Chapter 8 Anaerobic Treatment of Pulp and Paper Industry Effluents

Abstract The present status of Anaerobic treatment of pulp and paper industry effluents is presented in this chapter. The manufacturers of commercial reactors for waste water treatment and commercial installations are also presented.

Keywords Anaerobic treatment Pulp and paper industry Effluents Commercial reactors Waste water treatment Commercial installations · Forest industry wastewater

8.1 Present Status

Anaerobic technology is being used for the treatment of pulp mill effluents since the middle of 1980s. Earlier, the pulp and paper mill wastewaters were thought too dilute to be treated by the anaerobic process. Development of various high rate anaerobic processes and much more concentrated pulp mill effluents because of the extensive recycling make the economic benefit from anaerobic treatment more significant, which in turn increased the interest in the use of this technology. Anaerobic technologies are already in use for several types of forest industry effluents. Currently several full-scale system are in operation at pulp and paper industries. The most widely applied anaerobic systems are the upflow anaerobic sludge bed (UASB) reactor and the contact process. Most of the existing full-scale anaerobic plants are treating noninhibitory forest industry wastewater which are rich in readily biodegradable organic matter such as recycling waste water, thermomechanical pulping effluents. Full-scale application of anaerobic systems for chemical, semichemical and chemithermomechanical, bleaching and debarking effluents is still limited.

The application of anaerobic treatment for treatment of Kraft bleach plant effluent has been studied by several researchers (Lafond and Ferguson [1991;](#page-14-0) Raizer-Neto et al. [1991;](#page-15-0) Rintala and Lepisto [1992\)](#page-15-0). The COD removals have ranged from 28 to 50%. Removal of AOX was improved when easily degradable co-substrate was added to the influent. Several chlorophenolic compounds and chlorinated guaiacols were removed by more than 95% (Parker et al. [1993a](#page-15-0), [b](#page-15-0)).

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Fitzsmons et al. [\(1990](#page-13-0)) investigated anaerobic dechlorination/degradation of AOX at different molecular masses in bleach plant effluents. A reduction in AOX was observed with all molecular mass fractions. The rate and extent of dechlorination and degradation of soluble AOX reduced with the increase of molecular weight. As high molecular weight chlorolignins are not amenable to anaerobic microorganisms, dechlorination of high molecular weight compounds may be due to combination of growth, energy metabolism, adsorption and hydrolysis.

Buzzini and Pires [\(2002](#page-12-0)) reported 80% average COD removal when treating diluted black liquor from a kraft pulp mill by using an UASB reactor. The performance of a bench scale UASB was also examined by Buzzini et al. [\(2005](#page-12-0)) for the treatment of simulated bleached and unbleached cellulose pulp mill wastewaters. They obtained 76% COD removal and 71–99.7% AOX removal. They did not observe any inhibitory effect of the organochlorine compounds on the removal of COD during the experiments.

Chinnaraj and Rao ([2006\)](#page-12-0) observed 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 pulp and paper mill wastewater. Furthermore, they obtained a reduction of 6.4 Gg in carbon dioxide 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 carbon dioxide) in nine months.

Zhenhua and Qiaoyuan [\(2008](#page-16-0)) obtained 98% reduction in BOD5 and 85.3% reductions in COD from pulping effluents by using a combination of UASB and sequencing batch reactors (SBRs), whereas the removal efficiency when the substrate was just treated by a UASB reactor was considered to be 95% for BOD5 and 75% for COD, at HRT of one day.

Rao and Bapat [\(2006](#page-15-0)) observed 70–75 and 85–90% reductions of COD and BOD, respectively, and a methane yield of $0.31-0.33$ m³/kg of COD reduced, when using a full-scale UASB for treating the pre-hydrolysate liquor from a rayon grade pulp mill.

Puyol et al. [\(2009](#page-15-0)) used both UASB and anaerobic expanded granular sludge bed reactor (EGSB) for studying the effective removal of 2,4-dichlorophenol. They reported that EGSB reactor showed a better efficiency for the removal of both COD and 2,4-dichlorophenol (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-dichlorophenol/l/d.

Ali and Sreekrishnan ([2007\)](#page-12-0) treated black liquor and bleach effluent from an agroresidue-based mill using the anaerobic process. Addition of 1% w/v glucose yielded 80% methane from black liquor with concomitant reduction of COD by 71%, while bleach effluent produced 76% methane and produced 73 and 66% reductions in AOX and COD, respectively. In the absence of glucose, black liquor and bleach effluent produced only 33 and 27% methane reduction with COD reductions of 43 and 31%, respectively.

Thermomechanical pulping of waste water is found to be highly suitable for anaerobic waste water treatment (Sierra-Alvarez et al. [1990](#page-16-0), [1991;](#page-16-0) Jurgensen et al.

[1985\)](#page-14-0). In a mesophilic anaerobic process, loading rates up to $12-31$ kg COD/m³/d with about 60–70% COD removal efficiency have been obtained (Sierra-Alvarez et al. [1990,](#page-16-0) [1991;](#page-16-0) Rintala and Vuoriranta [1988\)](#page-15-0). In thermophillic anaerobic process conditions, up to 65–75% COD removal was obtained at 55 \degree C at loading rate of 14–22 kg COD/m³/d in a UASB reactors (Rintala and Vuoriranta [1988](#page-15-0); Rintala and Lepisto [1992\)](#page-15-0).

Kortekaas et al. [\(1998](#page-14-0)) studied anaerobic treatment of wastewaters from thermomechanical pulping of hemp. The wood and bark thermomechanical pulping waste waters were treated in a laboratory scale UASB reactor. For both types of wastewaters, maximum COD removal of 72% were obtained at loading rates of 13– 16 g COD/l/d providing 59–63% recovery of the influent COD as methane. The reactors provided excellent COD removal efficiencies of 63–66% up to a loading rate of 27 g COD/l/d, which was the highest loading rate tested. Batch toxicity assays showed the absence of methanogenic inhibition by hemp TMP wastewaters, coinciding with the high acetolastic activity of the reactor sludge of approximately l g COD/g VSS/d.

The anaerobic treatability of NSSC spent liquor together with other pulping and paper mill waste water streams was studied by Hall et al. [\(1986](#page-14-0)) and Wilson et al. [\(1987](#page-16-0)). The methanogenic inhibition by NSSC spent liquor was apparently the effect of the tannins present in these wastewaters (Habets and Knelissen [1985\)](#page-13-0). Formation of hydrogen sulfide in the anaerobic treatment of NSSC spent liquor has been reported but this is not related to the methanogenic toxicity. Apparently, the evaporator condensates from the NSSC production are responsive to anaerobic treatment because of their high volatile fatty acid content (Pertulla et al. [1991](#page-15-0)).

Unstable operations have been observed in anaerobic treatment of pulp mill effluents. The reason for these problems are not clear. It is believed that they may be associated with the toxicants in these effluents (Bajpai [2013\)](#page-12-0).

Research is continuing to develop treatment systems that combine aerobic technology with the ultrafiltration process. The sequential treatment of the effluent from bleached kraft pulp mill in anaerobic fluidised bed and aerobic trickling filters was found to be effective in degrading chlorinated, high and low molecular material (Haggblom and Salkinoja-Salonen [1991](#page-14-0)). The treatment substantially reduced the COD, BOD and AOX of the waste water. COD and BOD reduction was more in the aerobic process whereas dechlorination was more in the anaerobic process. With the combined aerobic and anaerobic treatment, over 65% reduction of AOX and over 75% reduction of chlorinated phenolics was seen. Measuring the COD/AOX ratio of the wastewater before and after treatment revealed that the chlorinated material was as biodegradable as the non-chlorinated.

Dorica and Elliott ([1994\)](#page-13-0) studied the treatability of bleached Kraft effluent using anaerobic plus aerobic processes. BOD reduction in the anaerobic stage was found to vary between 31 and 53% with hardwood effluent. Similarly the AOX removal from the hardwood effluents was higher (65–71%), for the single stage and the two stage treatment respectively, than that for softwood effluents (34–40%). Chlorate was removed easily from both softwood and hardwood effluents (99 and 96% respectively) with little difference in efficiency between the single-stage and two-stage anaerobic systems. At organic loadings rate between 0.4 and 1.0 kg COD/ m^3 /d, the biogas yields in the reactors were 0.16–0.37 $1/g$ BOD in the feed. Biogas yield was found to be reduced with increasing BOD load for both softwood and hardwood effluents. Anaerobic plus aerobic treatment was able to remove more than 92% of BOD and chlorate. AOX removal was 72–78% with hardwood effluents, and 35–43% with softwood effluents. From hardwood effluents, most of the AOX was found to be removed during feed preparation and storage. Parallel control treatment tests in non-biological reactors confirmed the presence of chemical mechanisms during the treatment of hardwood effluent at 55° C. The AOX removal that could be attributed to the anaerobic biomass ranged between 0 and 12%. The Enso-Fenox process was found to remove 64–94% of the chlorophenol load, toxicity, mutagenicity and chloroform (Hakulinen [1982](#page-14-0)).

Haggblom and Salkinoja-Salonen [\(1991](#page-14-0)) found the sequential treatment of bleached Kraft effluent in an anaerobic fluidized bed and aerobic trickling filter effective in degrading chlorinated material. The treatment reduced the COD, BOD and the AOX of the waste water. Reduction of COD and BOD was greatest in the aerobic process, whereas dechlorination was significant in the anaerobic process. When the combination of aerobic and anaerobic treatment, was used, over 65% reduction of AOX and 75% reduction of chlorinated phenolic compounds was observed (Table 8.1). Microorganisms capable of mineralizing pentachlorophenol constituted about 3% of the total heterotrophic microbial population in the aerobic trickling filter. Two aerobic polychlorophenol degrading Rhodococcus strains were found to degrade polychlorinated phenols, guaiacols and syringols in the bleaching effluent.

Singh ([2007](#page-16-0)) and Singh and Thakur ([2006\)](#page-16-0) investigated sequential anaerobic and aerobic treatment in a two-step bioreactor for removal of colour in the pulp and paper mill effluent. In anaerobic treatment, colour, lignin, COD, AOX and phenol were reduced by 70, 25, 42, 15, 39% respectively in 15 days. The anaerobically treated effluent was separately applied in a bioreactor in presence of a fungal strain,

Based on Haggblom and Salkinoja-Salonen ([1991](#page-14-0))

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Paecilomyces sp., and a bacterial strain, Microbrevis luteum. Data indicated reduction in colour, AOX, lignin, COD and phenol by 95, 67, 86, 88, 63% respectively with Paecilomyces sp. whereas M. luteum showed removal in colour, lignin, COD, AOX and phenol by 76, 69, 75, 82 and 93% respectively by third day when 7 days anaerobically treated effluent was further treated with aerobic microorganisms.

Swedish MoDo Paper's Domsjo Sulfitfabrik is using anaerobic treatment at its sulphite pulp mill and produces all the energy required at the mill (Olofsson [1996\)](#page-15-0). It also fulfills 90% of the heating requirements of the inner town of Ornskoldvik. Two bioreactors at the mill produce biogas and slime from the effluent. The anaerobic unit is used to 70% capacity. Reductions in $BOD₇$ and COD were 99 and 80% respectively. The slime produced can be used as a fertilizer.

In the Pudumjee Pulp and Paper Mill in India, the anaerobic pretreatment of black liquor reduced COD and BOD by 70 and 90% respectively (Deshpande et al. [1991\)](#page-13-0). The biogas produced is used as a fuel in boilers along with LSHS oil. The anaerobic pretreatment of black liquor has reduced organic loading at the aerobic treatment plant thereby reducing consumption of electrical energy and chemical nutrients.

Swedish researchers reported a process based on ultrafiltration and anaerobic and aerobic biological treatments (EK and Eriksson [1987](#page-13-0); EK and Kolar [1989;](#page-13-0) Eriksson [1990\)](#page-13-0). The ultrafiltration was used to separate the high molecular weight mass, which is relatively resistant to biological degradation. Anaerobic microorganisms more efficiently remove highly chlorinated substances than aerobic microorganisms. The remaining chlorine atoms were removed by aerobic microorganisms. The combined treatments removed 80% of the COD, AOX and chlorinated phenolics and completely removed chlorate (Table 8.2).

In recent years, AnMBRs which combine the advantages of anaerobic digestion process and membrane separation mechanisms are receiving attention because of their advantages for wastewater treatment such as lower energyrequirements and lower sludge production as compared to conventional anaerobic treatment methods (Jeison and Vanlier [2007\)](#page-14-0). Gao et al. [\(2011](#page-13-0)) reported that by using anaerobic

Parameter	UF plus anaerobic/aerobic predicted reductions $(\%)$	Aerated lagoon estimated reductions $(\%)$
BOD	95	$40 - 55$
COD	$70 - 85$	$15 - 30$
AOX	$70 - 85$	$20 - 30$
Colour	50	0
Toxicity	100	Variable
Chlorinated phenols	>90	$0 - 30$
Chlorate	>99	Variable

Table 8.2 Reduction of pollutants with ultrafiltration plus anaerobic/aerobic system and the aerated lagoon technique

Based on Eriksson [\(1990](#page-13-0)), EK and Eriksson [\(1987\)](#page-13-0), EK and Kolar [\(1989](#page-13-0))

membrane technologies, it is possible to obtain complete solid–liquid phase separation and, as a result, complete biomass retention. Since 1990s, some studies have been carried out to study the efficiency of such systems for the treatment of pulp and paper mill waste waters, and have shown 50–96% removal of COD (Hall et al. [1995\)](#page-14-0).

Xie et al. ([2010\)](#page-16-0) studied the performance of a submerged anaerobic membrane bioreactors (SAnMBRs) for the treatment of kraft evaporator condensateunder mesophilic temperature conditions. They obtained 93–99% COD removal under an organic loading rate of $1-24$ kg COD/m³/day. The methane production rate was found to be 0.35 ± 0.05 μ g COD reduced.

Lin et al. ([2009](#page-14-0)) obtained 97–99% COD removal from a kraft evaporator condensate at a feed COD of 10,000 mg/l in two pilot-scale submerged AnMBRs under thermophilic and mesophilic conditions.

Gao et al. [\(2010](#page-13-0)) obtained about 90% COD removal during the steady period (22nd–33rd day) of the performance of a submerged AnMBR, treating thermomechanical pulping (TMP) whitewater. Several types of membranes such as PVDF based membranes, hollow polymeric fibers, ceramic tubular etc. have been so far developed for the treatment of the various types of wastewaters (Masuelli et al. [2009;](#page-14-0) Kim et al. [2011;](#page-14-0) Stamatelatou et al. [2009](#page-16-0)). However, flat-sheets of polyvinylidine fluoride (PVDF), as a flexible, low weight, inexpensive, and highly nonreactive material, are the major membranes used for the treatment of pulp and paper mill effluents such as Kraft evaporator condensate (Lin et al. [2009](#page-14-0)) and TMP whitewater (Gao et al. [2010\)](#page-13-0) as internal configurations. The maintenance and operational costs arising from membrane fouling and the frequent cleaning requirement of such hydrophobic polymeric membranes and also being relatively energy intensive are nevertheless considered the main hurdle of such treatment systems dealing with various types of wastewaters. After studying the fouling mechanisms in AnMBRs, Charfi et al. [\(2012](#page-12-0)) reported that the cake formation is the main mechanism responsible for membrane fouling in AnMBRs. Such findings were also corroborated by Lin et al. ([2009\)](#page-14-0). Although some measures such as feed pre-treatment, optimization of operational conditions, broth properties improvements, and membrane cleaning have already been used for controlling the membrane fouling process (Lin et al. [2013](#page-14-0)), this issue demands further studies for improving the performance of AnMBR.

Yilmaz et al. ([2008\)](#page-16-0) studied the performance of two AFs under mesophilic and thermophilic conditions for the treatment of a paper mill wastewater. No significant differences at OLRs up to 8.4 g COD/l/d was observed. At higher OLRs, slightly better COD removal and biogas production were seen in the thermophilic reactor, which also denotes the effect of the OLR on the performance of the anaerobic digestion process.

Ahn and Forster [\(2002a\)](#page-12-0) reported that the specific methane production obtained in an anaerobic filter treating a simulated paper mill wastewater under thermophilic temperature was higher than the one obtained at a mesophilic temperature under all the studied HRTs from 11.7 to 26.2 h. They also observed that the performance of the two mesophilic and thermophilic upflow anaerobic filters treating a simulated paper mill wastewater can be affected either by a reduction 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 reduction in the operating temperature to 18–24 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 reduction in the treatment efficiency (Ahn and Forster [2002b](#page-12-0)). But, some studies have also shown that anaerobic biomass have a potential for good recovery after undergoing thermal shock (Buzzini and Pires [2002](#page-12-0)). The effect of the variations in the operating temperature can be affected significantly by the configuration of the reactor. When compared with other high-rate conventional anaerobic digesters AnMBR seems to be more resistant to temperature variation.

Lin et al. ([2009](#page-14-0)) did not observe any significant difference between the thermophilic and mesophilic anaerobic digestion, when treating pulping wastewater by using a pilot-scale SAnMBR. They also observed that the mesophilic SAnMBR can show a better filtration performance in terms of filtration resistance.

Gao et al. ([2011\)](#page-13-0) studied the effect of the temperature and temperature shock on the performance of a SAnMBR treating TMP pressate. They found that the COD removal at 37 and 45 \degree C was slightly higher than that at 55 \degree C. However, they observed no significant differences between the methane productions at the various temperatures. They also reported 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 anaerobic digestion has emerged in recent years, as an economic method to deal with cool, dilute effluents which were considered as inappropriate substrates for anaerobic digestion (Bialek et al. [2012](#page-12-0)).

McKeown et al. ([2012\)](#page-14-0), by reviewing the basis and the performance of the low temperature anaerobic treatment of wastewater, concluded that the adoption of effective post treatments for low temperature anaerobic digestion is a way to satisfy the stringent environmental regulations. Some recent studies have also indicated that low temperature anaerobic digestion can be more efficient by adopting the co-digestion approach (in pilot-scale application) (Zhang et al. [2013\)](#page-16-0). However, significant physical, chemical and biological improvements should be applied to high-rate anaerobic digestion under low-temperature conditions to enhance the efficiency of the present anaerobic digestion systems, and to improve the amount of the methane produced during the related anaerobic processes.

Anaerobic processes were earlier considered being very sensitive to inhibitory compounds (Lettinga et al. [1991](#page-14-0); Rinzema [1988](#page-15-0)). But now advances in the identification of inhibitory compounds and substances in paper mill effluents and also increasing insight into the biodegradative capacity and toxicity tolerance of anaerobic microorganisms has helped to establish that anaerobic treatment of various inhibitory wastewaters is feasible. The capacity of anaerobic treatment to reduce organic load depends on the presence of significant amounts of persistent organic matter and toxic substances. Most important toxicants are reported below (Pichon et al. [1988;](#page-15-0) Sierra-Alvarez and Lettinga [1991;](#page-16-0) McCarthy et al. [1990;](#page-14-0) Field et al. [1989](#page-13-0):

- Sulfate and sulfite
- Wood resin compounds
- Chlorinated phenolics
- Tannins.

These compounds are highly toxic to methanogenic bacteria at a very low concentration. In addition a number of low molecular weight derivatives have also been found as methanogenic inhibitors (Sierra-Alvarez and Lettinga [1991](#page-16-0)).

In CTMP effluents, volatile terpenes and resins may account for up to 10% of the wastewater COD (1000 mg/l) (Welander and Andersson [1985\)](#page-16-0). The solids present in the CTMP effluent were found to contribute to 80–90% of the acetoclastic inhibition (Richardson et al. [1991\)](#page-15-0). The inhibition caused by resin acids was solved by diluting anaerobic reactor influent with water or aerobically treated CTMP effluent which contained less than 10% of the resin acids present in the untreated wastewater (MacLean et al. [1990;](#page-14-0) Habets and de Vegt. [1991\)](#page-13-0). Similarly, inhibition by resin acids was solved by diluting the anaerobic reactor influent with water and by aerating the wastewater to oxidise sulfite to sulfate before anaerobic treatment (Eeckhaut et al. [1986](#page-13-0)).

The AOX generated in the chlorination and alkaline extraction stages are generally considered responsible for a major portion of the methanogenic toxicity in the bleaching effluents (Ferguson et al. [1990](#page-13-0); Rintala et al. [1991](#page-15-0); Yu and Welander [1994\)](#page-16-0). Anaerobic technologies can be successfully used for reducing the organic load in inhibitory waste waters if dilution of the influent concentration to subtoxic levels is feasible (Lafond and Ferguson [1991;](#page-14-0) Ferguson and Dalentoft [1991\)](#page-13-0). Dilution prevents methanogenic inhibition and favour microbial adaptation to the inhibitory compounds. Dilution with other non-inhibitory waste streams such as Kraft condensates and sulfite evaporator condensates(Sarner et ai. [1987\)](#page-15-0) before anaerobic treatment, is found to be effective for reducing this toxicity.

Tannic compounds present at very high concentrations are found to inhibit methanogenesis (Field et al. [1988,](#page-13-0) 1991). Dilution of wastewater or polymerization of toxic tannins to high molecular weight compounds by auto oxidation at high pH as the only treatment (Field et al. [1991\)](#page-13-0) was found to enable anaerobic treatment of debarking effluents.

A system consisting of an anaerobic process followed by an aerobic process appears to be a better option for the removal of COD, AOX and colour from pulp and paper mill effluents (Pokhrel and Viraraghavan [2004](#page-15-0)). Tezel et al. [\(2001](#page-16-0)) reported 91% removal in COD and 58% removal in AOX by using sequential anaerobic and aerobic digestion systems to treat pulp and paper mill wasrewater at a HRT of 5 and 6.54 h for the anaerobic and aerobic processes, respectively.

Bishnoi et al. ([2006](#page-12-0)) obtained a maximum methane production up to 430 ml/day. Furthermore, a COD removal up to 64% was obtained, while volatile fatty acids increased up to 54% at a pH of 7.3, a temperature of 37 $^{\circ}$ C and 8 days HRT during anaerobic digestion. 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. Treatment of the combined effluent of a pulp and paper mill by using a sequential anaerobic and aerobic treatment in two steps bioreactor was studied by Singh and Thakur ([2006\)](#page-16-0). They observed 70% reduction in colour, 42% reduction in COD and 39% reduction in AOX in 15 days. However, using a mixture of fungi and bacteria (Paecilomyces sp. and Microbrevis luteum) for the treatment of anaerobically treated pulp and paper mill effluents, about 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 were observed.

Combination of a UASB reactor (step 1) and two-step sequential aerobic reactor, involving Paecilomyces sp. (step 2) and Pseudomonas syringae pv myricae (CSA105) (step 3), as aerobic inoculums for the treatment of pulp and paper mill effluents, was studied by Chuphal et al. ([2005\)](#page-12-0). They found 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 obtained.

Balabanic and Klemencic ([2011](#page-12-0)) in a full-scale aerobic and combined aerobic-anaerobic treatment plants, obtained removal efficiencies of 87 and 87% for dimethyl phthalate, 73 and 88% for dibutyl phthalate, 79 and 91% for diethyl 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.

Sheldon et al. (2012) (2012) conducted a pilot plant study in a EGSB reactor. They reported reduction in COD by 65–85% over a 6 month period. The overall COD removal 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\)](#page-14-0) reported 50–65% COD removal from four different wastewaters from kraft mill using anaerobic process by using a pilot-scale packed bed column at an OLR of 0.2–4.8 kg COD/m^3 /d. The overall COD removal after combining with completely mixed activated sludge process, as anaerobic–aerobic sequential system, was found to be $55-70\%$. The methane production yield was 0.22–0.34 m³ methane/kg COD, with the biogas containing 80% of methane.

Grover et al. [\(1999](#page-13-0)) obtained a maximum of 60% COD removal from black liquor treatment by using an anaerobic baffled reactor at an organic loading rate of 5 kg/m³/d, a HRT of 2 d, a pH 8.0 and a temperature of 35 °C.

Table [8.3](#page-9-0) summarizes the performance of various reactor configurations for the anaerobic treatment of pulp and paper mill wastewaters.

Reactor configuration	Effluents origin	Initial COD (mg/l)	COD removal	References
UASB	Diluted black liquor	1400	76–86	Buzzini et al. (2005)
UASB	Bagasse-based P&P mill	2000-7000	$80 - 85$	Chinnaraj and Rao (2006)
$UASB + SBR$ UASB	Wheat straw explosion pulping effluent	$\overline{}$	85.3	Zhenhua and Qiaoyuan (2008)
UASB	Pre-hydrolysate liquor from a rayon grade Pulp mill	2500	$70-$ 75 d	Rao and Bapat (2006)
UASB	P&P mill	1133.9 ± 676	~ 81	Turkdogan et al. (2013)
SGBRe	P&P mill	1133.9 ± 676	~ 82	Turkdogan et al. (2013)
Submerged AnMBR	Kraftevaporator condensate	2500-2700	93-99	Xie et al. (2010)
Submerged AnMBR	TMPwhitewater	2782-3350	90	Gao et al. (2010)
ABR	Recycled paper mill effluents	3380-4930	Up to 71	Zwain et al. (2013)
ABR	Black liquor	$10,003 \pm 69$	60	Grover et al. (1999)

Table 8.3 Anaerobic treatment of pulp and paper mill wastewater

8.2 Manufacturers of Commercial Reactors for Waste Water Treatment and Commercial Installations

Most commercial anaerobic reactors for wastewater treatment are based on the upflow anaerobic sludge blanket (UASB) or internal circulation (IC) reactor principles (Kamali et al. [2016;](#page-14-0) Zhang et al. [2015](#page-16-0)). The reactors may also be based on combinations of the special features of different reactors so that their efficiency can be optimized. The commercial manufacturers of anaerobic digesters are listed in Table [8.4](#page-10-0). Van lier [\(2007](#page-16-0)) has reported that in pulp and paper industry 249 reactors have been installed.

The first full-scale low-rate anaerobic lagoon system for treating paper mill effluents was successfully operated in 1976 by Orient Paper mills, Amlai, India which is an integrated bleached sulphate pulp and paper mill (Dubey et al. [1982](#page-13-0)) and then in North America in 1978 by the Inland Container Corporation Newport, Indiana (Priest [1980](#page-15-0), [1983](#page-15-0)). In Orient Paper mill, the effluents from washing and screening from the pulp mill and from caustic extraction from the bleach plant are treated. The treatment system is presedimentation-anaerobic lagoon-aerated lagoon-clarification pond (Bajpai [2000](#page-12-0)). The treatment facility at Inland Container Corporation also has an aerobic polishing step following the anaerobic treatment. The BOD removal was about 85% by anaerobic treatment and 95% by

anaerobic-aerobic treatment. In Hartsville, South Carolina, Sonoco products company's recycle and paper board mill installed a similar anaerobic lagoon and aerobic polish system (Winslow [1988](#page-16-0)). Gwaliar Rayon mill, Mavoor, India manufactures is treating the prehydrolysis effluent in an anaerobic lagoon (Nambisan et al. [1980\)](#page-15-0). This mill is producing dissolving grade pulp by a prehydrolysis sulphate process. The treatment sequence is neutralization-sedimentation-cooling-anaerobic lagoon treatment and aerated lagoon treatment. Biogas is not collected from the lagoon. About 73% COD removal has been achieved at an influent COD of 80 t/d (flow rate $1700 \text{ m}^3/\text{d}$).

The first full-scale application of anaerobic contact systems in the pulp and paper industry was at Swedish sulphite mills in 1983, a semi-chemical pulp and waste paper mill in Spain and a sulphite pulping and cellulose derivative manufacturing facility in Sweden in 1984 and a ground wood mill in Wisconsin in 1986 (Janson [1984;](#page-14-0) Sarner et al. [1987;](#page-15-0) Schmutzler et al. [1988](#page-15-0)). Currently, there are several full-scale anaerobic contact systems in operation at pulp and paper mills worldwide (Bajpai [2000\)](#page-12-0). Reactor volatile solids concentrations reported for anaerobic contact systems operating in the pulp and paper industry have ranged from 3000 to

Mill	Wastewater source	Loading rate $(kg \text{ COD/m}^3/d)$	BOD ₅ (mg/l)	COD (mg/l)
Anaerobic contact reactor				
Hylte Bruk AB, Sweden TMP, groundwood, deink	TMP, groundwood, deinking	2.5	1300	3500
SAICA, Zaragoza, Spain	Waste paper, alkaline cooked straw	4.8	10,000	30,000
Hannover paper, Alfred, Germany	Sulfite effluent condensate	4.2	3000	6000
Niagara of Wisconsin of USA	CTMP	2.7	2500	4800
SCA Ostrand, Ostrand, Sweden	CTMP	6	3700	7900
Alaska Pulp Corporation, Sitka	Sulfite condensate, bleach caustic and pulp white water	3	3500	10,000
Upflow anaerobic sludge blanket				
Celtona, Holland	Pulp whitewater	3	600	1200
Southern paper converter, Australia	Tissue	10		10,000
Davidson, United Kingdom	Wastepaper	9	1440	2880
Chimicadel, Friulli, Italy	Linerboard	12.5	12,000	15,600
Quesnel River Pulp, Canada TMP/CTMP	Sulfite	18	3000	7800
Lake Utopia Paper, Canada	Condensate	20	6000	16,000
EnsoGutzeit, Finland Bleached	TMP/CTMP	13.5	1800	4000
McMillan Bloedel, Canada MP	NSSC	15	7000	17,500
Anaerobic filter: Lanaken, Belgium	TMP/CTMP	12.7	4000	7900
Anaerobic fluidized bed: D' Aubigne, France	NSSC/CTMP Paperboard	35	1500	3000

Table 8.5 Few examples of Using anaerobic technologies in the Pulp and Paper Industry

Based on Bajpai [\(2000](#page-12-0))

5000 mg/l to over 10,000 mg/l (Walters et al. [1988;](#page-16-0) Schmutzler et al. [1988\)](#page-15-0), resulting in volumetric loadings in the range of $1-2$ kg BOD removed/m³/d at BOD removal efficiencies greater than 90% and at optimum temperatures of 35 \pm 5 °C. These volumetric loading rates are perhaps 20–50% of those that can be obtained by other high-rate anaerobic treatment configurations.

Since early 1980s, the UASB has been used increasingly in pulp and paper industry (Jain et al. [1998;](#page-14-0) Habets [1986;](#page-13-0) Habets and Knelissen [1985;](#page-13-0) Habets [1986;](#page-13-0) Rekunen et al. [1985](#page-15-0); Habet et al. [1985](#page-14-0)) and other industries. The loading rates

achieved for pulp and paper industry effluents in full-scale UASB plants range from 5 to 27 kg COD/m³/d. The efficiencies vary from 50 to 80% of the COD depending mostly on the biodegradability of the particular wastewater being treated. The BOD removal efficiencies are high, in most cases between 75 and 99% indicating that anaerobic treatment is particularly useful for the elimination of readily biodegradable organic matter. Several UASB reactors are now operating worldwide for the treatment of pulp and paper mill effluents (Allen and Liu 1998; Rintala and Puhakka [1994\)](#page-15-0). In India, full-scale UASB plants are operating at Harihar Polyfibers and APR Ltd., Satia Paper Mills in Punjab, Warna plant in Maharashtra, India Jain et al. [1998\)](#page-14-0). Table [8.5](#page-11-0) presents few examples of using anaerobic technologies in the pulp and paper industry.

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