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Review

Review on recent developments on pulp and paper mill wastewater treatment

Mohammadreza Kamali [a], Zahra Khodaparast [b,*]

[a] University of Aveiro, Department of Environment and Planning, Portugal
[b] University of Aveiro, Department of Biology, Campus Universitario de Santiago, 3810-193 Aveiro, Portugal

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ABSTRACT

Economic benefits of the pulp and paper industry have led it to be one of the most important industrial sections in the world. Nevertheless, in recent years, pulp and paper mills are facing challenges with the energy efficiency mechanisms and management of the resulting pollutants, considering the environmental feedbacks and ongoing legal requirements. This study reviews and discusses the recent developments of affordable methods dealing with pulp and paper mill wastewaters. To this end, the current state of the various processes used for pulp and paper production from virgin or recovered fibers has been briefly reviewed. Also, the relevant contaminants have been investigated, considering the used raw materials and applied techniques as the subject for further discussion about the relevant suitable wastewater treatment methods. The results of the present study indicated that adopting the integrated methods, alongside a combination of biological (e.g., anaerobic digestion) and physicochemical (e.g., novel Fenton reactions) treatment methods, can be environmentally and economically preferable to minimize environmental contaminants and energy recycling.

Contents

* Corresponding author.
E-mail address: Khodaparast@ua.pt (Z. Khodaparast).

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1. Introduction

Pulp and paper (P&P) industry is considered a large user and producer of biomass based energy and materials (Svensson and Berntsson, 2014). To maintain their profitability and overcome the declining (Machani et al., 2014) and competitive (Karikallio et al., 2011) markets, P&P mills are no longer limited to production of pulp and/or paper; rather, they may adopt additional measures including waste heat delivery to district heating systems (e.g., Ericsson et al., 2011; Klugman et al., 2009) and production of the electricity, wood pellets, and dried bark as well as valuable chemicals such as ethanol (e.g., Fornell et al., 2012; Phillips et al., 2013) and materials like carbon fiber (see e.g., Maradur et al., 2012), biofuels, etc. (Jonsson et al., 2011).

However, the pulp and paper (P&P) industry is now facing challenges to comply with stringent environmental regulations. These factories commonly produce considerable amounts of wastewaters, especially from virgin raw materials processing. Such effluents have the potential to adversely affect the receiving aquatic environment through, for instance, slime production by microorganisms such as *Sphaerotilus sp.* (Pellegrin et al., 1999) and formation of scum, as well as toxicity to the exposed communities, thermal impacts, color problems, and aesthetical issues (Pokhrel and Viraraghavan, 2004), in case of incomplete treatment. The generated effluents, based on factors such as raw materials used and employed production process, commonly have a high COD (Table 1) and a low biodegradability (defined as the ratio of BOD_5/COD) and more than 200–300 different organic compounds and approximately 700 organic and inorganic compounds (Karrasch et al., 2006). Such substrates may include non-biodegradable organic materials, adsorbable organic halogens (AOX), color, phenolic compounds, etc. (Buyukkamaci and Koken, 2010), depending upon the applied pulping process, additive chemicals, and the amount of water consumed. Accordingly, in both traditional and emerging P&P producers (e.g., Chen et al., 2012) such as United States (Schneider, 2011), China (Zhu et al., 2012), and India (Afroz and Singh, 2014), P&P mills are considered a major source of environmental pollutants.

Pollutants which are released during several parts of P&P production process can be reduced by adopting several internal process improvements, especially in combination with management measures. In this regard, European Commission (2001) has described the best available techniques (BAT) to be adopted by P&P mills. Moreover, several studies have been carried out with the final purpose of reduction in the pollution load during the P&P making process (Martín-Sampedro et al., 2011). However, the external processes, including the primary clarification, secondary treatment, and/or tertiary processes have remained the main remediation ways used in P&P mills which can be simply divided into physicochemical and biological processes. In order to contribute to more development of these technologies, it is beneficial to demonstrate their current status. Hence, through a brief review of P&P manufacturing techniques and key pollutants released directly into the wastewater contents, recent and advanced P&P wastewater treatment methods have been reviewed and discussed in the present paper.

2. P&P production techniques and key pollutants

P&P are produced from virgin or recovered fibers (RCFs) as raw materials. Chemical, mechanical, or a combination of them are common pulp producing processes from virgin raw materials while recovered pulp is produced from fiber recovering processes. Produced pulp is further processed using additional non fiber materials, such as fillers, to obtain the paper web.

2.1. P&P from virgin fiber

2.1.1. P&P from virgin fiber – production techniques

Manufacturing processes of paper and paperboard can be generally divided into three steps: pulp making, pulp processing, and paper-making (Avsar and Demirer, 2008). Pulping is the process generally started by debarking which removes soil, dirt, and bark from the wood raw materials and converts the plant fiber into smaller pieces (chips) (Ali and Sreekrishnan, 2001). Resulting wood pieces are cooked at high temperature and under high pressure. Also, chemical techniques can be used to separate lignin and hemicelluloses from cellulose, used for making paper. This process is usually carried out by means of wet processes, which is responsible for removing large amounts of organic compounds from the processing wood (Vepsäläinen et al., 2011).

The yield of the mechanical pulping (MP), compared with chemical-based processes, is generally high (90–95%), but the quality of the products is significantly low (Pokhrel and Viraraghavan, 2004). Improvement of MP can be achieved by several techniques, such as thermo-mechanical pulping (TMP), chemo-mechanical pulping (CMP), and chemical thermo-mechanical pulping (CTMP). In TMP, the raw materials are exposed to pressurized steam for a short period of time, followed by refining. Chemical treatments (e.g., by using hydrogen sulfite (HSO_3)) can also be applied to TMP during the steaming stage for further modifications to form CTMP (Ekstrand et al., 2013). In recent years, some studies have been carried out to optimize the CTMP which produces fibers by biological (e.g., Lei et al., 2012) or chemical pre-treatment (e.g., Pan et al., 2013) of wood chips prior to refining. Chemical pre-processing of the raw materials, before exposing to mechanical pulping, is another common way to increase the efficiency of the process which is called CMP. Kraft pulp

Table 1
Typical characteristics of effluents from P&P production processes.

Unit operations	pH	COD (mg/L)	BOD_5 (mg/L)	BOD_5/COD	TSS (mg/L)	Reference
Wood yard and chipping[a]	7	1275	556	–	7150	Avsar and Demirer (2008)
Thermo-mechanical pulping	4.0–4.2	3343–4250	–	–	330–510	Qu et al.(2012)
Chemical thermo-mechanical pulping[b]	7.43	7521	3000	–	350	Liu et al. (2011)
Kraft cooking section	13.5	1669.7	460	0.27	40	Wang et al. (2007)
Pulping process operations[c]	5.5	9065	2440	–	1309	Avsar and Demirer (2008)
Bleaching[d]	8.2	3680	352	–	950	Kansal et al. (2008)
Paper machine	6.5	1116	641	–	645	Avsar and Demirer (2008)
Integrated pulp and paper mill	6.5	3791	1197	–	1241	Avsar and Demirer (2008)
Recycled paper mill	6.2–7.8	3380–4930	1650–2565	0.488–0.52	1900–3138	Zwain et al. (2013)

[a] Pulpwood storage, debarking, and chipping.
[b] Alkaline peroxide mechanical pulping (APMP).
[c] Pulping, pulp screening, pulp washing and thickening, bleaching, and kraft repulping.
[d] A combination of chlorination and alkaline extraction stages.