Recent Developments in Biogas Production from Pulp and Paper Industry Wastewaters

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Abstract: Increase in population and rapid developments in technology have enhanced production capacity in pulp and paper industry and have resulted in formation of huge amount of wastewaters, as high as 6-15 x 10^4 L per ton of paper produced. Depending on the pulping process, wastewaters can have a wide range of various pollutants characterized by biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), toxicity, and dark color. Untreated wastewaters from pulp and paper can be potentially very polluting especially for high COD concentrations which can be reach at 13000 mg/L. Thus a reliable treatment process is needed to reduce any possible impacts of wastewaters on the receiving media. To overcome this problem an environmentally friendly and economically viable treatment technology should be applied. Indeed, high organic content of pulp and paper industry wastewaters make anaerobic treatment a very attractive option for these wastes. Anaerobic processes not only remove the wastewater pollution but also can produce methane gas which is a valuable and renewable energy source. This review evaluates the recent developments of treatment technologies that highlight to practical use and economic availability of biogas production from pulp and paper wastewaters.

1. Introduction

The rapid increase in population and the increased industrialization to meet human requirements have created problems leading to the environmental danger. The pulp and paper industry which is the one of the most important industries produces a wide range of different types of papers we use today such as; channeled carton paper, newspaper, cleaning paper, cigarette paper, and bag paper. Normally paper production can be achieved by the help of so many process steps and each step generates a wide range of various pollutants. Generated pollutants from the wood pulping and production of the paper products have the potential of biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), toxicity, and color (Pokhrel andViraraghavan, 2004). Discharge of these wastewaters without any treatment poses a significant contributor to the environment pollution, such as; organic pollution, scum formation, color problems, loss of aesthetic beauty in the environment, and increase in toxic substances that affects terrestrial ecosystem (Berube and Kahmark, 2001). Thus a reliable treatment process is needed to reduce any possible impacts of wastewaters on the receiving media. Before introducing the applied treatment technologies for these wastewaters, the process of pulp and mill industry and characterization of the wastewaters generated in each step will be discussed briefly. Treatment methods widely used in order to remove the pollution in the process of papermaking will be deeply described in the subsequent sections.

2. Process Description of Pulp and Paper Mill Industry and Generated Effluents

2.1 Pulp and Paper Making Process

Pulping is the initial step of the paper making industry and represents the largest source of the pollution in the whole process of papermaking. The whole process from wood preparation to paper production can be classified into two categories, pulping and papermaking; respectively. Each process utilizes large amounts of waters which are then turn into a wastewater stream. The paper making operation generally consists of two parts. One is stock preparation by treating the pulp to the required degree of fitness and the other is paper making where the treated pulp is passed through continuous moulds/wires to form sheets (Pokhrel andViraraghavan, 2004) (Table 1).

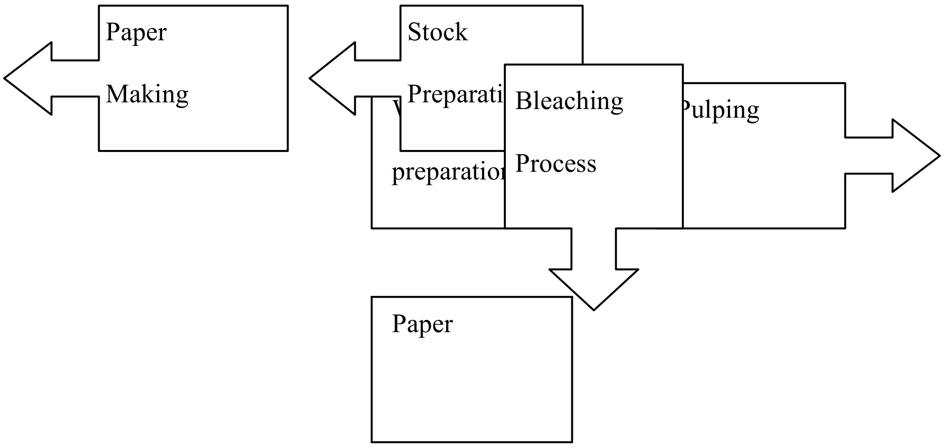

Table 1. Paper Process

Widely used pulping processes are mechanical pulping, chemical pulping and a combination of the two (chemical thermo-mechanical pulping). In the process of mechanical pulping wood is prepared for the subsequent steps by a rotating grindstone in which the fibers are stripped of. When the wood is broken down mechanically, the resulting pulp is known as *groundwood pulp*. Although mechanical pulping efficiency can reach about 90-95%, the quality of the generated pulp is highly colored, and contains short fibers. Additionally, this process does not require chemicals, but the lignin is not removed. In the process of the chemical pulping the wood chips are transformed into fibrous mass by using appropriate chemicals under elevated temperature and pressure in an aqueous solution. The main aim of this process is to remove the lignin by breaking it down and make it soluble (Smook, 1992). This process is performed under two different process, kraft process, and sulfite process; respectively. Kraft process requires alkali conditions in which woodchips are cooked in a solution of sodium hydroxide (NaOH) and sodium sulfide (NaS_2). Differently, in sulfite process woodchips are cooked in mixture of sulfurous acid (H_2SO_3) and bisulfide ions (HSO_3^-) to dissolve lignin (Pokhrel andViraraghavan, 2004). This process makes the wood free from lignin and hemi-cellulose and generated bagasse is used as energy source by burning. Remaining liquor from this step is called as black liquor (Soloman, 2009). In addition, the process in which the wood is first partially softened by chemicals and the remainder of the pulping proceeds with mechanical force is called the chemical thermo-mechanical pulping. By the help of this step, the wood chips are broken down and prepared for the next step.

The bleaching process is used for removal of colored compounds and lignin by chemical agents. In bleaching process chlorine based oxidation agents are used such as hypochlorite, NaOCl, Cl_2, ClO_2, etc. On the other hand there is also oxygen based oxidation agents used for bleaching such as (such as H_2O_2, Na_2O_2, O_3, etc) however their use as not widely as the chlorine based ones. Bleaching by the chlorine-based chemicals cause production of degradation products in which various chloro organic derivatives can be seen. The bleaching process technology and in-mill control is improving continuously. Finally, paper making processes is the last step in which generated pulps is used as paper production including two parts. Initially, a stock is prepared by treating the pulp to meet the required degree of fitness and then treated pulp is passed through continuous moulds/wires to form sheets (Pokhrel andViraraghavan, 2004). In the preparation of stock, pulp is diluted to at least 99% with water also some additives can be used such as optical brighteners and polyvinyl alcohol (Hentzschel, 1998).

2.2 Pulp and Paper Mill Effluent

Due to the diversity of processes and chemicals used in pulping and papermaking operations there is a significant difference between the qualities of wastewaters produced from the both (Billings and DeHass 1971). The major difference between the generated wastewaters is that pulp wastewater contains the dissolved wood derived substances which are extracted from the wood during the process of pulping. Additionally, the other difference between the pulp and paper mill effluents is the color of the effluents. Due to the dissolved lignin, all pulping effluents including papermaking effluents have some discoloration. Actually, lignin is responsible for the mechanical strength of the wood structure and gives the brownish color to the effluents (Leiviska, 2009). Except for the color, pulp and paper mill effluents represent some other pollutants. The sources of pollution and the generated pollutant features are summarized in Table 2. Although the availability of trace elements including heavy metals in the effluents is not mentioned above, there have been published reports on the discharges of metals and other elements from the pulp and paper industries.

Process Description	Wood preparation	Pulping	Paper Making
Features of wastewaters generated in each step	Suspended solids (SS) Biochemical oxygen demand (BOD) Fibers	High pH, Biochemical oxygen demand (BOD) Chemical oxygen demand (COD) Adsorbable organic halides (AOX) Volitile Organic Compounds (VOCs) Suspended solids Resins, Fatty acids Dissolved lignin, Carbohydrate, Color, Inorganic chlorine compounds Organo chlorine compounds	Chemical oxygen demand (COD) Particulate waste, Organic compounds, Inorganic dyes, Acetone

Table 2. The sources of pollution and the generated pollutant features (EPA, 1995)

3. Treatment of Effluents

Pulp and paper industry generates large quantities of highly polluted wastewaters. The high water usage, between 20,000 and 60,000 per ton of product results in large amounts of wastewater (Nemerow, 1991; Sinclair, 1990). Normally 150 m^3 effluents are generated per ton paper produced (Ali, 2001). Effluents of the pulp and paper making processes are widely expressed by its brownish color, high COD and high BOD. The effluent generated at the pulping stage, which is called as black liquor, contains a wide range of compounds like dissolved lignin and its degradation products, hemicelluloses, resin acid, fatty acids, tannins and phenols that are also responsible for giving the effluent its characteristic dark brown color and toxicity (Ali, 2001; Lara, 2003; Malaviya, 2007). Thus, the problems faced by the industry relate to the high organic content, toxicity and color. Discharging of these wastewaters without any treatment applications can cause serious pollution problems. Thus a reliable treatment method should be applied in order to meet discharge acceptance regulation. Mostly applied treatment methods are physical, chemical and biological treatment methods as well as combination of different methods in series. Application of chemical and physical methods has some disadvantages over the biological treatment methods such as their cost-effectiveness and residual effects. Biological treatment is known to be effective in reducing the organic load and toxic effects of pulp and paper mill effluent. There have been several attempts to use biological methods to decontaminate effluent from kraft mills because of their ability to degrade lignin by several microorganisms. The success of the biological treatment with respect to reduction organic load and toxic effects of pulp and paper making effluents have been proven in so many research articles. Biological treatment methods can be divided into two categories, aerobic and anaerobic; respectively. Aerobic treatment of the pulp and paper making effluents has long been known and widely used for these purposes. Aerobic treatments are effective for high COD and BOD removal efficiency (ranging from %70 to %90) but removal of AOX which are known to toxic and hardly biodegradable, cannot be removed effectively, the overall removal of

AOX from the effluents by aerobic treatment has been remained insufficient in so many situations (Savant, 2006). Alternatively, anaerobic treatment has become the most commonly used method not removes the wastewater pollution but also can able to produce methane gas that known as a renewable energy source (Rintala, 1994). Anaerobic treatment is simple to operate, relatively inexpensive technology, moreover; it consumes little energy. Pulp and paper making effluents are nutrient deficient. This feature of the effluent make anaerobic treatment more convenient since commonly used COD: C: N ratio in aerobic treatment is 100:5:1 while it is 350:5:1 in the anaerobic treatment (Maat, 1990). In a study anaerobic treatment was found to reduce AOX and COD by 73% and 66%, respectively. Also, when glucose was added to this effluent, there was generation of biogas containing 76% methane (Ali and Sreekrishnan, 2000).

Typical COD removal data for the treatment of papermill wastewaters shows that a relatively constant removal effciency of about 80% can be achieved and that the treated effluent has a COD concentration of about 800 mg/l. This COD concentration means that some form of additional treatment is required. Compairation of two system was studied, the three-step sequential bioreactor treatments by anaerobic and aerobic (fungus and aerobic bacteria) microorganisms and two step (fungus and aerobic bacteria), respectively and it was found that microorganisms exhibited significant reduction in colour (88.5%), lignin (79.5%), chemical oxygen demand (87.2%) and phenol (87.7%) in the two step aerobic sequential bioreactor, and colour (87.7%), lignin (76.5%), chemical oxygen demand (83.9%) and phenol (87.2%) in the three-step anaerobic-aerobic sequential bioreactor. They have concluded that in the anaerobic treatment, biogas is produced which can be utilized for energy generation; however; aerobic treatment (aerobic fungus + aerobic bacteria) was more significant than anaerobic–aerobic treatment (anaerobic + aerobic fungus + aerobicbacteria) (Chuphal et al. 2005). Numerous physico-chemical processes have also been developed to remove a variety of toxic materials from pulp effuents and to reduce parameters such as colour and COD. They include ozonation and adsorption, often in combination with coagulation, which is used as a pre-treatment stage (Thompson et al., 2001). Bishnoi et al. (2006) reported the biodegradation of pulp and paper mill effluent using anaerobic followed by aerobic treatment. Using a continuous stirred tank reactor (CSTR) for anaerobic digestion of black liquor, these authors reported a maximum methane production was found up to 430 ml /day.

a. Biogas Production

The interest in biogas production has grown considerably for the most of the industries. Anaerobic treatment producing methane that can be directly used as a source of energy has long been employed in industrial waste treatment. Anaerobic treatment is an effective means of decreasing the organic content of different wastewaters in the absence of oxygen (Noykova et al., 2002). Application of aerobic treatment is not commonly preferred due to the cost of oxygen supplementation and generation of higher sludge quantities and odors (Gavala et al., 1999). For the treatment of pulp and paper mill effluents, anaerobic digestion is essentially viable method due to waste reduction and energy potential. Actually anaerobic digestion consists of three main stages. The first step of anaerobic digestion called hydrolysis; complex organic molecules are broken down into simple sugars, amino acids, and fatty acids with the addition of hydroxyl groups which is accompanied by a rapid decrease in pH (Goblos et al., 2008). Step 2 is a fermentation process where acid-forming bacteria, also known as acidogens, convert the products of hydrolysis into simple organic acids, alcohols, carbon dioxide, and hydrogen gas. Finally, end-products of the fermentation process (acetate, butyrate, propionate etc.) are converted by methanogenic microorganisms into methane and carbon dioxide, together with trace quantities of other gases (Fig. 1).

In brief, two groups of methanogenic organisms are involved into the methane production; one group splits acetate into methane and carbon dioxide, and the second group uses hydrogen as electron donor and carbon dioxide as electron acceptor to produce methane. In general, biogas produced as end-product of anaerobic digestion consists of about 65–70% methane, 30–35% carbon dioxide and trace amounts of nitrogen, hydrogen, hydrogen sulphide and water vapor. It is the methane component of the biogas that will produce energy. The gas can be used to generate heat or electricity or both. Anaerobic treatment seems adequately not only removing the wastewater pollution but also producing methane gas which can be used for the energy requirement of the industry. Anaerobic wastewater treatment is typically used in different industries such as chemical, dairy, and pulp and paper mills. Application of anaerobic treatment of pulp and paper industry has been investigated by so many researchers. It has been noted that the adoption of this technology by pulp and paper industries has been limited, mainly due to the 30–60 day residence times required to process the sludge in conventional bioreactors (Elliott and Mahmood, 2007). The published reports that evaluate the recent developments of treatment technologies will be briefly discussed by means of biogas production from pulp and mill wastewaters and solid wastes.

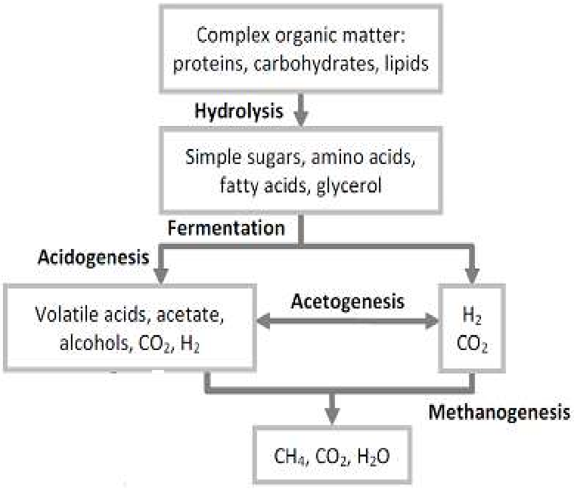

Figure 1. Anaerobic Methane Production

Anaerobic biogas production is actually a sensitive process. Presence of toxic materials in the effluent can be result in deterioration of the process which is undesirable. Unfortunately, pulp and paper industry effluents mainly contains high amount of lignin, adsorbable organic halide, color, low biodegradability (COD: BOD, 4–6) and potential toxicity problems. Inhibitory agents that can be found in pulp and paper industry effluents are summarized in Table 3. Providing that biomass is protected from toxic materials biogas production from pulp and paper industry can be successfully managed.

Wastewater	COD (mg/L)	Degradation (%)	Inhibitors
Pulping • Thermomechanical • Chemithermomechanical	 1000-5600 2500-13000	 60-87 40-60	 Resin Acids Resin Acids, fatty acids, sulfur
Sulfite condensate	7000	-	Sulfur, ammonia
Chlorine bleaching	900-2000	30-50	Chlorinated phenols, resin acids
Sulfite spent liquor	120000-220000	-	
Kraft condensate	1000-33600	83-92	Sulfur, resin acids, fatty acids, terpenes
Sulfite condensate	7500-50000	50-90	Sulfur, organic sulfur

Table 3. Inhibitors to methanogens in the effluent of pulp and paper industry (Rintala et al., 1994)

In the process of chlorine bleaching, so many toxic substances that affect the methanogens can be released. Also it is well known that chlorinated phenolics and chlorinated lignin derivatives are among the main chemical species responsible for the toxicity of pulp and paper mill effluents. Resin acids are tricyclic diterpenes that occur naturally in the resin of tree wood and bark and are transferred to process waters during pulping operations. Several workers have reported the accumulation of resin acids in anaerobic reactors treating mechanical pulping wastewaters. It was reported in a study that inhibition of methanogenic activity of the anaerobic consortium was noted at initial resin acid/biomass ratios exceeding 0.0031 mg resin acid/mg VSS. In addition to resin acids, unsaturated fatty acids, such as; oleic acids, linoleic acid and linolenic acid from pulp and paper mills employing softwood are also a source of toxicity. Since fatty acids can be degraded anaerobically, it is not entirely necessary to prevent them from entering the anaerobic reactors, however; the concentrations present in the wastewater should be kept below the maximum allowable level so that they do not cause significant inhibition to the anaerobic bacteria. For the removal of phenolic compounds white rot fungi have proved their potential in the lignin/phenolic wastewater treatment (Eaton et al. 1980). They have proved ideal organisms for decolorization as well as for the reduction of adsorbable organic halides (AOX) and the chemical oxygen demand (COD). Several researches have also shown that kraft mill effluents can be partly decolorized by white rot fungi (Gokcay and Dilek 1994).

For these reasons, the resent studies have been focused on the application of pretreatment technologies before anaerobic treatment in order to enhance biogas production. There are a number of physical, chemical or biological techniques (use of fungus and bacteria) to minimize the inhibitory effects of effluents prior to anaerobic treatment systems (Lettinga et al. 1991). Reactor design for anaerobic biogas production is also important. The use of thermophilic digesters has recently become more attractive due to their superior performance, better pathogen destruction, and higher digestion rates, which allow the anaerobic digestion facilities to operate at higher loading rates. Using two-stage systems, which segregate the formation of volatile fatty acids from methanogenesis, have also been developed, improving the overall digester performance. In a study performed by Yamini et al. (2009), Upflow anaerobic fixed packed bed reactor (UAFPBR) with brick ballasts as packing material was used in order to treat pulp and paper mill effluents. They have studied biogas production from paper and mill organic sludge in combination with fermented municipal sludge and cattle manure as inoculum. They have found that with a optimum hydraulic retention time (HRT) of 12 hr, reduction of 74.5% COD and 81% BOD was obtained. Additionally 30% inoculum concentration was best for the anaerobic treatment of the effluent with a maximum biogas production of 1.37 L / L effluent.

Beside pulp and paper effluents, pulp and paper industry solid wastes are also valuable for biogas production. In the late 1980s and early 1990s, several research articles have been published introducing anaerobic digestion for treating pulp and paper solid wates (Kowalczyk and Martynelis, 1989; Puhakka et al., 1988; Puhakka, 1991). The long residence time requirement of anaerobic sludge digestion has historically deterred its use in the pulp and paper industry. Techonological advancement that potentially can make anaerobic digestion more feasible has been the development and establishment of pretreatment of sludge prior to anaerobic digestion to accelerate the hydrolysis of sludge. Pretreatment enhances sludge digestion and the rate and quantity of biogas generated, thereby reducing the retention time requirement from 15 to 25 days to approximately 7 days. The studies were performed on both laboratory and pilot-scale systems. Generally, the results of these studies showed that anaerobic digestion of pulp and paper biosolids could reduce solid wastes by 30–70%, with the benefit of methane production. Studies were focused on cost and benefits of the anaerobic technology if pretreatment technologies, including high temperature, sonication, high-pressure homogenization, addition of acids and bases, or addition of enzymes, have been developed to solubilize the organic fraction of secondary sludge (Elliott and Mahmood, 2007; Barjenbruch and Kopplow, 2003; Bougrier et al., 2006; Chen et al., 2007; Khanal et al., 2007; Penaud et al., 1999; Tanaka et al., 1997; Valo et al., 2004). In addition to microbial biomass, pulp mill secondary sludge can contain residual cellulose, lignin and chemical components from the pulping process (Kyllönen et al., 1988). In a study performed by Wood (2009), thermal and caustic pretreatment can significantly increase both the extent and rate of anaerobic bioconversion of pulp mill secondary sludge to biogas.

4. Conclusion

The pulp and paper industry is considered to be a highly energy intensive and polluting industry. In recent years, the high cost of energy inputs and increased environmental concerns are forcing the pulp and paper industry to look for cost-effective and environmentally friendly alternatives. The general characteristics of the pulp and paper industry effluent can be listed as:

1. High lignin content,
2. High adsorbable organic halide (AOX) concentration (due to the bleaching process),
3. Color,
4. Low biodegradability which is indicated by their high chemical oxygen demand to biochemical oxygen demand ratios (COD/BOD), often in the range of 4–6,
5. Potential toxicity problems

Although physical and chemical methods are available for treatment of pulp and paper mill effluent, they are less desirable than biological treatment because of cost-ineffectiveness and residual effects. Biological treatment is known to be effective in reducing the organic load and toxic effects of pulp and paper mill effluent. Since the early 1980s anaerobic treatment of industrial effluents has found widespread application in the pulp and paper industry. Over 200 anaerobic plants are treating a large variety of different pulp and paper mill effluents. Anaerobic fermentation is especially valuable because its end product is methane, a renewable energy source. In the resent years, studies were performed on pretreatment techonologies to decrease toxicity of the effluent prior to anaerobic treatment. Advantages of anaerobic pretreatment are net production of renewable energy (biogas), minimised biosolids production and reduced emission of greenhouse gases. Anaerobic treatment of pulp and paper effluents combination with manure (co-digestion) has emerged among the new treatment perspectives for these effluents. Additionally, other energy source is the anaerobic pulp and paper solid wates. The long residence time requirement of anaerobic sludge digestion has prevented its use in the pulp and paper industry. In an attempt to decrease the residence time requirement, pretreatment technologies have been developed in the recent years such as; high temperature, sonication, high-pressure homogenization, addition of acids and bases, or addition of enzymes. These pretreatment techonologies have been developed to solubilize the organic fraction of secondary sludge. Some of these technologies, using physical or chemical principles, and often a combination of them, have demonstrated their ability to substantially reduce the digestion time and thereby the reactor size. Increased gas production and reduced excess sludge generation have been reported to be the added benefits associated with them.

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