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Review

Anaerobic digestion of pulp and paper mill wastes – An overview of the developments and improvement opportunities

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HIGHLIGHTS

- Historical perspective of P&P mill wastes anaerobic digestion is critically reviewed.
- Recent progress in anaerobic digestion of P&P mill wastes is reviewed and discussed.
- Combined methods are proposed as promising technologies for P&P wastes treatment.

GRAPHICAL ABSTRACT

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ABSTRACT

Various organic and inorganic hazardous substances are commonly originated during the processing of virgin or recovered fibers (RCFs), when the pulp and paper (P&P) are produced. Hence, pulp and paper industry (PPI) strongly need to employ advanced waste treatment processes as a powerful tool to comply with the stringent environmental regulations in one hand, and to increase their profitability in the current declining P&P markets, on the other hand. Among the treatment alternatives, anaerobic digestion (AD), is an interesting cost effective alternative with a small environmental footprint and has been increasingly adopted by the PPI to reach this goal. However, the application of AD to deal with wastes generated in P&P mills has been restricted due to a number of limitations, regarding the anaerobic reactor design and the operating conditions. Hence, the optimization of the AD performance would be a crucial step in order to increase the economic benefits, and also to satisfy the strict environmental protection standards. To this end, this paper presents an overview on the current state of the developments associated with AD treatment of P&P mill wastes to assess the applicability of this treatment process for the management of this type of complex wastes. In this context, suggestions are provided to maximize both biogas production and removal efficiency, focusing on the relationship between waste composition and reactor design and operational conditions, which will enhance methane capture and contribute to prevent global warming.

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Nomenclature

ABR	anaerobic baffled reactor
AD	anaerobic digestion
AFs	anaerobic filters
AOPs	advanced oxidative processes
AOXs	adsorbable organic halogens
AnMBRs	anaerobic membrane bioreactor
BI	biodegradability index
BOD	biochemical oxygen demand
COD	chemical oxygen demand
CP	chemical pulping
CTMP	chemical thermo mechanical pulping
DCP	dichlorophenol
ECF	elemental chlorine free
ENMs	engineered nanomaterials
FBRs	fluidized bed reactors
HRT	hydraulic retention time
KP	kraft pulp
LTAD	low temperature anaerobic digestion
MP	mechanical pulping
NPs	nanoparticles
OLR	organic loading rate
P&P	pulp and paper
PPI	pulp and paper industry
PPMW	pulp and paper mill wastewater
PPMS	pulp and paper mill sludge
PPS	pulp and paper sludge
PVDF	polyvinylidine fluoride
RCF	recovered fiber
SAnMBRs	submerged anaerobic membrane bioreactors
SBR	sequencing batch reactor
SCOD	soluble chemical oxygen demand
SCP	semi chemical pulping
SRT	solids retention time
SGBR	static granular bed reactor
SPC	sulfonated polycarbonate
TCF	total chlorine free
TCOD	total chemical oxygen demand
TDS	total dissolved solids
TSS	total suspended solids
TMP	thermomechanical pulping
UASB	upflow anaerobic sludge blanket
UAF	upflow anaerobic filter
UAPBR	upflow anaerobic packed bed reactor
VFAs	volatile fatty acids

1. Introduction

Various wood or non wood materials are the main raw materials for the production of pulp and paper (P&P) in many countries through the world (Fig. 1). Moreover, P&P manufacturing from recovered fibers (RCFs) has been increased during recent years [1]. After preparation of stock materials, steps including pulping, bleaching, and P&P making are applied, respectively, to yield pulp or paper as final products (Fig. 2). Based on the raw materials used and the manufacturing process adopted, P&P industry (PPI) produce relatively large amounts of both wastewater and solid wastes [2]. On site, reuse and recycling, and also modifications in the technology [3] are among the most efficient economic and environmental options dealing with the produced residues. In this regard, measures for minimizing the produced wastes, and recovery of energy and unavoidable wastes have been introduced [4] and adopted by PPI [5]. However, the external waste treatments are still the main ways to deal with the residues from PPIs, especially for small and medium size units which generally do not benefit of infrastructures for the recovery of chemicals [6]. So far, various types of treatments (primary, secondary, and tertiary) have been developed and applied in order to enhance the treatment efficiency of both pulp and paper mill wastewater (PPMW) and sludge (PPMS) with the aim of reducing the amount of the produced final wastes, and also to prevent the probable subsequent toxic effects induced by the presence of hazardous compounds when released into the receiving environment [7].

Anaerobic digestion (AD), defined as the biological degradation of organic compounds into different end products, including methane (50 75%), carbon dioxide (25 50%), hydrogen (5 10%), and nitrogen (1 2%) [8] by a microbial consortium in the absence of air [9], has been widely employed for primary or secondary treatment of various industrial residues. The development of methods for the AD process control and monitoring [10] as well as the operational conditions set up has raised a large interest in recent studies. This is mainly due to the advantages of AD over conventional biological P&P waste treatment, such as a significant reduction of the produced wastes and the production of biogas, mainly composed by methane. Despite these advantages, some improvements in the stability of the process, in methane yields,

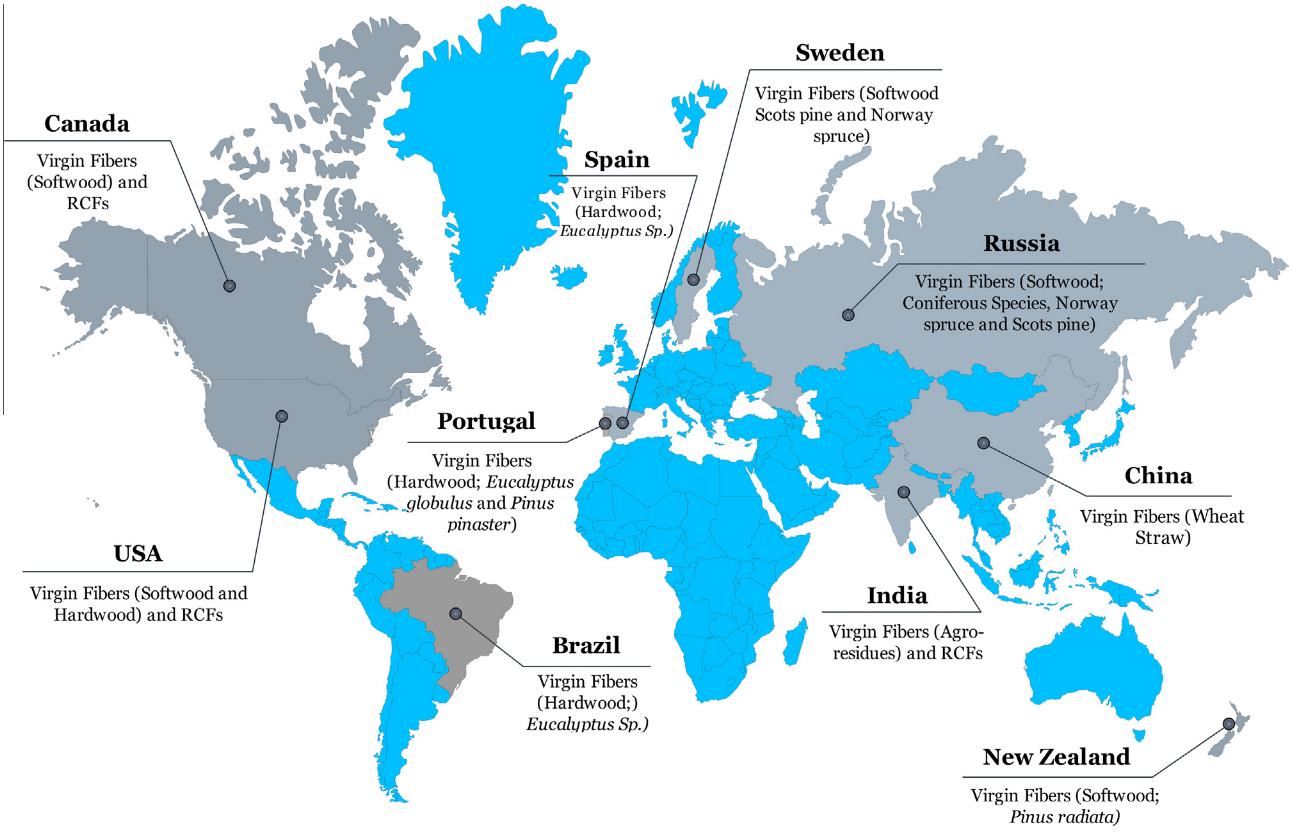

Fig. 1. Predominating raw materials for P&P production in some main [20] P&P producers [21–30].

and regarding inhibition problems are still necessary to enhance the AD performance, especially when dealing with non biodegradable and recalcitrant pollutants such as halogenated organic compounds present in P&P residues. Hence, when AD is used to treat wastes from P&P industry, the adoption of appropriate anaerobic reactor configuration and operating conditions can potentially promote methane production. Framed by this concern, the present study critically reviews the recent developments on AD bioreactor technologies used for the treatment of wastes generated by P&P mills and their relationship with the specific characteristics of the PPMW and waste sludge produced, depending on the P&P production process. In this context, previously published review papers addressing the various concepts of AD in general [11 17] or specific aspects of the AD of P&P mill wastes [18], [19] have also been taken into consideration to provide a broader overview and to emphasize that a choice among various available technologies are likely to be case specific, needing also an economic evaluation. However, to focus on the technology with the highest potential for implementation in the PPI, it is important to discuss the recently developed high rate anaerobic reactors together with the impact of the various environmental factors on the performances of the AD process. Hence, these aspects and their possible improvements are also discussed aiming at the optimization of the AD process and its adoption in the treatment of such high strength complex wastes. Furthermore, considering the remaining weaknesses and the developments of anaerobic reactors for the treatment of other streams, suggestions for further studies in the form of future outlook are presented in the manuscript.

2. Historical background

It is believed that biogas was used for the first time in Assyria in the 10th century B.C for bath water heating [31]. However, it was during the period 1804 1808 that John Dalton and Humphrey Davy discovered that the flammable gas in the biogas composition is methane [32]. Although the production of methane through the anaerobic conversion or digestion of animal and human wastes, as a source of energy, has a long history in many areas of the world [10], the first anaerobic digester was built in 1859 in a leper colony in Bombay, India, with the aim of converting the wastes to energy [33]. Bechamp (1868) and Popoff (1873) stated that biological processes are responsible for methane formation [34]. Omelianski, in the 1890s, and Sohngen in 1910 stated that the reaction between hydrogen and carbon dioxide, induced by biological agents is the probable pathway for methane formation [35].

Since the beginning of the 20th century, AD has been widely used in many parts of world, and China has had the largest number of AD systems since the late nineteenth century [36]. In the mid 20th century, this technology was mainly used for the treatment of sewage sludge rather than industrial effluents [37]. Since then, the AD systems have been rapidly developed, especially after the first energy crisis back in the 1970's [38], with an increasing interest to optimize the AD process to treat high strength industrial wastes [39]. Upflow anaerobic sludge blanket reactor (UASB) was developed during 1970's and applied by Dutch sugar industry. However, the development of the high rate generation of anaerobic digesters only took place in 1980's, in order to decrease the hydraulic retention time (HRT), which was the main weakness of such systems. Since 1990's, the development and application of AD systems for simultaneous treatment and methane production from PPMW and sludge have found a considerable success [40]. Nowadays, AD, as a mature technology in most of European countries, is utilized for household energy production [41], as well as for the treatment of various organic wastes such as agricultural wastes, sewage treatment, and different industrial wastes such as textile industry wastewater, etc. Although P&P mills generally produce a large amount of wastewater and solid wastes that contain

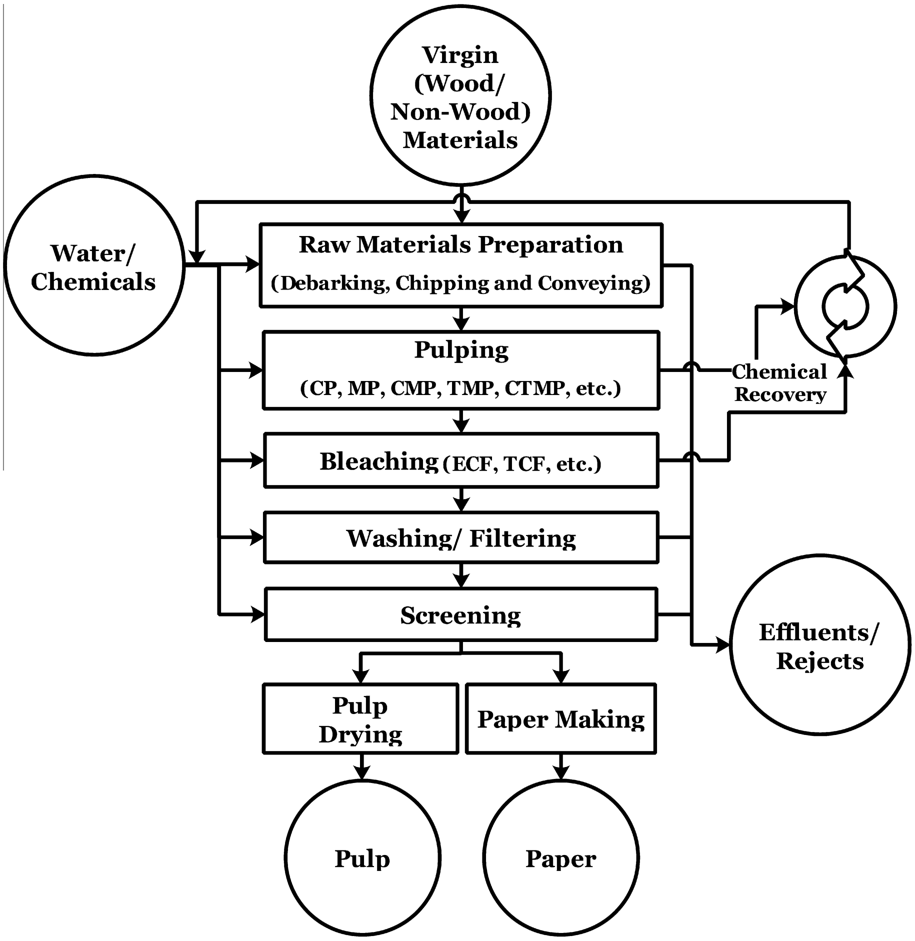

Fig. 2. A schematic P&P production process from virgin fibres.

various pollutants (Table 1), the effluents from mechanical pulping (MP), RCFs processing, chemical pulping (CP) and semi chemical pulping (SCP), as well as from both primary and secondary sludge originated by PPMW treatment plants are not commonly toxic to methanogenic bacteria. Hence, adoption of AD process for the treatment of P&P mill wastes has raised a large interest during the two recent decades. Designing new generations of anaerobic reactors, improving reactors operational conditions, and developing effective consortia of anaerobic bacteria have significantly enhanced the performance of the AD process for the treatment of various industrial wastes containing high levels of organic matter during the last decades [42].

3. Wastewater and sludge from P&P industry

3.1. Water cycle in P&P mills

P&P mill is a relatively high water-dependent industry when compared with many other industries and, according to the stringent environmental regulations, is responsible for the management of the water resources they use. Such resources are generally being obtained from the surface and ground waters and after being used in almost all the major process stages (Fig. 2), and also for cooling the machines, cleaning the equipment, etc., form the main part of the liquid reject (effluents) from a P&P industry (Fig. 3).

Due to the growing global concerns on the scarcity of water resources, the water management in water intensive industry, like PPI is of high importance and hence tough environmental regulations have been developed to ensure the sustainable use of the water resources in industrial water users. Although at the beginning of the last century the manufacturing processes in addition to other internal use required high amount of water (200–1000 m^3/tone paper), this amount has been considerably decreased due mainly to the technological advances occurred in the P&P production processes. As an example, German P&P industry has succeeded to reduce the water required for the production of a ton paper produced to just 13 m^3 [43]. Moreover, in many countries such as USA and Canada, the volume of recovered paper produced has significantly increased in the past two decades (e.g., from 17.4 million metric tons to 49.3 million metric tons in USA) [30] leading to a decrease in the amount of the wastewater generated for the production of P&P, due to the RCF mills being less water intensive when compared with virgin P&P producers [44].

Although the industry is a large user of water resources, only a small part of the water resource they use is consumed during the manufacturing related activities in a typical P&P mill. For instance, in United States, about 88% of the intake water is returned to the surface waters after being treated, while just 11% of it is evaporated and 1% is embedded in products or in solid wastes (Fig. 3) [45]. Accordingly, advanced treatment processes applied to the P&P mill wastes can significantly aid P&P producers to improve the quality of the effluents satisfying the environmental regulations. Moreover, some internal treatment processes can be provided in order to re-use the water during the manufacturing processes. For instance, Wang, Chen, Wang, Yuan, & Yu (2011) [46] through the application of aluminum chloride as a coagulant and a modified natural polymer (starch-g-PAM-g-PDMC) as a

Table 1
Main rejects to the PPMW from P&P making processes using virgin or RCFs.

Fibrous raw materials	Operation	Main processes	Main additives	Main rejects	Typical effluents parameters							References
					Process	pH	COD (mg/L)	BOD (mg/L)	TSS (mg/L)	Other parameters		
										Type	Quantity	
Virgin fiber	Raw materials operation	Debarking, chipping and conveying	–	Bark, tannin, lignin, hemicelluloses and some large amounts of organic compounds such as resin acids as well as soil and dirt	Wood yard and chipping	7	1275	556	7150	–	–	[28,54–56]
	Pulping (paper grade or dissolving grade)	Sulfate pulping (kraft) and sulfite pulping, Thermomechanical Pulping (TMP) Chemical thermo-mechanical pulping (CTMP)MPCMP	Sodium hydroxide (NaOH), sodium sulfide (NaS_2) (kraft pulping), and some other inorganic compounds, such as Na_2CO_3, $NaHCO_3$, Na_2SO_4, Na_2SO_3, and $Na_2S_2O_3$ (sulfite process), etc.	Knots, uncooked woods, bark particles, soluble wood materials Color, resin acids (Including Isopimaric, sandacopimaric, levopimaric, abietic, dehydroabietic, neoabietic and palustric acids), fatty acids, BOD, COD, and dissolved inorganics, Lignin, and hemicelluloses, also somechemical additives suchas soluble silicates ($3SiO_2$ Na_2O)	Kraft cooking	13.5	1669.7	460	40	–	–	[28,47,56–63]
					TMP	4.0–4.2	3343–4250	–	330–510	TN[a] TP[b]	0.01–0.02 (mg/L) 1.31–1.47 (mg/L)	
					APMP[c]	7.43	7521	3000	350	Lignin MTBE extractives	516 (mg/L) 147 (mg/L)	
					CTMP	12	25,000	6800	–	Color	42,000 (C.U.)	
					MP[d]	6.1–8.1	91–1150	6–69	3–45	–	–	
	Bleaching	Chemical or mechanical pulp bleaching	Elemental chlorine free (ECF): ClO_2 and H_2SO_4 (in an acidic environment) or NaOH, O_2, and hydrogen peroxide (in an alkaline phase). Total chlorine free (TCF): H_2SO_4, ozone, chelating agents, and/or hydrogen peroxide	Chlorophenols, AOX, EOXs, polychlorinated biphenyls, polychlorinated dibenzodioxines, dioxins, furans, chlorinated lignosulfonic acids, chlorinated resin acids, residual lignin, color, COD, carbohydrate, inorganic chlorines, VOCs, and halogenated hydrocarbons	Kraft pulp Bleaching	8.50	426	25.50	–	Lignin Phenol AOX	50.00 (mg/L) 0.535 (mg/L) 2.82 (mg/L)	[28,55,57,64–68]
					Bleaching[e]	8.2	3680	352	950	Residual chlorine Chloride content	9040 (mg/L) 1340 (mg/L)	
	Washing	Bleached pulp washing	Solutions containing chemicals like an alkali caustic soda	Residual lignin, bleaching agents and some hardly biodegradable organic compounds	–	–	–	–	–	–	–	[55]
	Paper-making	Dewatering, pressing and drying, finishing	Dyes, resins, fillers[f], sizing agents[g], binders, coating aids, strength agent[h], biocides, optical brighteners, colournts, pigments, etc.	Mineral additives, AOXs, resins, BOD, COD, resin acids, particulate wastes, etc.	Paper machine	6.5	1116	641	645	–	–	[58,69,70]

Table 1 (*continued*)

Fibrous raw materials	Operation	Main processes	Main additives	Main rejects	Typical effluents parameters							References
					Process	pH	COD (mg/L)	BOD (mg/L)	TSS (mg/L)	Other parameters		
										Type	Quantity	
RCFs	Pulping/ deinking	RCFs pulping	Caustic soda, sodium silicate, hydrogen peroxide, soap, etc.	Metallic components, sand, glass, plastic, coatings, fillers, organic compounds from the paints and printing inks such as 2,4,7,9-Tetramethyl-5-decyne-4,7-diol, pulping additive chemicals, compounds like Si and Ca, higher amounts of organics[i], thermoplastic resins[j], TCMTB, chlorophols, etc.	Newsprint mill	–	3500	–	250	Color	1000 (Pt-Co)	[50,58,71–76]
					Recycled paper mill	6.2–7.8	3380–4930	1650–2565	1900–3138	–	–	
					Recycled paper mill	6.36	4328	669	645	VFA[k] VSS[l]	501(mg/L) 850 (mg/L)	
	RCFs	De-inking	Substances like H_2O_2, NaOH, Na_2SiO_3, Na_2CO3, and other compounds like surfactants	Deinking additives and ink particles, fibers, fines, fillers, ash, etc.	De-inking effluents	7–8	–	–	–	Moisture Ash[m]	98.7 (%) 0.54 (%)	[73,77–79]

[a] Total nitrogen.

[b] Total phosphorus.

[c] Alkaline peroxide MP.

[d] Effluents from seven Canadian mills.

[e] Chlorination and alkaline extraction stages.

[f] e.g., clay, titanium dioxide, calcium carbonate.

[g] e.g., rosin, starch and styrene copolymers.

[h] Wet strength additives like synthetic resins (such as Urea formaldehyde and melamine formaldehyde) and Epichlorohydrin (ECH)-derived compounds (such as polyamine-epichlorohydrine resin (PAE)) as wet strength additives.

[i] From light-weight coated paper, because of the coating binders.

[j] In case of laser printing papers.

[k] Volatile fatty acids.

[l] Volatile suspended solids.

[m] Ash (after ignition at 900 °C) consisted of SiO_2 (16.70 %), Al_2O_3 (16.53 %), CaO (22.46 %), TiO_2 (32.39%), BaO (5.43%), CuO (2.59%), S_2O_3 (1.17%), Fe_2O_3 (0.92%), Na_2O (0.33%).

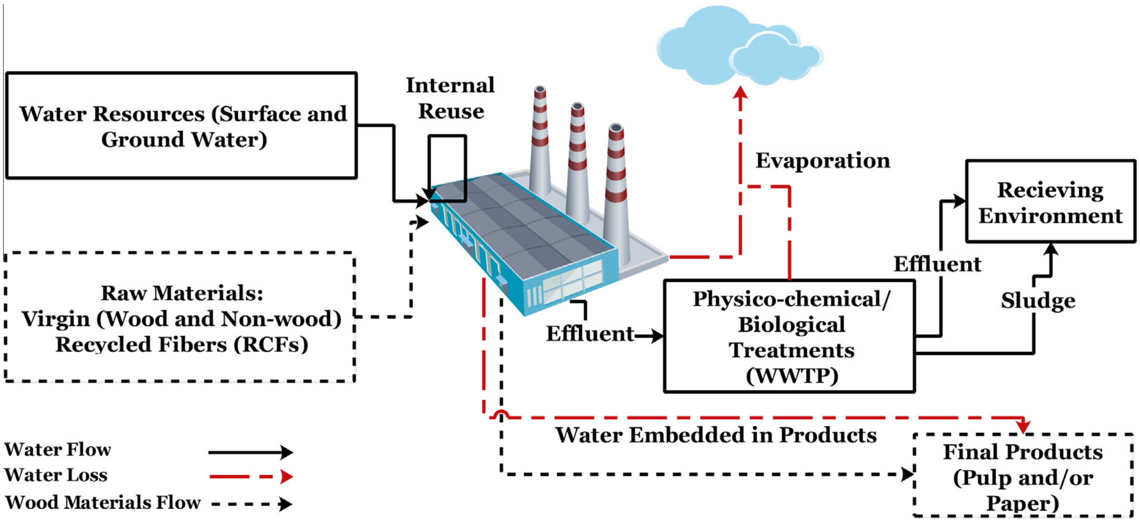

Fig. 3. A schematic of the raw materials flow, use and fate at a typical P&P mill.

Table 2
Efficiency of physicochemical and biological processes for the treatment of PPMW.

Type	Process	Parameters				References
		COD removal (%)	BOD removal (%)	Other parameters		
				Type	Removal (%)	
Physicochemical	Electrocoagulation (Al)	75	70	Lignin	80	[80]
				Phenol	70	
	Flocculation (polydiallyldimethylammonium)	>90	–	Turbidity	>90	[81]
				TSS	>90	
	Ozonation	~20	–	DOC	>15	[82]
				Color	>50	
	Fungi + solar photo-Fenton (Cryptococcus + Fe^{2+}/H_2O_2)	>90	–	DOC	90	[83]
Biological	Fungal (*Aspergillus niger*)	60	–	MTBE extracts	97	[84]
	Aerated stabilization basins	67	90	–	–	[85]
	Aeration pond	–	–	2,4-DCP	56.0–77.6	[86]
	Multiple stage activated sludge	65	95	–	–	[87]
	Activated sludge	76	–	Color	76	[6]
	Activated sludge	–	–	Sterols	>90	[88]
	Upflow anaerobic filter[a]	–	–	AOX	90.7	[89]
	Modified anaerobic baffled reactor	71	71	VFA	−32	[75]

[a] UAF.

flocculant at the optimal conditions (coagulant dosage of 871 mg/L, flocculant dosage of 22.3 mg/L and pH 8.35) recovered 72.7% of water as a result of the treatment of a PPMW from a primary sedimentation tank.

3.2. Wastewater and sludge from P&P production processes

Virgin or RCFs are used as raw materials for the production of P&P. For this raw materials, a variety of chemical, mechanical or a combination of both methods have been applied so far (Table 1). Chemical additives are used in the several stages of P&P production process, due to some reasons such as the reduction of the water consumption and saving the energy and raw materials. However, through the recovery of the chemical used for the manufacturing processes of P&P, the mills are able to reuse a portion of the required chemical raw materials. For instance, the black liquor from bleaching process can be concentrated and burned in order to recover inorganic smelt of Na_2CO_3 and Na_2S to be re used for cooking the unbleached pulps [47]. However, such strategies would require the infrastructures for the chemical recovery and many of the small and some of medium scale P&P mills (<100t/d) lack of such facilities and, as a result, they discharge the rejects directly into the receiving environment [48]. In addition to the production method applied, the nature and origin of the raw materials used can cause the presence of some toxic and non toxic substances such as resin acids (from conifer species), sterols (mainly β sitosterol), waxes, and β sitosterol esters (from the Kraft cooking and oxygen pre bleaching of Eucalyptus sp.) in the wastes produced from the P&P making processes [21,49].

Table 2 presents the results of some recent studies indicating the performance of physicochemical and biological P&P treatments methods. Various approaches applied for the treatment of PPMW have shown different capabilities to remove the generated pollutants from the PPMW. However, there are some main drawbacks that have restricted their adoption by the mills. For instance, in spite of the acceptable performance of physico chemical methods for the removal of various wastewater parameters (e.g., chemical oxygen demand (COD), biochemical oxygen demand (BOD), adsorbable organic halogens (AOXs), TSS, and lignin), main limitations such as to be relatively expensive as well as maintenance requirements besides technical barriers, such as membrane fouling for membrane reactors are restrict their wider applications.

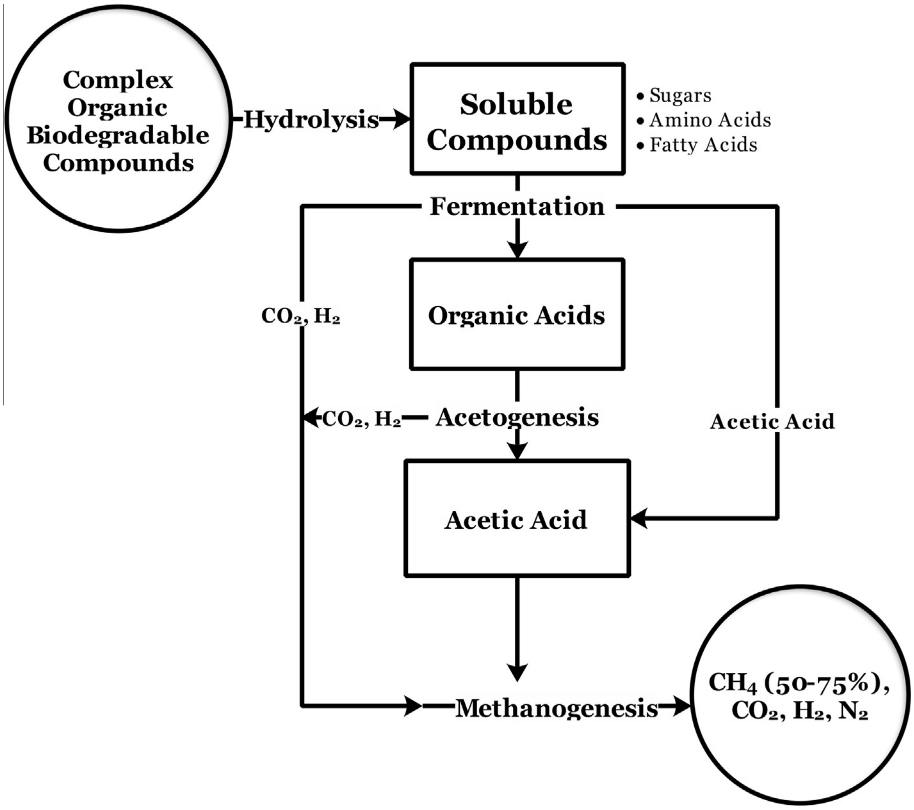

Fig. 4. A schematic of the AD steps.

Biological methods also have shown the feasibility for the treatment of wastewater from many types of P&P production processes. Although activated sludge processes are currently the major treatment for P&P mill effluents, AD has attracted a great amount of attention in recent years due to its inherent merits such as biogas production and minimizing the solid waste production, which has made it an attractive candidate for the treatment of PPMW. However, the toxic effect of some P&P effluents (e.g., kraft bleaching effluents) for the bacterial communities as well as the sensitivity of the biological systems to the environmental and operational conditions (e.g., restriction of AD and the fungal activity under high pH) are among the main problems of such systems to deal with PPMW. Having this in mind, the optimization of the efficiency of such biological systems is the most important step to achieve the desired performance and facilitation of transferring these technologies from lab scale to full scale applications [2,50,51].

In addition, the treatment of P&P wastewater normally produces a large amount of primary and secondary waste sludge which management and disposal are contributing to about 60% of the total PPMW treatment cost [52]. The characteristics of the primary and secondary sludge are highly dependent on the raw materials used, on the P&P production process, and on the applied subsequent wastewater treatment processes. Primary sludge consists mainly of higher size rejects such as fibrous materials (cellulose, hemicellulose and lignin), as well as the rejects from paper making process such as fillers and metallic components, sand, coatings, etc, in the case of paper making from RCFs (Table 1). However, non biodegradable compounds and other rejects from P&P production processes, based on the efficiency of the applied wastewater treatment processes [50], as well as the biomass from the microbial communities and the cell decay materials are the main constituents of the secondary sludge [53].

4. Anaerobic digestion of wastewater and sludge

Hydrolysis, acidogenesis, acetogenesis and methanogenesis are the main steps involved in the AD process (see Fig. 4). Lignocellulosic materials present in P&P wastes have the potential to slow down the hydrolysis step of the AD process. In addition, anaerobic reactor configuration, operational and environmental conditions (i.e., HRT, pH, temperature), and the presence of inhibitory compounds like ammonia, sulfide, chlorides, heavy metals, and hardly biodegradable compounds in the wastewater or sludge contents can potentially contribute to slow down the AD process, resulting in a low methane yield and process instability [11]. The factors that critically affect the performance of AD for the treatment of P&P wastewater and sludge are reviewed and discussed in the next sections.

4.1. AD of PPM wastewater

4.1.1. Reactor configuration

Among the high rate anaerobic reactors, anaerobic filters (AFs), upflow anaerobic sludge bed reactors (UASBs) and anaerobic membrane bioreactors (AnMBRs) have been mainly applied to treat the P&P mill wastewaters.

4.1.1.1. AFs. AFs are earlier types of high rate anaerobic reactors with relatively simple configuration, compared with other types of AD reactors such as fluidized bed reactors (FBRs) and UASB reactors [90]. Show & Tay (1999) [91] showed that the texture and the porosity of the media surface can significantly influence the removal of the chemical oxygen demand (COD) by anaerobic filter reactors. In recent years, novel filter media such as sludge fly ash ceramic particles [92], clay ceramic particles [93], and pumice stone [94] have been successfully applied in order to improve the AD by using AFs.

However, the application of such systems for the treatment of wastewater from P&P mills is limited, when compared to reactors with internal settlers, such as UASB reactors. Satyawali, Pant, Singh, & Srivastava (2009) [95] applied an upflow anaerobic packed bed reactor (UAPBR) with brick ballasts as packing material for the treatment of rayon grade pulp drain effluents. They observed 74.5% and 81% reductions in COD and BOD respectively, at an optimum HRT of 12 h. Deshmukh et al. (2009) [89] reported AOX degradation from a PPM bleaching effluent by using an AF with upflow. They observed 88% and 28% removals of AOX at initial concentrations of 28 mg AOX/L and 42 mg AOX/L, respectively, and HRT of 20 days. Bakhshi et al. (2011) [96] studied the removal of phenol from a synthetic wastewater by using a pilot scale UAPBR. Under mesophilic conditions and HRT of 24 h, the maximum biodegradation of phenol and biogas production achieved were 98% and 3.57 L/d, respectively. Jong & Parry (2003) [97] achieved more than 82% removal of sulfate from contaminated waters by using a bench scale UAPBR filled with silica sand at an organic and sulfate loading rates of 7.43, and 3.71 kg/d/m^3, respectively. Moreover, they observed removals of Cu and Zn >97.5%, removals of Ni of 77.5%, and removals of As and Fe >82%.

The performance of such reactors is mainly impaired by clogging due to the presence of high amounts of suspended solids leading to short circuiting of the wastewater [98]. Although some improvements have been proposed to solve this problem, such as a biological pre-treatment [99], further research and developments are critical and necessary, in order to find out technical and economical solutions for this problem.

4.1.1.2. UASBs. Among the several types of anaerobic reactors, UASB has been commonly adopted by pulp and paper industry since 1980's, due to its advantages when compared with other types of high rate anaerobic reactors, such as low investment requirements [13]. Buzzini & Pires (2002) [100] reached 80% on average removal of COD when treating diluted black liquor from a kraft pulp (KP) mill by using an UASB reactor. The performance of a bench scale UASB was also investigated by Buzzini, Gianotti, & Pires (2005) [101] for the treatment of simulated bleached and unbleached cellulose pulp mill wastewaters. They achieved 76% on average removal of COD and 71–99.7% on the removal of chlorinated organics. They also observed no inhibitory effect of the chlorinated organics on the removal of COD during the experiments. Chinnaraj & Rao (2006) [102] reported 80–85% reduction in COD, while producing 520 L/kg COD of biogas, after the replacement of an anaerobic lagoon by an UASB installation (full scale) for the treatment of an agro-based PPMW. Moreover, they achieved a reduction of 6.4 Gg in CO_2 emissions through the savings in fossil fuel consumption, and 2.1 Gg reduction in methane emissions from the anaerobic lagoon (equal to 43.8 Gg of CO_2) in nine months. Zhenhua & Qiaoyuan (2008) [103]achieved 98% and 85.3% reductions in BOD_5 and COD, respectively, from pulping effluents by using a combination of UASB and sequencing batch reactors (SBRs), while the removal efficiency when the substrate was just treated by a UASB reactor was considered to be 95% and 75% for BOD_5 and COD, respectively at an HRT of 1 day. Rao & Bapat (2006) [104] achieved 70–75% and 85–90% reductions of COD and BOD, respectively, and a methane yield of 0.31–0.33 m^3/kg of COD reduced, when using a full scale UASB for treating the pre-hydrolysate liquor from a rayon grade pulp mill. Puyol, Mohedano, Sanz, & Rodríguez (2009) [105] studied the effective removal of 2,4-DCP by using both UASB and anaerobic expanded granular sludge bed reactor (EGSB). Moreover, they indicate that EGSB reactor exhibited a better efficiency for the removal of both COD and 2,4-DCP (75% and 84%, respectively), when compared with UASB reactor (61% and 80%, respectively), at loading rates of 1.9 g COD/L/d and 100 mg 2,4-DCP/L/d.

4.1.1.3. AnMBRs. In recent years, AnMBRs which combine the advantages of AD process and membrane separation mechanisms have received considerable attention due to their advantages for wastewater treatment such as lower sludge production and energy requirements over conventional anaerobic treatment methods [106]. By adopting anaerobic membrane technologies, it is possible to achieve complete solid–liquid phase separation and, as a result, complete biomass retention [107]. Since 1990 s, some studies have been carried out to investigate the efficiency of such systems for the treatment of PPMW, and have shown 50–96% removal of COD [108]. Xie et al. (2010) [109] investigated the performance of a submerged anaerobic membrane bioreactors (SAnMBRs) for the treatment of kraft evaporator condensate at mesophilic conditions. They reached 93–99% COD removal under an OLR of 1–24 kg COD/m^3/day. Moreover, the methane production rate was observed to be 0.35 ± 0.05 L/g COD reduced. Lin et al. (2009) [110] achieved 97–99% COD removal from a kraft evaporator condensate at a feed COD of 10,000 mg/L in two pilot scale (thermophilic and mesophilic) submerged AnMBRs. Gao, Lin, Leung, & Liao (2010) [111] observed about 90% COD removal during the steady period (22nd–33rd day) of the performance of a submerged AnMBR, treating thermomechanical pulping (TMP) whitewater.

Several types of membranes such as PVDF based membranes [112], hollow polymeric fibers [113], ceramic tubular [114], etc. have been so far developed for the treatment of the various types of wastewaters. However, flat sheets of polyvinylidine fluoride (PVDF), as a flexible, low weight, inexpensive, and highly non-reactive material, are the dominant membranes used for the treatment of P&P mill effluents such as Kraft evaporator condensate [110] and TMP whitewater [111], as internal configurations. The maintenance and operational costs arising from membrane fouling and the frequent cleaning requirement of such hydrophobic polymeric membranes as well as being relatively energy intensive are nevertheless considered the main obstacles of such treatment systems dealing with various types of wastewaters. After studying the fouling mechanisms in AnMBRs, Charfi, Ben Amar, & Harmand (2012) [115] concluded that the cake formation is the main mechanism responsible for membrane fouling in AnMBRs. Such findings were also corroborated by other studies [110]. Although some measures such as feed pre-treatment, optimization of operational conditions, broth properties improvements, and membrane cleaning have already been applied to control the membrane fouling process [14], this issue demands further studies to enhance AnMBR performance.

4.1.1.4. Other types of AD reactors. The application of other types of anaerobic reactors has also been investigated for the treatment of PPMW, although the number of such studies is scarce in the literature. For instance, Grover, Marwaha, & Kennedy (1999) [116] achieved a maximum of 60% COD removal from black liquor treatment by using an anaerobic baffled reactor (ABR) at an organic loading rate (OLR) of 5 kg/m^{3}/d, a HRT of 2 d, a pH 8.0 and a temperature of 35 °C.

Table 3 summarizes the performance of various reactor configurations for the anaerobic treatment of PPMWs.

4.1.2. Operating conditions

4.1.2.1. HRT. HRT is one of the most significant influencing factors that can potentially affect the performance of an anaerobic reactor. In UASB reactors type, at high HRTs, the upflow velocity (V_{up}) decreases, and, as a result, the efficiency of the reactor for the removal of the suspended solids increases [119]. Moreover, elevated HRT can enhance the COD removal through the elevation

Table 3
Performance of various reactor configurations for the anaerobic treatment of PPMWs.

Reactor configuration	Effluents origin	Parameters					References
		COD		Other parameters			
		Initial (mg/L)	Removal (%)	Parameter/substance	Initial (mg/L)	Removal (%)	
UAPBR, (brick ballasts as packing material)	Rayon grade pulp drain effluent	3200[a]	74.5	BOD	–	81	[95]
				TSS[b]	–	62.7	
				TDS[c]	–	52	
UAF	Bleach composite wastewater	–	–	AOX	28	88	[89]
				AOX	42	28	
UAPBR	Synthetic phenolic wastewater	–	–	Phenol	1000	98	[96]
UAPBR, filled with silica sand	–		–	Sulfate	2280	82	[97]
		–		Cu	10.8	>97.5	
				Zn	10.3	>97.5	
				Ni	9.5	82	
				As	10.6	82	
				Fe	11.6	82	
UASB	Diluted black liquor	1400	76–86	–	–	–	[100]
UASB	Diluted black liquor	1400	76	Chlorinated organics	15	71–99.7	[101]
UASB	Bagasse-based P&P mill	2000–7000	80–85	–	–	–	[102]
				VFA	500–3500	–	
				SS	400–1000		
UASB + SBR	Wheat straw explosion pulping effluent	–	85.3	BOD_5	–	98	[103]
UASB		–	75	BOD_5	–	95	
UASB	Synthetic wastewater containing 2,4-DCP	1900	61	2,4-DCP	100 (mg/L/day)	80	[105]
EGSB	Synthetic wastewater containing 2,4-DCP	1900	75	2,4-DCP	100 (mg/L/day)	84	
UASB	Pre-hydrolysate liquor from a rayon grade pulp mill	2500	70–75[d]	BOD	–	85–90	[104]
UASB	P&P mill	1,133.9 ± 676	~81	TSS	1,063 ± 537	~67	[117]
				VFA	397 ± 347.7	~87	
SGBR[e]	P&P mill	1,133.9 ± 676	~82	TSS	1,063 ± 537	~57	[117]
				VFA	397 ± 347.7	~53	
Submerged AnMBR	Kraft evaporator condensate	2500–2700	93–99	–	–	–	[109]
Submerged AnMBR	Kraft evaporator condensate	10,000	97–99	–	–	-	[110]
Submerged AnMBR	TMP whitewater	2782–3350	90	–	–	–	[111]
ABR	Cornstalk fibrous pulp wastewater	4000	81.9[f]	–	–	–	[118]
ABR	Cornstalk fibrous pulp wastewater	4002	81.1[g]	–	–	–	
		6560	75.7[g]	–	–	–	[118]
ABR	Black liquor	10,003 ± 69	60	–	–	–	[116]
ABR	Recycled paper mill effluents	3380–4930	Up to 71	BOD	1650–2565	~70	[75]
				VFA	455–490	~−31	
				TSS	1900–3138	~45	

[a] The rate of the effluent generation was 6000–7000 m^3/day.
[b] Total dissolved solids.
[c] Total suspended solids.
[d] Full-scale installation with an optimum OLR of 10 and a methane yield of 0.31–0.33 m^3/kg of COD reduced.
[e] Static granular bed reactor.
[f] HRT 18 h.
[g] HRT 24 h.

of the contact time. Parker, Hall, & Farquhar (1993) [120] reported 27 65% removal of adsorbable organic halogens (AOX) when treating a kraft mill bleach wastewater by using a UASB reactor, depending on the HRT (3 48 h). Since then, the developments on the design and operational conditions of high rate reactors have led them to treat P&P mill wastes more efficiently. Turkdogan et al. (2013) [117] achieved 60% and 81% removals of COD by using a pilot scale UASB reactor at 4 and 9 h HRT, respectively. Moreover, they observed that the performance of a static granular bed reactor (SGBR) was better than that of a UASB reactor, with more than 70% COD removal at 4 h HRT. In addition, at 24 h HRT, the suspended solids removal was observed to be slightly higher in the SGBR. Sun et al. (2009) [118] investigated the effect of different HRTs on the performance of an ABR when treating the cornstalk fibrous pulp wastewater. They observed that with the initial COD of 4000 mg/L, when HRT decreased from 40 h to 19 h, the COD removal efficiency decreased from 81.9% to 75.7%, respectively. The performance of AD systems under various HRTs may also be affected by the operating temperature. Ahn & Forster (2002) [121] stated that with an increase in the HRT from 11.7 to 26.2 h, the performance of the thermophilic digestion increases, while no significant HRT related improvement in the mesophilic digester is observed in terms of COD removal when treating a simulated paper mill wastewater.

The presence of 2,4 dichlorophenol (2,4 DCP) can negatively affect the methanogenic phase [105]. Sponza & Uluköy (2008) [122] evaluated the removal of 2,4 DCP and COD from a synthetic wastewater at different HRTs ranging from 2 to 20 h using an UASB reactor. They observed a decrease in the COD removal from 83% to 65% when the HRT was decreased from 20 to 2 h. In these conditions, the removal of 2,4 DCP was 99% and 83%, respectively. Sponza & Cigal (2008) [123] identified *Methanobacterium bryantii*, *Methanobacterium formicicum*, *Methanobrevibacter smithii*, *Methanococcus voltae*, *Methanosarcina mazei*, *Methanosarcina acetivorans*, *Methanogenium bourgense*, and *Methanospirillum hungatei* as the microorganisms involved in the treatment of 2,4 DCP, when

Table 4
The effect of HRT on the performance of AD for the treatment of PPMWs.

Reactor	Effluents origin	Parameters						References
		COD			Other parameters			
		Initial (mg/L)	Removal (%)	HRT (h)	Parameters	Initial (mg/L)	Removal (%)	
UASB	Black liquor	1400	76	24	BOD	800	–	[100]
					Sulfide	8.8	–	
					P_{total}	6.5	–	
UASB	Black liquor	1400	86	14.4	–	–	–	[124]
		1400	75	24	BOD	660	–	
					P_{total}	4.0	–	
					VFA	–	30	
UASB	Black liquor	1400	78	30	VFA	–	29	
UASB	Synthetic effluents	514	83	20	2,4 DCP[a]	12	99	[122]
		2000	65	2	2,4 DCP	232	83	
UASB	Segregated kraft bleaching effluents	–	–	3	AOX	–	27	[120]
		–	–	48	AOX	–	65	
UASB	TMP paper mill wastewater	1,133.9	60	4	TSS	1,063	92	[117]
					VFA	397	71	
		1,133.9	85	9	TSS	1,063	55.57	
					VFA	397	84	
		1,133.9	81	24	TSS	1,063	50	
					VFA	397	88	
ABR	Cornstalk fibrous pulp wastewater	4000	81.9	40	–	–	–	[118]
			75.7	19	–	–	–	
AF[a]	Simulated paper mill wastewater		85	13	–	–	–	[121]
			>90	23	–	–	–	
MAHB[b]	RCFs	1000–4000	97.69	–[c]	VFA	35[d]	–	[125]
			78.37	–[e]	VFA	$\sim$10[f]	–	

[a] Thermophilic conditions (55 °C).
[b] Anaerobic hybrid baffled.
[c] OLR of 1.33 gm COD/lit/day.
[d] VFA concentration at OLR of 2.00 gm COD/lit/day.
[e] OLR of 2.00 gm COD/lit/day.
[f] VFA concentration at OLR of 1.33 gm COD/lit/day.

Table 5
Optimal conditions for the growth of some methanogenic bacteria [15,139,144].

Genus	Optimal temperature range	Optimal pH range
Methanobacterium	37–45	6.9–7.2 (*Methanobacterium bryantii*)
Methanobrevibacter	37–40	7.8–8 (*Methanobrevibacter arboriphilus*) $\sim$7 (*Methanobrevibacter smithii*)
Methanosphaera	35–40	$\sim$7
Methanolobus	35–40	$\sim$7
Methanococcus	35–40	5–7 (*Methanococcus voltae*)
Methanosarcina	30–40	6.5–7.5 (*Methanosarcina acetivorans*)
Methanocorpusculum	30–40	6.4–7.2 (*Methanocorpusculum aggregans*)
Methanoculleus	35–40	$\sim$7
Methanogenium	20–40	6.2–6.6 (*Methanogenium cariaci*)
Methanoplanus	30–40	6.6–7.2 (*Methanoplanus endosymbiosus*)
Methanospirillum	35–40	–
Methanococcoides	30–35	$\sim$7
Methanolobus	35–40	$\sim$7
Methanohalophilus	35–45	$\sim$7
Methanohalobium	50–55	$\sim$7
Methanosarcina	50–55	6.5–7.5 (*Methanosarcina acetivorans*)

using a UASB reactor. Table 4 presents the results from some studies investigating the effects of the HRT on the performance of anaerobic reactors for the treatment of PPMW.

4.1.2.2. Environmental conditions.

4.1.2.2.1. Temperature. The operating temperature is a significant variable that can potentially affect the efficiency of the COD removal and biogas production from various wastewaters through, for instance, an increase in the microbiological activity [126]. This process is generally carried out at mesophilic conditions (35–37 °C). However, several studies on the AD of various substrates have clearly indicated that the thermophilic conditions allow a better COD removal and biogas production [127]. Moreover, benefits like higher maximum specific growth rate of microorganisms (μ_{max}), and therefore better organic matter degradation in a shorter operating time [126], higher colour removal efficiency [128], more favorable disinfection capability, improved AD steady state stability [129], and being more feasible for co digestion approaches than mesophilic processes [130] can be expected by operating under thermophilic conditions.

Yilmaz et al. (2008) [90] studied the performance of two AFs under mesophilic (35 °C) and thermophilic (55 °C) conditions for the treatment of a paper mill wastewater. They observed no significant differences at OLRs up to 8.4 g COD/L/d. At higher OLRs, slightly better COD removal and biogas production were observed in the thermophilic reactor, which also denotes the effect of the

OLR on the performance of the AD process. Ahn & Forster (2002) [121] showed that the specific methane production obtained in an AF treating a simulated paper mill wastewater under thermophilic digestion was higher than the one obtained at a mesophilic temperature under all the studied HRTs from 11.7 to 26.2 h. In the same study, they also indicated that the performance of the two mesophilic and thermophilic upflow AFs treating a simulated paper mill wastewater can be affected either by a drop or an increase in the operating temperature. They showed that the performance of both digesters, in terms of COD removal efficiency and biogas production at an OLR of 1.95 kg COD/m^3/day, was negatively affected by a drop in the operating temperature to 18 24 °C and to 35 °C for mesophilic and thermophilic digesters, respectively. When the temperature was increased to 55 and 65 °C in mesophilic and thermophilic digesters, respectively, they also observed an immediate decrease in the treatment efficiency [131]. However, some studies have also shown that anaerobic biomass have a potential for good recovery after undergoing thermal shock [100]. The effect of the variations in the operating temperature can be significantly affected by the configuration of the reactor. SAnMBR seems to be more resistant to temperature variation when compared with other high rate conventional anaerobic digesters. Lin et al. (2009) [110] observed no significant difference between the thermophilic and mesophilic AD, when treating pulping wastewater by using a pilot scale SAnMBR. They also observed that the mesophilic SAnMBR can exhibit a better filtration performance in terms of filtration resistance. Gao et al. (2011) [107] investigated the effect of the temperature and temperature shock on the performance of a SAnMBR treating TMP pressate. Their results indicated that the COD removal at 37 and 45 °C was slightly higher than that at 55 °C. However, they observed no significant differences between the methane productions at the various temperatures. They also indicated that temperature shock can affect the diversity and richness of the species. A COD removal efficiency of 97 99% was observed at a feed COD of 10,000 mg/L in both SAnMBRs.

In spite of the advantages of conventional mesophilic and thermophilic treatments, low temperature AD has emerged in recent years, as an economic method to deal with cool, dilute effluents which were considered as inappropriate substrates for AD [132]. McKeown, Hughes, Collins, Mahony, & O'Flaherty (2012) [133], by reviewing the basis and the performance of the low temperature AD for wastewater treatment, concluded that the adoption of effective post treatments for low temperature anaerobic digestion (LTAD) is a way to satisfy the stringent environmental regulations. Some recent studies have also indicated that LTAD can be more efficient by adopting the co digestion approach (in pilot scale application) [134]. However, significant physical, chemical and biological improvements should be applied to high rate AD under low temperature conditions to enhance the efficiency of the present AD systems, and to improve the amount of the methane produced during the related anaerobic processes.

4.1.2.2.2. pH. The anaerobic digesters are very sensitive to changes in the pH of the system. This occurs mainly due to the restriction of the methanogens growth below pH 6.6 [135] (Table 5). Methanogens are more sensitive to pH, compared to fermentative microorganisms which can survive in a wider pH range between 4.0 and 8.5 [136]. By inhibiting the methanogens, VFAs are produced and converted to acetic acid, hydrogen and carbon dioxide and thus they are accumulated in the medium. As a result, the pH will decrease leading to a further inhibition of the microbial activities [137]. Allowing methanogens to be reproduced by stopping the substrate feeding is considered to be one of the possible ways [15] In order to correct the pH failure. Moreover, co digestion of the main substrate with an appropriate ratio of another (co)substrate is an applicable way to provide the system

Table 6
Performance of some AD systems for the treatment of PPMWs.

Reactor	Effluents origin	Parameters						Considerations	References
		Temp.	pH	COD		Biogas production (L/day)	Methane yield (L CH_4/g COD)		
				Initial (mg/L)	Removal (%)				
AF	Paper mill wastewater	Mesophilic	7–7.6	3144	77	2.957	0.274	At HRT of 6 h	[90]
		Thermophilic	7–7.6	3144	80	3.204	0.291	At HRT of 6 h	
SAnMBR	kraft evaporator condensate	Mesophilic	7.0	10,000	97–99	–	0.35	–	[110]
		Thermophilic	7.0	10,000	97–99	–	0.35	–	
Serum bottles	ECF bleaching process effluents at kraft mills (softwood)	Mesophilic	3.2	1700	–	–	0.35[a]	–	[143]
	Kraft cooking effluent (softwood)	Mesophilic	10.0	620	–	–	0.660[b]	–	
SAnMBR	TMP whitewater	Mesophilic	7.0	2782–3350	~90	–	0.41	–	[111]
		Mesophilic	8.0	2782–3350	83	–	0.38	pH shocks from 7 to 8, 9.1, and 10, respectively	
		Mesophilic	9.1	2782–3350	75	–	~0		
		Mesophilic	10	2782–3350	30	–	~0		
AF	Simulated paper mill wastewater	Thermophilic		–	93		~0.25	At HRT of 25.1 h	[121]
		Mesophilic		–	77		~0.18	At HRT of 26.2 h	

[a] NL CH4/g TOC, COD/TOC: 2.3.

[b] NL CH4/g TOC, COD/TOC: 6.5.

Table 7
AD performance with physico-chemical methods for pre-treatment of PPMWs.

Wastewater	Pre-treatment method	Parameters				References
		COD		Biodegradability		
		Initial (mg/L)	Removal (%)	Initial	Final	
Bleaching effluent	Precipitation	1510	Up to 90	0.11	0.26	[153]
Blending black liquor	Coagulation + Flocculation	1358	—	—	—	[46]
Synthetic wastewater	Electrocoagulation	2500	~95	–	–	[154]
Effluents from equalization tank	Flocculation	2900 ± 90	>90	–	–	[81]
Cardboard industry wastewater	Flocculation	500–1800	>80	–	–	[155]
Effluents from aerated lagoons	Electrocoagulation	426	75	–	–	[81]
TCF effluents	Fungi-solar photo-Fenton	1802	>90	–	–	[83]

with a suitable pH, and to increase its buffering capacity [138]. However, the most appropriate pH range for such reactors is between 6 and 8 [139]. The variation in the pH can also influence the activities of the microorganisms including metabolism and degrading efficiency of the system [140]. Moreover, the morphology of the bacterial communities may be influenced by the changes in the pH. Sandberg & Ahring (1992) [141] stated that disintegration of microbial granules can be expected at alkaline pH values. This is a very important issue because the kraft wood pulping effluent is alkaline [142] which may lead to the failure of the system. Moreover, the ECF acidic effluents from the KP mills have been shown to be very toxic to the AD microorganisms [143] and this can directly affect the methane production from such effluents. Gao et al. (2010) [111] indicated that although a pH shock of 8.0 had no important adverse effects on the performance of a SAnMBR in terms of COD removal, biogas production and membrane filtration, the long lasting negative effects of pH shocks of 9.1 and 10.0 were significant. They also observed that after providing the normal pH (7.0), it took approximately 30 days for the total recovery of the reactor performance after the pH shock of 10, compared with 1, and 6 days for pH shocks of 8.0 and 9.1, respectively.

Table 6 presents the results of some studies on the performance of AD under various operating conditions, especially temperature and pH, for the treatment of PPMWs.

4.1.3. Inhibitory elements

The efficiency of an AD system may be limited by the presence of some elements. Relatively high amounts of soluble forms of nitrogen and phosphorous are required to ensure the sufficient growth and activity of all microorganisms, involved in all AD stages. This is considered a significant feature for the treatment of PPMW, due to the low amount of nitrogen, as a key nutrient, which normally occurs in such type of residues [145]. In addition, the ratio of key elements is of high importance to avoid the failure of the AD process. Bouallagui (2003) [146] applied an optimum ratio of 100 130:4:1 for COD:N:P, as an optimal condition for AD of vegetable biomasses. Qu et al. (2012) [61] reported the adjustment of this ratio to 100:5:1 for appropriate biomass growth. The successful adoption of this ratio has been also indicated by other studies [121]. Furthermore, the ratio of carbon to nitrogen (C:N) is of importance to ensure the desirable efficiency of an AD system. In this regard, a low C:N ratio may cause the accumulation of total ammonia nitrogen or VFAs, which are inhibitor factors for AD performance. Moreover, the inhibition of the methane production is considered to be a result of a high C:N ratio, through the rapid consumption of the nitrogen by methanogens. The optimal amount of 25:1 has been determined for C:N [147].

In addition, the PPMW often contains high amounts of sulfide compounds which may inhibit the AD process. Air purging is considered an effective way to increase the efficiency of the system and to remove the adverse toxic effects caused by sulfide compounds. Lin et al. (2014) [148] achieved a considerable improvement in the COD removal (from 20 30% to 65 75%) by using a UAPBR anaerobic digester, when a foul condensate from a PPI was purged with air for at least 2 h before the pre digestion stage. Zhou, Imai, Ukita, Li, & Yuasa (2007) [149] achieved a 40% increase (from 40% to 80%) in the removal of COD from a sulfite pulp mill evaporator condensate, by applying a direct limited aeration in the UASB, at an OLR of 8 kg COD m^3/d and a HRT of 12 h. This extra COD removal occurred due to sulfide oxidation and H_2S removal, which can lead to the methanogens improvements.

4.1.4. Pre treatment strategies

Although many attempts have been made to enhance the removal of the persistent pollutants from PPMWs (Table 7), the number of published papers investigating the direct effects of the physico chemical and biological pre treatments on the performance of AD facilities is still scarce. Kim, Yeom, Ryu, & Song (2004) [150] achieved 60% removal of the calcium hardness in the CO_2 stripper when a UASB/CO_2 stripper system was used for the treatment of liner paper wastewater. In this situation, more than 60% removal efficiency for the anaerobic process of COD was also observed. Yue, Li, & Yu (2013) [151] by reviewing the performance of the rumen microorganisms for AD of lignocellulosic biomass showed the higher hydrolytic and acidogenic activity of such microbial inoculums, compared to other microorganisms. Yuan et al. (2012) [152] indicated that pre treatment of the filter paper, office paper, newspaper, and cardboard with a microbial consortium, containing *Clostridium straminisolvens* CSK1 and *Clostridium* sp, resulted in a significant increase in the soluble chemical oxygen demand (SCOD) and, as a consequence, an improvement in the methane production with all studied substrates. Baba, Tada, Fukuda, & Nakai (2013) [153] achieved a 2.6 times higher methane production (73.4% of the theoretical methane yield), when the waste paper was soaked with rumen fluid for 6 h at 37 °C before treatment in a semi continuous AD, compared to that of untreated paper.

4.1.5. Anaerobic aerobic combinations

According to most references [51] a system consisting of an anaerobic followed by an aerobic process is a better option for the removal of COD, AOX and colour from P&P mill streams. Tezel, Guven, Erguder, & Demirer (2001) [156] observed 91% and 58% removals of COD and AOX, respectively, by using sequential anaerobic and aerobic digestion systems to treat a PPMW, at a HRT of 5 h and 6.54 h for the anaerobic and aerobic processes, respectively. Bishnoi, Khumukcham, & Kumar (2006) [157] achieved a maximum methane production up to 430 mL/day. Moreover, a COD removal up to 64% was obtained, while VFAs increased up to 54% at a pH of 7.3, a temperature of 37 °C and 8 days HRT during AD. Afterwards, COD and BOD removals were 81% and 86%, respectively, at 72 h HRT in activated sludge process.

It also seems that a combination of fungal and bacterial strains can help for a more effective removal of recalcitrant pollutants from streams. For instance, a treatment of the combined effluent of a PPM by using a sequential anaerobic and aerobic treatment

Table 8
Changes in the P&P mill wastewater parameters after treatment by anaerobic–aerobic combinations.

Process	Parameters					References
	COD		Other parameters			
	Initial (mg/L)	Removal (%)	Parameter	Initial (mg/L)	Removal (%)	
EGSB + MLE + UF	1600–4400	96	–	–	–	[161]
Packed bed AD column + ASP	2973 ± 142[a] 2886 ± 381[b] 3901 ± 1940[c] 4498 ± 2020[d]	55–70				[149]
Sequential anaerobic–aerobic process	–	42	Colour	–	70	[158]
			Lignin	–	25	
			AOX	–	15	
			Phenol	–	39	
Sequential anaerobic–aerobic[e] process	–	88	Colour	–	95	[158]
			Lignin	–	86	
			AOX	–	67	
			Phenol	–	63	
UASB + Two-step sequential aerobic reactor[f]	5280	83.9	Colour	5205.5 cu	87.7	[159]
			Lignin	6380.56 mg/L	76.5	
			Phenol	54 mg/L	87.2	

[a] Foul condensates.
[b] Chlorine dioxide bleaching effluents.
[c] Alkaline extraction reinforced with oxygen and peroxide bleaching effluents.
[d] Dewatering operation of plant wasted sludge.
[e] A combination of fungal and bacterial strains.
[f] Involving *Paecilomyces sp.* and *Pseudomonas syringae pv myricae* (CSA105), respectively.

in two steps bioreactor was studied by Singh & Thakur (2006) [158]. They observed 70%, 42% and 39% removals of colour, COD and AOX, respectively, in 15 days. However, using a mixture of fungi and bacteria (*Paecilomyces* sp. and *Microbrevis luteum*) for the treatment of anaerobically treated PPM effluents, it was observed 95%, 67%, and 88% reductions in colour, AOX, and COD after 7 and 3 days in the anaerobic and aerobic treatment of the effluents, respectively. Combination of a UASB reactor (step I) and two step sequential aerobic reactor, involving *Paecilomyces* sp. (step II) and *Pseudomonas syringae pv myricae* (CSA105) (step III), as aerobic inoculums for the treatment of PPM effluents, has been also investigated by Chuphal, Kumar, & Thakur (2005) [159]. They indicated that by using such three step fixed film sequential bioreactors, 87.7%, 76.5%, 83.9% and 87.2% removals of colour, lignin, COD, and phenol, respectively, can be achieved. Balabanič & Klemenčič (2011) [160], by using full scale aerobic and combined aerobic anaerobic treatment plants, reached removal efficiencies of 87% and 87% for dimethyl phthalate, 79% and 91% for diethyl phthalate, 73% and 88% for dibutyl phthalate, 84% and 78% for di(2 ethylhexyl) phthalate, 86% and 76% for benzyl butyl phthalate, 74% and 79% for bisphenol A and 71% and 81% for nonylphenol from paper mill effluents, respectively. In a study carried out by Sheldon, Zeelie, & Edwards (2012) [161], a pilot plant EGSB reactor effectively lowered the COD by 65 to 85% over a 6 month period. The overall COD removal efficiency after the combination of an EGSB with a modified Ludzack Ettinger process coupled with an ultra filter membrane was consistent at 96%. Lin et al. (2014) [148] observed 50 65% COD removal from four different KP wastewaters (Table 8) under AD by using a pilot scale packed bed AD column at an OLR of 0.2 4.8 kg COD/m^3/d. The overall COD removal efficiency after combining with completely mixed activated sludge process (ASP), as anaerobic aerobic sequential system, was 55 70%. Moreover the methane production yield was 0.22 0.34 m^3 CH$_4$/kg COD, with the biogas containing 80% of methane.

4.1.6. Future outlook in AD of PPMW

Inherent capabilities of AD reactors can play a significant role in their adoption by P&P mill to treat various types of PPMW (Table 1). Some of the technologies reviewed in this paper have started to make their way into full scale implementation. The technologies that appear to be at the forefront of AD of PPMW include systems based on suspended growth microorganisms (UASB, SAnMBR and ABR) and fixed film reactors (AFs, UAPBR). Among the first type of technologies, UASB reactors are currently the dominant full scale facilities adopted by P&P mills through the world. However, in spite of their high levels of stability (based on the ratio of VFA/Alk indicator) and moderate efficiencies for the removal of COD, BOD and TSS from PPMWs they mainly fail to treat recalcitrant compounds such as AOX released to the wastewater from the processes involving the use of chlorinated compounds during the bleaching sequences (Table 1). In addition, relatively long HRT requirement of UASBs can also affect their efficiencies when operating in low HRTs which is an urgent need for the P&P industry to deal with a large amount of the wastewater produced. These can reflect the importance of the adoption of corrective measures such as adoption of appropriate pre treatments methods before AD by UASB reactors. Recent studies have introduced low operating cost reactor configurations such as SGBR, having better efficiencies than UASBs at low HRTs in the lab scales, although not yet widely used to test their performance in full scale treatment of PPMWs. In addition, some measures can also be proposed for the UASB systems in order to maintain their removal efficiency while decreasing the HRT. Partial recirculation of the effluent, or cultivation of specific microbial strains [123] are among the tested methods in lab scale [124] which need precise cost benefit evaluations in full scale operation to be applicable by the P&P mills.

Submerged anaerobic membrane reactors (SAnMBR) can be also acceptable choices for the treatment of highly polluted effluents such as kraft evaporator condensate and TMP whitewater, in spite of their main technical difficulties, especially for treatment of PPMW having high TSS and fibrous materials, where membrane fouling has to be overcome. In this sense, low cost methods such as back flush cycles or relaxation are not able to remove the cake sludge (dominate cause of the membrane fouling). Hence, innovation and application of economic ways to deal with this phenomenon, like optimization of the most important operating conditions such as transmembrane pressure can help their wider application by P&P mills. Such improvements are especially of high importance because SAnMBR exhibit a better stability and resistance to temperature variation when compared with conventional high rate anaerobic digesters for the treatment of PPMW and, hence, can be a promising alternative for the conventional high rate anaerobic digesters to be used by P&P mills. Surface functionalization is a rapidly developing way to this end. For instance, fouling resistance of PVDF can be enhanced via attachment of appropriate materials to the surface of the membrane. Liang et al. (2013) [162] improved the hydrophobicity of the PVDF through post fabrication tethering of silica nanoparticles (NPs) to the membrane surface in order to form a highly hydrophilic membrane. Electrical treatment of the membrane surface can also be a good candidate to limit the hydrophobic behavior of the membranes, and so less attachment of the solutes to the membrane surface. Synthesis and application of new polymers having well defined characteristics is another possibility to optimize the membrane performance. As an example, a polymeric membrane based on sulfonated polycarbonate (SPC) and PVDF developed by Masuelli, Marchese, & Ochoa (2009) [112] resulted in lower fouling when treating an emulsified oily wastewater, as SPC content increased. Other types of membranes applied so far for the treatment of a variety of effluents such hollow fiber for tofu processing waste [113] and ceramic tubular for olive mill wastewater [114], are among the applied membranes with external/side stream configurations which can be also evaluated for the treatment of P&P mill effluents. Such a configuration can also provide benefits such as easer membrane replacement and providing high flux with more direct control of fouling [163].

ABRs have been rarely applied for the treatment of PPMW, despite having inherent advantages including simplicity, no requirement for gas separation system, low bacterial washout, and the adaptability to the changing operational conditions such as HRT and OLR, which can make them favorable choices, especially in the low income countries.

Among the second type of reactors, UAFs and anaerobic fixed film reactors, are good candidates for the efficient removal of AOXs from the P&P mill effluents, mainly those from ECF bleaching processes, as observed in lab scale experiments. AFs also have shown the applicability for the removal of sulfate, dominant specie in kraft mill effluents (Table 1), as well as other trace metallic materials which can be found in the effluents from RCFs processing processes. However, in spite of inherent advantages of AFs, such as negligible power requirements, technical difficulties including clogging (as a result of the presence of high amount of suspended solids in P&P mill effluents), and the cost of the packing materials must be overcome to facilitate their transfer from lab scale to full scale applications. Some innovations such as periodic irradiation of ultrasound waves and the fabrication of low cost and high efficient filter media (i.e. biotrickling filters [164]), can be proposed as the main areas for further studies to overcome such deficiencies.

Thermophilic digesters can also give a superior stability when compared to mesophilic digesters for a wide range of highly polluted PPMWs like those from chemical pulping (especially ECF). However, utilization of high temperature conditions may alter the energy saving strategies of P&P mills. In this regard, it would be also of high importance for future studies to evaluate the performance of low temperature AD by adopting some strategies like co digestion with other substrates for the treatment of PPMW.

The pre treatment methods have been applied so far for the remediation of wastes containing AOXs (Table 2), are also mainly unable to degrade and remove these compounds from the wastes content. In this sense, state of the art technologies, especially application of engineered nanomaterials (ENMs), can assist the degradation of AOXs from the PPMW, and enhance the biodegradability of the streams, providing a potentially cost effective and efficient solution. It is also of high importance to develop novel methods for the green fabrication of ENMs having enhanced and modified properties for such application as well as the facile and applicable methods for the collection of the used ENMs.

Some other features of the PPMW, such as the alkaline nature of the wastes from some P&P production processes (such as Kraft pulping) or toxic effects of the acidic effluents, like those from ECF (Table 1) may considerably restrict the efficiency of any AD technology. Innovation on multi stage AD reactors, able to separate the hydrolysis/acidification from acetogenesis/methanogenesis phases (Fig. 4) with acceptable performance criteria (i.e. HRT, OLR, removal efficiency, etc.), and adoption of strategies such as co digestion with appropriate substrates, in order to increase the buffering capacity and neutralization of the P&P effluents, are the subject for further studies in this field. Sequential bioreactors including anaerobic and aerobic digestion systems (especially a combination of fungal and bacterial strains) has been also of high effectiveness for COD removal and to some extent removal of AOXs, lignin and colour from PPMWs. This combined strategy could also be used as a solution for the problems of the conventional anaerobic digesters (such as UASB) when the HRT decreases; because the experimental analysis have shown relatively high performance for this combined systems at relatively low HRTs. In addition, it should also be mentioned that the performance of the AD systems for the treatment of PPMW when exposed to shocks in the operating conditions, and their recovery potential has not been well documented so far.

Anaerobic digestion of PPMW rate can be limited by the quantity of the most limiting elements (i.e. nitrogen phosphorous), according to the Liebig's law [165]. An applicable method for the nutrient deficiency compensation seems to be the co digestion of PPMW with appropriate substrates. However, real applications of such strategies are highly scarce, whereas it can be a very interesting choice in order to do the integration of different treatment plants. However, In some cases, such as the effluents from *Eucalyptus* sp. P&P making processes (Fig. 1), there may be relatively high amounts of phosphorous which may need novel techniques to prevent discharging the phosphorus based compounds, in higher amounts than their limits according to the environmental protection standards. On the other hand, the presence of some toxic compounds can limit the AD of P&P mill wastes. With respect to sulfide, some measures such as pre oxidization [148] can be a possible solution. However, in the presence of sulfate reducing bacteria, H_2S will be released, which is the most toxic form of the sulfide species for the microbial communities. Such species can also promote the corrosion of the concrete in full scale reactors, caused by the hydrogen sulfide released in the media, or interrupting the methane yield through for instance the anaerobic oxidation of the methane through the following equation [166]:

$$CH_4 + SO_4^{2} \rightarrow HCO_3 + HS + H_2O \qquad (1)$$

However, studies on the conversion or removal of sulfide from the P&P mill effluents are scarce. Multi stage reactors may be a good option for this purpose. Moreover, there is a lack for studies on the presence of sulfate reducing bacteria in the AD microbial population and their effects on the inhibition of the methane yield. For other inhibitory elements, such as tannins, which are considered as the main portion of the P&P mill effluents (Table 1), AOXs, resin acids, etc., in spite of their evident toxic effects on the microbial communities, there is still a need for further comparative studies to quantify their exact effects on the methane production, as well as the economic and effective innovative methods for the degradation (or removal) of these compounds from the streams. One effective way to deal with the inhibitors and also with non biodegradable compounds is applying a physico chemical and biological pre treatment. However, there is a lack of knowledge on the direct effects of such methods on both the methane yield and AD removal efficiency. Coagulation, flocculation, precipitation, oxidation, adsorption, and filtration are the main physico chemical techniques that have been applied so far for the treatment of P&P wastewater (Table 7). However, several technical and economic considerations have limited their wider application at full scale. Membrane based technologies are mainly struggling with technical deficiencies (such membrane fouling) and conventional oxidation processes are of high expense to be adopted economically by the P&P mills. Moreover, applying methods such as sedimentation can remove high weight fibrous materials from the content of P&P wastewater which may affect the yield of the following AD. In spite of innovation of some economic and theoretically applicable methods such as advanced oxidative processes (AOPs) by using nano catalytic materials, they have not been used for the pre treatment of PPMW. Ultrasonic irradiation (20 kHz 10 MHz), which has been used previously as a pre treatment for some types of effluents, such as municipal wastewaters [167] can also be applied before AD of PPMW. It may increase the homogeneity of the effluents and transform some hardly biodegradable fractions, as a result of direct high intensity energy of ultrasonic irradiation or, indirectly, under the effect of high speed jets or shock waves (400 km/h) produced by collapsing the bubbles which form and grow under ultrasonic irradiation, and experience instantaneous implosive collapse [168].

Although pre treatment methods have been applied so far for the remediation of wastes containing AOXs (Table 2), they are also mainly unable to degrade and remove these compounds from the wastes content. In this sense, an evolution had occurred in the state of the art technologies, especially the application of engineered nanomaterials (ENMs), which can assist the degradation of AOXs from the PPMW, and enhance the biodegradability of the streams, providing a potentially cost effective and efficient solution. In this area of study, it is also of high importance to develop novel methods for the green fabrication of ENMs having enhanced and modified properties for such application as well as to develop facile and applicable methods for the collection of the used ENMs.

4.2. AD of PPM sludge

Pre treatment methods and co digestion strategies are the main approaches used so far to enhance the AD of PPMS.

4.2.1. Pre treatment strategies

It seems that pre treatment methods are very effective in order to reduce the residence time and to enhance the performance of the AD systems, and, hence, to reduce the treatment costs. Yunqin, Dehan, Shaoquan, & Chunmin (2009) [169] investigated the effects of the pre treatment of the PPMS with NaOH, prior to AD. They observed that by performing this pre treatment, the SCOD of the sludge increased, and, as a consequence, a 54 88% improvement in the methane production was achieved. Park et al. (2012) [52] achieved no significant methane production improvement when the thickened PPMS (65 g/kg TS) was subject to a pre treatment with NaOH (0.261 g/g TS), or to an ultrasonic pre treatment (16.8 MJ/kg TS) before AD. However, the initial rate of methane production increased and, as a result of the pre treatment, 80% of total methane yield was reached 5.5 6.5 days faster. Moreover, Bayr, Kaparaju, & Rintala (2013) [170] indicated that ultrasound method could not improve the methane yield, when used as pre treatment for AD of secondary PPMS. They investigated 12 different pre treatment methods in this regard and concluded that hydrothermal pretreatment (150 °C, 10 min), alone or in combination with enzymatic and/or ultrasound pretreatment can result in the highest methane yield. Wood, Tran, & Master (2009) [171] achieved similar results with respect to the efficiency of the thermal pre treatment of the kraft and sulfide sludge samples, when compared to other studied pre treatments, including thermochemical (caustic) and sonication. Saha, Eskicioglu, & Marin (2011) [172] studied the effects of the microwave (2450 MHz, 1250 W), ultrasonic (20 kHz, 400 W) and chemo mechanical (MicroSludge® with 900 mg/L NaOH followed by 83,000 kPa) pre treatments on the methane production from pulp mill wastewater treatment sludge. They observed that the microwave pretreatment was the most effective method, resulting in a 90% increase in the specific methane yield, when compared to controls after 21 days under mesophilic digestion of secondary sludge. Moreover, although sonication showed a better effect on the COD solubilization, it resulted in soluble non biodegradable compounds. Table 9 summarizes the results of the recent studies on the PPMS pre treatments.

Moreover, there is a potential improvement in the treatment process through the application of advanced materials and technologies such as ENMs which experienced a rapid transfer from laboratory to field scale applications in various scientific fields

Table 9
The AD performance with pre-treatment methods for treatment of PPMS.

Sludge	Method	SCOD (Before pre-treatment) (mg/L)	SCOD (AD)		Methane production improvement (%)	References
			Initial (mg/L)	Removal (%)		
Mixture of primary and secondary sludge	Alkali pre-treatment (8 g NaOH/100 g TS_{sludge})	–	14778.6	93	83	[169]
Secondary sludge (TMP)	Alkali + Ultrasound pre-treatment	–	~13,000	–	3–7	[52]
Secondary sludge (KP)[a]	Hydrothermal pretreatment	800	9000	–	54	[170]
	Hydrothermal + Enzymatic pretreatment	800	9000	–	41	
	Ultrasound + Hydrothermal pretreatment	800	9000	–	52	
	Ultrasound + Hydrothermal + Enzymatic pretreatment	800	10,000	–	57	
Secondary sludge (pulp mill[b])	Thermal pretreatment	1.4 ± 0.03	8.5 ± 1.0	–	50	[171]
	Thermochemical pretreatment	1.4 ± 0.03	9.7 ± 1.0	–	18	
Mixture of primary and secondary sludge[c]	Microwave pre-treatment (175 °C)	1926	–[d]	–[e]	~80[f]	[172]
	Ultrasonic (90 °C)	1926	–[g]	–[h]	~90[c]	

[a] Integrated bleached (chlorine dioxide, oxygen) KP (softwood and birch) and paper mill (producing coated magazine paper).
[b] Ammonium sulfite mill, and a kraft mill.
[c] Pulp mill WAS and WAS + PS (40:60% v/v) mixed sludge.
[d] SCOD/total chemical oxygen demand (TCOD): 41 ± 2.1%.
[e] TCOD removal: 30%.
[f] Based on the specific methane yield (mL/mg $TCOD_{added}$) after 21 days.
[g] SCOD/TCOD: 42 ± 2.1%.
[h] TCOD removal: 30%.

Table 10
Characteristics of the primary, secondary and mixed PPMS.

Sludge type	Characteristics					References
	COD (mg/L)	TS (%)	VS (% of TS)	pH	C/N ratio	
Primary sludge[a]	–	3.4	86	6.2	–	[53]
Secondary sludge[a]		4.0	82	7.6	–	[53]
Secondary sludge[b]	29,800	24.2	77.0	7.3	10.5:1	[52]
Secondary sludge[c]	–	4.7	83	–	–	[170]
Secondary sludge[d]	11,700	11.1 (mg/L)	–	–		[171]
Secondary sludge[e]	27,000	24.4 (mg/L)	–	–		[171]
Secondary sludge	39,579	2.50	80	6.5		[172]
Primary + secondary sludge	34,229	2.21	83	6.2		[172]
Primary + secondary sludge	–	31.45	62.3	7.82	30.05	[169]

[a] Integrated bleached kraft pulp (softwood and birch) and paper mill.
[b] Bleached CTMP and TMP.
[c] Integrated bleached kraft P&P mill.
[d] Sulfite mill.
[e] Kraft mill.

[173]. Such novel materials are used to remove trace elements such as Ni, Cd, and Pb [174] which may be found in PPMS [175], mainly through sorbtive techniques [176]. Moreover, they seem to be able to break down non biodegradable compounds like cellulosic biomass (i.e., cellulose, hemicellulose, and lignin [177] which resists the hydrolytic enzymes [178]. This may lead to enhance the biodegradability index (BI), and an improvement in the yield of the biological treatment.

4.2.2. Co digestion

Nutrient deficiency, and also lignin and sulphur containing substances are considered the main drawbacks which may cause an incomplete anaerobic treatment of P&P mill wastes. Hagelqvist (2013) [179] indicated the feasibility of the secondary sludge from CTMP, from KP process, and from food packaging board to be co digested with municipal sewage sludge, without significant reduction in methane production, but a small increase in the solid residue's cadmium content. Bayr & Rintala (2012) [53] achieved methane yields of 150 170 $m^3/t\ VS_{fed}$ by anaerobic co digestion of primary and secondary sludge with OLR of 1 $kg\ VS/m^3$ d and HRT of 25 31 d. In order to do adjustments of the C/N ratio, Lin et al. (2011) [147] investigated co digestion of the PPMS with monosodium glutamate waste liquor by using a bench scale anaerobic digester under mesophilic conditions. They observed no inhibitions due to VFAs and ammonia on the anaerobic co digestion process, with an accumulative methane yield attained of 200 $mL/g\ VS_{added}$ and a peak value of daily methane production of 0.5 m^3. Lin et al. (2013) [14] designed a mesophilic anaerobic bio hydrogen production and a mesophilic anaerobic process for methane production, for co digestion of PPMS and food wastes. They achieved 64.48 $mL/g\ VS_{fed}$ and 432.3 $mL/g\ VS_{fed}$ yields for hydrogen and methane production, respectively, at an optimal ratio of PPS and food wastes (1:1 VS), as the feedstock. In this situation, a maximum of 87% removal efficiency on the SCOD was achieved.

4.2.3. PPMS: criticisms and future outlook

AD has been traditionally utilized for decades, as an attractive way to stabilize primary, secondary and mixed sludge having high levels of biodegradable materials, and to produce biogas, as a source of renewable energy form these types of wastes. However, compared to PPMW, there are a limited number of reports about AD of PPMS, especially for the (semi) continuous AD of P&P primary sludge (Table 10). This may be to the fact that the primary sludge from P&P mill production processes are rich in fibrous materials and, hence, is recovered instead of being anaerobically digested. However, the PPMS is generally low in organic matters, especially biodegradable compounds; they have typically low methane potentials. It is mainly attributed to the fact that they have been already degraded by physico chemical or biological treatments. In this regard, application of pre treatment technologies, especially chemical (e.g., alkali) ones as cost effective ways, can promote the biogas production, through the disintegration of sludge cells and enhancing the availability of the biodegradable compounds for AD microorganisms. However, it seems that in order to achieve the maximum energy production, in line with environmental considerations, the main priority must be to develop and promote the efficient methods to AD treatment of PPMW to maximize the biogas production resulting in a low sludge production which can meet discharge standards to be used, for instances, in land applications safely.

In spite of the recent advances in the anaerobic digestion of the P&P mill wastes, digested streams may still contain compounds like lignin, tannin, etc. (Table 1); contributing to color of the leachate/ effluents, as well as microorganisms, suspended solids and other pollutants including non biodegradable compounds and relatively low quantities of remained biodegradable organics [82,180]. Hence, tertiary treatments such as membrane separation [82], adsorption [181], ion exchanging [182], and chemical oxidation process [180,183,184] may be vital if the sludge (or wastewater) is desired to be recycled in the manufacturing processes. Composting for the AD residual to form a soil conditioner can also be performed on the AD residuals [185].

5. Conclusion

High COD concentrations contributing to the 55 60% of the original weight of the wood [11] and additives used (Table 1) can strongly support the idea of the AD of P&P mill wastes in order to reduction of pollution load, and production of biogas, as a renewable source of energy. However, several factors are involved in the AD of P&P mill wastes (graphical abstract) which should be taken into consideration carefully to achieve the desirable methane production and treatment efficiency for this process. Anaerobic digesters having internal settlers such as UASB reactors are the dominant reactor systems for the treatment of PPMWs. Such reactors have shown a moderate to high performance to reduce the COD and various removal efficiencies for other parameters including BOD, TSS, AOX, etc., depending on the reactor design, operating conditions and the properties of the streams. While the relatively long HRT has been the main shortfall in the performance of UASB systems, the maintenance and the additional costs are considered the most significant obstacles for AnMBRs. In addition, the cost of the packing materials has been considered the cause of the limited applications of AFs to deal with PPMWs. The microbial activity and its impact on the overall performance of the AD reactors for methane production and COD (and other pollutants) removal can be highly influenced by the reactor operating conditions including HRT, OLR, operating temperature, and pH, as well as the presence of inhibitory elements such as sulfide compounds. Nevertheless, the performance of the AD systems for the treatment of P&P mill wastes when exposed to shocks in the operating conditions, and their recovery potential has not been well documented so far. In addition, the development of reliable sensing systems for a continuous measurement and adjustment of the operating conditions would be an essential need to promote the methane yield from AD, especially when applied to P&P mill wastes as complex high strength substrates. In addition, there is a lack in the investigation of the direct effects of physico chemical and biological pre treatments on both the methane yield and removal efficiency of AD reactors. The research on the PPMS has clearly indicated that chemical (e.g., alkali) pre treatments are acceptable and cost effective ways to enhance the AD of both primary and secondary sludge, when compared to other studied methods. Combination of aerobic and anaerobic technologies have also been identified as a promising way to enhance either the overall performance of the treatment process for P&P mill wastes, or to satisfy the stringent environmental regulations. However, most of the developments in the AD of P&P mill wastes which have been reviewed in this paper have not been implemented in full scale applications. In this regard, further work is required to evaluate and enhance the performance of these promising lab scale technologies for large scale operation in P&P mills.

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