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FULL SCALE EXPERIENCES WITH ANAEROBIC PRE-TREATMENT OF WASTEWATER IN THE FOOD AND BEVERAGE INDUSTRY IN GERMANY

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ABSTRACT

In Germany, there are currently 106 full-scale anaerobic treatment plants treating industrial wastewater. This paper describes the operational experiences of several industries (beet sugar, starch, pectin, brewery, distillery, vegetable) which undertake anaerobic wastewater treatment, with particular emphasis on specific wastewater problems and their solutions. Also presented are experiences of the handling of high nitrate concentrations, with the treatment of mixtures of industrial wastewater from different origins, with the chance to prevent the emergence of lime, magnesium ammonium phosphate (MAP) or aluminium precipitation.

This paper deals with the first municipal wastewater treatment plant combined with a separate anaerobic stage to treat a wastewater mixture of several small factories. One particular asset of this plant is the construction of the acidification tank: using the "teapot effect" to enrich the solid material in the centre of the bottom, the solids can be taken from the bottom of the tank and pumped to the municipal sludge digester. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Acidification combined with solids removal; food industry, beet sugar, starch, pectin, brewery, distillery, mixtures of industrial wastewater; high rate denitrification; lime precipitation; MAP precipitation.

INTRODUCTION

Currently (January 1996), there are 106 full scale anaerobic treatment plants in Germany for industrial wastewaters (see Table 1). Thirty-nine plants are working with contact process, 26 plants sport sludge blanket reactors, and 30 plants work with fixed-film methane reactors. The other 11 plants have completely stirred tank reactors (CSTR), self-made constructions, hybrid reactors, or unspecified reactor types.

The ISAH (Institute of Sanitary Engineering and Waste Management) has been involved in the research, design, or operation at 24 of these plants. The experiences were made with all different kinds of reactor systems. The main subject of this paper will be the description of typical problems and their solutions in different industries. An overview is given below (see Table 2).

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Table 1. Anaerobic wastewater treatment plants in Germany

industry	number	type of methane reactor			
		contact	UASB	fixed-film	others
sugar	27	22	3	0	2
paper	15	1	11	2	1
alcohol	9	1	2	5	1
animal meal	9	0	0	9	0
cellulosis	8	5	1	1	1
brewery	8	0	4	4	0
starch	5	2	0	3	0
potato processing	4	1	0	1	2
fruit and vegetable	3	2	0	1	0
soft drink bottling	3	0	1	2	0
yeast	3	2	1	0	0
fruit juice	2	1	1	0	0
abattoire	2	0	0	0	2
dairy	1	0	1	0	0
malting house	1	0	0	1	0
pectin	1	1	0	0	0
citric acid	1	1	0	0	0
tannery	1	0	0	0	1
fibre board	1	0	0	0	1
others	2	0	1	1	0
sum	106	39	26	30	11

Table 2. Several industries with their special problems and solutions

industry	special problem	solution
beet sugar factories	lime precipitation	cyclone
	pH lower than 5 in the pond system	lowering the pH in the circuit system
potato and wheat starch industry	precipitation of MAP (magnesium ammonium phosphate)	pH-regulation
pectin factories	high nitrate concentrations over 1000 mg NO_3-N/l	denitrification stage before methane reactor
breweries	considerable pH variations	equalising tanks, pH-regulation
	kieselguhre contents	treatment together with municipal sludge
	aluminium precipitation in the acidification stage	settling tank
distilleries (alcohol production from molasses slops)	discontinuous production	equalising tanks and pH regulation
anaerobic/aerobic treatment	carbon/nitrogen relation bulking sludge	bypassing the anaerobic stage, pre-treatment
anaerobic pre-treatment of wastewater from different industries in one plant	different small factories with high loaded wastewater and campaign processing	anaerobic pre-treatment of the waste-water mixture of a brewery, two vegetable and one fish processing factory at the municipal sewage treatment plant

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BEET SUGAR FACTORIES

The sugar industry was one of the first industries in Germany to carry out anaerobic wastewater treatment. The first methane reactor for a sugar factory started to work in 1979. Today, over 50% of the sugar factories in Germany clean their wastewater anaerobic/aerobically.

Due to increasing awareness of water consumption and the resulting closing of water recirculation systems, the discharged wastewater could be reduced from 40 m^3/t beet sugar to about 0.5 m^3/t by driving a nearly closed circuit. To keep the water bacteriologically as clean as possible, the pH of the water is adjusted with lime to a pH level of at least 11, an exclusive asset of the German sugar industry. As a result of the lime dosage, the calcium concentrations in the water range from 800 to 2500 mg/l Ca^{++}, depending on the factory. Lime precipitation and caking cause problems in all steps of wastewater clarification. Lime precipitation prevent the use of fixed-film reactors. Lamella separators used in methane reactors must be cleaned approximately every three years; moreover, only coarse bubble aeration systems can be used in the aerobic stages. Lime precipitation can be seen especially in the inorganic part of the suspended solids (SS). In anaerobic treatment plants running with a pH of about 7.2, it is normal that only 28 to 50% of the SS is organic, this means only 28-50% are volatile suspended solids (VSS) at COD sludge loading rates of 0.7 to 1.1 kg COD/(kg VSS.d). The experiences of the ISAH have shown that it is possible to separate large parts of precipitated lime by injecting a hydrocyclone (Sulzer, Butzbach, FRG) into the recirculation pipe of anaerobic or aerobic systems.

The same positive effect could be observed when hydrocyclones were used in the anaerobic treatment of wastewater in paper factories which use waste paper as raw material.

Another problem of the high pH in the circuit is the sudden drop in the storage ponds based on acidification (cf. Figure 1). In full scale experiences it was found that when the pH in the circulation system in the factory is higher than 11, the pH in the ponds drops to a level of 5 and below, which causes problems in the following anaerobic stage. Keeping the pH in the circulation system of the factory in a range of 8-11, the pH in the ponds dropped only to values of 5.5 to 6.5. 2,000 to 6,000 mg/l of lactic acid could be analysed in the effluent of the ponds; these amounts were converted into acetic, propionic and butyric acids in nearly the same proportion in the following acidification with a hydraulic retention time (HRT) of 14 h. Under these conditions there were no more problems in running the anaerobic contact process.

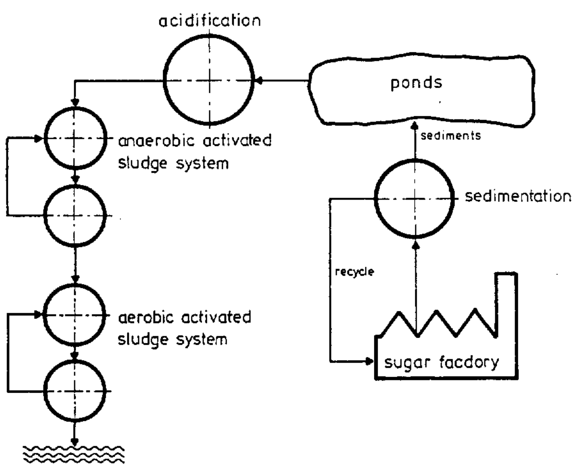

Figure 1. Flow diagram of a water system as used in German beet sugar factories.

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POTATO AND WHEAT STARCH INDUSTRY

Wastewater of wheat and potato starch factories contains high concentrations of magnesium, nitrogen and phosphate (Table 3). Magnesium, ammonium and phosphate form the slightly soluble salt $MgNH_4PO_4.6H_2O$ *magnesium ammonium phosphate* (MAP). The formation depends on several factors, such as the concentrations of the elements, pH, temperature and turbulence (Borgerding, 1972). In methane reactors, on the one hand the organic nitrogen is changed into ammonium by ammonification, and on the other hand the pH rises by degradation of the organic acids formed in the acidification stage. This causes the problem that, especially at places with a higher turbulence (pumps and pipes) or at places with a momentary ascent in pH (degassing of CO_2), MAP precipitation will occur.

Table 3 shows the ammonium, phosphate and magnesium concentrations in the effluent of methane reactors used in a potato and wheat starch factory, respectively. The concentration in the original wastewater is referred to as C_0, the concentration in the same water after pH adjustment with NaOH is called C_e. By raising the pH in the batch test, MAP precipitation in a N:P:Mg mol ratio of 1:1.4:1.0 occurs without any addition of magnesium or other chemicals.

Table 3. Ammonium, phosphate and magnesium concentrations in the effluent of methane reactors of starch factories before and after pH-regulation

Parameter	potato starch factory			wheat starch factory		
	C_o	C_e	elimination	C_o	C_e	elimination
	mg/l	mg/l	%	mg/l	mg/l	%
NH_4^+-N	436	393	27	641	146	77
PO_4^{3-}-P	140	31	78	84	2.3	97
Mg	87	9	90			
pH	6.9	10			9.2	
N:P:Mg mol ratio	1:0.14:0.12			1:0.9:1.5		

Even at a pH of 7.0, MAP salt does emerge. To protect some fixed-film reactors running in a full scale anaerobic treatment plant of a potato starch factory (Seyfried and Austermann-Haun, 1990) against MAP precipitations throughout the campaign, the pH in the methane reactor is kept at exactly 6.9 with hydrochloric acid.

If a UASB reactor is used to treat the wastewater of a potato starch factory, MAP precipitation will happen; this, however, is tolerable. In such cases, it is necessary to dose chemicals to prevent coating in pumps and pipes. The MAP crystals are flushed out of the methane reactor and separated in the clarifier of the aerobic stage. When the same agents were dosed into a fixed-film methane reactor instead of hydrochloric acid, there occurred considerable MAP precipitation on the PE support material.

PECTIN FACTORIES

Some kinds of industrial wastewater with high organic loads are usually highly loaded with nitrate at the same time, which is due to the usage of nitric (azotic) acid in the production. In a full scale methane reactor (3500 m^3) of a pectin factory designed as a contact process, the sporadic denitrification or nitrate ammonification led to problems with the COD elimination. As a consequence, the COD in the effluent of the methane reactor varied between 1,000 and 8,000 mg/l (Seyfried and Austermann-Haun, 1990).

Based on the analysis results (Bode, 1985), the existing anaerobic treatment process was adjusted by a high-grade denitrification stage, consisting of two denitrification tanks (120 m^3 each) and a special separator. This separator (175 m^3) is a combination of a flotation tank and a sedimentation tank: the sludge sometimes floats and sometimes settles depending on the amount of residual NO_3. The separated biomass is recycled into the first denitrification tank. This process is exothermic; it is effected at temperatures between 43 and 55°C by an inflow water temperature of about 30°C. The water has to be cooled down after the high rate

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denitrification to keep a temperature of about 37°C in the methane reactor. Table 4 gives some current data about the actual load and operating results of the full scale high-grade denitrification.

Table 4. Load and operating results of a full scale high rate denitrification

Parameter	dimension	value
Influent data:		
COD	mg/l	15,000-22,000
NO_3-N	mg/l	1,280-2,990
pH	--	1.24-11.4
Daily COD load	kg COD/d	11,600
Daily NO_3-N load	kg NO_3-N/d	1,378
Loading		
NO_3-N space loading rate	kg NO_3-N/(kg $m^3 \cdot d$)	5.74
Sludge content	g/l	11.6
NO_3-N sludge loading rate	kg NO_3-N/(kg SS $\cdot$d)	0.49
Effluent data:		
COD	mg/l	10,285
NO_3-N	mg/l	20
NH_4-N	mg/l	400

Normally, the NO_3-N effluent concentration of the first denitrification tank is below 10 mg/l. The second tank is necessary to prevent extreme values. 45% of the COD is removed by denitrification.

BREWERIES

Over a period of one year, semi-technical pilot plants using fixed-film reactors and a UASB-reactor were operated in parallel at a brewery (Birkenstock, 1991). The best results were obtained with a UASB-reactor with a COD removal efficiency of more than 80% at space loading rates between 3.5 and 14.9 kg COD/(m^3.d), with an average ratio of 6.7 kg COD/(m^3.d). The plant proved to be environmentally more sound and more efficient than a high rate aerobic pre-treatment plant. It became apparent that to reach these very favourable results, the acidification and equalisation, the pH-regulation and separation of aluminium precipitations are extraordinarily important.

A high pH level and high pH variations between 7.1 and 11 (mostly about 10) in the influent of the acidification tank caused some problems. Even at hydraulic retention times of 20 to 27 hours, the pH in the effluent of the acidification tank varied between 6.5 and 10.3. The methane reactors operated in a much more stable fashion as soon as the pH in the acidification tank was dropped to a level of about 7 with hydrochloric acid.

The raw brewery wastewater (mixture of all wastewater streams) included aluminium at concentrations of about 12 mg/l as a result of the metal-coloured bottleneck wrappers which in Germany are used for premium beers. When the pH dropped in the acidification tank, aluminium precipitation took place. It was found that these very settleable aluminium precipitations have to be removed by a settling tank because otherwise the granulated sludge in the UASB-reactor would be covered with the aluminium sludge within a few days. In the effluent of the clarifier, the aluminium concentrations were below 1.6 mg/l. The aluminium content of the separated sludge was about 20 g/kg SS.

Because there was insufficient acidification, it was decided to switch to another acidification tank after the clarifier. It was found that it was necessary to regulate the pH to a constant level of 7 in the influent of the UASB-reactor.

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As a result of these analyses, the optimal hydraulic retention times were found to be 21 hours in the equalisation and acidification tank, 2.5 h in the settling tank, 21 h in the acidification tank I, and 4.8 h in the second acidification tank and at least 5 h in the UASB-reactor.

The design of the full scale plant was based on the experiences presented. The full scale plant, running data, and details of operation were presented by Austermann-Haun and Rosenwinkel (1997).

Kieselguhre is a filter aid which is used in most German breweries for the beer filtration. Kieselguhre contains about 11-12% organic matter and 8% protein stemming from yeast and albumen particles. There are several options to deal with the kieselguhre: in agriculture as fertiliser, deposition and recycling. The co-fermentation in a municipal sludge digester has successfully been practised over a couple of years. The kieselguhre is pumped into the primary clarifier and then pumped into the sludge digester together with the primary sludge.

DISTILLERY

One distillery at Hannover, which produces alcohol from beet sugar molasses, runs the fermentation in a continuous mode, in contrast to the batch fermentation which is usually used. The molasses slops are thickened to vinasse in an evaporator. Because of this process, the concentration of calcium is as low as in molasses slops. For that reason, it is possible to sell the vinasse which is used as a by-product in the animal food industry. Thus, it was possible to decrease the specific sewage flow from 3 m^3/t molasses to 0.9 m^3/t.

The condensate of the evaporator is the wastewater which has to be treated because the city of Hannover forbids to discharge wastewater with a COD over 2,000 mg/l into the municipal sewer system. For that reason the wastewater is treated anaerobically/aerobically.

Limits for indirect discharging: COD $\leq$ 2,000 mg/l, $PO_4 \leq$ 100 mg/l, $NO_2 \leq$ 20 mg/l, NH_4 and $NH_3 \leq$ 100 mg/l.

Wastewater situation: daily flow 100 m^3/d, COD 12,000 to 20,000 mg/l; pH $\approx$ 3.2. Depending on the operation of the evaporator, there is normally a lack in nitrogen, phosphorus and trace elements. The wastewater mainly consists of organic acids and ethanol. For that reason, it is not necessary to have an acidification tank in the plant.

The distillery mainly runs periodically from autumn to spring, as the molasses is bought from the beet sugar factories which work from September to December. From the first day of operation onwards, there is the full amount of wastewater flow. This situation requires a storage tank.

Wastewater treatment plant: storage tank 2,500 m^3, equalising tank with pH-regulation and dosage of nutrient salts 100 m^3; two fixed- film methane reactors running in parallel, each 140 m^3, 100 m^3 of the volume filled with a PE fixed-film material, intermediate clarifier 13 m^3 (diameter 2.6 m), two activated sludge tanks with a total volume of 48 m3, a final clarifier 7.6 m^3 (diameter 2.5 m) and a biofilter to treat the air of the storage and equalising tank.

The anaerobic/aerobic treatment plant is a custom-made construction which has had to be modified several times since it went into operation in 1986. The following important points were noticed: it is necessary to raise the pH from 3.2 to at least 4.0 before it enters the methane reactor. Since there is a storage tank (October, 1995) and the flow rate to the fixed-film methane reactors is regulated by the pH, which is measured in the recirculation pipe of the methane reactor, the COD removal efficiency is $\leq$ 80% at COD loading rates of 4 to 6 kg COD/(m^3.d).

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ANAEROBIC/AEROBIC TREATMENT

In most cases (beet sugar factories, potato processing industry, breweries, potato and wheat starch factories) when the wastewater is anaerobically pretreated and the aerobic stage has to run with nitrification and denitrification, it is necessary to run a bypass (fresh or acidified wastewater) around the methane reactor to make sure that there is enough carbon for denitrification. The decision as to which water has to be directly led to the activated sludge system depends on the water. The use of acidified water in a potato starch factory led to bulking sludge within a few weeks. The bulking sludge disappeared within three months when the dosage of acidified water was stopped. To keep the necessary carbon source as small as possible, 50 to 70% of the activated sludge tank should be used for denitrification. In a sugar factory, the bypass could easily be regulated by an on-line measurement of NO_3-N installed in the effluent of the denitrification zone in the activated sludge tank.

ANAEROBIC PRE-TREATMENT OF WASTEWATER FROM DIFFERENT INDUSTRIES IN ONE PLANT

The highly loaded wastewater streams of a brewery, a fish factory and two vegetable-processing plants are anaerobic/aerobically pretreated in one common stage in the area of a municipal sewage treatment plant. The concept and design was made by ISAH. The industrial pre-treatment started in 1992.

The industrial part of the wastewater treatment plant consists of a buffering, sedimentation and acidification tank (270-1125 m^3) with solid matter removal, a fixed-film methane reactor (1584 m^3), an anaerobic settling tank (495 m^3, 133 m^2), and a trickling filter (820 m^3). Pretreated wastewater can be added at different stages of the municipal treatment plant which is working with nitrification, denitrification and phosphorus-precipitation.

Equalisation, sedimentation and acidification tank. The fluid volume in the tank varies between at least 270 m^3 and a maximum of 1125 m^3. This tank has several functions: equalisation of wastewater flow, equalisation of concentrations, acidification, and removal of solid material. The solid matter removal is realised by a tangential inflow which induces a motion of rotation in the tank and brings the solids down to the middle of the conical bottom of the tank (teapot effect). The separated solid matter from the acidification tank is led to the municipal sludge digester (flush-out reactor).

A part of the acidified wastewater from this tank is directly led to the denitrification tank if there is not enough organic carbon to bring down the nitrate concentrations. This bypass is regulated manually each day.

Fixed-film methane reactor. The fluid volume of the fixed-film methane reactor is 1584 m^3. The top 4.8 m of the fluid volume (34% of the effective volume) are filled with loosely poured swimming curlers called BIO-NET (NSW Umwelttechnik, Nordenham, FRG) as a support medium with a specific surface of 100 m^2/m^3.

Trickling filter. The high-rate plastic media biological filter has the function of a buffer system to obtain stable COD concentrations in the influent of the activated sludge system. The support medium in the trickling filter is called SESSIL (NSW Umwelttechnik, FRG) with a specific surface of 100 m^2/m^3.

The main indirect dischargers of industrial wastewater are two vegetable processing factories. They work throughout the year but they also have seasonal variations, as the availability of the vegetables and demand for particular products varies considerably. Thus, the wastewater flow and composition also varies a great deal. Vegetable manufacturing can be divided into two periods: the main campaign lasting from July to December, and the intermediate campaign lasting from January to June. Wastewater flow and load are presented in Table 5.

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Table 5. Wastewater flow and load of the main industrial indirect dischargers

main industries	campaign (July-December)		January- June	
	flow [m³/d]	load [kg COD/d]	flow [m³/d]	load [kg COD/d]
brewery	230	390	230	390
fish factory	105	330	105	330
vegetable manufacturing I	150	1500	90	260
vegetable manufacturing II	230	4000	110	320
total	715	6220	535	1300

During the main campaign, only the wastewater of the vegetable processing industry is treated anaerobically. Meanwhile, the effluent of the brewery and the fish factory are led directly to the trickling filter. The rest of the year, all industrial wastewaters are treated anaerobically. The design data of the different processing steps are given in Table 6.

Table 6. Design data of the industrial pre-treatment plant for several different industries

Main industry	Campaign (July-December)				January- June			
industrial pre-treatment	flow m^3/d	load $\frac{kg\ COD}{d}$	OLR $\frac{kg\ COD}{m^3 \cdot d}$	HRT d	flow m^3/d	load $\frac{kg\ COD}{d}$	OLR $\frac{kg\ COD}{m^3 \cdot d}$	HRT d
acidification	380	5,500	4.5-14.5	0.7-3.2	535	1,300	4.5-14.5	0.5-2.3
methane reactor	270	4,000	2.5	5.8	380	930	0.59	4.2
	flow m^3/d	load $\frac{kg\ BOD_5}{d}$	OLR $\frac{kg\ BOD_5}{m^3 \cdot d}$	SFR m/h	flow m^3/d	load $\frac{kg\ BOD_5}{d}$	OLR $\frac{kg\ BOD_5}{m^3 \cdot d}$	SFR m/h
trickling filter	840	1,110	1.4	1.5	384	325	0.41	1.5

OLR = Organic Loading Rate; HRT = Hydraulic Retention Time; SFR = Surface Flow Rate

SUMMARY

Since 1958 when the first full scale anaerobic wastewater treatment plant started to work, a great number of analyses have been carried out. As a result, there are currently 106 methane reactors in Germany which process industrial wastewater. This paper about experiences gained in the operation of anaerobic treatment plants in Germany shows that each industry has its own specific problems. Therefore, specific investigations have to be undertaken to find specific solutions. Furthermore, it became apparent that it is possible to treat several different industrial wastewaters together in one plant, which is particularly interesting for small factories, especially in the food industry.

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