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# Pulp Mill Wastewater: Characteristics and Treatment

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<http://dx.doi.org/10.5772/67537>

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## Abstract

The production of chemical pulp in recent times is 180 million tons per year; while the production of eucalyptus pulp has increased intensively, especially in the southern hemisphere. The pulp and paper industry has long been considered a large consumer of natural resources (wood and water) and one of the largest sources of pollution to the environment (air, water courses and soil). Important efforts are being made to reduce the pollutant levels and water consumption of the industry. The wastewater composition, and therefore, the efficiency of effluent treatments and characteristics of the discharges to water are strongly dependent on the applied technology and raw materials. Despite a large body of literature on softwood-based wastewater, few studies have examined the characteristics of kraft eucalyptus bleaching effluents and their behaviour in the different biological treatments. The largest secondary treatment systems today use the activated sludge process. Sixty to seventy-five per cent of all the biological effluent treatment plants within the pulp and paper industry use this kind of treatment system. This chapter reviews the current pulping technologies at mills and compares the chemical composition and biological treatment of wastewater between softwood and hardwood bleached pulps.

**Keywords:** pulp mills, hardwood, softwood, kraft pulping, ECF-TCF bleaching

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## 1. Introduction

The pulp and paper mill industry is an intensive consumer of water and natural resources (wood), discharging a variety of liquid, gaseous and solid wastes to the environment. Since the 1970s, a growing awareness of the effects of pulp and paper wastes in the ambience had prompted water and energy consumption levels and the loads of toxic compounds discharge to reduce. One of the most important implemented changes in this regard was made within the mill, wherein chlorine was completely substituted by, that is, chlorine dioxide as the bleaching

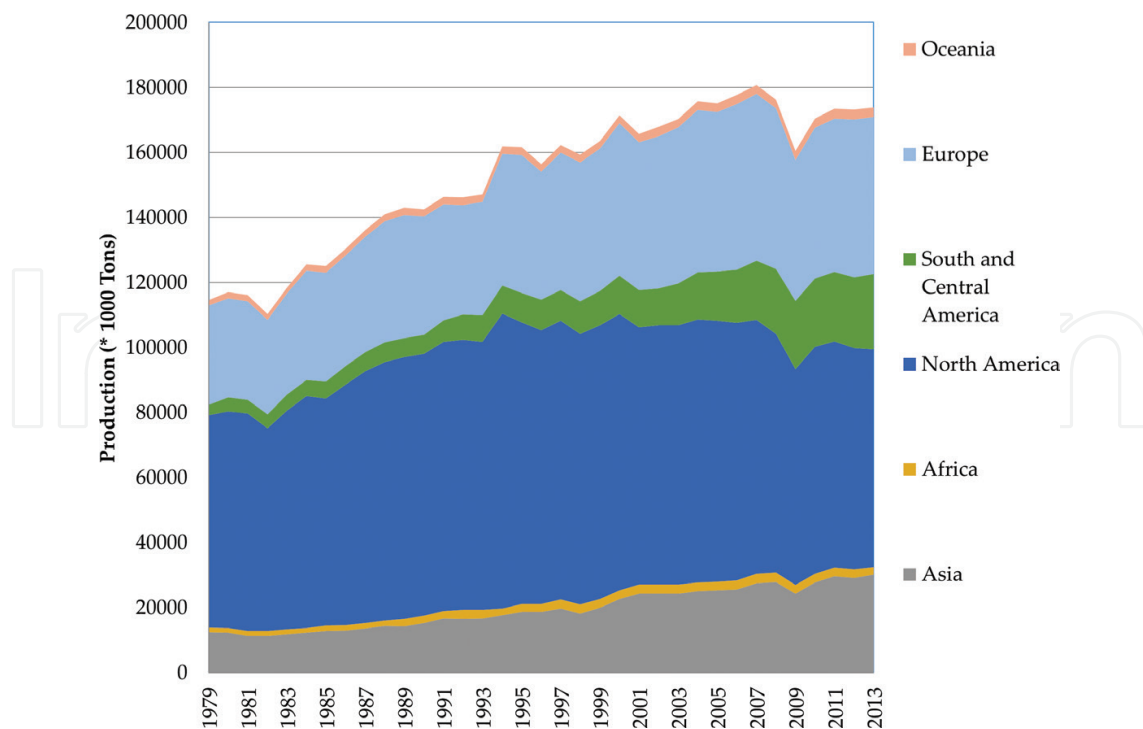
chemical agent. Another major issue was the implementation of secondary biological treatments. The wastewater composition and hence the effluent treatment efficiencies and characteristics of the discharges are strongly dependent on the technology applied and the raw materials. In the last 25 years, however, the global distribution of pulp producers has significantly changed and so have the species of wood used. Eucalyptus pulp production, for example, is becoming a leader in the hardwood pulp market; Brazil went from being a pulp consumer to a world leader in hardwood pulp production, and since 2008, it has been the fourth largest pulp producer in the world.

2. Wood pulp market

Cellulose pulp is the main raw material in the production of different types of paper and paperboard. It is also used as the absorbent material in diapers and other sanitary products.

The global pulp market has changed intensely in recent years. A few decades ago, this industry was characterized as national character as a supply industry inputs for domestic production of paper and paperboard. Globalization has led to increased competitiveness in the international market, as new players have emerged both at the level of producers and consumers. Within the latter, the appearance of China and India have strongly modified cellulose demand worldwide [1].

**Figure 1** graphically shows the evolution of world’s production of wood pulp between 1979 and 2013 according to the data published by FAO [2–6].



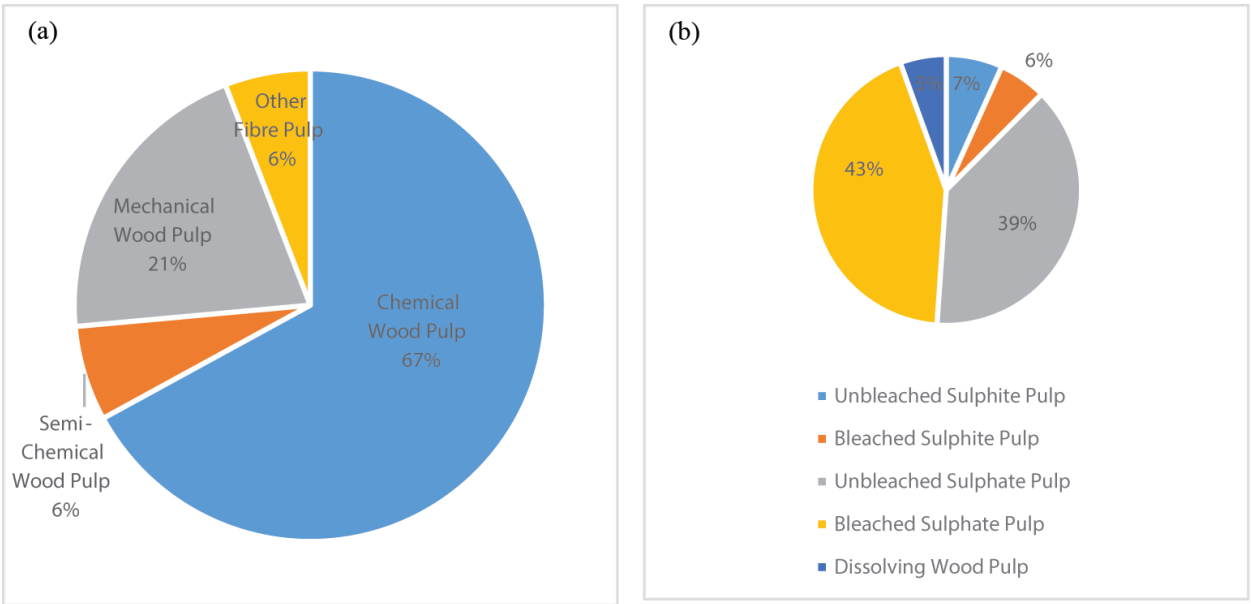
**Figure 1.** World pulp production 1979–2013. Data obtained from Ref. [2].

It is clearly shown that the world’s wood pulp production increased to about 50% in this period, from 120 million tons in 1979 to nearly 180 million tons in 2013. Part of this growth can be explained by the explosive increase in production in non-traditional wood pulp producing regions such as Asia and South America. The main producing regions are still North America with 38% and Europe with 28%, even though in 2013, Asia produced 17% of the wood pulp and South America about 13% [6].

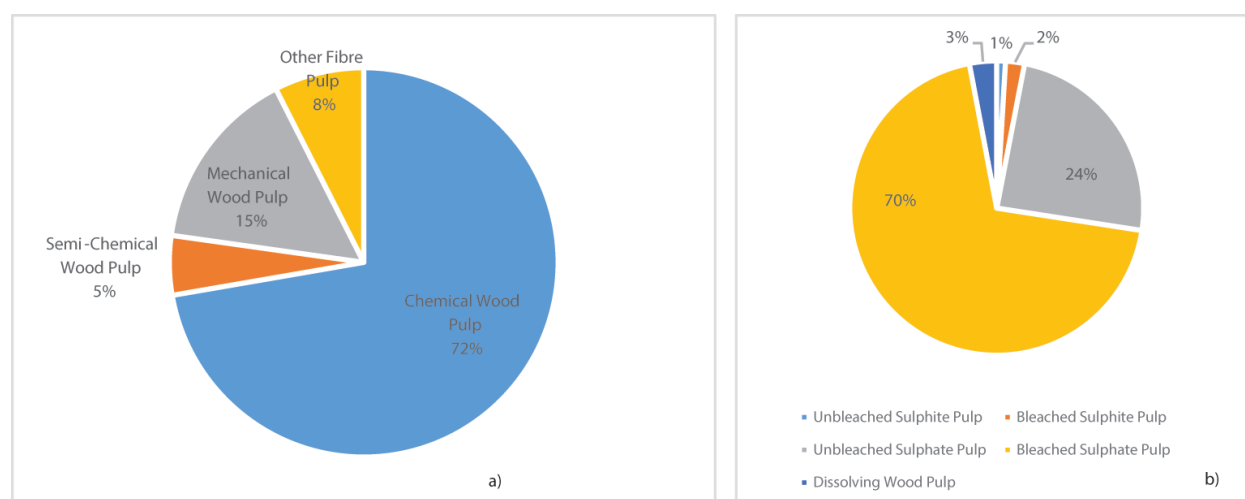
Wood pulp grades are categorized according to the pulping process, which can be classified as mechanical, semi-chemical and chemical pulps. In a mechanical process, logs or wood chips are mechanically grinded by abrasive action. In a chemical cooking process, a significant part of the wood components (mainly lignin) is chemically dissolved to obtain a solid compound with high cellulose fibre content. There are two main methods of chemical pulping: (1) sulphite pulping and (2) sulphate (kraft) pulping. The first process—sulphite cooking process—uses aqueous sulphur dioxide ( $\text{SO}_2$ ) and a base of calcium, sodium, magnesium or ammonium. The kraft process uses a treatment comprising a mixture of sodium hydroxide and sodium sulphide, known as white liquor, at a high pressure and temperature. The semi-chemical pulping process combines chemical and mechanical methods, where wood chips are first softened or partially cooked with chemicals and then mechanically pulped [7].

**Figures 2** and **3** illustrate the different kinds of pulp produced in 1979 and 2013.

The rise in wood pulp production is due to an increase in chemical pulp production, as the production of mechanical pulp has declined in the same period. Mechanical pulping has the advantage of converting up to 95% of dry weight wood into pulp, although considerable



**Figure 2.** (a) World pulp production by type of pulp in 1979; (b) different kinds of chemical pulps produced in 1979 (Data from FAO [2]).



**Figure 3.** (a) World pulp production by type of pulp in 2013; (b) different kind of chemical pulps produced in 2013 (Data from FAO [6]).

amounts of energy are required to do so. The pulp obtained produces a highly opaque paper with good printability, but the physical properties are inferior than chemical pulps and yellowing when exposed to light. Moreover, mechanical pulps are mainly produced from softwood [7].

There are significant changes in the production of chemical pulp. The use of sulphite cooking process in pulp production compared to kraft pulping technology decreased steadily, from 60% in 1925 to 20% in 1967 and 9.2% in 1979 to only 2.4% in 2013 [6, 8]. The superiority of kraft pulping process is explained by the following facts: (1) all wooden materials including low-quality wood can be used as raw material; (2) superior fibre strength of pulp compared to other chemical pulping methods; (3) more simple chemical and energy recovery process; (4) scale of economy of kraft methods prevents competition and (5) low environmental risks in modern mills [9].

A second classification considers the type of wood used by distinguishing softwood or long fibre (produced mainly from pine and spruce) from hardwood or short fibre (produced from eucalyptus, birch, poplar, etc.) [10]. A gradual move from softwood to hardwood can be observed. In 2013, 56% of bleached kraft pulp was produced with long-fibre wood (softwood), while the remaining 44% was produced with short-fibre wood (hardwood) (according to data from Ref. [6]). In 1980, the production capacity of bleached kraft pulp corresponded to 63% of softwood pulp. The entry into the market of non-traditional producing countries such as Brazil, Indonesia, Spain and Portugal, significantly increased the production of hardwood pulp. Eucalyptus bleached pulp production is rapidly increasing (from 8 million tons in 2003 to nearly 15 million in 2015), and eucalyptus wood is thus considered to be the most important raw material of hardwood bleached market pulp in the world [11].

As kraft pulping is by far the most common process used these days, this chapter will focus in the wastewaters generated in this process.

### 3. Main processes description

#### 3.1. Mechanical pulping

The oldest method of mechanical pulping is the groundwood process. In this process, round logs are forced against a rotating pulp stone (revolving at peripheral speeds of 1000–1200 m/min), under specified conditions of pressure and temperature. Atmospheric grinding, pressure grinding and thermo-grinding could be done according to the applied temperature and pressure. In all of them, the temperature levels obtained from the heat applied or from rubbing the logs on the stone soften and break down the fibres structure; and cracks the fibres from the wood matrix [7, 8].

Another common method is the refiner mechanical pulping (RMP). The wood chips are pulled between two rotating disks. Among them, thermomechanical pulping operates like RMP, but under higher temperature and pressure. The high temperature and pressure levels soften the lignin even more than frictional heat, making fibres separation easier. Thermomechanical pulp is stronger than refined mechanical pulp, and still retains the high-yield and cost-effectiveness of mechanical pulps [7].

#### 3.2. Chemical pulping

##### 3.2.1. Sulphite pulping

Sulphite process is very versatile, and covers the entire pH range, achieving high fibre flexibility in pulp yields and properties. The cooking process involves the use of aqueous sulphur dioxide ( $\text{SO}_2$ ) and a base: calcium, sodium, magnesium or ammonium. Sulphite pulping was developed in the second half of the nineteenth century and for several decades, the calcium acid sulphite process was the most common method. However, since 1950, the utilization of bases other than calcium has been a major development. The specific base used will determine the process's chemical and energy recovery system and water use. The use of the relatively cheap calcium base has become obsolete because the cooking chemicals cannot be recovered. Magnesium and sodium bases allow chemical recovery, and magnesium bases are currently the dominant choice in sulphite pulping process [7, 12].

##### 3.2.2. Kraft pulping

In kraft pulping, white liquor, containing mainly active chemicals—sodium hydroxide and sodium sulphide—is used for cooking the chips at a high temperature (150–170°C) and pressure. Approximately, half of the wood composition degrades and dissolves during cooking. The spent cooking liquor (black liquor) contains reaction products of lignin and hemicelluloses, and is concentrated and burned in a recovery boiler that recovers the cooking chemicals and generates energy. The smelt is dissolved into water to form green liquor (mostly sodium carbonate and sodium sulphide), which then reacts with lime to convert the sodium



carbonate into sodium hydroxide regenerating the white liquor. After cooking and washing, a brown pulp (brown stock pulp) is obtained. Printing, writing and tissue papers require the pulp to be bleached which removes the excess lignin and chromophores to produce a “white” pulp.

#### 4. Background of pulp mill effluents: environmental fate and effects

The pulp and paper industry consumes enormous amounts of water and natural resources and is also one of the largest effluents generators. Before the 1970s, wastewaters from the pulp and paper mills were normally discharged directly to the rivers or lakes, without any treatment or even a rough primary treatment. The high organic loads and solid content in the effluents affected the aquatic ecosystem in several ways such as localized damage to the benthic community, oxygen depletion in large areas and numerous changes in fish reproduction and physiology. In the 1980s, studies in Scandinavia, along the Baltic Coast and the Gulf of Bothnia, showed alterations in fish reproduction and increase of diseases and parasites [13, 14]. Studies conducted in USA and Canada in the beginning of the 1990s, under the Environmental Effects Monitoring (EEM) program [15, 16], revealed delayed sexual maturity, smaller gonads, changes in fish reproduction and depression in secondary sexual characteristics in species living downstream of pulp and paper mills discharges.

From the end of the 1970s until now, the main concern regarding effluents is the formation of chlorinated compounds in bleaching plants. In 1985, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) was discovered in the pulp mill effluents, which led to a general concern over the formation of chlorinated organic matter in chlorine bleaching. Consequently, the use of chlorine in the bleach plants gradually decreased until it was completely substituted with chlorine dioxide. In many countries, the environmental control authorities set strict restrictions on the discharges of chlorinated organics, measured as adsorbable organic halogen (AOX), into the aquatic environment. In 1992, the Swedish Environmental Protection Agency limited organochlorines emissions to 1.5 kg AOX/t of pulp and in 1995, Finland’s official limit was set at 1.4 kg AOX/t of pulp [14].

Several authors reported that with the replacement of chlorine with chlorine dioxide, the effluent quality improved in AOX levels and the elimination of detectable amount of dioxins, polychlorinated compounds and chloroform [12, 13, 17].

The European Integrated Pollution and Prevention Control [12] has created reference documents (BREF) that set the Best Available Techniques (BAT) for several industrial sectors. The pulp and paper industry has a very defined set of operations to be especially applied in the new mills. Similarly, the International Finance Corporation [18] among others has defined directives that could be required to give financial support for the construction of new mills. For kraft pulp, the most important guidelines are listed in **Table 1**.

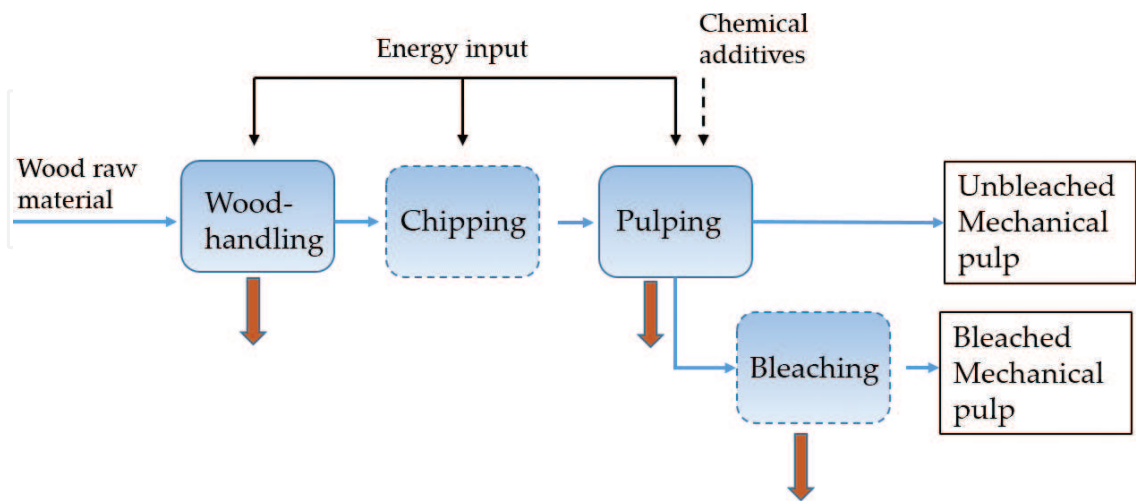
|  |
|--|
| Dry debarking of wood  |
| Extended modified cooking to a low kappa number (batch or continuous)  |
| Systems for collection and recycling of temporary and accidental discharges from process water spills                                    |
| Closed screening   |
| Efficient washing of the pulp ahead of the bleaching   |
| Oxygen delignification ahead of the bleach plant   |
| Elemental chlorine free (ECF) or total chlorine free (TCF) bleaching   |
| Removal of hexenuronic acids by mild hydrolysis at the beginning of the bleaching process, for hardwood pulp, especially eucalyptus      |
| Partial closure of the bleach plant combined with increased evaporation  |
| Sufficient and balanced volumes of pulp storage, broke storage and white water storage tanks to avoid or reduce process water discharges |
| Recycling of wastewater, with or without simultaneous recovery of fibres   |
| Separation of contaminated and non-contaminated (clean) wastewaters  |
| Biological secondary wastewater treatment  |

**Table 1.** Main BAT guidelines from IFC [18] and/or IPPC Bureau [12] regarding wastewater load minimization in bleached kraft pulp mills.

5. Mechanical pulping: wastewater characteristics

Figure 4 shows a block diagram of the main part of the mechanical pulp production indicating the sources of emissions to the water from a pulp mill.

Table 2 shows the specific water consumption and loads before wastewater treatment from the mechanical pulping [12].



**Figure 4.** Main unit operations of the mechanical pulping. Light brown arrows indicate wastewater sources.



| Pulping process | BOD <sub>5</sub> (kg/ADt) | COD (kg/ADt) | Nitrogen (kg/ADt) | Phosphorous (kg/ADt) |
|-----------------|---------------------------|--------------|-------------------|----------------------|
| GW              | 8.5–10                    | 20–30        | 80–100            | 20–25                |
| PGW             | 10–13                     | 30–50        | 90–110            | 20–30                |
| RMP             | 10–15                     | 40–60        | 90–110            | 20–30                |
| TMP             | 13–22                     | 50–80        | 100–130           | 30–40                |

BOD<sub>5</sub>: Biochemical Oxygen Demand; COD: Chemical Oxygen Demand; GW: groundwood pulping; PGW: pressurized groundwood pulping; RMP: refined mechanical pulping; TMP: thermomechanical pulping; ADt: air dry tone (10% water and 90% oven-dry pulp).

**Table 2.** Specific water consumption, organic and nutrient loads before wastewater treatment from the mechanical pulping. Data taken from Ref. [12].

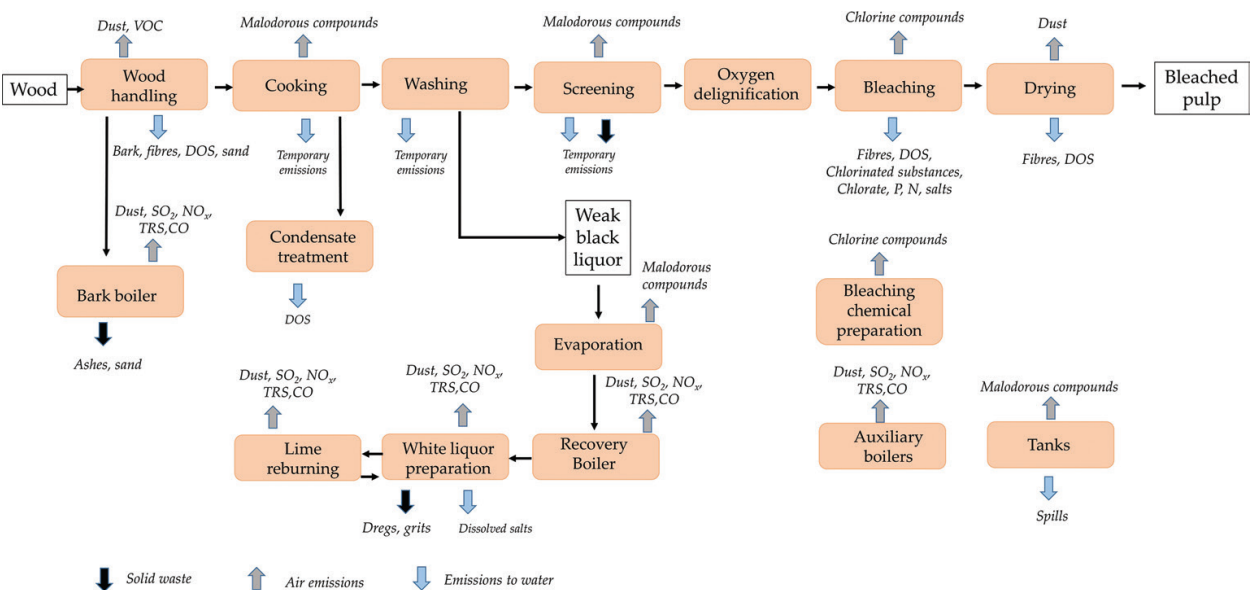
## 6. Kraft pulping: wastewater characteristics

### 6.1. Process description and emissions to water

A kraft pulp mill can be divided into four main parts: (1) raw material handling; (2) pulping line with an almost closed chemical and energy recovery system; (3) bleaching with an open water system and (4) the external wastewater treatment system. **Figure 5** shows the emissions sources to water from a kraft pulp mill.

**Table 3** shows the typical figures for the parameters in different sectors of a kraft pulp mill.

Data on current discharges to water (after wastewater treatment) expressed as loads based on available data from kraft pulp mills within the European Union are given in **Table 4**. **Figure 6** presents a comparison of the discharges to water of different existing mills with the performance of the new mills in South America that are processing eucalyptus wood and apply-



**Figure 5.** Main unit operations of kraft pulping. DOS: dissolved organic substances. Adapted from Ref. [12].

| Department            | Flow | TSS | BOD | AOX | COD | P  | N     |
|-----------------------|------|-----|-----|-----|-----|----|-------|
| Debarking             | 2.5  | 4   | 2   | 0   | 5   | 20 | 0.2   |
| Washing and screening | 0.5  | 3   | 1   | 0   | 2   | 1  | 0.015 |
| Bleaching             | 31   | 2   | 10  | 1.2 | 35  | 47 | 0.075 |
| Condensates           | 1    | 0   | 1   | 0   | 3   | 0  | 0     |
| Others                | 3    | 4   | 4   | 0   | 10  | 7  | 0.002 |
| Total                 | 38   | 13  | 18  | 1.2 | 55  | 75 | 300   |

Flow in m<sup>3</sup>/ADt, TSS, BOD, AOX, COD and Nitrogen in kg/ADt. Phosphorous in g/ADt.

**Table 3.** Sources of effluents and effluents loads from kraft pulp mill [12, 19].

|                 | Flow  | COD                                      | AOX   | TSS     | Total P <sup>1</sup> | Total nitrogen |
|-----------------|-------|--|-------|---------|----------------------|----------------|
| Unbleached pulp | 14–82 | 1.2–23                                   | –     | 0.02–3  | 0–0.05               | 0.01–1.0       |
| Bleached pulp   | 20–94 | 5–20 <sup>2</sup><br>7.5–42 <sup>3</sup> | 0–0.3 | 0.015–7 | 0.003–0.11           | 0.01–0.6       |

Flow in m<sup>3</sup>/ADt, COD, BOD<sub>5</sub>, AOX, TSS, nitrogen and phosphorous in kg/ADt.

<sup>1</sup> Eucalyptus strands contain higher levels of phosphorus compared to other forest species used for pulp production. The average level discharged with the effluent is up to 0.12 kg total-P/ADt.

<sup>2</sup> Emissions from eucalyptus pulp mills.

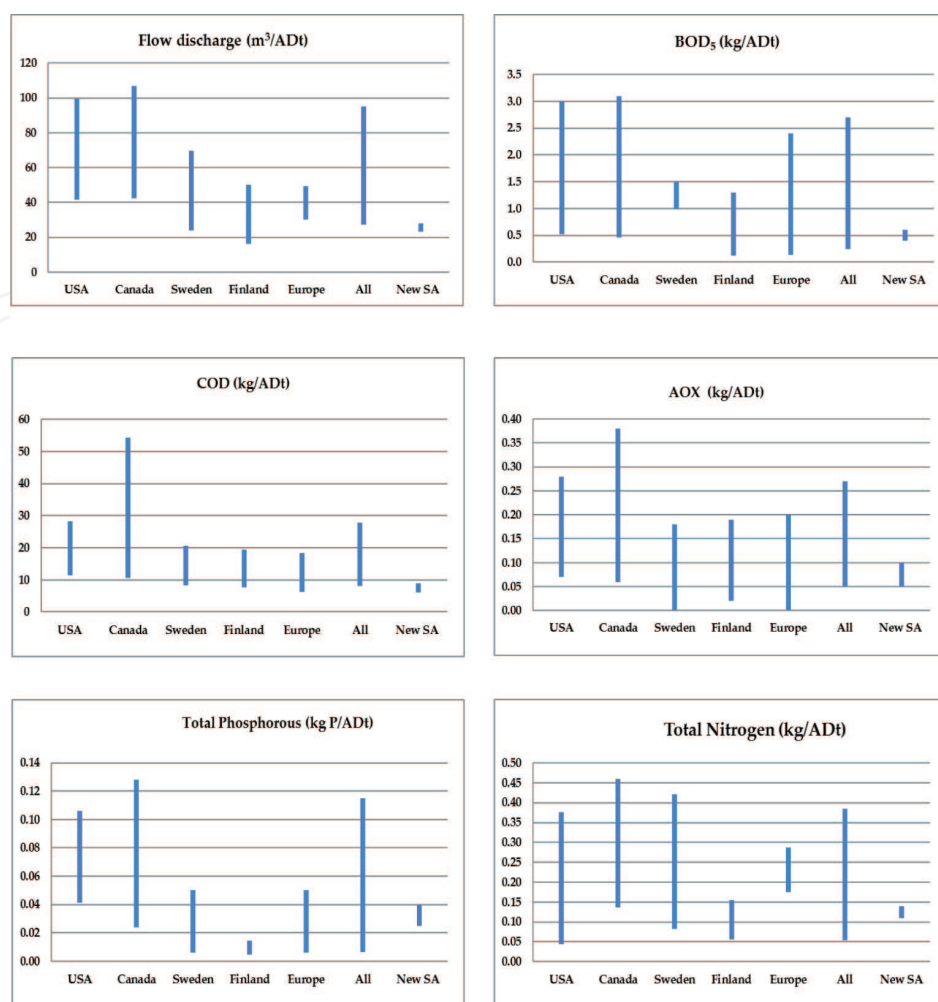
<sup>3</sup> Emissions from other hardwood (no eucalyptus) and softwood.

**Table 4.** Reported annual average discharges from kraft pulp mills within the EU [12].

ing the Best Available Techniques (according to the European IPPC Bureau [12] and the IFC Guidelines [18]).

## 6.2. Bleaching effluents

Up to 85% of the total effluent volume is generated in the bleaching stage. Therefore, this part of the mill is broadly studied in order to minimize the effluent organic loads (especially the organo-chlorines loads) without impacting the pulp yield and brightness. Effluent loadings depend on the production process and the raw materials. The degree of delignification of the unbleached pulp, the bleaching process, the washing loss, type of wood, final brightness desired, chemical and water consumption and the degree of plant closure are important indicators of wastewater characteristics [12, 19]. To this end, kappa number is an important mill control parameter. The kappa number quantifies by a redox reaction to the amount of lignin (or the delignification degree) still in the pulp. The higher the kappa number, the higher the lignin content in the pulp. The low lignin amounts to be removed during bleaching, decreases the utilization of bleaching chemicals, which consequently reduces the load to the wastewater treatment. However, if the kappa number were to decrease too much during the cooking then the pulp yield and physical properties will be considerably low [10]. **Table 5** provides performance data of the different processes [12].



**Figure 6.** South America new mills performance compared with mills in North America and Europe (Data from EKONO and author personal sources). The vertical bars depicted in the graphs correspond to the 10th percentile to 90th percentile range. The column “All” corresponds to the average of the values reported.

| Delignification technologies                  | Kappa for hardwood | Kappa for softwood | Calculated COD load (kg/t) from the bleach plant |          |
|---|--------------------|--------------------|--|----------|
|   |                    |                    | Hardwood   | Softwood |
| Conventional cooking                          | 14–22              | 30–35              | 28–44  | 60–70    |
| Conventional cooking + oxygen delignification | 13–15              | 18–20              | 26–30  | 36–40    |
| Extended/modified cooking                     | 14–16              | 18–22              | 28–32  | 36–44    |
| Extended cooking + oxygen delignification     | 8–10               | 8–12               | 16–20  | 16–24    |

**Table 5.** Kappa number currently achieved with different delignification technologies and comparison of the calculated effluent COD without considering the washing losses [12].

### 6.2.1. *Hardwood and softwood bleaching effluents*

The effluents from kraft pulp bleaching constitute varying quantities of organic and inorganic substances. The organic typically represents one-third of the dissolved material while the inorganics comprise two-thirds. The solid matter includes mainly fibres, pieces of fibres and the additives used in bleaching. The dissolved organic matter is composed of various species derived from the raw material and formed in the pulping and bleaching process (residual lignin, hemicelluloses and extractives) [19].

Wood material impact on the values of the effluents parameters can be assessed by comparing the figures for bleaching effluents derived from softwood and hardwood pulp. The former has higher COD and colour content than those of hardwood pulp. The compounds responsible for colour are lignin fragments of high molecular weight (HMW), which represents low biodegradability in the biological treatment [20]. Research has compared effluents from softwood and eucalyptus pulps [13, 20, 21] through AOX, COD, BOD<sub>5</sub> and colour behaviour of the different kinds of pulp production (conventional bleached pulps and oxygen delignified bleached pulps). According to the findings, softwood and eucalyptus effluents have the same trend in AOX levels. For both conventional pulps, the AOX levels were higher than the corresponding oxygen delignified pulps. Furthermore, as it mentioned earlier, the total COD levels are dependent on the initial kappa numbers. The COD compositions of eucalyptus and softwood effluents are significantly different, where the effluents from the eucalyptus pulps are more biodegradable. The compounds forming the kappa number in softwood and hardwood (especially eucalyptus) differ as well: in softwood, the kappa number mainly representative of lignin, whereas in eucalyptus, the hexenuronic acids (HexA) are a large contributor [22, 23]. In this regard, the most common way to remove the hexenuronic acids is in the early bleaching stages through hot acid hydrolysis (A) and hot chlorine dioxide bleaching (D<sub>H</sub>) technologies [11, 22, 24].

### 6.2.2. *Chemical composition of the wastewater*

The two main types of bleaching methods in use are elemental chlorine free (ECF), when no molecular or gaseous chlorine is dosed in the bleaching, and totally chlorine free (TCF) bleaching [12]. ECF is dominating the bleached chemical pulp market. In 2012, ECF pulp production reached approximately 93% of bleached kraft pulp's world market share. TCF production has declined a little over the last 10 years [25].

Owing to the differences between both the bleaching technologies and chemical composition of the bleaching effluents, it is necessary to study in order to predict and understand the environmental impact associated, and consequently to develop the most suitable treatment that decreases effluent loads and toxicity. A significant number of studies pertaining to the chemical composition of bleaching effluents have been published. Several authors have worked in identifying the chemical compounds in filtrates. More than 500 organic compounds have been identified in bleaching effluents so far. Most compounds identified in bleaching effluents are derived from lignin or other wood components, such as extractives or carbohydrates [26].

The most important difference, when comparing softwood effluents with the eucalyptus effluents, is the higher lignin content in the former and the hexenuronic acid content in the latter [20].

Lignin degradation products were commonly considered as the major precursors of chlorinated compounds. However, the presence of monochlorinated compounds derived from glucuronoxylans were identified to be the major components of chlorine dioxide bleaching filtrates of eucalyptus kraft pulps [27, 28].

Other important compounds found in the effluents are wood-derived components: resin acids, fatty acids, phytosterols and retene. Lipophilic hardwood extractives consist of a complex mixture of compounds such as sterols, long chain aliphatic acids and alcohols, waxes, glycerides and sterol esters. If high amounts of these compounds are found in kraft mill effluent, their origin is frequently the spills of black liquor and soap or black liquor transported with the pulp [14, 29].

### 6.2.3. Molecular weight distributions

Several authors [14, 30, 31] have worked in determining the molecular weight distribution of the components in the effluents. The importance of determining the molecular weight distribution comes from the fact that significant removal in the biological treatment system is achieved from the low molecular weight (LMW) material. Evidence of this is the increment in the proportion of organic compounds with high molecular weight after biological treatment. Improvements in the removal of high molecular weight material would lead to greater efficiency and improve the effluent quality. Traditionally, the separation between low molecular weight (LMW) and high molecular weight (HMW) is done at 1000 Da. Bleach kraft mill effluents have an extended molecular weight distribution; from diverse kinds of monomeric compounds to large and complex molecules with molecular weights between 10,000 and 30,000 g/mol. The molecular weight distribution depends on the raw material and the bleaching process used. For example, the average molecular weight of organic matter in hardwood kraft pulp effluents is lower than the corresponding softwood effluents [14].

The molecular weight fractions in the bleaching filtrates of oxygen delignified eucalyptus pulps were studied. The HMW fraction contributed to approximately 40% of the total effluent load of COD both in softwood and hardwood ECF bleached pulps production, and about 30–40% to TCF bleached pulps effluents [30, 31]. Additionally, the most remarkable differences between softwood- and hardwood-derived effluents are in the aromatic region. The aromatic lignin-derived structures such as syringyl and guaiacyl units are not important structural elements in HMW effluent materials from ECF bleaching of oxygen delignified hardwood kraft pulps, but are important in softwood HMW effluents [31, 32]. Similarly, the results show that all HMW effluents contained carbohydrates. The carbohydrates found in the examined HMW could have had oligosaccharides, polysaccharides or both present in the effluent, either in dissolved or colloidal form. As can be expected, the HMW hardwood kraft pulps fraction contained more carbohydrates (mainly xylan) than the corresponding samples from softwood kraft pulps. Concerning the presence of carboxylic acids, the HMW samples showed high levels of these groups. They were formed due to the oxidation of lignin structures in the bleaching process [30–32].

Regarding the low molecular weight (LMW) compounds, it can be broadly classified into three main classes: acids, phenolic compounds and neutral compounds. The phenolic compounds



and some of the acids are degradation products from lignin, while the resin acids, fatty acids, terpenes and sterols are residues of extractives presents in the raw material [14].

#### 6.2.4. ECF and TCF wastewaters treatability

The biological treatment of the effluents from ECF and TCF is almost the same. There is a slight difference in the organic matter constitution among these bleaching effluents, but it is less than other parameters such as raw materials, effluents from the unbleached line, than the bleaching effluent itself.

TCF eucalyptus pulp produced an effluent with 3.5 times the BOD and twice the COD than ECF eucalyptus pulp effluent [30]. Similarly, TCF bleaching effluent had approximately twice the COD in softwood than the ECF effluents [33]. The larger amounts of COD and TOC in the TCF effluents can be explained because the bleaching reagents used in the TCF sequences ( $O_3$ ,  $H_2O_2$ ) are less selective towards residual lignin than the  $ClO_2$  use in the ECF sequences. Bleaching of pulps with ozone is known to produce aldehyde and keto groups on carbohydrates, which are highly susceptible to oxidative degradation under alkaline conditions. An alkaline peroxide stage is used to further bleach ozone-treated pulps, resulting in an oxidative degradation of these carbohydrates and thus contributing to higher COD and TOC values in the TCF effluents. Moreover, the hardwood TCF effluents contained more carbohydrates (mainly xylan) than the ECF effluents. An explanation of these differences was that the process conditions in P-stage (long retention time under alkaline conditions) may favour dissolution of xylan from the pulp [30, 33].

However, while TCF effluent contains more dissolved organic matter, it is less coloured than ECF effluent, mainly because of the action of residual reagents (i.e.  $H_2O_2$ ) in the TCF effluent. Normal values of colour at 525 nm in TCF effluents are 300 and 1300 C.U. in ECF effluents [31].

## 7. Kraft pulping: wastewater treatment

The typical pulp mill wastewater treatment should include primary treatment (neutralization, screening or sedimentation), principally to remove suspended solids, and biological/secondary treatment. The secondary treatment is mainly done to diminish the organic matter, which is removed by biological degradation, and is particularly useful for the removal of low molecular mass organic matter with a molecular weight of 800 Da or less. Some mills have tertiary treatment to further reduce toxicity, suspended solids, organics or colour [12, 13, 34].

Secondary biological treatment is applied in most types of pulp and paper mills. The most usual methods are activated sludge and aerated lagoons. Some variations of these systems include the use of filters and sequences reactors—Mobil Bed Bioreactor (MBBR) and Membrane Bioreactors (MBR). Sometimes anaerobic treatment is used followed by an aerobic biological stage [12, 18].

Aerated ponds and activated sludge methods are the most common treatment systems in pulp and paper industry. In an aerated pond, wastewater is treated through a combination of



physical, biological and chemical processes. They have large residence times between 3 and 20 days, and consequently a large volume. They work with low microorganism concentration (low solids concentration) about 100–300 mg/L. These ponds use aeration devices to add oxygen to the wastewater (normally surface turbine aerators or bottom aerators) and mix the contents of the pond, thereby enhancing the microbial activity. However, due to low efficiency levels and the large surface required, the use of aerated lagoons has drastically diminished [12, 13, 34].

The largest secondary treatment system is activated sludge (60–75% of all the biological effluent treatment plants in pulp and paper industry use activated sludge systems); even in new plants. The advantages of the aerated activated sludge systems compared to the aerobic ponds are that they achieve high removal efficiencies, the process can be well controlled, requires less surface and the microorganisms are adapted to the receiving wastewater. The disadvantages are the high construction and operation costs (especially the energy cost of the aeration systems), the high rate of sludge production and the loss of efficiency due to bulking problems, and consequently, the need to add nutrients to avoid this problem. Sludge handling and nutrient dosage are additional to the energy cost, which is the major component contributing to the operational cost of the biological treatment of process effluents within the pulp and paper industry [34].

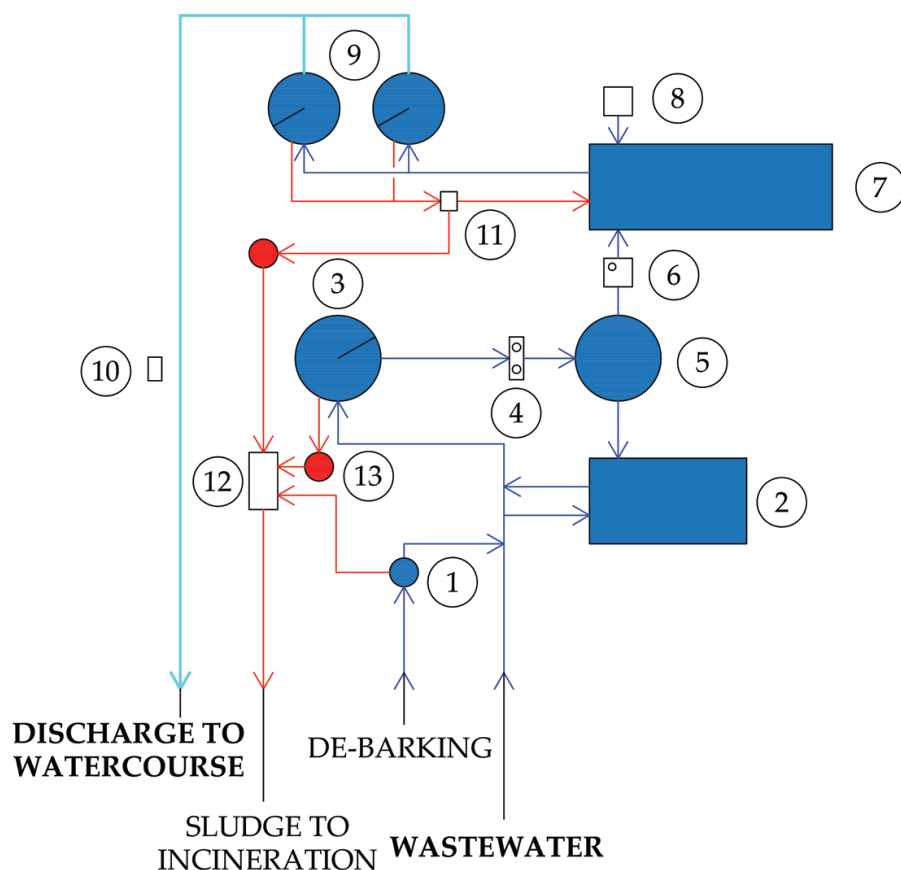
### 7.1. Characteristics of activated sludge treatment

Two main units of the activated sludge plant are the aeration basin and the sedimentation basin. In the aeration basin, the effluent is treated with a culture of microorganisms (the activated sludge), which is present in a high concentration. **Figure 7** shows a diagram of a pulp mill treatment with the activated sludge system. Activated sludge plants at kraft pulp mills have a retention time of about 15–48 h. The solids concentration in the activated sludge systems is typically 2000–6000 mg/L. The hydraulic residence time is 4–8 h for a conventional system and the cellular residence time (sludge age) is normally 5–15 days. Normal loads are between 0.05 and 0.1 kg BOD/kg sludge for extended aeration and 0.1–0.3 kg BOD/kg sludge for low load process. The common operating temperature is about 35–37°C and the dissolved oxygen (DO) concentration is 1.5–2.0 ppm. The nutrients concentration in relation to the organic matter is important in effluent treatment. Effluents from the wood processing industry generally have a BOD:N:P ratio of 100:(1–2):(0.15–0.3) and the addition of supplemental nutrients is normally required [13, 34].

The removal efficiencies reached vary according to the wastewater residence time and the operating conditions. Normal efficiencies figures are between 85 and 98% BOD<sub>5</sub> removal and 60–85% for COD removal. For AOX, the reduction is about 40–65%, 40–85% for phosphorus and 20–50% for nitrogen. The overall efficiency of TSS removal using primary and secondary treatment is about 85–90% [12].

### 7.2. Aerobic treatability of the different effluent fractions

The COD of treated effluent represents how effective a treatment technology is in its ability to remove the total organic material present in the influent. BOD measurements by themselves



1-DE-BARK WATER CLARIFIER, 2-SPILL LAGOON, 3-CLARIFICATION, 4-COOLING TOWER, 5-EQUALISATION BASIN, 6-NEUTRALISATION AND NUTRIENT ADDITION, 7-AERATION BASIN, 8-COMPRESSOR STATION, 9-SECONDARY CLARIFICATION, 10-MEASUREMENT AND SAMPLING, 11-SCREEN PUMP, 12-SLUDGE HANDLING, 13-FIBRE SLUDGE THICKENER.

**Figure 7.** Diagram of a pulp mill treatment plant with activated sludge as biological treatment.

do not quantify the non-biodegradable or slowly biodegradable organic portion of the effluent. Moreover, studies seem to indicate that the residual colour in pulp mill effluents could be linked to the recalcitrant COD [35].

Recalcitrant organic matter is supposed to be partly responsible for long-term toxicity in receiving waters [21]. As discussed earlier, it is widely reported that the residual recalcitrant organic matter is composed predominantly by high molecular weight components, which are not metabolized due to its size. However, the contributions of high and low molecular weight fractions in bio-treated effluents are dissimilar [36]. In the LMW fraction, a large-scale removal of the chlorinated phenolic compounds, chlorinated resin acids and sterols occurs. In the HMW fraction, the carbohydrates are strongly affected; however, other compounds such as oxidized lignin were less affected [30].

Some findings are possible by comparing the high molecular weight (HMW) and low molecular weight (LMW) fractions of the acidic and alkaline filtrates post biological treatment [32]. In the alkaline filtrate, the COD and TOC in the HMW fraction increased after treatment. The same behaviour was observed with the AOX and lignin content in the acidic filtrate. This is attributable to the formation of soluble bacterial products or to the adsorption of the LMW into HMW matter [32, 35]. In the LMW filtrates, the COD/TOC decreased after biological treatment, as a result of the large removal of highly oxidized organic carbon. The colour increased in the HMW fractions of acid and alkaline filtrates. The biological treatment often leads to increased colour in ECF bleaching effluents due to the creation of new chromophores in the HMW fractions [13, 32].

### 7.3. Bulking problems in the activated sludge systems

Two critical operational aspects of an activated sludge plant are maintaining proper control of the dissolved oxygen (DO) concentration in the aeration tank and preserving a good settling sludge. Reduced settleability results in poor plant performance, as it is difficult to maintain a low concentration of suspended solids in the plant effluent [13, 34]. Activated sludge plants that treat pulp and paper mill wastewaters seem to be particularly prone to this. There are several reasons for poor separation properties, such as filamentous bulking sludge, bulking due to excessive extracellular polymeric substances (EPS), production or formation of small flocs and dispersed biomass [37, 38]. In pulp mill wastewater, bulking is often due to the presence of filamentous bacteria. Common conditions that favour bulking are working at feeding loads ratios out of normal range, deficiencies in nitrogen and phosphorous species or in the level of DO [13]. In kinetic terms, the floc forming microorganisms have a competitive advantage at lower substrate concentrations because that allows the compounds to utilize oxygen and nutrients more efficiently than the not floc forming microorganisms [37].

The presence of filamentous bacteria was examined for two years in 15 French pulp, paper and board mills wastewater. The study of 25 bulking cases attributed the source in 10 cases to be COD hydraulic overloads, in 8 cases to deficient aeration and in 5 cases to nutrient deficiency [39].

## 8. Partial closure in water circuits

The current market and environmental demands facing pulp and paper mills are the increased closure of the plant circuits and a further reduction or elimination of the wastes produced. The concept of a closed loop mill aims to eliminate discharges to the aquatic environment, recycle and reuse all possible solid and liquid process wastes, and reduce air emissions to the lowest possible quantity and toxicity. However, until today, no kraft mills are operating with complete closure and complete reutilization of the effluents. The most important problem experienced in mills that try to operate for long periods with zero discharge was corrosion caused by chlorides in a number of positions. Nevertheless, great progress has been made in minimizing impacts associated with pulp mill effluents. Water circulation closure methods include dry debarking, effective liquor spilling control, closed screening and washing, condensate stripping and other methods to minimize the loss of wood-derived organic mat-

ter. Extended and oxygen delignification can significantly reduce bleach plant effluent loads from kraft pulp mills. The bleach plant is the most important source of effluent within a pulp mill and the chlorinated effluents are more complicated to reutilize within the mill. For this reason, an important trend in bleaching development is to reduce volumes and decrease the effluent loads, especially of chlorinated compounds [40–42].

Up to now, a complete water closed circulation is not available; nevertheless, a partial closure of the water circuits is possible. This can be done segregating the acid and alkaline effluent streams and recirculating the liquids countercurrently from the last bleach stage through the sequence to the brown stock washer. The alkaline effluent could be used for washing the pulp in the unbleached part of the process.

## 9. Conclusions

The pulp and paper industry has been considered a large consumer of wood, energy and water, and an important contributor of pollutant discharges to the environment (air, water courses and soil). However, the last decades have seen a lot of effort in creating solutions such as generating less pollutant wastewaters and reducing the amount and load of the emissions to the environment. The implementation of several measures like the dry debarking of wood, the introduction of extended cooking and oxygen delignification, the reuse of condensates, improvements in washing efficiency and especially the total substitution of chlorine, has brought a significant reduction in effluent flows and in the chlorinated and organic loads generated within the mill. In addition, the introduction of end-of-pipe secondary, and even tertiary, treatments have reduced large amounts of pollutant loads to the environment. However, the need for tertiary treatment is not yet well proven; while it purifies the effluent, the energy costs are high and even forms sludge.

Effluent characteristics are dependent on the production process and the raw materials. ECF eucalyptus pulp production is increasing appreciably but not much information on its effluents is available. The main difference between softwood and eucalyptus pulps is in the kappa number: the kappa number is mainly formed by lignin content in softwood pulp, and the Hexenuronic acids are important contributors to kappa number in eucalyptus pulp. Hence, the bleaching conditions for eucalyptus are less severe and consequently the effluents characteristics are different. Eucalyptus bleaching effluents have lower COD, AOX and colour content and higher biodegradability than the softwood effluents.

The environmental impact of effluent loads and the appropriate treatment can be determined by studying the chemical composition and molecular weight distribution of the bleaching effluents. The HMW in hardwood bleaching wastewaters constituted an important but not prevailing fraction of the wastewater composition (30–65% of the total). The hardwood HMW fraction is mainly composed of non-aromatic structural compounds.

Aerated activated sludge is the most common treatment system in pulp mills. BOD<sub>5</sub> removals of 85–98% and COD removals of 60–85% are normally achieved with these systems. For AOX, the reduction is about 40–65%, 40–85% for phosphorus and 20–50% for nitrogen. Bulking

problems are common in these systems mainly due to nitrogen deficiencies and phosphorous concentration or the level of DO.

Nowadays, plants that apply the best available technologies have their emissions controlled and present minimum environmental impact at the receiving waters.

The new developments are in the way to close even more the internal circuits in the plant, to reduce the flow discharged. Membrane technologies and similar technologies may be key in this regard.

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