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Review

Wastewater treatment in the pulp-and-paper industry: A review of treatment processes and the associated greenhouse gas emission

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ABSTRACT

Pulp-and-paper mills produce various types of contaminants and a significant amount of wastewater depending on the type of processes used in the plant. Since the generated wastewaters can be potentially polluting and very dangerous, they should be treated in wastewater treatment plants before being released to the environment. This paper reviews different wastewater treatment processes used in the pulp-and-paper industry and compares them with respect to their contaminant removal efficiencies and the extent of greenhouse gas (GHG) emission. It also evaluates the impact of operating parameters on the performance of different treatment processes. Two mathematical models were used to estimate GHG emission in common biological treatment processes used in the pulp-and-paper industry. Nutrient removal processes and sludge treatment are discussed and their associated GHG emissions are calculated. Although both aerobic and anaerobic biological processes are appropriate for wastewater treatment, their combination known as hybrid processes showed a better contaminant removal capacity at higher efficiencies under optimized operating conditions with reduced GHG emission and energy costs.

1. Introduction

The wastewater produced by industrial operations has a significant impact on the environment. Pulp-and-paper industry is a large consumer of fresh water and an important source of wastewater, generated during various stages of pulping and papermaking activities. The produced wastewater has detrimental impacts on the environment and poses a serious threat to the wild and human life. This industry produces the third largest amount of wastewater after primary metals and chemicals industries (Savant et al., 2006). The World Bank Group (1999) reported that in Canada the pulp-and-paper industry produces 20–100 m^3 of wastewater per ton of air-dried pulp. This wastewater contains a variety of organic and inorganic contaminants that mostly originate from tannins, lignins, resins, and chlorine compounds (Buzzini and Pires, 2007). COD, TSS, nitrogen compounds, and adsorbable organic halides (AOX) are the major contaminants that should be removed and/or minimized in wastewater treatment plants (WWTPs) through a series of treatment processes. The treated wastewater can be recycled for reuse in the pulp-and-paper industry, if its quality permits, or it can be released to the environment if its quality meets the environmental standards. Wastewater treatment processes used in the pulp-and-paper industry produce solid sludge and greenhouse gases (GHGs) that have significant impacts on the environment and they are subjected to environmental regulations. The on-site sources for the production of GHGs in WWTPs of pulp-and-paper industry are various biological, chemical or mechanical treatment processes. It has been reported that major GHGs namely carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) are produced in this industry (Ashrafi et al., 2013b). The detailed estimation of GHG emission helps to identify the important GHG emission sources and leads to control and/or reduce their production. The GHG reduction assists the industry to protect the environment and provide financial benefits by exchanging CO_2 credits on the market. The principal objective of this paper is to examine various wastewater treatment processes employed in the pulp-and-paper industry and their associated GHG emission.

2. Pulp-and-paper industry: an important source of wastewater

Wastewater is generated in various processes of the pulp-and-paper industry, including wood debarking or chip making, pulp

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manufacturing and bleaching, paper manufacturing and fiber recycling. All of these processes are consumers of fresh water and producer of a large volume of wastewater.

2.1. Major pulp-and-paper processes

The main processes in pulp manufacturing and paper making are divided into five major groups including mechanical, chemical, chemo-mechanical, and thermo-mechanical pulping as well as papermaking (see Supplementary Materials, Table S1), each producing a high volume of wastewater with special characteristics.

2.2. Wastewater production in the pulp-and-paper processes

Wood preparation, pulp washing, pulp bleaching and paper making processes as well as the digester house are the major wastewater producers in the pulp-and-paper industry. The volume of wastewater produced in each process is closely related to the quantity of generated pulp in that particular process (The World Bank Group, 1999). The generated wastewaters have a high content of BOD and various concentrations of other contaminants that depend on the types of applied processes, as presented in Table 1. For instance, wood preparation wastewater has suspended solids, BOD, dirt, and fibers while the produced wastewater in the digesters house contains resins, fatty acids, color, BOD, COD, AOX, and VOCs (Pokhrel and Viraraghavan, 2004). These contaminants can be removed or reduced by treatment processes. WWTPs consume energy while generating GHGs through several processes and technologies, energy production units, combustion, and transportation (Ashrafi et al., 2013b). The magnitude of GHG emission in the WWTPs depend on the concentrations of nutrients in wastewater, reactor operating temperature, type of treatment processes employed and the contaminant removal efficiency.

3. Wastewater treatment

The growing concerns about the use of fresh water, increased economic considerations and stringent environmental regulations have highlighted the importance of water use and efficient wastewater treatment in the pulp-and-paper industry. The recycling and reuse of the generated wastewater after its proper treatment is the key to reduce fresh water use. This procedure will minimize external discharges to the environment while advancing environmental conservation by reducing fresh water consumption. In view of this, the main objective of WWTPs is to remove contaminants from wastewater using a series of physicochemical, biological, and integrated treatment processes. Ashrafi et al. (2013a; 2013b) developed comprehensive mathematical models (steady-state and dynamic models) to estimate the generated GHG emission by WWTPs. In the development of these models, it was assumed that the bioreactors are completely mixed:

$$\text{Accumulation} = \text{influent} - \text{effluent} + \text{net growth (production by reaction)} \quad (1)$$

The estimation of GHG emission was based on the BOD concentrations, available from different pulp-and-paper mills. It should be mentioned that the Intergovernmental Panel on Climate Change (IPCC) recommended that the generated CO_2 from biogenic sources should not be considered in the estimation of GHGs. However, this assumption does not apply to the GHGs generated in industrial WWTPs, such as the pulp-and-paper industry. It is only valid when GHGs has been produced without using fossil fuel. The kinetics of chemical and biological relationships as well as mass balances around relevant processes and activities were used to estimate GHG emission. The calculated substrate and biomass concentrations in bioreactors led to the estimation of the magnitude of GHGs produced in the treatment systems. The steady-state model was used to estimate total GHG emission in each treatment system while the dynamic model was used to predict major variations in the output of each treatment plant and to identify time-dependent GHG emissions. Since reliable data on GHG emission by industrial WWTPs is not available, the predictions of the models were validated by comparing the calculated BOD removal efficiency of given processes with the literature-cited results (see Supplementary Materials, Table S2). The estimated values of GHG emissions are all related to on-site activities of WWTPs and off-site GHG emissions are not considered in this study. The common wastewater treatment processes and their associated GHG emissions are discussed in the following sections:

3.1. Physicochemical treatment

Physicochemical processes are used to remove suspended solids, colloidal particles, toxic compounds, floating matters, and colors from wastewaters. These processes include sedimentation, ultra-filtration (Bhattacharjee et al., 2007), flotation (Hogenkamp, 1999), screening (El-Ashtoukhy et al., 2009), coagulation,

Table 1
Characteristics of wastewaters generated in various pulp-and-paper processes (Dubeski et al., 2001; Pokhrel and Viraraghavan, 2004; Rintala and Lepistö, 1992).

Process	Parameters						
	pH	TS (mg/l)	SS (mg/l)	BOD_5 (mg/l)	COD (mg/l)	N (mg/l)	Color (Pt–Co)
TMP whitewater	4.6	–	127	1541	2713	7	–
TMP	4.2	–	810	2800	5600	12	–
CTMP[a]	6.2	–	500	2500	7300	–	–
Kraft mill	8.2	8260	3620	–	4112	350	4667.5
Bleach Kraft mill	10.1	–	37–74	128–184	1124–1738	2	–
Sulfite mill	2.5	–	–	2000–4000	4000–8000	–	–
Pulping	10	1810	256	360	–	–	–
Bleaching	2.5	2285	216	140	–	–	40[b]
Bleached pulp mill	7.5	–	1133	1566	2572	–	4033
Wood preparation	–	1160	600	250	–	–	–
Paper making	7.8	1844	760	561	953	11	Black
Newsprint mill	–	3750	250	–	3500	–	1000
Chip wash	–	–	6095	12,000	20,000	86	–
Digester house	11.6	51,583	23,319	13,088	38,588	–	16.6[b]

[a] Chemi-thermomechanical pulping.
[b] Unit Optical Density (OD) at 465 nm.

flocculation (Wong et al., 2006), ozonation and electrolysis (Kishimoto et al., 2010). Physicochemical processes are commonly used in the preliminary, primary, or tertiary stages of wastewater treatment. These processes contribute to GHG generation either directly, through the treatment process itself, or indirectly, due to their energy requirement, commonly satisfied by using electricity. The concentration of contaminants present in wastewaters and their desired removal efficiencies are important factors in choosing the type of physicochemical treatment process.

The presence of lignin and its derivatives contribute to strong color in most pulp-and-paper wastewaters (Dilek and Gokcay, 1994). These wastewaters also contain high concentrations of suspended solids and floating matters. Therefore, the use of a primary treatment, commonly sedimentation (Mulligan, 2002), is essential for the treatment process. Thompson et al. (2001) reported the possibility of removing 80% of suspended matters from wastewater by sedimentation. Bhattacharjee et al. (2007) used sedimentation combined with adsorption and ultra-filtration for the treatment of Kraft black liquor and achieved 60% and 87% total solid removal, respectively. Although ultra-filtration has a better removal efficiency, its use in the pulp-and-paper industry is not common due to its associated high cost. Sevimli (2005) compared ozonation, combined ozonation and hydrogen peroxide oxidation, and Fenton's oxidation for the removal of COD and color from the pulp-and-paper wastewater. The results showed that ozonation and ozonation with hydrogen peroxide were successful in removing color, while the COD removal efficiency was not satisfactory. However, the Fenton's oxidation process was more efficient in removing both color and COD. This process has a lower operating cost in comparison with ozonation alone and combined ozonation and hydrogen peroxide oxidation. De los Santos Ramos et al. (2009) used chemical precipitation by sulfuric acid followed by ozonation for the treatment of paper-making wastewater with a large content of high molecular weight contaminants. This process removed 96% and 60–70% of color and BOD, respectively. They showed that the pH level, varied with the quantity of sulfuric acid used in the process, affected the efficiency of ozonation.

Although few types of tertiary treatment processes are used in pulp-and-paper mills because of their high cost (Mulligan, 2002), coagulation and flocculation are used in this industry for additional polishing of the effluent. Dilek and Gokcay (1994) examined the efficiency of coagulation process in removing suspended solids and COD from the pulp-and-paper wastewater in different mills. The COD removal rate in this work varied from 20% to 96% depending on the wastewater characteristics and treatment process conditions and color removal was around 80% which made the treated wastewater suitable for reuse. Mansour et al. (2007) treated paper-making wastewater using coagulation and electroflotation to remove color, suspended solids, and COD. They used batch and continuous processes for wastewater treatment, and showed that both processes were capable of removing color and suspended solids and producing a clear effluent. Their experimental results revealed that the continuous process was more effective in removing COD. However, despite the removal of color and suspended solids, the obtained COD and BOD removal efficiencies were not completely satisfactory under all examined conditions. Therefore, these processes should be combined with biological processes to achieve acceptable results.

3.1.1. Greenhouse gas emission

Most physicochemical processes contribute to GHG emission due to their energy requirements, while some, such as the coagulation/flocculation, produce GHGs directly as a result of the applied processes. The concentration of contaminants present in the wastewaters and the desired removal efficiencies determine the energy requirements and the extent of produced GHGs during physicochemical processes. Since coagulation and flocculation are common processes for color removal in the pulp-and-paper industry, the estimation of produced GHG by these processes is presented in the following relationship. Using the characteristics of wastewater from the Kraft process presented in Table 2, the CO_2 emission is estimated to be 30 g/kg BOD by assuming the use of ferric chloride ($FeCl_3$) as the coagulant, according to the following stoichiometric relationship:

$$2\,FeCl_3 + 3\,Ca(HCO_3)_2 \rightarrow 2\,Fe(OH)_3 + 3\,CaCl_2 + 6\,CO_2 \qquad (2)$$

The GHG emission during the production and transportation of ferric chloride was considered as up-stream GHG emission and was not considered in the calculations.

3.2. Biological treatment

Most WWTPs use aerobic and/or anaerobic biological processes to remove organic contaminants in wastewaters. Aerobic processes are preferably used in most pulp-and-paper mills because of their ease of operation as well as the relatively low capital and operating costs (Mulligan, 2002). Among aerobic technologies, activated sludge (AS) and aerated lagoons are commonly used in the pulp-and-paper industry (Pokhrel and Viraraghavan, 2004). Although the use of anaerobic processes in the pulp-and-paper industry is not common, a number of mills have employed different anaerobic technologies because of lower sludge production, renewable energy production (biogas), smaller area requirements and facility in further degradation of pollutants (Buzzini et al., 2005; Habets and Driessen, 2007). Both aerobic and anaerobic processes have certain disadvantages which includes the high sludge production of aerobic processes and sensitivity of anaerobic bacteria to toxic materials. Salkinoja-Salonen et al. (1984) showed that high sulphur content of chemical pulping wastewater had a detrimental effect on the contaminant removal capacity of anaerobic processes, especially at low pH values. In order to benefit from different treatment processes, integrated treatment consisting of combined biological processes operating under different environmental conditions (aerobic and anaerobic), or physicochemical and biological processes have been used to treat the pulp-and-paper wastewaters (Pokhrel and Viraraghavan, 2004).

GHG emission of WWTPs is an important factor that can be used for the selection of the appropriate type of biological process employed in the treatment system. While aerobic processes produce only CO_2, anaerobic processes produce biogas that contains methane which is a potent GHG. Ashrafi et al. (2013b) recommended recovering and using the generated biogas as a source of energy, if possible. Consequently, the GHG emissions and energy requirements of these processes are considerably different with respect to their operating conditions and the generated end-products.

3.2.1. Aerobic processes

AS and aerated lagoons or aerated stabilization basins (ASB) are the most common aerobic processes used in WWTPs of the pulp-and-paper industry. Thompson and Forster (2003) used AS to remove COD from different pulp-and-paper wastewaters in a laboratory-scale plant. Although this study showed the capability of the AS process in removing COD from most wastewaters, there were considerable differences between the produced effluents at laboratory-scale and full-scale operations of WWTPs. Bengtsson et al. (2008) treated wastewater from a paper mill, producing liner board from recycled fibers by AS in a batch process and removed 95% of soluble COD. Other investigations (Hansen et al.,

Table 2
Operating and kinetic parameters used for the estimation of GHG emission.

	Operating parameter	Value	Kinetic parameter	Value
Influent	Flow rate	1000 m^3/day		
	BOD	2000 g/m^3		
	Alkalinity	150 g $CaCO_3/m^3$		
	VSS	1200 g/m^3		
Aerobic reactor	Temperature	25 °C	Yield	0.6 g VSS/g BOD
	SRT[a]	5 days	Decay coefficient	0.1 g VSS/g VSS day
	HRT[b]	0.5 day	Half velocity constant	20 g BOD/m^3
			Nitrification yield	0.12 g VSS/g NH_4–N
			Nitrification decay	0.08 g VSS/g VSS day
			Waste to influent rate	0.01
Anaerobic reactor	Temperature	30 °C	Yield	0.08 g VSS/g BOD
	SRT	20 days	Decay coefficient	0.03 g VSS/g VSS day
	HRT	0.5 day	Half velocity constant	360 g BOD/m^3
			Waste to influent rate	0.01
Anaerobic digester	Temperature	35 °C	Yield	0.08 g VSS/g BOD
	SRT	20 days	Decay coefficient	0.03 g VSS/g VSS day

[a] Solid retention time.
[b] Hydraulic retention time.

1999; Lerner et al., 2007b; Mahmood and Elliott, 2006; Norris et al., 2000) showed that the AS process can effectively decrease the concentration of contaminants such as BOD, COD, AOX and chlorinated compounds from pulp-and-paper wastewaters. Because of the high removal efficiency of COD, BOD, and AOX in the AS process which amounted to 70%, 90%, and 60%, respectively, it was concluded that AS was a suitable process for the treatment of pulp-and-paper wastewaters regardless of high sludge production. In these studies, the effect of bulking related to bacterial growth that caused reduction in the removal efficiency was ignored.

Bryant et al. (1997), Achoka (2002), Mahmood and Paice (2006), and Ghoreishi and Haghighi (2007) treated various pulp-and-paper wastewaters with ASB. It was shown that ASB process could remove 50%–70% BOD, 30%–40% COD, as well as AOX and chlorinated compounds, while the amount of nutrient addition in ASB system was lower than that required in the AS process. The reported characteristics of ASB systems are long HRT, large area requirements compared to the AS process and biological solid production during the treatment of low flow rate wastewaters. Clark et al. (1997) treated Kraft mill wastewater with ASB while measuring nitrogen and phosphorous flows during the process. They showed the dependency of BOD removal efficiency on the rate of nutrients addition. Bryant (2010) simulated the treatment process of pulp-and-paper wastewater in ASB and showed that although the treatment system could remove up to 67% COD from the wastewater, certain limitations such as nitrogen supply affected the removal efficiency of contaminants. Schnell et al. (2000) compared three different laboratory-scale systems, namely AS, facultative stabilization basin (FSB) and ASB, in treating high rate and low rate Kraft mill wastewaters. Although the SRT in their experiments was quite long, the results showed that all three systems were capable of removing up to 70% COD and 56% AOX from the wastewater. They reported no difference between FSB, ASB and AS systems in removing AOX from the wastewater, while the efficiency of ASB was lower in removing chlorinated compounds.

An alternative treatment process in the pulp-and-paper industry is sequencing batch reactor (SBR). Dubeski et al. (2001) treated chemi-thermomechanical pulping (CTMP) wastewater using a lab-scale SBR and removed up to 77% BOD from wastewater. They recommended the use of SBR for wastewater treatment rather than the AS process because of the production of less sludge, possible treatment of wastewater at a greater organic loading rate, and better sludge settling properties. Table 3 presents the performance of different aerobic processes used for wastewater treatment in the pulp-and-paper industry.

3.2.1.1. Greenhouse gas emission. Aerobic processes produce CO_2 and a large amount of sludge through the removal of carbonaceous contaminants. GHGs are also produced during the sludge treatment process. The supply of oxygen for aerobic treatment processes is the main energy consuming operation that produces large amounts of up-stream GHG. The production of GHG by an aerobic process (i.e. AS process) can be estimated by the addition of CO_2 emission from BOD removal processes and the microbial biomass decay (Ashrafi et al., 2013b).

$$\text{GHG emission} = CO_2^{\text{BOD removal}} + CO_2^{\text{biomass decay}} \tag{3}$$

Oxygen consumption is estimated from the following relationship:

$$\text{Oxygen consumption} = \text{BOD removed} - \text{BOD remained in the sludge} \tag{4}$$

GHG emissions, oxygen consumption and sludge production have been estimated by using the characteristics of Kraft pulping wastewater and the operating conditions of AS process (Table 2). All estimations are based on the BOD removal efficiency of 99% for the AS process. The steady-state model (Ashrafi et al., 2013b) showed that 330 g CO_2/kg BOD is released by the AS process and 190 g sludge/kg BOD is produced. The produced sludge can be sent to the sludge treatment system for further treatment. During the wastewater treatment process, 452 g O_2/kg BOD is needed for the biological treatment and 227 kWh/day electricity is required for aeration.

Ashrafi et al. (2013a) used a dynamic model to show the impact of daily variations of operating conditions on the biological process (see Supplementary Materials, Table S3 for the range of examined operating conditions in the dynamic model). The results showed significant variations of CO_2 generation during 140 days of operation, equal to 240–450 g CO_2/kg BOD, in response to varying operating conditions. Oxygen consumption also varied up to 68% and changed energy consumption by the aeration system by 55% and the associated GHG emission from electricity generation system. The overall change of GHG emission, predicted by the dynamic model, was up to ±30%.

3.2.2. Anaerobic process

Anaerobic processes such as up-flow anaerobic sludge blanket

Table 3
Treatment performance of different aerobic processes.

Treatment process	Source of wastewater	Contaminants removal efficiency (%)				References
		COD	BOD	Color	Other compounds	
AS	Paper mill whitewater	74–95	–	–	–	Bengtsson et al., 2008
	Kraft pulp mill	60	90	40	36 (Tannin and Lignin)	Diez et al., 2002
	Integrated pulp mill	60–70	95	–	60 (TOC)	Leiviska et al., 2008
Multiple stage (AS)	Black liquor	65	95	–	–	Sandberg and Holby, 2008
ASB	Kraft pulp mill	67	90	–	–	Bryant, 2010
	Kraft pulp mill	40	60	–	–	Clark et al., 1997
SBR	Paper mill	75	–	–	–	Ammary, 2004
	CTMP and TMP	53–62	88–94	–	–	Dubeski et al., 2001
	Hardwood Kraft mill	69	–	–	>80 (TSS)	Morgan-Sagastume and Allen, 2003
Biofilter	TMP	52	79	–	–	Kantardjieff and Jones, 1997
MBR[a]	Paper mill	80	97	–	>90 (TSS)	Lerner et al., 2007b
	Paper mill	92	>98	–	84 (Ammonia), >99 (TSS)	Zhang et al., 2009
FSB[b]	Kraft mill	62	>95	–	51 (AOX), 69 (chlorinated compounds)	Schnell et al., 2000

[a] Membrane bioreactor.
[b] Facultative stabilization basin.

(UASB) reactor and fluidized-bed reactor (FBR) have been used to treat pulp-and-paper wastewaters. Chen and Horan (1998) used a UASB reactor to treat newsprint paper mill wastewater to remove COD and sulfite, and achieved 66% and 73% removal efficiency, respectively. They monitored methane and sludge production during the COD removal, and showed that the production rates of sludge and methane were independent of the process duration. The estimated GHG emission in this study was approximately 60% of the theoretical emission with respect to the strength of wastewater. Chinnaraj and Venkoba Rao (2006) replaced anaerobic lagoon with a UASB reactor for the treatment of agro-based pulp-and-paper mill wastewater and obtained COD removal efficiencies in the range of 80%–93%. The new system had a higher COD removal efficiency, smaller area requirement, and easier biogas recovery. In the anaerobic lagoon without biogas recovery system, methane is released to the atmosphere.

Buzzini and Pires (2007) and Buzzini et al. (2005) used UASB reactors to treat both bleached and unbleached Kraft mill wastewaters. The results of these studies showed high removal efficiencies of COD and chlorinated organics between 79%–82% and 71%–99%, respectively, and the insignificant impact of partial recycling of effluent on the COD removal efficiency. Rintala and Lepisto (1992) treated thermo-mechanical pulping (TMP) whitewater using a UASB reactor at the influent temperatures of 35 °C, 55 °C and 65 °C and obtained COD removal efficiencies of 82%, 92%, and 86%, respectively. Moreover, the removal efficiencies of carbohydrates and volatile fatty acids were in the range of 50%–60% by applying an AS process after the UASB reactor. They concluded that the application of aerobic post-treatment enhances the quality of treated effluent. Kortekaas et al. (1998b) used two laboratory-scale UASB reactors for the treatment of wastewaters with low and high molecular weight lignins produced by the TMP process. They showed the suitability of UASB technology for the treatment of TMP wastewaters. The system was able to remove low molecular weight lignin and COD with an acceptable removal efficiency of around 73% for COD.

Ortega-Clemente and Poggi-Varaldo (2007) used packed-bed reactor (PBR) and FBR for the treatment of anaerobically pretreated weak black liquor from Kraft pulping wastewater. They improved the performance of the treatment process by adding ligninolytic fungi to both reactors to improve the contaminants removal efficiencies. The results showed that higher COD and color removal efficiencies in the PBR resulted from the presence of different fungi in the two reactors. Rajeshwari et al. (2000) studied the treatment of wastewaters with various types of anaerobic reactors including UASB, fixed-film, and fluidized-bed and compared them with respect to the ease of operation, energy consumption, and capital cost. They concluded that the UASB reactor had less energy consumption and the fixed-film reactor had a lower capital cost, while the contaminant removal of FBR was higher during the treatment of pulp-and-paper wastewaters. Deshmukh et al. (2009) used up-flow anaerobic filter (UAF) to remove BOD, COD, and AOX from bleaching wastewater and obtained removal efficiencies of 70%, 50%, and 50%, respectively. To improve the efficiency of UAF in the removal of AOX, they added acetate as an electron donor and increased AOX removal efficiency to about 90%. The results showed the cost effectiveness of electron donor addition to the anaerobic treatment process compared to the addition of physicochemical or other biological processes. Table 4 shows the performance of anaerobic treatment processes for different types of pulp-and-paper wastewaters.

3.2.2.1. Greenhouse gas emission. Methane is a potent GHG with a global warming potential of 34 times higher than CO_2 produced in anaerobic treatment processes and can be used as a source of energy. The quantity of the produced methane is significantly affected by the operating parameters (Ashrafi et al., 2014). If the generated methane is recovered and used to satisfy the energy requirements of the WWTP, the use of anaerobic processes can be more cost effective than aerobic processes. Moreover, GHG emission from the sludge treatment in anaerobic processes is significantly lower than that resulting from the aerobic processes due to the lower volume of sludge production. Therefore, many operational aspects of anaerobic processes offer energy saving and GHG emission reduction. Nevertheless, the requirement for the supply of alkalinity in anaerobic processes increases energy consumption and GHG generation. While alkalinity is produced during the BOD utilization and VSS digestion, the production of carbonic acid by the dissolution of CO_2 in wastewater consumes a significant amount of alkalinity to maintain the liquid pH at an optimum level (Ashrafi, 2012). The average alkalinity requirement in anaerobic processes is commonly in the range of 2000–4000 mg $CaCO_3$/l to control and maintain the pH. The production and transportation of the required alkalinity are significant up-stream sources of GHG emission.

The GHG emission from an anaerobic process (i.e. UASB reactor) can be estimated as presented below:

Table 4
Treatment performance of different anaerobic processes.

Treatment process	Source of wastewater	Contaminants removal efficiency (%)			References
		COD	Color	Other compounds	
UASB	Kraft pulp mill	79	≈0	71–99.7 (chlorinated compounds)	Buzzini et al., 2005
	Paper mill	66	–	73 (sulphate)	Chen and Horan, 1998
	Bagasse wash	80–85	–	–	Chinnaraj and Venkoba Rao, 2006
	TMP	73	45	–	Kortekaas et al., 1998b
	Pulping whitewater	65–70	–	90 (TSS)	Rintala and Lepistö, 1992
UAF[a]	Bleaching process	50	–	88 (AOX)	Deshmukh et al., 2009
ABR[b]	Paper mill	88	95	67 (AOX), 86 (Lignin), 63 (Phenol)	Singh and Thakur, 2006

[a] Up-flow anaerobic filter.
[b] Two step anaerobic bio-reactor.

$$\text{GHG emission} = CO_2^{\text{BOD removal}} + CO_2^{\text{biomass decay}} + CO_2^{CH_4\ \text{combustion}} + CO_{2-eq}^{CH_4\ \text{leakage}} \quad (5)$$

CO_2-equivalent for leakage was estimated using the GWP of methane and considering 5% leakage of the generated methane during the recovery process while a small fraction of methane is dissolved in the effluent and is later released to the atmosphere (Ashrafi et al., 2013b; Lelieveld et al., 2005). The amount of dissolved methane was calculated using the CH_4 and CO_2 partial pressures inside the bioreactor along with the Henry's law. To calculate the alkalinity (Alk) requirements, the carbonic acid concentration was calculated using the Henry's law.

$$\text{Alk requirements} = \text{Alk}^{\text{acid carbonic}} - \left(\text{Alk}^{\text{influent}} + \text{Alk}^{\text{BOD removal}} + \text{Alk}^{\text{biomass decay}}\right) \quad (6)$$

The reported values for the characteristics of Kraft wastewater and operating conditions of UASB reactor were used for the estimation of GHG emission, alkalinity requirements and sludge production. The BOD removal efficiency of the UASB reactor was calculated to be 87%. The steady-state model estimated 235 g CO_2/kg BOD, 124 g CH_4/kg BOD and 25 g sludge/kg BOD production by the UASB reactor. The total GHG generation by the anaerobic process was equal to 992 g CO_2-eq/kg BOD after considering biogas combustion and leakage. In addition, the produced energy by burning the generated biogas was 2050 kWh/day. This energy can be used in the production of electricity for the plant. The produced sludge is sent to the sludge treatment system for further treatment. The alkalinity requirement during the anaerobic process was estimated to be 968 g $CaCO_3$/kg BOD, resulting in a high off-site GHG emission associated with the production and transportation of this material. The dynamic model predicted considerable variations in CO_2 and CH_4 generation in the UASB reactor in response to varying operating parameters. These variations amounted to 190–380 g CO_2/kg BOD and 90–200 g CH_4/kg BOD and changed the daily GHG emission by up to ±19% in this system. In addition to GHG emission, the dynamic model showed 32% and 13% variations in the produced sludge and consumed alkalinity, respectively.

3.2.3. *Nutrients removal from wastewater*

In addition to carbon, hydrogen and oxygen as essential elements for COD removal and microbial activity in biological processes, nitrogen and phosphorous should also be present in the treatment system. The mean concentration of nitrogen in different types of woods was reported to be approximately 0.1%, which is mostly transferred to black liquor (Wiegand, 2007). Based on the BOD:N:P ratio of 100:5:1 that is essential for biological wastewater treatment, pulp-and-paper wastewaters have insufficient amount of nutrients (Table 1). The required BOD:nutrient ratio may be lower or higher for different biological processes. For example the BOD:N:P is reported to be 100:3.5:0.7 for aerated lagoons (Slade et al., 1999). In order to raise the concentration of nitrogen and obtain the required BOD:nutrient ratio and to support the growth and proliferation of microorganisms, pulp-and-paper mills commonly add nutrients to the wastewater in the form of ammonium nitrogen (NH_4^+–N). It should be noted that the concentration of nutrients is controlled by either the influent BOD concentration or by controlling their corresponding residual concentrations in the effluent. Therefore, the balance between nutrient addition/consumption and wastewater characteristics is a critical factor in minimizing nutrient addition to the influent wastewater (Wiegand, 2007). However, most physicochemical and biological treatment processes used in the treatment of pulp-and-paper wastewaters are not designed for the removal of nutrients, and hence, nitrogen and phosphorus persist in the effluent of WWTPs, often in excess of environmental standards. These nutrients have to be removed due to their associated health hazards, contribution to algal blooms and depletion of oxygen in lakes and rivers, which threatens aquatic life (de-Bashan and Bashan, 2004).

Jarvinen (1997) measured nitrogen concentrations in the influent and effluent of AS processes at two pulp-and-paper mills and found organic and inorganic nitrogen in both streams. The author concluded that the addition of nitrogen should be precisely controlled in order to prevent its presence in the effluent. Bhathena et al. (2006) studied the effect of nutrient limitation on the performance of AS process using a laboratory-scale bioreactor for the treatment of Kraft mill wastewater while tracking AS treatment properties. They showed minor impact of nitrogen limitation on the performance of AS process, while demonstrating the controlling effect of phosphorous limitation on bulking and dewatering properties of the generated sludge. It was concluded that inadequate nitrogen and phosphorous caused lower cell growth rate and less BOD removal from wastewater. Slade et al. (1999) investigated the impact of nutrient concentration on the performance of ASB systems in three different WWTPs treating bleached Kraft mill wastewater and showed significant impact of BOD:N ratio on the BOD removal efficiency. It was also reported that for wastewaters having high BOD:N ratios (around 100:0.8), nitrogen addition was an appropriate solution to adjust the level of nitrogen while for wastewaters with lower BOD:N ratios (around 100:2.1), benthic recycling showed the best result.

3.2.3.1. *Greenhouse gas emission.*

The removal of nutrients from the effluent of WWTP is essential for improving the quality of effluent and protecting the environment by reducing the potential damage to aquatic eco-system. Nitrogen removal by biological nitrification and denitrification processes is a viable option that has shown to reduce the concentration of ammonia-, nitrite- and nitrate-nitrogen below environmental standards. Both processes are known to generate nitrous oxide (N_2O), a potent GHG with a global warming potential of 298 times higher than CO_2. The removal of phosphorus by biological processes, although possible, is uncommon in the pulp-and-paper industry (Wiegand, 2007). Nitrogen removal by nitrification and denitrification processes consumes oxygen and alkalinity while producing CO_2 and N_2O. In order to estimate the impact of nitrogen removal processes on GHG emission by the WWTPs, the amount of CO_2 consumption during nitrification and its generation during denitrification should be calculated. These parameters in the overall nitrogen removal process are considered in the estimation of GHG emission, as follows:

$$\text{GHG emission} = CO_2^{\text{BOD removal}} + CO_2^{\text{biomass decay}} + CO_2^{\text{denit}} - CO_2^{\text{nit}} + CO_{2-\text{eq}}^{N_2O} \quad (7)$$

The oxygen consumption during the nitrification process is added to its consumption during the AS process. The characteristics of Kraft pulping wastewater and operating conditions of AS process were used for the calculation of GHG emission and oxygen consumption. According to IPCC the magnitude of N_2O production was considered to be 0.5% of the nitrogen content of the wastewater (Yerushalmi et al., 2013; Kampschreur et al., 2009). The steady-state model predicted the production of 531 g CO_2-eq/kg BOD and consumption of 551 g O_2/kg BOD by the AS process with the nitrogen removal processes. This is approximately 38% and 18% higher than the generated GHG and consumed oxygen, respectively, by the AS process without nitrification and denitrification processes. Approximately 267 kWh/day of electricity is required to support aeration. Results of the dynamic model estimated up to 12% variation in GHG emission associated with N_2O production by nitrogen removal processes.

3.3. Integrated systems

The application of integrated systems, also known as hybrid systems, has gained considerable attention in an effort to enhance the efficiency of treatment and improve the quality of effluents. The integrated system could be a combination of two physicochemical processes, a physicochemical and a biological process or two biological processes. Helble et al. (1999) achieved more than 80% COD removal from paper mill wastewater by combining ozonation with fixed-bed biofilm reactor in a pilot-scale plant. In addition to COD, other contaminants such as color, AOX, and spores were also removed from the wastewater. Kantardjieff and Jones (1997) used an aerobic biofilter followed by an aerated lagoon for the treatment of TMP wastewater, and obtained 82% BOD removal efficiency. This process achieved an improved efficiency of BOD removal at SRT values lower than that used in the aerated lagoon. Buzzini et al. (2006) used electrochemical oxidation with a UASB reactor for the treatment of bleached pulp mill wastewater, and compared the effluent characteristics with those obtained from each individual process. Although the high operating cost of the electrochemical process is prohibitive, it offers a high COD and color removal from the wastewater, equal to 93% and 96%, respectively.

Ruas et al. (2007) used ozone treatment to improve COD removal from bleaching wastewater in the SBR process while comparing the effect of pre- and post-ozonation. They showed that ozone treatment improved COD, BOD, and lignin removal efficiencies by 11%, 40%, and 46%, respectively, while its effects on color removal was not significant. The comparison of pre- and post-ozonation showed the capability of pre-ozonation in removing higher concentrations of BOD, color and lignin from the wastewater. Kortekaas et al. (1998a) treated black liquor from chemical pulping with a combination of aerobic reactor and UASB process to benefit from both types of biological processes. The effluent was recycled to dilute the influent black liquor and to elevate the COD removal efficiency. The addition of aerobic post-treatment to the anaerobic UASB reactor increased the BOD removal efficiency to 97%, while the anaerobic reactor alone could only remove up to 83% of the BOD. These investigators also showed that the developed process can remove 58% lignin and established the role of bacterial degradation in lignin removal. Lerner et al. (2007a) combined a UASB reactor and the AS process for the treatment of a paper mill wastewater and achieved a higher removal of COD, BOD, and TSS in comparison with the AS process. They also reported fewer fluctuations in the effluent COD concentration compared to the AS process and showed that COD, BOD, and TSS removal efficiencies improved by approximately 6%. According to this study, the operating cost before and after the addition of UASB to the AS process were reduced by about 50% resulting from lower nutrient addition, electricity requirement and sludge production. Saravanan and Sreekrishnan (2005) used a fluidized bed reactor with fungus followed by treatment with a poly-electrolyte to remove color from pulp-and-paper wastewaters. They removed 81% color and reduced both sludge disposal and toxicity. Although the color removal efficiency of this process was lower than that commonly obtained in coagulation/flocculation processes (90–95%), using poly-electrolyte as a post-treatment reduced the operating costs and made this process simple and eco-friendly. Table 5 presents the performance of hybrid systems for the treatment of pulp-and-paper wastewaters.

3.3.1. Greenhouse gas emission

The operating cost, GHG emission and energy consumption of a hybrid system depends on the type of treatment processes employed. A common hybrid system used for wastewater treatment is composed of an anaerobic biological process followed by an aerobic biological process. In these systems, since the anaerobic process is the primary process for contaminant removal, the operating parameters of the anaerobic reactor control the performance of the system. The hybrid systems benefit from the advantages of anaerobic processes, such as energy generation by the produced methane and low sludge production, while offering BOD removal efficiencies comparable to those obtained in aerobic processes. The main source of GHG generation in a hybrid system is the combustion of biogas. In addition, the treatment process requires a significant amount of alkalinity for the anaerobic process to control and maintain the liquid pH, contributing to the generation of GHG due to the production and transportation of alkalinity. GHG emission from a typical hybrid system, i.e. UASB reactor followed by the AS process, is calculated from the following relationship (Ashrafi et al., 2013b):

$$\text{GHG emission} = CO_2^{\text{BOD removal}} + CO_2^{\text{biomass decay}} + CO_2^{CH_4\ \text{combustion}} + CO_{2-\text{eq}}^{CH_4\ \text{leakage}} \quad (8)$$

The CO_2 emission from BOD removal and biomass decay is related to both aerobic and anaerobic processes. The alkalinity requirement of the hybrid system is the sum of total alkalinity requirements of the anaerobic and aerobic processes. In addition, a hybrid system requires oxygen in the aerobic process. The alkalinity requirement and oxygen consumption are obtained as follows:

Table 5
Treatment performance of different hybrid systems.

Treatment process	Pulp-and-paper mill wastewater	Contaminants removal efficiency (%)				References
		COD	BOD	Color	Other compounds	
UASB + electrochemical	Kraft pulp mill	93	–	96	–	Buzzini et al., 2006
AS + hydrogenation	Kraft pulp mill	95	98	97.5	97 (TSS)	Ghoreishi and Haghighi, 2007
UASB + aerobic reactor	Black liquor	72	97	57	–	Kortekass et al., 1998a
SBR + ozone treatment	Kraft pulp mill	40–70	90–95	Clear	46 (Lignin)	Ruass et al., 2007
FBR + poly-electrolyte	Black liquor	78	–	81	60 (TSS)	Saravanan and Sreekrishnan, 2005
Anaerobic + aerobic + ozonation	White liquor and Black liquor	83	–	95	–	Sevimli, 2005

$$\text{Alkalinity requirements} = \text{Alk}^{\text{UASB process}} + \text{Alk}^{\text{AS process}} \tag{9}$$

$$\text{Oxygen consumption} = \text{BOD removed}^{\text{AS process}} - \text{BOD remained in the sludge}^{\text{AS process}} \tag{10}$$

The quantity of GHG emission, alkalinity requirement, oxygen consumption and sludge generation were estimated using the reported characteristics of Kraft process wastewater and the operating conditions of the system, shown in Table 2. A BOD removal efficiency of 99% was used during all calculations. Predictions of the steady-state model showed the production of 267 g CO_2/kg BOD, 124 g CH_4/kg BOD and 77 g sludge/kg BOD. Total GHG emission by the hybrid system was estimated to be 1.1 kg CO_2-eq/kg BOD when considering biogas combustion and leakage. The biogas combustion produced approximately 2050 kWh/day energy that could cover all the energy requirements of the WWTP (electricity and heat). The produced sludge in the process is sent to a sludge treatment system (i.e. anaerobic digester) for further treatment. The steady-state model also predicted the consumption of 1011 g $CaCO_3$/kg BOD that creates an important source of off-site GHG emission. During the treatment process, 43 g O_2/kg BOD is consumed to support aeration. The dynamic model showed significant variations in the estimated values of GHG emission and methane generation in response to the varying operating parameters. These variations were equal to 190–370 g CO_2/kg BOD and 90–200 g CH_4/kg BOD. The dynamic model also predicted 10%, 21%, and 40% variations in the amount of alkalinity requirement, sludge generation and oxygen consumption, respectively. Overall, the dynamic model predicted ±17% change in the quantity of GHG emission in the hybrid system.

3.4. *Effect of operating parameters on the treatment process*

Operating parameters of the treatment process have a major impact on the BOD removal efficiency, energy consumption, effluent quality and the type and concentrations of end-products. Temperature, pH, concentration of substrate and nutrients, SRT, HRT, recycle rate, ammonia and sulfite concentrations, as well as microbial competition in the system are important parameters which affect the performance of WWTPs (Bogner et al., 2008; El-Fadel and Massoud, 2001). Temperature is an important parameter that controls the type and concentration of microorganisms in biological processes as well as the COD removal efficiency (LaPara et al., 2001). Morgan-Sagastume and Allen (2003) tested the effect of temperature on the performance of an AS process treating bleached Kraft wastewater, while monitoring COD and suspended solids removal efficiencies and sludge properties. They employed two methods to increase the temperature; first, fast increase of temperature from 35 to 45 °C and second, temperature oscillations between 31.5 °C and 40 °C. It was shown that the first approach reduced COD removal efficiency and increased the concentration of suspended solids while temperature oscillations had only a slight effect on these parameters. It was also concluded that temperature elevation affected sludge characteristics and deteriorated its compressibility and settleability.

Diez et al. (2002) treated bleached Kraft mill wastewater by the AS process and studied the effect of HRT, F/M ratio, and nutrient concentration on the effluent quality. To achieve the highest BOD and COD removal efficiencies of 90% and 58%, respectively, the optimum values for BOD:N:P and F/M ratios were reported to be 100:5:0.3 and 0.12–0.23 g BOD/g MLVSS day, respectively. It was also shown that the decrease of HRT lowered the lignin removal efficiency in this system. Under optimum operating conditions, the maximum removal efficiencies for N and P were 87% and 84%, respectively. Wang et al. (2009) modeled the effect of nutrient concentration, temperature, dissolved oxygen (DO), pH, SRT, and HRT on the reactor volume and effluent quality in terms of COD and nitrogen concentrations during wastewater treatment with membrane bioreactor (MBR). They showed that nutrient concentration, temperature, DO, and SRT were the controlling parameters in the examined treatment system. Elliott and Mahmood (2008) investigated the effect of DO concentration on the sludge production during the treatment of pulp-and-paper wastewater in an aerobic basin of an AS process. The laboratory- and pilot-scale tests for the treatment of wastewater from TMP and integrated Kraft pulping process showed that the increase of DO concentration decreased sludge production while increasing COD removal and improving the settling and dewatering properties of the sludge.

3.4.1. *Greenhouse gas emission*

The detailed investigations of Ashrafi et al. (2014) on aerobic (AS process), anaerobic (UASB reactor) and hybrid (UASB reactor & AS process) systems showed that the operating temperature and SRT exert the highest influence on the performance of WWTPs and consequently, on the associated GHG emission. The impact of these operating parameters on the BOD removal efficiency and GHG emission of the examined treatment systems are reported below. Table 6 presents the effective range of operating parameters in each treatment system, corresponding to the optimum BOD removal efficiency (Metcalf et al., 2002).

3.4.1.1. Effect of reactor temperature. The change of aerobic bioreactor temperature from 25 °C to 30 °C had a minor impact on its

Table 6
Effective range of operating parameters.

Operating parameter	Bioreactor	Range
Reactor temperature	Aerobic	25–30 °C
	Anaerobic	30–35 °C
SRT	Aerobic	5–15 days
	Anaerobic	15–30 days

performance, reducing the BOD removal efficiency by less than 1% and sludge production by 11 g sludge/kg BOD. The reduced sludge production contributes to a lower methane generation in the sludge treatment system. The temperature elevation enhanced oxygen and alkalinity consumption in the system, by 8% and 10%, respectively, resulting in higher GHG emissions by the aeration system and an increased demand for material production and transportation. In addition, the increase of temperature enhanced N_2O emission by the nitrification and denitrification processes by approximately 9%.

The change of temperature from 30 °C to 35 °C in the anaerobic bioreactor increased the BOD removal efficiency by 10%, causing higher CO_2 and CH_4 production, equal to 24 and 18 g/kg BOD, respectively. This rise in the temperature increased sludge production by approximately 10%. The impact of temperature rise on alkalinity requirement in the anaerobic system was more pronounced, decreasing it by 188 g $CaCO_3$/kg BOD.

The increase of temperature in the aerobic bioreactor had no significant impact on the GHG emission by the hybrid system, while increasing the temperature of anaerobic bioreactor increased CO_2 and CH_4 emissions (24 and 18 g/kg BOD). The increase of anaerobic bioreactor temperature reduced oxygen consumption and sludge production in the follow up aerobic bioreactor, since more BOD had been removed in the anaerobic bioreactor. Temperature increase also decreased alkalinity requirement in this system by 160 g $CaCO_3$/kg BOD.

3.4.1.2. Effect of SRT. As reported in Table 6, a 10-day increase of SRT in the aerobic bioreactor increased CO_2 emission by 201 g/kg BOD, while reduced sludge production by 34%, hence decreasing the GHG emissions associated with the sludge treatment system. The increase of SRT increased alkalinity and oxygen consumption by 20 g $CaCO_3$/kg BOD and 252 g O_2/kg BOD, respectively. In addition, the increase of SRT raised N_2O emission by 30% and consequently increased the overall GHG emission by 94 g CO_2-eq/kg BOD.

In the anaerobic process, the increase of SRT by 15 days had a minor impact on the GHG emission, alkalinity consumption and sludge production in the anaerobic bioreactor. This change increased GHG emission by only 90 g/kg BOD, while reducing the alkalinity consumption and sludge production by 4% and 5%, respectively.

In the hybrid system, the change of SRT in the anaerobic bioreactor had a significant impact on the performance of the system and consequently on the overall GHG emission. However, the change of SRT in the aerobic bioreactor had a minimal impact on the performance of the system. The 15 days increase of anaerobic SRT increased GHG emission by 154 g/kg BOD and sludge production by 10% while decreasing oxygen and alkalinity consumption by 57% and 3%, respectively. The impact of SRT on N_2O emission by the system with nitrification and denitrification processes was insignificant.

4. Sludge treatment

An important end-product of WWTPs is the biological sludge that must be treated before disposal. The pulp-and-paper industry allocates a large amount of operating cost for the handling and treatment of the produced sludge by processes such as dewatering and incineration (Strmen et al., 2006). Two common methods of solid handling in the pulp-and-paper industry are first, mechanical dewatering and landfilling or composting, and second, mechanical dewatering and incineration with landfilling of the generated ashes (Stoica et al., 2009). Although sludge digestion, especially anaerobic digestion, results in energy minimization and GHG reduction, it is rarely used in the pulp-and-paper industry (Greenfield and Batstone, 2005). Pulp-and-paper mills incinerate solids with black liquor in recovery boilers, or mix them with bio-fuels and incinerate them in bio-fuel boilers, which produce ash and contribute to SO_2 and/or N_2O emissions (Singh and Thakur, 2006).

It has been shown that anaerobic digestion reduces GHG production compared to incineration, while removing AOX and producing biogas that can be used as a source of energy (Savant et al., 2006; Zitomer et al., 2008). Elliott and Mahmood (2007) used anaerobic digestion to treat pulp-and-paper wastes. They improved the treatment performance by adding a variety of pretreatment processes such as ultrasound, ozone oxidation, and mechanical digestion. It was shown that the applied pretreatment processes reduced the digestion time, sludge production and digester size, while increasing biogas production.

4.1. Greenhouse gas emission

The extent of GHG emission in the anaerobic digester is proportional to the percentage of solid digestion and can be calculated from the following relationship:

$$\text{GHG emission} = CO_2^{\text{sludge treatment}} + CO_2^{CH_4\ \text{combustion}} + CO_{2-\text{eq}}^{CH_4\ \text{leakage}} \tag{11}$$

It should be mentioned that the average alkalinity requirement in the digestion process is high (2000–4000 mg $CaCO_3$/l) for the control and maintenance of pH.

Ashrafi et al. (2013b) reported that sludge production by aerobic, anaerobic and hybrid bioreactors were 188, 38, and 77 g/kg BOD, respectively. The generated sludge was treated in an anaerobic digester and produced CO_2 and CH_4, equal to 409, 83, 161 g CO_2-equivalent/kg BOD in the three examined systems, respectively. Anaerobic digester contributes 100%, 37% and 41% of the total methane generation in aerobic, anaerobic and hybrid treatment systems, respectively. GHG emission related to other sludge treatment processes such as landfilling or composting is considered as off-site GHG emissions and was not considered in the present study.

5. Discussion

The treatment of the generated wastewater in pulp-and-paper industry serves to remove contaminants, conforming to environmental regulations, while offering the possibility of using the treated effluent as the process water in the production mills, if its quality permits. Among the different treatment methods examined, aerobic processes, especially AS and ASB, are more commonly used in the pulp-and-paper industry (Mahmood and Paice, 2006) because of the simplicity of their operation and high COD removal efficiencies. It has also been shown that among different aerobic processes, MBRs offer high COD removal efficiencies, in the range of 80–92%, from a variety of pulp-and-paper wastewaters (Table 3), while minimizing sludge generation, improving liquid/bio-solids separation, having higher sludge retention times, and smaller footprints (Lerner et al., 2007b). Despite the high capital cost and high control and maintenance requirements of MBR systems, the numerous advantageous of this technology make it a potential candidate for the treatment of pulp-and-paper wastewaters. Alternative aerobic treatment processes such as SBR and FSB have also been used to treat pulp-and-paper wastewaters because of their ability to remove TSS and AOX. However, the excessive sludge production and energy consumption of aerobic processes have attracted attention to the use of anaerobic processes.

The established application of UASB process in the treatment of pulp-and-paper wastewaters has enhanced the use of a variety of anaerobic technologies including PBRs and FBRs (Table 4). These processes offer higher removal efficiencies for AOX and lignin. Nevertheless, biological processes do not exhibit satisfactory color removal efficiencies, an important pollution that needs to be removed. Therefore, hybrid systems have been frequently used in an effort to increase the removal of color and improve the quality of emerging effluents. Table 5 presents the performance of different integrated processes in the removal of wastewater color, which was shown to be up to 97%, as well as producing acceptable removal efficiencies for other contaminants such as lignin and TSS. Although most hybrid systems have higher operating and capital costs, the combined use of physicochemical and biological treatment methods has demonstrated elevated removal efficiencies for contaminants.

The estimated amount of GHG emission by using the steady-state model developed by Ashrafi et al. (2013b) was a total of 739, 1075, and 1261 g CO_2-equivalent/kg BOD by aerobic, anaerobic and hybrid treatment systems, respectively. The estimated GHG emissions are from biological wastewater treatment (AS process and UASB reactor for aerobic and anaerobic systems, respectively) and anaerobic sludge digestion. Since biochemical reactions involved in aerobic and anaerobic processes were used in the applied models for all WWTPs, the estimation of GHG emission could be generalized for other aerobic, anaerobic and hybrid systems. The results showed higher sludge production by the aerobic systems which results in higher GHG emissions from the sludge treatment unit. In addition, the high oxygen requirement of this system constitutes an important source of off-site GHG emission. On the contrary, anaerobic and hybrid systems produce lower amounts of sludge and have no or small oxygen requirements, while producing biogas that could be used for energy production (electricity or heat). This helps WWTPs to cover a part or all of their energy requirements and reduce operating costs related to electricity and fuel consumption. However, these processes need high amounts of alkalinity during the operation that increases the operating costs and off-site GHG emission. The dynamic model developed by Ashrafi et al. (2013a) showed major variations of CO_2 emission in the three examined bioreactors in response to varying operating parameters, equal to 210, 190, and 180 g CO_2/kg BOD, respectively. Methane emission is also varied by 110 g CH_4/kg BOD in the anaerobic and hybrid processes. This change in the amount of methane generation in the anaerobic and hybrid systems resulted in 17% and 14% change in energy production by biogas recovery in these systems. The estimated GHG emissions by the developed models for the three examined systems were summarized (see Supplementary Materials, Table S4).

6. Conclusion

In this review, different wastewater treatment processes in the pulp-and-paper industry were investigated and compared with respect to the extent of GHG emission and contaminant removal efficiencies. Steady-state and dynamic models were used to estimate GHG emission in common biological treatment processes used in the pulp-and-paper industry. The following conclusions result from this study:

i. Both aerobic and anaerobic biological processes are appropriate for the treatment of pulp-and-paper wastewaters.
ii. Although COD removal efficiencies in both treatment methods can be satisfactory, anaerobic treatment is generally more successful in the removal of AOX and lignin.
iii. The use of hybrid systems, a combination of either biological and physicochemical processes or two biological processes, showed a better contaminant removal performance with higher efficiencies, especially for color removal.
iv. The extent of GHG production during wastewater treatment depends mainly on whether CH_4 or N_2O is produced. Therefore, GHG emission relates to the type of process used for wastewater treatment.
v. The steady-state model estimated a higher GHG emission by the anaerobic and hybrid systems compared to the aerobic system because of methane production in the anaerobic bioreactor.
vi. The recovery and use of methane for energy generation can reduce the required energy consumption in WWTPs and accordingly decline operating costs and off-site GHG emission.
vii. The dynamic model showed significant variations in the quantity of CO_2 and CH_4 emissions in WWTPs. The hybrid system had the most stable operation and the lowest variations in response to varying operating parameters in comparison with aerobic and anaerobic systems.
viii. The use of hybrid systems for wastewater treatment under optimized operating conditions is the most appropriate option for pulp-and-paper industry to obtain a satisfactory treatment performance, reduce GHG emission and energy costs, and meet environmental regulations.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2015.05.010.

References

Achoka, J.D., 2002. The efficiency of oxidation ponds at the kraft pulp and paper mill at Webuye in Kenya. Water Res. 36, 1203–1212.
Ammary, B.Y., 2004. Nutrients requirements in biological industrial wastewater treatment. Afr. J. Biotechnol. 3, 236–238.
Ashrafi, O., 2012. Estimation of Greenhouse Gas Emission in Wastewater Treatment Plants of Pulp and Paper Industry. Concordia University. Montreal (PhD dissertation).
Ashrafi, O., Yerushalmi, L., Haghighat, F., 2013a. Application of dynamic models to estimate greenhouse emission by wastewater treatment plants of the pulp and paper industry. Environ. Sci. Pollut. Res. 20, 1858–1869.
Ashrafi, O., Yerushalmi, L., Haghighat, F., 2013b. Greenhouse gas emission by wastewater treatment plants of the pulp and paper industry – modeling and simulation. Int. J. Greenh. Gas. Control 17, 462–472.
Ashrafi, O., Yerushalmi, L., Haghighat, F., 2014. Greenhouse gas emission and energy consumption in wastewater treatment plants: impact of operating parameters. Clean – Soil Air Water 43, 207–220.
Bengtsson, S., Werker, A., Christensson, M., Welander, T., 2008. Production of polyhydroxyalkanoates by activated sludge treating a paper mill wastewater. Bioresour. Technol. 99, 509–516.
Bhathena, J., Driscoll, B.T., Charles, T.C., Archibald, F.S., 2006. Effects of nitrogen and phosphorus limitation on the activated sludge biomass in a kraft mill biotreatment system. Water Environ. Res. 78, 2303–2310.
Bhattacharjee, S., Datta, S., Bhattacharjee, C., 2007. Improvement of wastewater quality parameters by sedimentation followed by tertiary treatments. Desalination 212, 92–102.
Bogner, J., Hashimoto, S., Diaz, C., Mareckova, K., Diaz, L., Kjeldsen, P., Monni, S., Faaij, A., Qingxian, G., Tianzhu, Z., Ahmed, M.A., Sutamihardja, R.T.M., Gregory, R., 2008. Mitigation of global greenhouse gas emissions from waste: conclusions and strategies from the intergovernmental panel on climate change (IPCC) fourth assessment report. working group III (mitigation). Waste Manage. Res. 26, 11–32.
Bryant, C.W., 2010. Updating a model of pulp and paper wastewater treatment in a partial-mix aerated stabilization basin system. Water Sci. Technol. 62, 1248–1255.
Bryant, C.W., Barkley, W.A., Garrett, M.R., Gardner, D.F., 1997. Biological nitrification of kraft wastewater. In: Proceedings of the 1996 5th IAWQ International Symposium on Forest Industry Wastewaters. Elsevier Science Ltd, Vancouver, Canada, pp. 147–153.
Buzzini, A.P., Gianotti, E.P., Pires, E.C., 2005. UASB performance for bleached and unbleached kraft pulp synthetic wastewater treatment. Chemosphere 59, 55–61.
Buzzini, A.P., Miwa, D.W., Motheo, A.J., Pires, E.C., 2006. Use of electrochemical oxidation process as post-treatment for the effluents of a UASB reactor treating

cellulose pulp mill wastewater. Water Sci. Technol. 54, 207–213.
Buzzini, A.P., Pires, E.C., 2007. Evaluation of a upflow anaerobic sludge blanket reactor with partial recirculation of effluent used to treat wastewaters from pulp and paper plants. Bioresour. Technol. 98, 1838–1848.
Chen, W., Horan, N.J., 1998. The treatment of a high strength pulp and paper mill effluent for wastewater re-use II) biological sulphate removal from effluent with a low COD/Sulphate ratio. Environ. Technol 19, 163–171.
Chinnaraj, S., Venkoba Rao, G., 2006. Implementation of an UASB anaerobic digester at bagasse-based pulp and paper industry. Biomass Bioenergy 30, 273–277.
Clark, T.A., Dare, P.H., Bruce, M.E., 1997. Nitrogen fixation in an aerated stabilization basin treating bleached kraft mill wastewater. Water Environ. Res. 69, 1039–1046.
de-Bashan, L.E., Bashan, Y., 2004. Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003). Water Res. 38, 4222–4246.
De los Santos Ramos, W., Poznyak, T., Chairez, I., Cordova, R.I., 2009. Remediation of lignin and its derivatives from pulp and paper industry wastewater by the combination of chemical precipitation and ozonation. J. Hazard. Mater. 169, 428–434.
Deshmukh, N.S., Lapsiya, K.L., Savant, D.V., Chiplonkar, S.A., Yeole, T.Y., Dhakephalkar, P.K., Ranade, D.R., 2009. Upflow anaerobic filter for the degradation of adsorbable organic halides (AOX) from bleach composite wastewater of pulp and paper industry. Chemosphere 75, 1179–1185.
Diez, M.C., Castillo, G., Aguilar, L., Vidal, G., Mora, M.L., 2002. Operational factors and nutrient effects on activated sludge treatment of Pinus radiata kraft mill wastewater. Bioresour. Technol. 83, 131–138.
Dilek, F.B., Gokcay, C.F., 1994. Treatment of effluents from hemp-based pulp and paper industry: I – waste characterization and physico-chemical treatability. In: Proceedings of the IAWQ International Specialized Conference on Pretreatment of Industrial Wastewaters. Pergamon Press Inc, Athens, Greece, pp. 161–163.
Dubeski, C.V., Branion, R.M.R., Lo, K.V., 2001. Biological treatment of pulp mill wastewater using sequencing batch reactors. J. Environ. Sci. Health. Part A 36, 1245–1255.
El-Ashtoukhy, E.S.Z., Amin, N.K., Abdelwahab, O., 2009. Treatment of paper mill effluents in a batch-stirred electrochemical tank reactor. Chem. Eng. J. 146, 205–210.
El-Fadel, M., Massoud, M., 2001. Methane emissions from wastewater management. Environ. Pollut. 114, 177–185.
Elliott, A., Mahmood, T., 2008. An evaluation of maintaining elevated oxygen concentrations in activated sludge systems. J. Residuals Sci. Technol. 5, 137–144.
Ghoreishi, S.M., Haghighi, M.R., 2007. Chromophores removal in pulp and paper mill effluent via hydrogenation-biological batch reactors. Chem. Eng. J. 127, 59–70.
Greenfield, P.F., Batstone, D.J., 2005. Anaerobic digestion: impact of future greenhouse gases mitigation policies on methane generation and usage. Water Sci. Technol. 52, 39–47.
Habets, L., Driessen, W., 2007. Anaerobic treatment of pulp and paper mill effluents – status quo and new developments. In: Forest Industry Wastewaters VIII. IWA Publishing, London, United Kingdom, pp. 223–230.
Hansen, E., Zadura, L., Frankowski, S., Wachowicz, M., 1999. Upgrading of an activated sludge plant with floating biofilm carriers at Frantschach Swiecie S.A. to meet the new demands of year 2000. In: Proceedings of the 1999 6th IAWQ Symposium on Forest Industry Wastewaters. Elsevier Ltd, Tampere, Finland, pp. 207–214.
Helble, A., Schlayer, W., Liechti, P.A., Jenny, R., Mobius, C.H., 1999. Advanced effluent treatment in the pulp and paper industry with a combined process of ozonation and fixed bed biofilm reactors. In: Proceedings of the 1999 6th IAWQ Symposium on Forest Industry Wastewaters. Elsevier Ltd, Tampere, Finland, pp. 343–350.
Hogenkamp, H., 1999. Flotation: the solution in handling effluent discharge. Pap. Asia 15, 16–18.
Jarvinen, R., 1997. Nitrogen in the Effluent of the Pulp and Paper Industry. Proceedings of the 1996 5th IAWQ International Symposium on Forest Industry Wastewaters. Elsevier Science Ltd, Vancouver, Canada, pp. 139–145.
Kampschreur, M.J., Temmink, H., Kleerebezem, R., Jettenm, M.S.M., van Loosdrecht, M.C.M., 2009. Nitrous oxide emission during wastewater treatment. Water Res. 43, 4093–4103.
Kantardjieff, A., Jones, J.P., 1997. Practical experiences with aerobic biofilters in TMP (thermomechanical pulping), sulfite and fine paper mills in Canada. In: Proceedings of the 1996 5th IAWQ International Symposium on Forest Industry Wastewaters. Elsevier Science Ltd, Vancouver, Canada, pp. 227–234.
Kishimoto, N., Nakagawa, T., Okada, H., Mizutani, H., 2010. Treatment of paper and pulp mill wastewater by ozonation combined with electrolysis. J. Water Environ. Technol. 8, 99–109.
Kortekaas, S., Vidal, G., Yan-Ling, H., Lettinga, G., Field, J.A., 1998a. Anaerobic-aerobic treatment of toxic pulping black liquor with upfront effluent recirculation. J. Ferment. Bioeng. 86, 97–110.
Kortekaas, S., Wijngaarde, R.R., Klomp, J.-W., Gatze, L., Field, J.A., 1998b. Anaerobic treatment of hemp thermomechanical pulping wastewater. Water Res. 32, 3362–3370.
LaPara, T.M., Nakatsu, C.H., Pantea, L.M., Alleman, J.E., 2001. Aerobic biological treatment of a Pharmaceutical wastewater: effect of temperature on COD removal and bacterial community development. Water Res. 35, 4417–4425.
Leiviska, T., Nurmesniemi, H., Poykio, R., Ramo, J., Kuokkanen, T., Pellinen, J., 2008. Effect of biological wastewater treatment on the molecular weight distribution of soluble organic compounds and on the reduction of BOD, COD and P in pulp and paper mill effluent. Water Res. 42, 3952–3960.
Lelieveld, J., Lechtenbohmer, S., Assonov, S.S., Brenninkmeijer, C.A.M., Dienst, C., Fischedick, M., Hanke, T., 2005. Greenhouse gases: low methane leakage from gas pipeline. Nature 434, 841–842.
Lerner, M., Stahl, N., Galil, N., 2007a. Aerobic vs. anaerobic-aerobic biotreatment: paper mill wastewater. Environ. Eng. Sci. 24, 277–285.
Lerner, M., Stahl, N., Galil, N.I., 2007b. Comparative Study of MBR and Activated Sludge in the Treatment of Paper Mill Wastewater. In: Forest Industry Wastewaters VIII. IWA Publishing, London, United Kingdom, pp. 23–29.
Mahmood, T., Elliott, A., 2006. Activated sludge process modification for sludge yield reduction using pulp and paper wastewater. J. Environ. Eng. 132, 1019–1027.
Mahmood, T., Paice, M., 2006. Aerated stabilization basin design and operating practices in the Canadian pulp and paper industry. J. Environ. Eng. Sci. 5, 383–395.
Mansour, L.B., Ksentini, I., Elleuch, B., 2007. Treatment of wastewaters of paper industry by coagulation-electroflotation. Desalination 208, 34–41.
Morgan-Sagastume, F., Allen, D.G., 2003. Effects of temperature transient conditions on aerobic biological treatment of wastewater. Water Res. 37, 3590–3601.
Metcalf, Eddy, Tchobanoglous, G., Burton, F.L., Stensel, H.D., 2002. Wastewater Engineering: Treatment and Reuse, Fourth ed. McGrow-Hill, New York, United states.
Mulligan, C.N., 2002. Environmental Biotreatment: Technologies for Air, Water, Soil, and Waste. Government Institutes, Maryland, United States.
Norris, P., Marshall, R., Richard, M., 2000. High temperature effects on activated sludge treatment performance and sludge quality in a recycle mill. In: Proceedings of the 2000 TAPPI International Environmental Conference and Exhibit. Technical Assoc. of the Pulp and Paper Industry Press, Denver, United states, pp. 383–406.
Ortega-Clemente, A., Poggi-Varaldo, H.M., 2007. Comparison of two types of fungal bioreactors with immobilized Trametes versicolor for posttreatment of anaerobically pretreated weak black liquor from kraft pulp mills. In: 9th International in Situ and On-site Bioremediation Symposium. Curran Associates Inc, Baltimore, United states, pp. 514–524.
Pokhrel, D., Viraraghavan, T., 2004. Treatment of pulp and paper mill wastewater - a review. Sci. Total Environ. 333, 37–58.
Rajeshwari, K.V., Balakrishnan, M., Kansal, A., Lata, K., Kishore, V.V.N., 2000. State-of-the-art of anaerobic digestion technology for industrial wastewater treatment. Renew. Sustain. Energy Rev. 4, 135–156.
Rintala, J.A., Lepistö, S.S., 1992. Anaerobic treatment of thermomechanical pulping whitewater at 35-70 °C. Water Res. 26, 1297–1305.
Ruas, D.B., Mounteer, A.H., Lopes, A.C., Gomes, B.L., Brandao, F.D., Girondoll, L.M., 2007. Combined chemical biological treatment of bleached eucalypt kraft pulp mill effluent. In: Forest Industry Wastewaters VIII. IWA Publishing, London, United Kingdom, pp. 143–150.
Salkinoja-Salonen, M., Apajalahti, J., Silakoski, L., Hakulinen, R., 1984. Anaerobic fluidised bed for the purification of effluents from chemical and mechanical pulping. Biotechnol. Adv. 2, 357–375.
Sandberg, M., Holby, O., 2008. Black liquor and alkaline shocks in a multiple stage biological treatment plant. J. Environ. Eng. Sci. 7, 335–344.
Saravanan, V., Sreekrishnan, T.R., 2005. Bio-physico-chemical treatment for removal of colour from pulp and paper mill effluents. J. Sci. Ind. Res. 64, 61–64.
Savant, D.V., Abdul-Rahman, R., Ranade, D.R., 2006. Anaerobic degradation of adsorbable organic halides (AOX) from pulp and paper industry wastewater. Bioresour. Technol. 97, 1092–1104.
Schnell, A., Hodson, P.V., Steel, P., Melcer, H., Carey, J.H., 2000. Enhanced biological treatment of bleached kraft mill effluents - II. Reduction of mixed function oxygenase (MFO) induction in fish. Water Res. 34, 501–509.
Sevimli, M.F., 2005. Post-treatment of pulp and paper industry wastewater by advanced oxidation processes. Ozone: Sci. Eng. 27, 37–43.
Singh, P., Thakur, I.S., 2006. Colour removal of anaerobically treated pulp and paper mill effluent by microorganisms in two steps bioreactor. Bioresour. Technol. 97, 218–223.
Slade, A.H., Nicol, C.M., Grigsby, J., 1999. Nutrients within integrated bleached kraft mills: sources and behaviour in aerated stabilisation basins. In: Proceedings of the 1999 6th IAWQ Symposium on Forest Industry Wastewaters. Elsevier Ltd, Tampere, Finland, pp. 77–84.
Stoica, A., Sandberg, M., Holby, O., 2009. Energy use and recovery strategies within wastewater treatment and sludge handling at pulp and paper mills. Bioresour. Technol. 100, 3497–3505.
Strmen, J., Elliott, A., Mahmood, T., Roy, L., 2006. Pilot-scale evaluation of the low sludge production (LSP) process. J. Residuals Sci. Technol. 3, 15–23.
Thompson, G., Forster, C., 2003. Bulking in activated sludge plants treating paper mill wastewaters. Water Res. 37, 2636–2644.
Thompson, G., Swain, J., Kay, M., Forster, C.F., 2001. The treatment of pulp and paper mill effluent: a review. Bioresour. Technol. 77, 275–286.
The World Bank Group, 1999. Pollution prevention and abatement handbook, 1998: toward cleaner. The International Bank for Reconstruction and Development (Washington D.C., United states).
Wang, Z., Chu, J., Song, Y., Cui, Y., Zhang, H., Zhao, X., Li, Z., Yao, J., 2009. Influence of operating conditions on the efficiency of domestic wastewater treatment in membrane bioreactors. Desalination 245, 73–81.
Wiegand, P., 2007. Synthesis of NCASI information on the management of nutrients for biological treatment of pulp and paper mill wastewaters. NCASI Tech. Bull. 1–51.
Wong, S.S., Teng, T.T., Ahmad, A.L., Zuhairi, A., Najafpour, G., 2006. Treatment of pulp

and paper mill wastewater by polyacrylamide (PAM) in polymer induced flocculation. J. Hazard. Mater. 135, 378–388.
Yerushalmi, L., Ashrafi, O., Haghighat, F., 2013. Reductions in greenhouse gas (GHG) generation and energy consumption in wastewater treatment plants. Water Sci. Technol. 65, 1159–1164.
Zhang, Y., Ma, C., Ye, F., Kong, Y., Li, H., 2009. The treatment of wastewater of paper mill with integrated membrane process. Desalination 236, 349–356.
Zitomer, D.H., Adhikari, P., Heisel, C., Dineen, D., 2008. Municipal anaerobic digesters for codigestion, energy recovery, and greenhouse gas reductions. Water Environ. Res. 80, 229–237.