Anaerobic Industrial Wastewater Treatment; Perspectives for Closing Water and Resource Cycles.

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Introduction

Decades of developments and implementations in the field of high-rate anaerobic wastewater treatment have put the technology at a competitive level. With respect to sustainability and cost-effectiveness, anaerobic treatment has a much better score than many alternatives. Particularly, the energy conservation aspect, i.e. avoiding the loss of energy for destruction of organic matter, while energy is reclaimed from the organic waste constituents in the form of biogas, was an important driving force in the development of such systems. At present, other advantages such as the extremely low production of excess sludge and the system compactness are important selection criteria. Compared to conventional aerobic treatment systems, the most striking advantages of high-rate anaerobic wastewater treatment are:

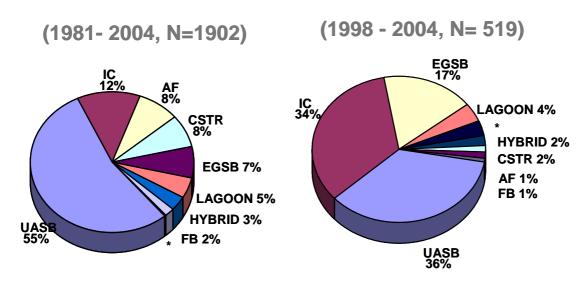
- 1. Reduction of excess sludge production up to 90%
- 2. Excess sludge has a market value
- 3. No use of fossil fuels for treatment, saving \pm 1 kWh/kg COD removed
- 4. Production of energy in the form of methane gas at a theoretical value of 3.8 kWh/kg COD removed (assuming 100% treatment efficiency, and 100% conversion to electricity).
- 5. Up to 90% reduction in space requirement
- 6. High applicable COD loading rates reaching 20-35 kg COD.m⁻³ reactor volume.day⁻¹
- 7. No or very little use of chemicals
- 8. Rapid start-up (< 1 week), using granular anaerobic sludge as seed material
- 9. Anaerobic sludge can be stored unfed; reactors can be operated during agricultural campaigns only (e.g. 4 months per year in the sugar industry)
- 10. Plain technology with high treatment efficiencies
- 11. High rate systems facilitate water recycling in factories (towards closed loops)

The ever rising energy prices and the overall concern on global warming puts again the attention on the traditional advantages as mentioned under points 3 and 4. On the other hand, for economic reasons, point 1 is more and more decisive in choosing for anaerobic high-rate systems, particularly when incineration of excess sludge /biowaste is the only option at costs of 400-450 € / ton. The compactness of the system can be illustrated by a full-scale example where, an anaerobic reactor with a 6 m diameter and a height of 25 m, can treat up to 25 tons of COD daily, producing 7000 m³ methane (assuming 80% CH₄ recovery), with a usable energy potential of 1-1.5 MW at an assumed 30-50% energy conversion efficiency. The produced sludge, which is less than 1 ton/day in the above example, is not a waste product, but is marketed as seed sludge for new reactors. Such compactness makes the system suitable for implementation on the industry

premises or sometimes even inside the factory buildings. The latter is of particular interest in densely populated areas and for those industries aiming to use anaerobic treatment as the first step in a treatment for reclaiming process water.

Reactor Technology

Key to the worldwide interest in anaerobic treatment is the development of high-rate reactor systems allowing for an extreme uncoupling of the solid retention time from the hydraulic retention time. This uncoupling can be achieved by various ways of sludge retention, such as sedimentation, immobilization on a fixed matrix or moving carrier material, and granulation High-rate systems can be divided in suspended growth and attached-growth processes including expanded/fluidized bed reactors and fixed-film processes. In suspended growth systems bacterial sludge is present as flocs or granules, whereas in attached growth systems micro-organisms are adhered to a moving a fixed medium. In an expanded/fluidized bed reactor, suspended carrier media (such as sand or porous inorganic particles) are used to develop an attached film. Fixed film processes rely on the bacteria attaching to a fixed media, like rocks, plastic rings, modular cross-flow media, etc. Some systems, such as the anaerobic hybrid process, combine suspended-and attached-growth processes in a single reactor to utilize the advantages of both types of biomass.



Super high rate based: 21% Super high rate based: 52% Granular sludge based: 76% Granular sludge based: 88%

Figure 1. Implemented anaerobic technologies for industrial wastewater pictured for the period 1981-2004 (left) and the period 1998-2004 (right). UASB: upflow anaerobic sludge blanket; EGSB: expanded granular sludge bed; Hybrid: combined system with sludge bed at the bottom section and a filter in top; IC: internal circulation reactor; type of EGSB system with biogas-driven hydrodynamics AF: anaerobic filter; FB: fluidized bed reactor; CSTR: continuous stirred tank reactor.

The upflow anaerobic sludge bed (UASB) reactor technology is considered a breakthrough in the development and application of anaerobic high-rate technology for industrial wastewater. After the initial first trials in the seventies, the system became rapidly popular in particularly the agrofood sector. The worldwide applied technologies, implemented between 1980 and 2005 are depicted in Figure 1. The right graph shows the relative number of the same technologies in the time frame 1998-2005. Figure 1 indicates that the granular sludge based technologies (UASB, IC. EGSB) dominated the market in the passed decades. This is confirmed by the newly installed systems in the most recent period. Interestingly, competitive technologies like anaerobic filters of hybrid systems were not able to be consolidating in the market. But also the super high rate technology of Fluidized Bed (FB) almost vanished, most likely due to technology problems in various full scale systems. An interesting observation in Figure 1 is the increasing popularity of the super high rate reactors EGSB and IC. At present the major Dutch constructors (Pagues and Biothane) sell more IC and EGSB reactors than conventional UASB systems. Most likely, the vast growing experiences and the higher availability of the indispensable seed material for these systems, i.e. methanogenic granular sludge, have lead to the success of the super high-rate reactors.

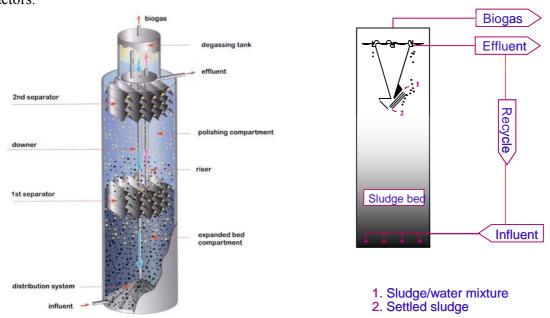


Figure 2. Paques IC reactor (left) and Biothane EGSB reactor (right), inoculated with granular sludge. Applicable loading rates: 15-45 kg COD/m³.day.

In addition to the anaerobic reactor technology, there is an increasing experience in pre- and post treatment systems, safe-guarding stable operation and guaranteeing the contracted effluent discharge criteria. Effluents containing fatty, oily and greasy compounds (FOG), such as dairy, are in some cases pre-treated to such extent that all FOG and suspended solids are removed from the wastewater prior to feeding it to the super high-rate system. However, in other situations, the resulting treatment train becomes so complex that decisions are made to apply conventional CSTR systems that treat the entire flow in a single step. Even with relatively simple wastewater flows like those coming from the beer brewery process, adequate pre- and post- treatment is essential for the success of the system. In some cases the actual anaerobic reactor volume is only 20-25% of the totally installed wastewater treatment volume for brewery effluents. Novel

developments in anaerobic reactor technology are directed to integrated multifunctional bioreactors, such as sequencing batch reactors (SBR) and a simplification of the treatment trains.

End-of-the-pipe-treatment

Recent surveys showed a total registered number of over 2000 anaerobic reactor systems for the end-of-the-pipe treatment of various types of industrial wastewater worldwide. This number is much higher when all reactor systems are added that are constructed by local suppliers. Generally, anaerobic high-rate treatment is applied for wastewaters coming from food processing industries such as, sugar, potato, distilleries, wineries, fruit juices, starch, beer and soft drinks, etc. Table 1 gives an overview of application in the most important industrial sectors.

Table 1. Application of anaerobic technology to industrial wastewater

Industrial sector	Wastewater			
Agro-food industry	Sugar, potato, starch, yeast, pectin, citric acid, cannery, confectionary			
	fruit, vegetables, dairy, bakery			
Beverage	Beer, malting, soft drinks, wine, fruit juices, coffee			
Alcohol distillery	Can juice, cane molasses, beet molasses, grape wine, grain, fruit			
Pulp & paper industry	Recycle paper, mechanical pulp, NSSC, sulphite pulp, straw, bagasse			
Miscellaneous	Chemical, pharmaceutical, sludge liquor, landfill leachate, acid mine			
	water, municipal sewage			

The number of anaerobic applications in the non-food sector is rapidly growing. Common examples are the paper mills and the chemical wastewaters, such as those containing formaldehyde, benzaldehydes, terephthalates, etc. Especially the chemical industries are difficult to enter with anaerobic technology, owing to the general prejudices against biological treatment in general and anaerobic treatment in particular. However, most of the reactors listed in Table 2 perform better than expected and the number of chemical applications is steadily growing.

Table 2. Anaerobic treatment in chemical industries.

Wastewater	Reactor type	Loading (ton COD/day)	COD removal	Number of reactors
Poly ethylene therephthalate	UASB,	1.7 - 6	N.A.	2
(PET)	Hybrid			
Purified therephthalic acid	UASB, IC	6 - 81	75 – 85%	9
(PTA)	EGSB,			
	Hybrid, UAF			
Pure Chemicals (formaldehyde,	EGSB,	2 -10	60 - 90%	8
alcohols, organic acids, amines,	Hybrid			
etc.)	,			
Others (Metallurgic, soaps, pH	UASB, UAF,	2 - 40	75 – 95%	5
liquor, dyestuff, plastics, etc.)	EGSB, IC,			
	Hybrid			

N A · not available

With regard to the chemical compounds it is of interest to mention that certain compounds, such as poly chloro aromatics and poly nitro aromatics as well as the azo-dye linkages can only be degraded when a reducing (anaerobic) step is introduced in the treatment line. Anaerobics are then complementary to aerobics for achieving full treatment. With the ongoing research and full-scale applications in chemical industries the application potential of anaerobic treatment in this sector is rapidly growing. As such, anaerobic high-rate treatment has become a matured technology.

Despite the many advantages of anaerobic wastewater treatment, the global market share of anaerobic reactors in the total treatment capacity is still very low. The latter can be ascribed to a general lack of knowledge, the 'fear of the unknown', prejudice, and a possible bad image in the past. However, the fact that in densely populated countries like the Netherlands, the major part of the agro-food processing wastewater is treated by anaerobic reactor systems indicates that these prejudices are based on perception rather than on verifiable facts. Encouraging, in this respect, is that companies that have selected an anaerobic system for effluent treatment, which has been constructed by recognized suppliers, will stick to the technology for all factories belonging to the company. A good example is the brewery and beverage sector.

Zero-effluent-discharge

Reduction in industrial water consumption is generally achieved by good housekeeping and redesigning the process water loops. Benefits to the companies include cost savings resulting from e.g. less tax, less energy consumption, and less costs for wastewater treatment. Also environmental improvement (green label), increased throughput, and risk and liability reduction may result from optimized process water cycles. In clean industrial production processes, water use reduction is essential.

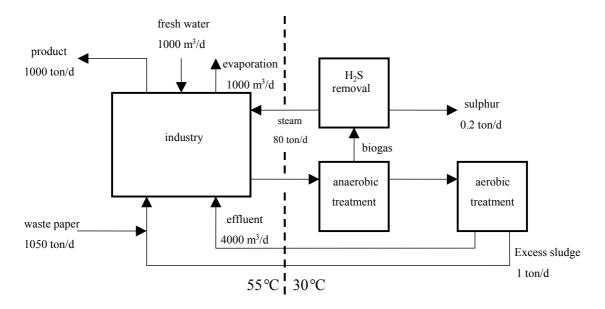


Figure 3. 'Zero-discharge' cardboard and packaging industry of the Smurfit Kappa Group in Zülpich, Germany.

After good housekeeping, a generally warm and more concentrated process water stream is left that can be more easily treated by anaerobic high-rate reactors. Particularly when the treated warm effluent is recovered for reuse, concomitant energy conservation is experienced that goes far beyond the energy production from the anaerobic system itself. An interesting example is the pulp and paper industry where 'zero-effluent-discharge' already can be achieved in the cardboard and packaging paper manufacturers. Compared to an open system that consumes 10 m³ of water per ton of paper produced, the closed system saves 1045 MJ.ton⁻¹, assuming a fresh water temperature of 10°C and an effluent of 35°C. The surplus energy of the anaerobic system adds another 200 MJ.ton⁻¹, bringing down the energy costs considerably. In this case, the role of the anaerobic reactor is more than a treatment system: its cost-effectiveness leads to a more rapid implementation of the zero-discharge approach with all its benefits for the industry. With regard to the closed paper mill, it must be noted that in addition to COD removal, the anaerobic reactor also eliminates sulphate as sulphide from the process water cycle, reducing the smell inside the factory. And in fact, the anaerobic reactor is the only place for an efficient sulphur bleed at zero costs. The anaerobic-aerobic treatment concept in closed water loops is already applied at various full-scale situations (Figure 3).

Although not yet feasible in many industries, the zero-discharge approach is now being researched for various types of industries (e.g. white paper, textile). Also here, anaerobic reactor systems can be considered as a crucial step in closing the cycles. The next step will be the agroindustrial production lines that are subjected to more stringent hygienic standards. However, reuse of treated water for low-grade applications, such as washing and transportation has been applied for several decades (Figure 4).

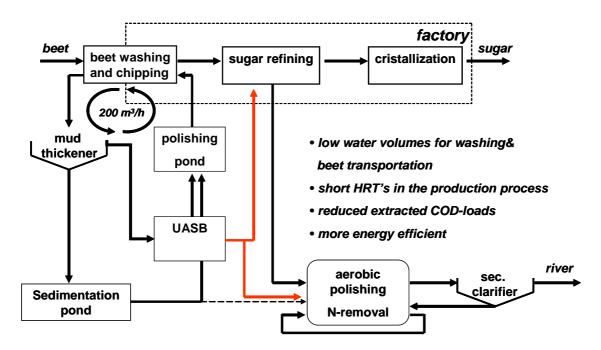


Figure 4. Implementing anaerobic high-rate technology for optimising internal water loops in sugar beet processing industries.

Anaerobic treatment using the sulfur cycle: recovery of inorganic resources

A complete other field of application of anaerobic treatment is the use of the sulphur cycle in environmental technology. Sulphur has the interesting property to accept or donate a different number of electrons and thus can be reduced or (partially) oxidised, depending on the reactor conditions. SO_2 - containing flue gas can be transformed in S-free gas by a sequence of an anaerobic and micro-aerophilic reactor. While in the first reactor sulphide is produced, in the latter biological sulphur is formed together with alkaline (OH) that on its turn is reused to scrub the SO_2 from the flue gas. The similar strategy is also used for the desulphurization of biogas from anaerobic reactors where the H_2S is entrapped in a slightly alkaline scrubbing liquid and the alkalinity is recovered in the subsequent sulphide oxidation step, according to:

$$H_2Sgas + OH^- \rightarrow HS^-aq + H2O$$

 $HS^- + \frac{1}{2}O_2 \rightarrow S^0 + OH^-$

The resulting technology does not consume chemicals, while the produced biological sulphur can be marketed (Figure 5).

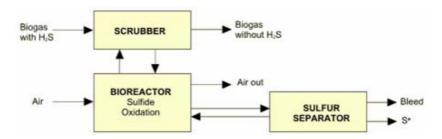


Figure 4. Biogas desulphurization unit combining an alkaline scrubber with a partial oxidation of HS and alkalinity recovery.

At present the technology is also used for natural gas desulphurization at large scale, e.g. at the AMOC natural gas refinery in Alexandria, Egypt, producing 50 ton elemental sulphur per day (Paques, personal communication). The S-cycle can also be used to (selectively) recover heavy metals from wastewater streams (Figure 5). An interesting full-scale example recovers both the waste zinc and the sulphur to be reused as raw oar and sulphuric acid in the metal industry. Lens & Hulshoff Pol (2000) made an overview of the current state on the S-technology.

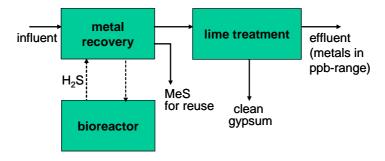


Figure 5. Biological metal recovery applying the S-cycle in anaerobic technology.