ultrafiltration & nanofiltration of extraction-stage bleach effluent	COD: 85-90%	A volume reduction factor of 30 was achieved, allowing reuse.	Zaidi <i>et al.</i> 1992
Paper mill	Chemical	Coagulation with alum and flocculation with polyacrylamide	TSS: 76-99% BOD: 26-87% COD: 26-97% NH <sub>3</sub> : 6-57%	Parameters were adjusted to achieve high removal.	Žarković <i>et al.</i> 2011
Paper mill	Mechanical, biological	Integrated membrane process with anaerobic & aerobic tanks and reverse osmosis	Conductivity: Turbidity: COD:	The treated water could be reused in papermaking.	Zhang <i>et al.</i> 2009
Paper mill	Chemical	Electrocoagulation with aluminum or iron plates	DOC: 24-46% COD: 32-68%	Settling was better with the aluminum plates.	Zodi <i>et al.</i> 2011