

THE IMPORTANCE OF ANAEROBIC DIGESTION FOR GLOBAL ENVIRONMENTAL DEVELOPMENT

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The general performance of anaerobic digesters and the diversity of wastes which they can treat have been increasing steadily as a result of new reactor design, operating conditions, or the use of specialised microbial consortia, during the last decade. This paper illustrates examples of prospects and challenges of anaerobic digestion. Anaerobic ammonium oxidation and phosphate fermentation to phosphine are new nutrient removal methods to be coupled to anaerobic digestion. Approaches to recover organic acids and biohydrogen prior to methane fermentation are attracting interest. Solid waste digestion should evolve towards integration of the concepts of energy recovery and Kyoto-agreed CO₂ reduction.

Key Words : anaerobic digestion, biogas, hydrogen, phosphine, biotechnology

1. INTRODUCTION

The range of waste types that can or is being treated via anaerobic digestion processes has, in the recent past, been expanding at a rapid pace due to new reactor designs. For example, the low strength wastewaters can now be treated, even under psychrophilic conditions, by using specific hydraulic conditions in the Expanded Granular Sludge Bed (EGSB) reactor¹. Solid wastes are treated anaerobically with the thermophilic 'high-solids' fermentation technology². New reactor designs permit S⁰ recovery from SO₂-rich waste gases³. Another significant trend of anaerobic digestion technologies is higher treatment efficiency. Higher efficiency is made possible by adequate pre- or post-treatments and by various types of additives or co-substrates that improve sludge retention, composition, metabolic diversity, or resistance toward toxicants^{4,5,6}.

The breakthroughs] dealing with reactor design and operating conditions offer practical solutions to many of the drawbacks that were initially thought to limit the scope of anaerobic digestion, such as high K_m values, instability, temperature requirement, shock loads, and feed composition. There remain,

however, inherent drawbacks to anaerobic digestion technologies, which require further developments in the area of sludge engineering. The granular sludge inocula necessary for the start-up of Upflow Anaerobic Sludge Blanket (UASB) reactors are commercially available throughout the world. Yet, sludge adaptation to new recalcitrant and/or toxic xenobiotics may require several months and up to a year. Moreover, although one can adapt anaerobic reactors to treat "exotic" wastes such as those produced by the terephthalic acid industry, minor incidents such as a short interruption of the food supply can give rise to excessively long (up to several months) periods of low activity⁷.

Engineered anaerobic consortia are therefore needed to expand the catabolic diversity of sludge and shorten the period of sludge adaptation to recalcitrant and toxic substrates. Such consortia were shown to fasten the degradation of PCBs⁸. Another potential benefit associated with the large-scale availability of specialised microbial consortia could be 'biochemical re-routing', i.e. the induction of desirable biochemical pathways as, e.g., the degradation of malodorous primary amines, anaerobic ammonium oxidation, or homoacetogenesis. This re-routing could be based

on the principles of the genetic engineering of microbial species, but is as yet with respect to anaerobic consortia, still in its infancy.

2. SPECIFIC WASTE TYPES

(1) Sewage treatment

Few attempts have been made to explore the variety of physical, chemical, and microbiological processes taking place in the sewer system. The latter can be considered as an anaerobic reactor and certain processes such as the N, P, and S conversions certainly could be optimised. Moreover, totally new approaches could be considered such as the separate handling of the anthropogenic nutrient solution (ANS, i.e. urine) as proposed by Larsen and Gujer⁹⁾.

Phosphine (PH_3) is a very poisonous colourless gas that is prepared by the hydrolysis of phosphide. It is commercially used in grain fumigation and microelectronics. It was established by Eismann et al.¹⁰⁾ that gaseous phosphine inhibits biogas formation during the anaerobic fermentation of swine manure. Phosphine was reported to be present in river and sea sediments as well as in the faeces of human, ruminants and swine¹¹⁾.

The phosphine concentrations in biogas is of the order of 100 mg/m^3 ¹²⁾. To this day it is not clear how this phosphine is formed: chemically, microbiologically or a combination of both. The discovery of phosphine has not yet led to biotechnological applications. Exploration of this potential is warranted.

(2) Industrial wastewaters

A possible recovery product, tied in a scheme of anaerobic digestion is biohydrogen. Hydrogen production by micro-organisms is the final product of reductant disposal from hydrogenase or nitrogenase activity. The primary electron donor for both enzymes is ferredoxin, which received electrons in its turn from the reduced products of glycolysis i.e. NADH or NADPH¹³⁾. Organic matter can in principle be totally converted to biohydrogen (Fig. 1). In a first phase, heterotrophic fermentation (clostridia, facultative anaerobes and even aerobes) bring about the conversion of the biomass to hydrogen and organic acids. Generally, the yield of hydrogen is only 20-30% but rates of up to $4 \text{ L H}_2 \text{ L}_{\text{reactor}}^{-1} \text{ d}^{-1}$ are typically for *Clostridium* species¹⁴⁾. Ueno et al.¹⁵⁾ nicely demonstrated that provided one works at low HRT of 0.5 days, one can pre-treat sugary wastewater in a reliable way to produce a hydrogen rich gas (64% H_2 , 36% CO_2 and 0.1% CH_4). The latter authors also reached 4 L biohydro-

Biotechnical hydrogen production by anaerobic fermentations

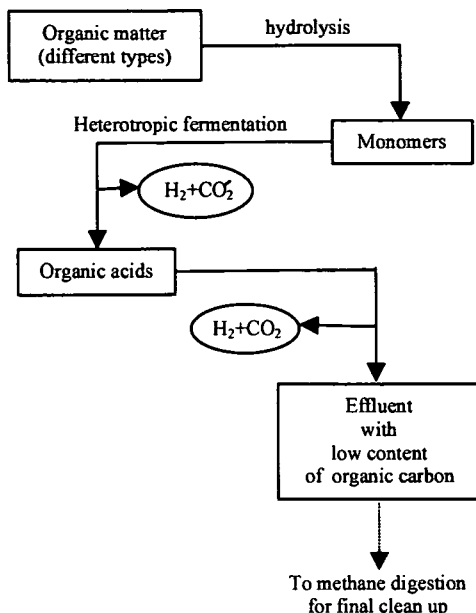


Fig. 1 Biohydrogen production from biomass.

$\text{gen.L}_{\text{reactor}}^{-1} \text{ d}^{-1}$ at a production of 2.5 mol H_2 per mol glucose (the theoretical maximum is $12 \text{ mol H}_2/\text{mol glucose}$). It is conceivable that hyper thermophilic strains and reactor conditions may permit to operate this heterofermentative step in a more effective way¹⁶⁾.

In a second phase, the organics can be photofermented. Photosynthetic bacteria such as *Rhodospseudomonas*, *Rhodobacter* and *Rhodospirillum* can convert the carbohydrates to CO_2 and H_2 . The yield can be 100%, but the rates are limited by the fact that the photosystem of the cells becomes light saturated at low light intensities. Seghers and Verstraete¹⁷⁾ reported e.g. that axenic cultures of the latter bacteria, when grown with glutamate as the nitrogen source converted lactate, acetate and butyrate to H_2 and CO_2 . Conversion rates ranged from 100 to $926 \text{ mL H}_2 \text{ L}_{\text{reactor}}^{-1} \text{ d}^{-1}$ and efficiencies up to 100% were achieved. Yet, the axenic cultures were quite vulnerable to contamination. In this respect, Liessens and Verstraete¹⁸⁾ used selective inhibitors to control the growth of algae, sulphate reducers and methanogens. By applying a combination of chloroxuron (10 mg/L) and cyclo-heximide (10 mg/L) against algae, isohumulones ($30 \text{ bitter units/L}$) and molybdate (0.5

g/L) against sulphate-reducing bacteria and isohumulones and chloroform (10 mg/L) against acetogens and methanogens, photoreactors could be operated in a non-axenic way and continued to produce hydrogen gas at rates depending on the feed quality varying from 333 to 676 ml $H_2 \cdot L_{\text{reactor}}^{-1} \cdot d^{-1}$, for a period of 116 d without apparent interference from other microbial contaminants.

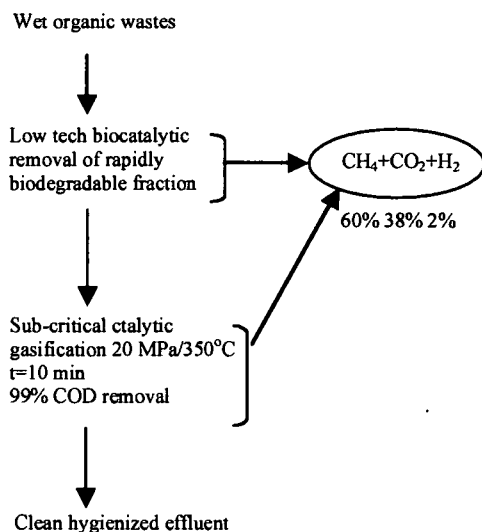
Chlorine chemistry has been in the forefront of public concern, since organochlorine compounds constitute a large group of environmental pollutants that adversely affect the health of humans and wildlife. Today, chlorine is used in a vast range of processes to create thousands of often indispensable products that serve our everyday needs at work, home and play.

In the last decade, the ability of anaerobic microorganisms to reductively dechlorinate some of these chemicals has become more widely recognized. This process has the following advantages: (i) reduction in the degree of chlorination making the product more susceptible to mineralisation by aerobic microorganisms if it is not completely degraded by the anaerobic community, (ii) reduction in toxicity of the parent compound, and (iii) the relative ease to establishment of the appropriate *in situ* conditions conducive of dechlorination in many environments that contain these pollutants. Hence, reductive dechlorination is becoming an important technology to be considered for remediation of chlorinated pollutants. Typical examples of pollutants thus treatable are e.g. chlorinated solvents such as tetrachloroethene (PCE)¹⁹⁾, pentachlorophenol (PCP)^{20,21)} and PCB²²⁾.

(3) Digestion of organic slurries

Proteins are, under anaerobic conditions, incompletely broken down, producing amines, which give rise to foul odours. The challenge is to stimulate degradation pathways of amino acids other than the decarboxylation pathway or, alternatively, to enhance the fermentative degradation of primary amines. H_2 -driven cleavage of primary amine is thermodynamically favourable but has not yet been demonstrated. Reductive conversion of amines to the respective fatty acids has been shown to require unusual isomerisation reactions or unusual supplies such as selenium²³⁾.

Anaerobic digestion does not remove NH_4^+ . To achieve this, an energy-intensive nitrification/denitrification post-treatment is required. A new NH_4^+ removal 'ANAMMOX' pathway has been described for the effluent from methanogenic reactors. It was found that NH_4^+ was oxidised anaerobically to N_2 in the presence of NO_2^- , with a



Advantages

- Water remains solvent
- energy saving
- excellent heat exchange
- easy separation of gas/oil/water
- * No formation of organochlorines
- * $NH_4^+ + NO_3^-$ to N_2 is possible

Disadvantages

- * Catalyst intoxication by Cl^- , SO_4^{2-} , Ca^{2+}
- * High investment cost; yet total costs are of the order of 1 EURO/kg COD removed

Fig. 2 Concept of total methanogenesis by combining two types of thermal catalysis for wet organic wastes.

lab-scale reactor achieving a removal rate of 0.6 kg $N \cdot m^{-3} \cdot d^{-1}$ ²³⁾. The full-scale implementation of this process would significantly enlarge the future of anaerobic digestion.

Another potential development is the OLAND process, i.e. Oxygen Limited Autotrophic Nitrification and Denitrification. In this process, conventional autotrophic nitrifiers are under oxygen limited conditions capable to oxidise part of the NO_3^- with part of the NO_2^- already produced²⁴⁾. This process could if further developed, have the advantage that the biocatalyst is easily produced on a large scale.

More complete conversion of the organic matter has been investigated by Elliot et al.²⁵⁾. The catalytic gasification of organics is demonstrated at the engineering development scale as an option for chemical manufacturing wastewater cleanup. A high-pressure of about 20 MPa (200 bar) and high temperature (about 350°C) liquid water-processing environment was used to treat wastewaters. Organic by-products from chemical manufacturing were converted primarily to methane and carbon dioxide

in the presence of a fixed bed of nickel/ruthenium catalyst. This process has potential to be used, with the appropriate catalyst, to clean up wastewater and recover waste organics as useful fuel gas. Subsequently, biotechnological gasification could deal with the remaining fraction. Alternatively, the process of sub-critical gasification could be applied after normal digestion and be set to completely remove the remaining organics and moreover achieve a full hygienisation (Fig. 2).

(4) Municipal solid waste (MSW) treatment

The remaining digested residue can be considered as quite stable organic carbon which upon proper storage conditions (e.g., water logged or acidic soils or even controlled landfills) will have a very slow turnover on the order of at least several decades. Hence, proper technology and land planning can make the end product of the biowaste digestion a form of sequestered carbon. This opens new perspectives for anaerobic digestion in the framework of the decreasing global greenhouse effect²⁷.

(5) Anaerobic treatment of soils and sediments

At present, it has become clear that there is a diverse array of anaerobic technologies implementable to clean up soils and sediments. Interesting examples are the removal of organochlorines (PCB) in river sediments by seeding of the latter with specially cultivated anaerobic granules⁸. Another domain is the anaerobic binding of nitro-aromatics such as TNT into soil humus complies. Indeed, by simply mixing the soil with protein and compost, blocking the influx of air and oxygen, TNT is microbiologically converted to a non-toxic Meisenheimer-complex in a matter of days. Subsequently, the thus treated soil can be opened up to air, sown with grass and be re-integrated in normal land-use without any risk of re-appearance of free TNT or toxicity²⁸.

A most remarkable paper by the group of Widdel²⁹ demonstrates that in soils and sediments, in contrast to what was known thus far, also hydrocarbons such as hexadecane are converted to methane and carbon dioxide by microorganisms. The authors demonstrate that the reaction is exergonic: Hexadecane + water \rightarrow CH₄ + CO₂. $\Delta G = -1596$ kJ per mol. The process proceeds in several steps. First, there is acetogenesis; the latter is possible when the pH₂ remains below 2 Pa. Then the acetate and hydrogen are converted to methane. The authors identified by 16S ribosomal RNA gene cloning the causal bacteria as delta subclass of the *Proteobacteria* and as *Archaea*. This finding can explain why in deeper soils there are so many

bacteria; they thrive on geological oil deposits. This finding also provides the challenge of in the future expanding oil recovery from depleted oil reservoirs by anaerobic hydrocarbon biomethanation.

(6) Removal and recovery of SO_x from waste gases

At present, there are developments to scrub flue gases from full-scale power plants to treat the waters by means of anaerobic conversion techniques. Yet, the high costs of the electron donor (hydrogen) and the low value of the recovered product (S-powder) restrict the application of this process.

The overall public perception of incineration is very critical. Indeed, emissions of dioxines and related polychlorinated organics are very much feared. The overall monitoring and control for these compounds must be very rigorous because levels of 0.1 ng per m³ of gaseous effluent have to be detected. Such analyses are moreover very costly (5000 EURO/analysis) because a variety of different organics and isomers of dioxines have to be examined for. The major danger from the current approach of chemical analysis is that one looks for 'specific' compounds described in the literature. Hence, unexpected organochlorines might go unnoticed. In view of the fact that anaerobic digestion apparently can achieve broad-range dechlorination, it appears interesting to explore the possibility of sampling wastegases, subjecting the sample to general or specific anaerobic dechlorination, and then to monitor for chloride release. Any signal of such occurrence would be a valuable element in overall risk assessment.

3. OUTLOOK

(1) Considering anaerobic digestion in all its diversity and potentials, one should not overlook the most preponderant anaerobic digestion processes which are occurring in all multicellular structures consuming organic components. Indeed, as soon as oxygen has to diffuse above some 100 μ m layer, there is already a niche for the anaerobes. Hence, higher organisms ranging from the meso- to the macrobiota strongly depend on anaerobic microbial processes³⁰. There is a formidable need to better understand and to possibly better engineer respectively use these mixed microbial populations.

(2) Anaerobic biocatalysis offers a possibility to live (more) comfortable with the variety of organochlorine chemicals used for commodity purposes.

(3) Anaerobic digestion is in terms of energy production relying on organic carbon. The latter

originates in principle from primary production, i.e. plant photosynthesis in recent or in geological time scales. Yet, a direct tapping of photosynthetate via anaerobic microbial metabolism is possible. Indeed, Feijtel et al.³¹⁾ demonstrated that various legumes can be brought to hydrogen production at the order of 3 to 15 ml per day per g plant dry weight over prolonged periods of time. Such activities correspond for 10 ton biomass dry matter per ha with a production potential of 30 to 150 m³ of hydrogen gas per day. The coupling of plant photosynthesis to direct anaerobic fermentation of the photosynthetate to hydrogen remains a startling potential to explore.

(4) In view of increasing need to respect the 1997 Kyoto agreements on CO₂ emission, it is obvious that anaerobic digestion deserves to be considered as a key process. First, all energy recovered by anaerobic digestion corresponds with fossil fuel saved. Secondly, by means of controlled biomethanation, disperse production and release to the atmosphere of the strong greenhouse-gas methane is avoided. Moreover, during digestion, in view of the high CO₂ partial pressure, a considerable amount of the latter gas dissolves in the water phase and often precipitates as CaCO₃.³²⁾ Anaerobic digestion can be set to act as a CO₂-sink. Finally, the organics leaving the organic digester qualify as slowly degradable organic carbon. The latter carbon, call it humus or sequestered carbon, is of intrinsic value for the blue planet and therefore deserves to be fully re-appraised in the context of the above mentioned agreements.

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地球環境の発展に対する嫌気性消化の重要性

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嫌気性消化槽の一般的性能とそれらが処理可能な廃棄物の多様性は、過去 10 年間、新しい反応槽の設計、操作条件あるいは特殊な微生物群の使用の結果として、確実に向上してきている。本論文は、嫌気性消化の展望と可能性の実例について示すものである。嫌気性アンモニア酸化およびリン化水素を生成するリン酸発酵のような新しい栄養塩除去気性消化に付加される必要がある。メタン発酵に先立って有機酸や水素を回収するアプローチが関心を引き起こしつつある。有機性固形廃棄物の嫌気性消化は、エネルギー回収と京都議定書の二酸化炭素の削減の考え方を統合する方向に発展させるべきである。