ANAEROBIC WASTEWATER TREATMENT PROCESS

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Abstract Anaerobic wastewater treatment differs from conventional aerobic treatment. The absence of oxygen leads to controlled conversion of complex organic pollutions, mainly to carbon dioxide and methane. Anaerobic treatment has favourable effects like removal of higher organic loading, low sludge production, high pathogen removal, biogas gas production and low energy consumption. Psychrophilic anaerobic treatment can be an attractive option to conventional anaerobic digestion for municipal sewage and industrial wastewaters that are discharged at moderate to low temperature. **Keywords** anaerobic biodegradation, anaerobic processes, anaerobic wastewater treatment, energy recovery

INTRODUCTION

Aerobic treatment systems such as the conventional activated sludge (CAS) process are widely adopted for treating low strength wastewater (< 1000 mg COD/L) like municipal wastewater. CAS process is energy intensive due to the high aeration requirement and it also produces large quantity of sludge (about 0,4 g dry weight/g COD removed) that has to be treated and disposed off. As a result, the operation and maintenance cost of a CAS system is considerably high. Anaerobic process for domestic wastewater treatment are an alternative, that is potentially more cost-effective, particularly in the sub-tropical and tropical regions where the climate is warm consistently throughout the year.

Anaerobic wastewater purification processes have been increasingly used in the last few decades. These processes are important because they have positive effects: removal of higher organic loading, low sludge production and high pathogen removal, methane gas production and low energy consumption (Nykova et al., 2002).

Reviews of anaerobic processes encompasses both fundamental and applied research performed in this area. The review is subdivided into a number of sections including microbiology, biotransformation of toxic and recalcitrant compounds, toxicity, model development, reactor systems, municipal solid waste treatment and new methods for testing of anaerobic processes. In the past decade has been an increased research activity in the application of reactor technology for treatment of various types of industrial wastewaters, such as those from food processing, textile industry, paper and pulp industry (Rumana et al., 2000; Pantea and Romocea, 2008). Is was stated that high rate anaerobic systems represent low cost and sustainable technology for industrial wastewaters treatment, because of its low construction, operation and maintenance cost, small land requirements, low excess sludge production and production of biogas.

Anaerobic digestion consists of several interdependent, complex sequential and parallel biological reactions, during which the products from one group of microorganisms serve as the substrates for the next, resulting in transformation of organic matter mainly into a mixture of methane and carbon dioxide. Anaerobic digestion takes place in four phases: hydrolysis/liquefaction, acidogenesis, acetogenesis and methanogenesis. To ensure a balanced digestion process it is important that the various biological conversion processes remain sufficiently coupled during the process so as to avoid

the accumulation of any intermediates in the system. Microorganisms from two biological kingdoms, the *Bacteria* and the *Archaea*, carry out the biochemical process under strict anaerobic conditions (Parawira, 2004).

Anaerobic reactors have been used mainly for industrial wastewater treatment. Researches have shown than anaerobic systems such as the Upflow Anaerobic Sludge Blanket (UASB), the Anaerobic Sequencing Batch Reactor (AnSBR) and the Anaerobic filter (AN) can successfully treat high-strength industrial wastewater as well as low-strength synthetic wastewater.

Application of anaerobic systems for municipal sewage treatment is so far very limited. The predominant reason given for is, that municipal sewage are to weak (to low BOD or COD) to maintain high biomass (in the form of granules – suspended solids or fixed film) content in reactor. There are however, some successful examples in pilot and full scale. Orozo (1997) investigated a full scale anaerobic baffled reactor (AnBR) to treat municipal sewage of an average BOD of 314 mgO₂/L for a hydraulic retention time of 10.3 hours, (organic loading rate 0.85 kg/m³·d) and achieved a 70% removal efficiency. It has to be stressed that the process was run at very low temperature between 13 and 15 °C. Treatment of domestic wastewater in a UASB and two anaerobic hybrid (AnH) reactors was conducted by Elmitwalli et al. (1999) at a temperature of 13 °C. For pre-settled wastewater treatment, the AnH reactors removed 64 % of total COD, which was higher than the removal in the UASB reactors.

The majority of anaerobic digestion plants are operated under mesophilic conditions (approx. 35 °C), however, most wastewaters are released for treatment at temperatures below 18 °C. Therefore many wastewaters are heated prior to treatment, thus consuming up to 30% of energy produced.

The main objective is to decrease the cost of sewage treatment and minimise the amount of excess sludge produced. There is however, another important aspect, which can make application of anaerobic treatment as the first step of municipal or industrial treatment attractive. It was many times proven that many refractory difficult biodegradable organic compounds can be decomposed (at least to simpler substances) under anaerobic conditions.

PSYCHROPHILIC ANAEROBIC TREATMENT PROCESS

Although anaerobic wastewater treatment plants for municipal wastewater have been successfully operated in tropical countries such as Mexico, Columbia, India and China, the process until now has not been applied in countries with moderate and low temperatures. At such temperatures, chemical oxygen demand (COD) removal is limited and long hydraulic retention time is needed for one step system to provide sufficient hydrolysis of particulate organics (Gasparikova, 2005). Low temperature causes deleterious effect on anaerobic digestion because of relatively longer generation time of anaerobic bacterial populations and lower biochemical activity, resulting in the decrease of biogas yield and digester failure (Singh et. al., 1999). The start-up and treatment of municipal wastewater in cold regions was investigated in two UASB reactors operated at temperatures of 32, 20, 15, 11, and 6° C with several HRTs ranging from 48 to 3 h (Singh and Viraraghavan, 1999). Biomass aggregation (granulation) was achieved in approximately 281 d at 20° C.

However, low temperature or psychrophilic (< 20 °C) anaerobic digestion has recently been proven feasible for the treatment of a range of industrial wastewater representing a technological breakthrough for environmental management. Therefore psychrophilic anaerobic treatment is an attractive option to conventional anaerobic digestion for wastewaters that are discharged at moderate to low temperature.

Biodegradation of persistent organic compounds

Under psychrophilic conditions, chemical and biological reactions proceed much slower than under mesophilic conditions. Most reactions in the biodegradation of organic matter require more energy to proceed at low temperatures than at a temperature optimum of 37° C (mesophilic conditions) (Table 1). However, some reactions, such as hydrogenotrophic sulfate reduction, hydrogenotrophic methane production and acetate formation from hydrogen and bicarbonate, require less energy (Table 1; reactions 9, 10 and 11, respectively). A strong temperature effect on the maximum substrate utilization rates of microorganisms has been observed by many researchers. In general, lowering the operational temperature leads to a decrease in the maximum specific growth and substrate utilization rates but it might also lead to an increased net biomass yield (g biomass g⁻¹ substrate converted) of methanogenic population or acidogenic sludge (Lettinga et. al, 2001).

Table 1. Stoichiometry and Gibbs free-energy changes of acetate, propionate, butyrate and hydrogen anaerobic conversion in the presence and absence of sulphate (Lettinga et. al, 2001).

	$\Delta G' kJ/reaction$	
Reactions	37 °C	10 °C
1. $CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 3H_2$	+71.8	+82.4
2. $CH_3CH_2COO^- + 0.75SO_4^{2-} \rightarrow CH_3COO^- + HCO_3^- + 0.75HS^- + 0.25H^+$	-39.4	-35.4
3. $CH_3CH_2COO^- + 1.75SO_4^{2-} \rightarrow 3HCO_3^- + 1.75HS^- + 0.25H^+$	-88.9	-80.7
4. $CH_3CH_2CH_2COO^- + 2H_2O \rightarrow 2CH_3COO^- + H^+ + 2H_2$	+44.8	+52.7
5. $CH_3CH_2CH_2COO^- + 0.5SO_4^{2-} \rightarrow 2CH_3COO^- + 0.5HS^- + 0.5H^+$	-29.3	-25.9
6. $CH_3CH_2CH_2COO^- + 2.5SO_4^{2-} \rightarrow 4HCO_3^- + 2.5HS^- + 0.5H^+$	-128.3	-116.4
7. $CH_3COO^- + SO_4^{2-} \rightarrow 2HCO_3^- + HS^-$	-49.5	-45.3
8. $CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$	-32.5	-29.2
9. $4H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O$	-148.2	-157.1
10. $4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O$	-131.3	-140.0
11. $4H_2 + 2HCO_3^- + H^+ \rightarrow CH_3COO^- + 4H_2O$	-98.7	-111.8

Interactions of methanogens and denitrifiers were investigated by Fang and Zhou (1999) in an upflow anaerobic sludge blanket reactor (UASB) treating phenol (200 mg/L) and m-cresol (100 mg/L) containing wastewater. Over 98 % phenol and 60 % m-cresol were degraded jointly by methanogens and denitrifiers with 1 day hydraulic retention time (HRT), when the ratio of COD to NO₃-N was 5.23. A continuous flow fixed-film anaerobic bioreactor was seeded with a consortium and reduced the concentration of phenol and phenolic compounds by 97 and 83%, respectively, at an HRT of 6 h. Anaerobic biofilm reactors inoculated with mixed microbial populations degraded contaminants like phenol, o-cresol, quinoline, debenzofuran, acenaphthene and phenonthrene by more than 90% at an HRT of 3 h or more (Guieysse and Mattiasson, 1999). Collins et al. (2005) has proven feasible low temperature or psychrofilic (< 20 °C) anaerobic digestion treatment of phenolic wastewater. They observed efficient COD and phenol removal at organic and phenol loading rates of 5 kgCOD/m³·d and 0.4 - 1.2 kg phenol/m³·d. They had proven also that methanogenic activity was developed under psychrophilic conditions.

Decolorisation of textile effluents in anaerobic biological process has very often failed while many dyes are recalcitrant to biodegradation. It was however, shown that anaerobic reductive cleavage by microbes could be potentially useful. For example Cariel et al. (1995) and Donlon et al. (1997) employed anaerobic digeste sludge for microbial dyes structure cleavage. As a result of azo-reactive dyes destruction under anaerobic conditions, cancerogenic aromatic amine intermediates are produced.

They can further degraded under aerobic biological treatment to become less harmful end products. The biodegradation of two azo dyes, 4-phenylazophenol and Mordant Yellow-10, was evaluated by Tan et al. (1999) in batch systems where anaerobic and aerobic conditions were integrated by exposing anaerobic granular sludge to oxygen. The azo dyes were reduced, resulting in a temporal accumulation of aromatic amines. Own investigations (Mrowiec and Suschka, 2006) have shown an anaerobic-aerobic system to be effective for real textile wastewater in admixture with textile effluents. Only at the first anaerobic stage – consisting of a fixed bed filter, operated at a hydraulic retention time of 7.7 hours, a COD reduction of 79 % and colour reduction of 75 % was possible.



Figure 1. Schematic representation of anaerobic-aerobic textile wastewater treatment.



Figure 2. Laboratory system of the anaerobic-aerobic textile wastewater treatment.



Figure 3. COD removal in the anaerobic-aerobic textile wastewater treatment process.



Figure 4. Colour removal in the anaerobic-aerobic textile wastewater treatment process.

The effects of acetate and benzoate on anaerobic degradation of terephthalate (1,4-benzenedicarboxylate) by a syntrophic methanogenic culture were studied by Kleerebezem et al. (1999). They observed that decarboxylation of terephthalate resulting in the formation of benzoate, was strictly dependent on the concomitant fermentation of benzoate.

Cometabolic and biotic conversions were observed to be significant mechanisms for the transformation of chlorinated ethanes by the methanogenic consortium in a UASB reactor by van Eekert et al. (1999). The effect of 1,1,2,2-tetrachloroethane (TCE) on a UASB reactor fed with a

synthetic wastewater was determined by Navarrete et al. (1999). The results showed that the UASB had the potential to treat industrial wastewaters containing TCE.

Anaerobic/anoxic fluidized-bed granular activated carbon (GAC) bioreactor in series with an activated sludge reactor was used to treat 2,4-dinitrotoluene (DNT) by Vanderloop et al.

(1999). DNT was transformed to 2,4-diaminotoluene (DAT) in the anaerobic stage. Under denitrification conditions in the fluidized bed, 5 % of DAT was transformed to 2-amino-4-nitrotoluene, 4-amino-2-nitrotoluene, and unknown products, and about 45 % remained as DNT. The fate of four nitroaromatic compounds (5-nitrosalicylate, 4-nitrobenzoate, 2,4-dinitrotoluene,

nitrobenzene) was investigated by Razo-Flores et al. (1999), in laboratory-scale UASB reactor. All the nitroaromatic compounds were transformed stoichiometrically to their corresponding aromatic amines.

Effect of low temperature on the physical and chemical properties of wastewater

A drop in temperature is accompanied with a change of the physical and chemical properties of the wastewater, which can considerably affect design and operation of the treatment system. For instance, the solubility of gaseous compounds increases as the temperature decreases below 20°C. This implies that the dissolved concentrations of methane, hydrogen sulfide and hydrogen will be higher in the effluent of reactors operated at low temperatures than those from reactors operated at high temperatures. The high increase of solubility of CO_2 indicates that a slightly lower reactor pH might prevail under psychrophilic conditions.

At low temperatures, the viscosity of liquids is also increased. Therefore, more energy is required for mixing and sludge bed reactors become less easily mixed, particularly at low biogas production rates. In psychrophilic reactors, particles will settle slower because of a decreased liquid–solid separation at low temperatures. Moreover, related to the higher liquid viscosity, the diffusion of soluble compounds

will drop at lower temperatures. The diffusion constant of soluble compounds is about 50% lower at 10°C compared with the mesophilic temperature range (30–40°C), (Lettinga et. al, 2001).

SUMMARY

The feasibility of high-rate anaerobic wastewater treatment (AnWT) systems for cold wastewater depends primarily on: (1) the quality of the seed material used and its development under submesophilic conditions; (2) an extremely high sludge retention time under high hydraulic loading conditions because little if any viable biomass can be allowed to wash out from the reactor; (3) an excellent contact between retained sludge and wastewater to utilize all the available capacity within the bioreactor; (4) the types of the organic pollutants in the wastewater; and (5) the reactor configuration, especially its capacity to retain viable sludge.

It is not clear, as yet, whether high-rate psychrophilic anaerobic wastewater treatment requires the development of psychrophilic or psychro-tolerant sub-populations, nor to what extent mesophilic sludges can become psychro-tolerant.

Anaerobic treatment often is very cost-effective in reducing discharge levies combined with the production of reusable energy in the form of biogas. Anaerobic treatment of domestic wastewater can also be very interesting and cost-effective in countries were the priority in discharge control is removal of organic pollutants.

Economy and technologies today largely depend upon energy resources that are not renewable. It is therefore necessary to identify and develop alternative sources of energy that are sustainable.

REFERENCES

Elmitwalli, T. A.; Zandvoort, M. H.; Zeeman, G.; Bruning, H.; and Lettinga, G. (1999). Low temperature treatment of domestic sewage in Upflow Anaerobic Sludge Blanket and Anaerobic Hybrid Reactors. *Water Science Technology*, **39**, (5), 177-185.

Fang, H. H. P., and Zhou, G. M. (1999). Interaction of methanogens and denitrifiers in degradation of phenols. *J. Environ. Eng.*, **125**, (1), 57-63.

Gasparikova E., Kapusta S., Bodik I., Derko J., Kratochvil K. (2005). Evaluation of anaerobic-aerobic wastewater treatment plant operation. *Polish Journal of Environmental Studies*, **14**, (1), 29-34. Guieysse, B., Mattiasson, B. (1999). Fast remediation of coal-tar-related compounds in biofilm bioreactors. *Appl. Microbiol. Biotechnol.* **52**, 600-607.

Kleerebezem, R., Hulshoff Pol, L. W., Lettinga, G. (1999). The role of benzoate in anaerobic degradation of terephthalate. *Biodegradation*, **10**, 63-73.

Lettinga G., Rebac S., Zeeman G. (2001). Challenge of psychrophilic anaerobic wastewater treatment. *Trends in Biotechnology*, **19**, (9), 363-370.

Mrowiec B., Suschka J. (2006). Oczyszczanie ścieków włókienniczych w warunkach beztlenowotlenowych sposobem ciągłym. XIII Conference: Zapobieganie zanieczyszczeniu, przekształcaniu i degradacji środowiska, November 24-25 2005 Szczyrk Poland, *Zeszyty Naukowe. Inżynieria Włókiennicza i Ochrona Środowiska, Akademia Techniczno-Humanistyczna w Bielsku-Białej*, **24**, 240-251.

Navarrete, M., Rodriquez, N., Amils, R., Sanz, J. L. (1999). Effect of 1,1,2,2-tetrachloroethane on the performance of Upflow Anaerobic Sludge Bed (UASB) Reactors. *Water Science Technology*, **40**, 8, 153-160.

Nykova N., Muller T. G., Gyllenberg M., Timmer J. (2002). Quantitative analyses of anaerobic wastewater treatment processes: identifiability and parameter estimation. *Biotechnology and Bioengineering*, **78**, (1), 89-103.

Orozco A. (1997). Pilot and full scale anaerobic treatment of low strength wastewater at sub-optimal temperature (15°C) with a hybrid plug flow reactor. Proceedings of 8th International Conference on Anaerobic Digestion, Sendai, Japan , **2**, 183-191.

Pantea E.V., Romocea T. (2008). Thermophilic anaerobic wastewater treatment. *Protectia Mediului, Analele Universitatii din Oradea*, **8**, 454-458.

Parawira W. (2004). Anaerobic treatment of agricultural residues and wastewater. Application of highrate reactors, *Doctoral Dissertation*, *Department of Biotechnology*, *Lund University*, *Sweden*.

Razo-Flores, E., Lettinga, G., Field, J. A. (1999). Biotransformation and biodegradation of selected nitroaromatics under anaerobic conditions. *Biotechnol. Prog.*, **15**, 3, 358-365.

Rumana R., Somchai D., Kannitha K. (2000). Anaerobic processes. Literature Review, *Water Environment Research*, **72**, (5), 576-656.

Singh L., Alam S.I., Ramana K.V. (1999). Effect of fluctuating temperature regime on psychrophilic anaerobic digestion of nightsoil. *Defence Science Journal*, **49**, (2), 135-140.

Singh, K. S., Viraraghavan, T. (1999). Municipal wastewater treatment by UASB process: Start-up at 20° C and operation at mesophilic and psychrophilic temperatures. *Proc. Water Environ. Fed.* 72_{nd} *Annu. Conf. Exposition*, New Orleans, LA.

Tan N. C., Prenafeta-Boldu F. X., Opsteeg J. L., Lettinga G., Field J. A. (1999). Biodegradation of azo dyes in coculture of anaerobic granular sludge with aerobic aromatics amine degrading enrichment cultures. *Appl. Microbiol.* Biotechnol., **51**, 865-871.

Van Eekert M. H., Stams A. J., Field J. A. (1999). Gratuitous dechlorination of chloroethanes by methanogenic granular sludge Gratuitous dechlorination of chloroethanes by methanogenic granular sludge. *Appl. Microbiol. Biotechnol.*, **51**, 46-52.

Vanderloop S. L, Suidan M. T., Moteleb M. A., Maloney S. W. (1999). Biotransformation of 2,4dinitrotoluene under different electron acceptor conditions. *Water Research*, **33**, (5), 1287-1295.