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The Biogas Potential of Pulp and Paper Mill Wastewater: An Essay

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Abstract Currently the economic benefits of the pulp and paper industries have become one of the most important industrial segments in the world; however, the treatment of effluents is still a challenge and an environmental barrier. The effluent from pulp and paper mills can contain a high amount of organic matter including toxic and hardly degradable compounds depending on the production process. The generated wastewaters can be polluting and very hazardous; they should be treated in wastewater treatment plants before being released to the environment. For high COD (Chemical Oxygen Demand) concentrations anaerobic digestion seems to be the favorable wastewater treatment to reduce the organic matter compared to the activated sludge process, since increasing energy costs, the industrial utilization of biogas (CH_4), and technical advances in the anaerobic technology made anaerobic digestion more cost effective. Also the produced primary and activated sludge can be used for biogas production and to reduce the sludge amount at the same time. Possible pretreatment methods are presented and discussed. Preconditioned sludge is often claimed to hold a potential for higher methane recovery with reduced excess sludge and lower retention times, but not economically feasible yet. Thermophilc process running was also shown to increase the methane potential and to lower the retention time.

Keywords Effluent, Biogas, Pulp and paper, Anaerobic digestion

1. Introduction

In pulp- and paper production, high amounts of water are required for:

- suspension as well as for transport of fibers and fillers;
- as solvent for chemical additives;
- as a medium to build hydrogen bridge bonds between the fibers, what creates the stability of the paper.

At conditioning and formation fiber fleece 250 and 1000 L/kg of water of the product are required, depending on type of product [1]. The Technical Bulletin of 2009 from USA National Council for Air and Stream Improvement reported that in this year the installed capacity of the world's pulp and paper industry is more than 100 million metric tons of pulp and more than 120 million metric tons of paper and paperboard per year. Flinders et al [2] assumes that the average amount of effluent from pulp and paper mills is 200 m^3/t of pulp and paper and the total of effluent discharged from the world pulp and paper industry would be about 40.000 million m^3 per year.

To purify the pulp and paper mill wastewater activated sludge treatment in the form of activated sludge plants or aerated lagoons is an often used process, because of high organic matter removal efficiency. But this aerobic process is highly sensitive concerning internal and external disturbances like sudden changes in pH, loading rate or toxicity [3]. This can result in a reduced biomass activity, foaming and increasing concentrations in the effluent. Furthermore a high energy input is needed for the biological carbon oxidation. The aerobic treatment of wastewater includes a cost for the mills and does not make use of its potential energy and nutrient content.

Due to the mentioned high water consumption of pulp and paper mills, recycling and reuse water in the production process is an important issue in paper industry. This leads to a reduction of fresh water use but also to concentrate the wastewater produced. Both, the disadvantages of the activated sludge treatment and the decreasing concentrations of organic compounds in the wastewater are leading to a growing popularity of anaerobic applications.

There can be already found reports about full scale anaerobic treatment plants for pulp and paper mill wastewater in different countries like for instance Canada, Israel or Germany [4-7]. In this essay the biogas potential of pulp and paper mill effluent is evaluated by relating to scientific literature. Furthermore possibilities to improve the biogas potential with high rate reactor types, pretreatment methods or thermophilic process running are discussed and advantages of anaerobic sludge and wastewater treatment are pointed out.

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2. Potential of Possible Substrates

For evaluating the biogas potential it is important to have a closer look on the carbon rich streams within the wastewater treatment process. Figure 1 presents the wastewater treatment of pulp and paper mill effluent, emphasizing the carbon rich flows and showing the possibility of methane (CH_4) recovery.

In general, the ingredients of the pulp or paper mill wastewater depends strongly on the applied process and can contain a big variety of organic substrates like lost cellulose fibers, resin acids, plant sterols, lignin, starch, chlorinated organic compounds, fatty acids, sulfur compounds, and dyes [6]. Some of those compounds are considered to be toxic.

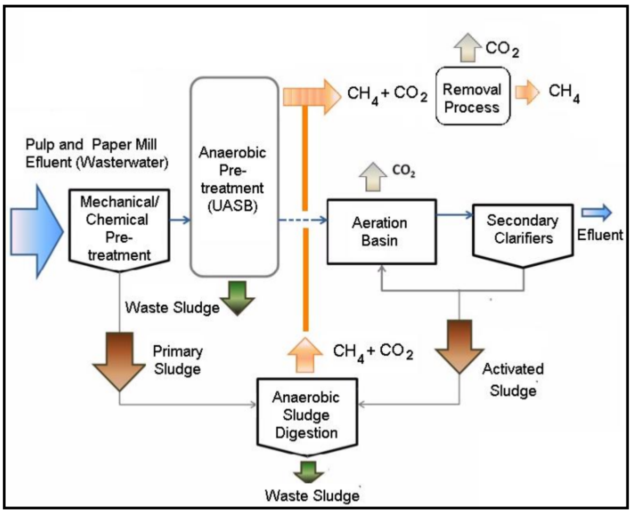

Figure 1. Wastewater treatment of pulp and paper mill effluent

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Besides naturally occurring wood extractives like tannins, xenobiotic compounds are formed during the process of pulp and paper making like chlorinated lignin, resin acids and phenols, dioxins or furans [8], which are considered to have a high toxicity and can decrease or completely stop aerobic and also anaerobic biological degradation if high concentrated. Howbeit, the microorganisms can adapt to the potentially toxic substrate to a certain amount and reduce the grade of inhibition. It should, however, be pointed out that adaptation depends on several factors, like e.g. the concentration of the toxicant and the operating conditions [9]. Ali and Sreekrishnan [10] reviewed the aquatic toxicity from pulp and paper mill effluents including an overview of the different organic pollutants. They reported that the pulp and paper industry was the sixth largest polluter after oil, cement, leather, textile, and steel industries, discharging a variety of gaseous, liquid, and solid wastes into the environment.

The concentrations of organic matter are often expressed with the Chemical Oxygen Demand (COD). Möbius [1] reports COD values for different pulp and paper mill effluents varying between 20 mg/L up to 5500 mg/L. Especially paper production using secondary fibers, like newspapers or carton board, shows high COD concentrations with more than 1000 mg/L in the paper mill effluent. In comparison, the average COD of European municipal wastewater is around 500 mg/L.

Only in some cases of wood free or low freeness paper, produced with a high freshwater use, the COD can be so low (<100 mg/L) that a biological treatment is difficult and rather ineffective [1].

Generally the biological treatment is subsequent to a mechanical-chemical pretreatment i.e. sedimentation, flotation or filtration which eliminates suspended solids in order to protect the following biological reactors. The produced so called "primary sludge" consists of wood fibers (cellulose, hemicellulose and lignin), papermaking fillers like kaolin and calcium carbonate, pitch, lignin by-products and ash [11]. Bayr and Rintala [12] suggested that primary sludge might be a better substrate for methane production than waste activated sludge, which is already partly degraded and shows only half of the soluble COD. In the literature there is a wide range of observed methane (CH_4) production potentials between 45 m^3/tVS [13] and 210m^3/tVS [12]. Primary sludge probably can contain a various amount of anaerobically hardly- or even non-degradable compounds, depending on the paper producing process. So further pretreatment or thermophilic conditions might be a possibility to higher and fasten degradation, but dewatering and incinerating the primary sludge is nowadays the economically favored solution.

In comparison to primary sludge, waste activated sludge is more common as a substrate for biogas production. It consists of microbial biomass, cell-decay products and non-biodegradable lignin precipitates [14, 15]. Karlsson et al. [16] investigated the biogas production potential of the activated sludge from six different pulp and paper mills. Their results ranged from 100-200m^3CH_4/tVS and are closely related to the used paper production process as well as to the sludge age, since younger sludge is less degraded and has a higher biogas potential. Bayr and Rintala [12] also studied the co-digestion of primary and waste activated sludge.

However, since primary sludge is mostly difficult to degrade under anaerobic conditions and activated sludge treatment requires high energy input for aeration, the anaerobic digestion of the paper mill effluent after particle separation becomes more favorable especially when dealing with toxic compounds or high COD concentrations. Not at least because of the invention of high rate reactor types with Hydraulic Retention Time (HRT) less than five days [17], allowing to treat high wastewater flows compared to Continuously Stirred Tank Reactors (CSTR) used for sludge digestion. Lerner et al. [18] reports that after pre-treating the wastewater in an anaerobic reactor, no foaming or sludge bulking was observed in the activated sludge treatment. Also, the risk of gaining metabolites with an increased toxicity during the degradation of toxic compounds is lower if using anaerobic processes.

3. High Rate Reactors

There have been developed several different types of high rate reactors for anaerobic degradation of pulp and paper mill effluent [19, 20]. Today's preferred reactor types are so called "tower reactors" based on the up flow Anaerobic Sludge Blanket (UASB) process [21, 22]. In a UASB reactor, the biomass is retained by forming granular sludge particles of high density. This biomass granulates float due to the up streaming wastewater and form the characteristic sludge blanket (also called sludge bed). Fixed separators ensure the retention of the biomass in the reactor. The produced biogas is collected at the top of the reactor.

However, this high rate reactor types are only economically profitable with relatively high organic substrate concentrations. So the COD should be higher than 1000 to 2000 mg/L. The COD elimination efficiency is strongly related to the wastewater composition but may be expected between 60% to 70% [1].

Two-stage digestive systems, which separate the formation of volatile fatty acids from methanogenesis, can further improve the overall reactor performance [4].

UASB reactors show a high sensitivity for suspended solids [17], which can cause plugging of the sludge bed. So a good mechanical and chemical pretreatment is necessary to eliminate particles like fibers.

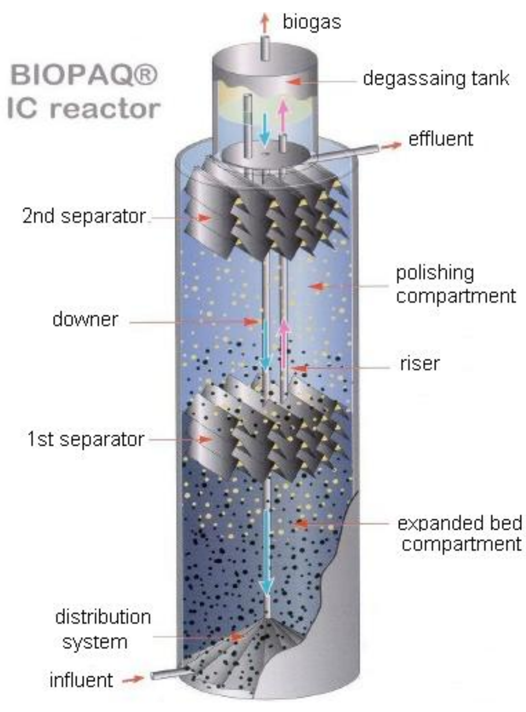

Figure 2. Internal circulation (IC) reactor, Paques [23]

Beside suspended solids, also a low sulfate carbon ratio can cause problems in the UASB process, since sulfate reducing bacteria are not involved in granular forming and can inhibit methanogens.

By modifying the basic USAB concept, improved reactor designs were created, showing an increased retention of suspended solids and new gas separation systems. Two main examples for these new generations of UASB reactors are the high rate Internal Circulation (IC) reactor [23] and the Expended Granular Sludge Bed (EGSB) reactor [24] which can be seen on Figure 2 and 3.

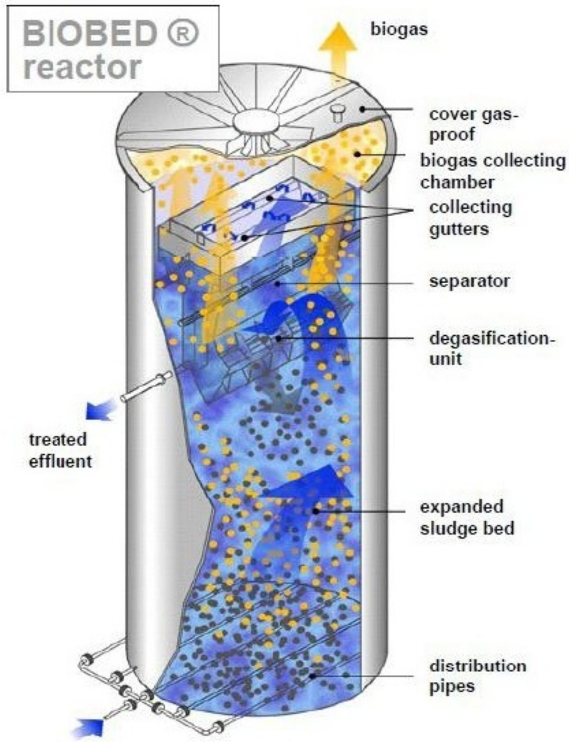

Figure 3. Expended granular sludge bed (EGSB], Veolia Water, [24]

4. Potential of Treatment

Wastewater from pulp and paper mills and especially the produced sludge can contain compounds that are more hardly degradable, like lignin and cellulose fibers. Especially lignin, an irregular and therefor insoluble polymer, consisting of phenyl-propanoid subunits [4, 25]. These complex macromolecules are difficult to break down to readily available organic matter for acidogenic micro-organisms. So hydrolysis becomes mostly the rate limiting step, what causes long retention times and a low overall degradation efficiency.

During the pretreatment slowly degradable, particulate organic matter is converted to low molecular weight, easy biodegradable compounds. There are many articles reviewing the following pre-treatment methods of waste activated sludge mostly from municipal wastewater:

- Thermal pretreatment;
- Mechanical pretreatment;
- Chemical pretreatment (ozonation, peroxidation);
- Ultrasound;

- Bacterial and enzyme hydrolysis [4, 26].

The leading technologies of preconditioning sludge seem to be based on sonication, thermal processing and mechanical disintegration. The combination of those technologies, using physical or chemical principles at the same time, have demonstrated their ability to substantially reduce the digestion time and thereby the reactor size, with increased gas production and reduced excess sludge generation. Elliott and Mahmood [4] suggest that pulp and paper mill activated sludges could be more amenable to pretreatment technologies than municipal activated sludge, because of the higher volatile fraction.

On the contrary Karlsson et al. [16] reported that ultrasonic and enzymatic pretreatment did not show any significant effect on the methane production potential of waste activated sludge from different pulp and paper mills.

Recent developments in sludge preconditioning technologies for activated sludge have substantially reduced the sludge residence time requirement in a biogas reactor from 15 to 25 days to 7 days [4], but from today's point of view, it is difficult to assume which pretreatment technology holds the greatest potential for pulp and paper sludge, because the composition of the sludge differs depending on the paper production process and there is only rare literature investigating pretreatment effects on the specific wastewater and sludges.

5. Potential of Thermophilic Process Running

The majority of anaerobic digesters operating in the municipal sector use single-phase mesophilic reactors [4, 27]. 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 [27] with smaller reactor volumes. The pulp and paper mill effluent is furthermore often characterized by a high temperature.

Habets [28] reported that in modern mills the temperature is often around 50 to 55ºC and the water has to be cooled down to 30°C for activated sludge treatment in most cases. Using thermophilic processing only a small amount of energy input is needed to heat the wastewater stream to the optimum temperature for termophilic digestion which amounts to 50-60°C. The temperature increases the activity of acidogenic and methanogenic micro-organisms but also the mass transport and the bio-availability of the substrate.

Thermophilic digestion can reduce the amount of difficult degradable organic materials, thus improving the overall removal efficiency of organics. The low biodegradability of the sludges is related to the lignin content. However, on Bayr and Rintala [12] studies, the cellulose removals was 70-73% using AD. The authors consider that anaerobic microbes are able to degrade cellulose better than aerobic ones, because they contain membrane-bound enzyme complexes containing cellulose hydrolyzing enzymes [12]. The higher cellulose content of the primary sludge compared to activated sludge could lead to higher methane yields.

In a recent study of anaerobic digestion of pulp and paper mill, primary sludge and co-digestion of primary and secondary sludge were studied for the first time in semi-continuously fed continuously stirred tank reactors (CSTR) under thermophilic conditions, by Bayr and Rintala [12]. Primary and secondary sludge were incubated in batch assays at 55°C, for 42 days. They reported greater methane potentials under thermophilic than under mesophilic conditions. The highest methane yield obtained was 240 m^3CH_4/tVS with an OLR (Organic Load Rate) of 1 $kgVS/m^3d$ and HRT of 29-32 d in the digestion of primary sludge. For the co-digestion of primary and secondary sludge the highest methane yield was 170 m^3CH_4/tVS obtained with HRT of 25 d.

In combination with thermophilic digestion, thermal pretreatment seems to be feasible. Elliott and Mahmood [4] studied the conditioning of municipal sludge at 110–134ºC (for 20–90 min) and at 70 °C (for 9–72 h) before thermophilic anaerobic digestion. Pretreatment of activated sludge can increase methane production for both mesophilic (43-145%) and thermophilic (4–58%) anaerobic digestion processes.

There are also negative aspects of thermophilic digestion mentioned in articles including increased operator attention, higher odor potential, higher susceptibility to process upsets and poorer quality of dewatering filtrate [27, 29, 30, 31].

6. Conclusions

The effluent from pulp and paper mills can contain a high amount of organic compounds depending on the production process. If the COD is higher than 1000 g/L, anaerobic digestion seems to be the favorable wastewater treatment for COD reduction, compared to the activated sludge process, since high rate reactors allow to treat high wastewater flows.

Anaerobic digestion uses the energetic potential of the substrate for biogas production and requires furthermore less energy for aeration, produces less sludge, consumes less space, enables more stable process running (no problems with bulking sludge in aerobic treatment) and has a lower risk of metabolites with increased toxicity. Also the produced primary and activated sludge can be used for biogas production and to reduce the sludge amount. A lot of research is focused on possible pretreatment methods.

Preconditioned Sludge is often claimed to hold a potential for higher methane recovery with reduced excess sludge and lower retention times, but at present, it is difficult to assess which pretreatment technology holds the greatest potential for pulp and paper sludge and if it is economically reasonable.

Thermophilc process running was also shown to increase the methane potential and to lower the retention time. The already high temperature of the pulp and paper mill effluent could make this technology energetically and also economically feasible.

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