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Combined anaerobic removal of COD, N and S from industrial waste water

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Abstract Anaerobic treatment of industrial effluent is increasingly accepted in various industries. Not only in industries that are normally associated with the application of anaerobic technology like breweries, pulp & paper and food & vegetable, but also in the chemical, metallurgical and power plant industries. Anaerobic removal of COD combined with the production of methane is well developed and has been applied since the 1980's. Anaerobic sulfate removal has been applied in full-scale applications since the 1990's. In some cases sulfate removal is combined with metals removal by sulfide precipitation. The latest addition are a number of innovative nitrogen removal technologies of which the Anammox® technology is now also applied in a full-scale application. This paper analyses the trend towards the combined removal of various contaminants. As examples a number of recently realized full-scale references will be used. The integration of the high rate anaerobic IC® technology with the more recently developed THIOPAQ® technology for sulfur removal and the Anammox® technology for nitrogen removal will be discussed and start up and operational data of three plants will be discussed.
Keywords Anaerobic industrial effluent treatment, Anammox® ammonia removal, sulfate removal, COD removal, full-scale plant performance evaluation.

Trends towards integrated industrial waste water treatment

After the successful introduction of anaerobic technology into the industrial wastewater treatment market, several thousand references were realized until now which mainly focus on the reduction of the COD content of the water. Depending on the effluent quality requirements the water is discharged into the sewer, aerobically treated, polished, recycled and/or discharged into a waterway. The anaerobic COD removal is combined with the reduction of other components in the wastewater like sulfate and nitrogen. The reduced components like sulfide and nitrite might as an added advantage assist in the removal of other contaminants like metals. Disadvantages of these reduced components are normally inhibiting effects on the biological activity and a negative influence on the formation of high quality anaerobic biomass pellets.

More recently anaerobic sulfate removal was introduced. The sulfate is first anaerobically converted to sulfide and then aerobically to solid sulfur. An external electron donor (COD source) is normally added like methanol, ethanol or hydrogen. This external electron donor forms a significant part of the operational cost of this technology. Since sulfate removal can be applied in industries where metals are also present in the wastewater, an added bonus is the precipitation of metal sulfides in the anaerobic treatment step.

During the last five years a number of innovative nitrogen removal technologies were introduced of which Anammox® was most recently realized in a full-scale reference. Traditional nitrification / denitrification is replaced with more or less direct ammonia removal. Major advantages of these technologies are:

1. Reduction of external carbon source that needs to be added during the denitrification step.
2. Reduction of amount of air that is added during the nitrifying step.

Indirect advantages are of course a reduction of the energy consumption and the CO_2 production. For the Anammox® technology the reduction percentages could be 100% on methanol consumption and 60% on aeration.

The applications of anaerobic technology described above are all aimed at the removal of one specific component. They all have their specific investment cost and chemicals are normally added to control the biological removal of these components. A number of market drivers have developed in this new Millennium, which started a trend towards further integration of these different anaerobic technologies:

1. Increasing pressure from an environmental legislation point of view.
2. Significant increase in the sewer discharge fees of companies.
3. The perception of customers that some of these technologies have high operational costs due to chemicals consumption.
4. The need to treat more complicated wastewaters to environmental standards.
5. The need to reduce the emission of CO_2.

As a response to these drivers integration of the various anaerobic technologies is becoming more and more important. Through integration significant operational and economical advantages can be achieved. The normally required pre- and post treatment steps can be simplified. The addition of neutralizing agents and the removal of solids can be optimized when these anaerobic technologies are logically integrated.

Various examples of integration of anaerobic technologies are:

1. Combined sulfate and metals removal.
2. Combined sulfate, COD and metals removal.
3. Combined sulfate, COD and nitrogen removal.
4. Combined SO_2, COD and metals removal.

Three examples

Three reference plants were selected as examples for the trend that is described in the previous section:

- WWTP for South African Coal Estates (SACE), Anglo Coal, in South Africa.
- WWTP for Lenzing AG in Austria.
- WWTP for Royal Dutch Hulshof Tanneries in the Netherlands.

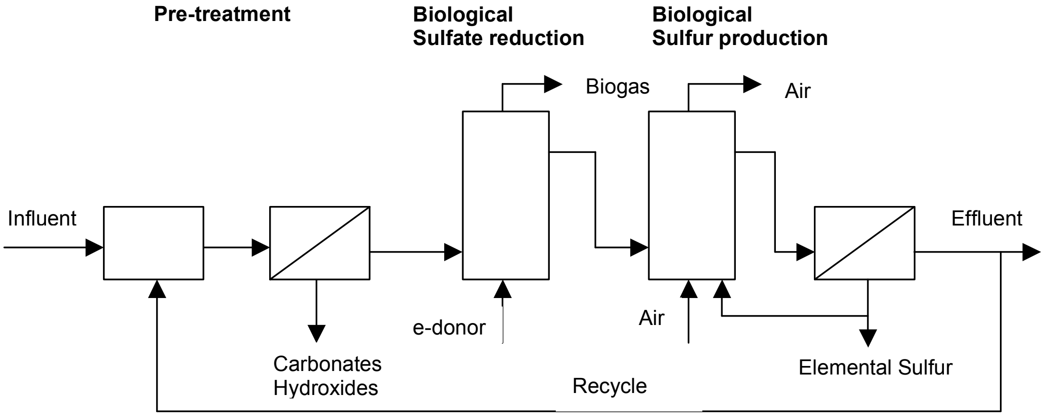
The SACE WWTP offers a solution for the removal of calcium, sulfate and heavy metals from mine wastewater. The Lenzing WWTP offers a solution for the removal of zinc, COD and sulfate from pulp and viscose fiber production wastewater. The Hulshof WWTP offers a solution for the removal of chromium, COD, sulfate and ammonium.

WWTP for South African Coal Estates (SACE), Anglo Coal, in South Africa

The SACE water is an acidic mine water that is treated in the Sulfate Reduction Demonstration Plant (SRDP).

The Thiopaq® SRDP is designed for a feed flow between 3000 m^3/day and 4500 m^3/day depending on the sulfate level and a sulfate removal capacity of 6.6 tpd SO_4. The simplified flow scheme is shown in figure 1.

Figure 1: Simplified flow scheme of SACE WWTP.



By recycling the effluent with the influent the alkalinity in the effluent is used to raise the pH of the acidic influent water, which drops out part of the metals as hydroxides and part of the calcium as calcium carbonate. Sulfate reduction to sulfide occurs in the first bioreactor using ethanol as electron donor:

$$3\ SO_4^{2-} + 2\ C_2H_5OH \rightarrow 3\ HS^- + 3\ HCO_3^- + CO_2 + 3H_20$$

The partial oxidation of sulfide occurs in the second bioreactor:

$$HS^- + 0.5\ O_2 \rightarrow S^0 + OH^-$$

The products of the process are a hydroxide/carbonate sludge, which is disposed in a nearby dam and a sulfur slurry, which can be upgraded to a marketable sulfur product. The process was selected by the customer based on an economic evaluation. The results in table 1 shows that the integration of various biological treatment steps is starting to pay off:

Table 1: Results economic analysis for treatment of acid mine water.

Process	Effluent	Water recovery	Products	Costs	Proven
Lime treatment	--	>98%	--	-	++
Reverse Osmosis	++	80%	--	+ / -	++
Electrolysis	++	65%	--	+ / -	++
Ion exchange	++	75%	--	+ / -	++
THIOPAQ®	++	> 97%	++	+	++

Typical influent and effluent characteristics are shown in table 2:

Table 2: Composition of the most important process streams of the Thiopaq® plant for the treatment of Landau Acid Mine Water.

Variable	Units	LAMW	Final effluent
Flow	m^3/h	125	125
PH		2,9	7,5-8,0
Elect.cond.	mS/m	361	125
TDS	mg/l	3778	1300
Acidity	mg/l $CaCO_3$	554	0
Alkalinity	mg/l HCO_3^-	0	900
Ca^{2+}	mg/l	512	150
Mg^{2+}	mg/l	158	158
Na^+	mg/l	49	49
K^+	mg/l	6	6
SO_4^{2-}	mg/l	2398	<300
Cl^-	mg/l	40	40
Fe	mg/l	65	<1
Mn^{2+}	mg/l	20	<1
Al^{3+}	mg/l	16	<1
HS^-	mg/l	0	<1
COD	mg/l	<50	<50
Susp. Solids	mg/l	203	<20
Temperature	^oC	19	24

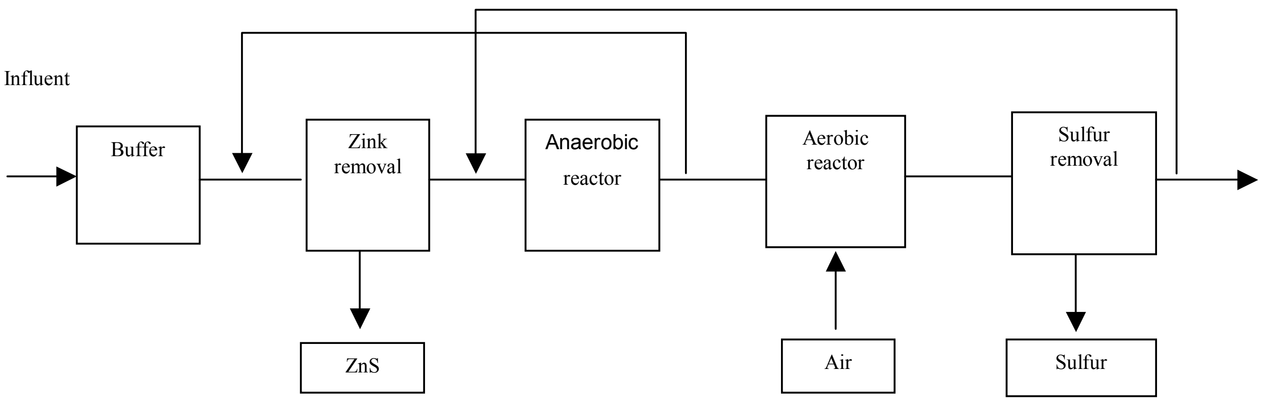
The plant was started up in March 2003 and has reached the operating capacity of 6.6 tons per day sulfate removed. The plant is processing Landau Acid Mine Water only. Appendix 1 contains a picture of the plant.

WWTP for Lenzing AG in Austria

Lenzing A.G. in Lenzing Austria, is a world leader in the viscose fiber production.

A high rate biological system was installed to treat several waste streams, both acidic and alkaline, thus removing COD, sulfate and Zinc. The plant produces dischargeable water, sulfur (S^0) and zinc sulfide (ZnS). The simplified flow scheme is shown in figure 2.

Figure 2: Simplified flow scheme of Lenzing WWTP



The influent is first contacted with sulfide produced in the anaerobic bioreactor to produce ZnS. The solid product is removed while part of it is recycled to enhance particle growth. The COD present in the waste water is used to reduce the sulfate to sulfide. The sulfide is then oxidized to solid sulfur and this product is removed in a tilted plate settler (See SACE WWTP section for chemical reactions). The design influent characteristics of the Lenzing WWTP are shown in table 3.

Table 3: Design influent characteristics of Lenzing WWTP

Variable	Unit	Stream 1	Stream 2	Stream 3
Flow	m^3 / hr	235	52.5	10.5
Sulfate	mg / l	13000	900	0
COD	mg / l	3500	6000	32000
Methanol	mg / l	0	900	0
Zn	mg / l	400	0.8	0
Ca	mg / l	700	500	0
PH		5.5	6	> 12
Temperature	°C	35	45	20

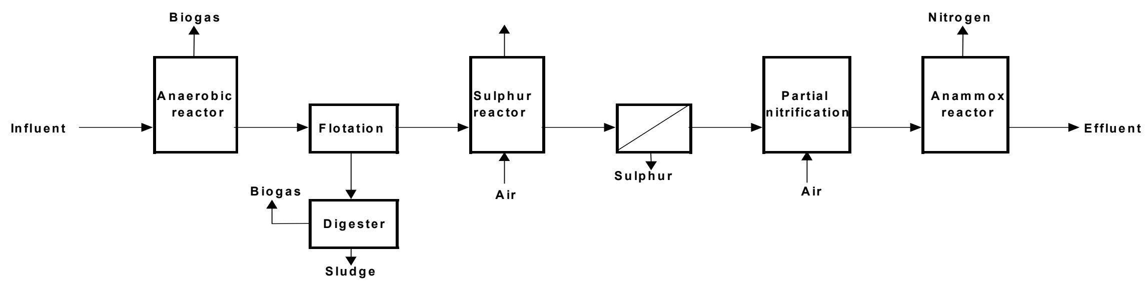
The plant is designed to remove 15 tons per day of sulfate, 10 tons per day of COD and 2 tons per day zinc as zinc sulfide. The plant was started in January 2004. At the moment it is building its capacity up to design level, which will be achieved in the middle of 2004. Appendix 2 contains a number of graphs showing the progress during the first months of operation.

WWTP for Royal Dutch Hulshof Tanneries in the Netherlands

Koninklijke Hulshof Leerlooierijen (or Royal Dutch Hulshof Tanneries) is Holland's largest tannery. Their location in the heart of the city Lichtenvoorde and their constant expansion forced Hulshof to move and expand the existing chemical wastewater treatment facility. Waterstromen B.V, a company resulting from private public cooperation and specialized in industrial Own & Operate concepts would operate the WWTP and solids handling. The project is supported by LIFE EU for its innovative and sustainable nature.

Based on the complex tannery wastewater a rather unique and complex flow sheet for the treatment of all pollutants was developed. Figure 3 gives a simplified flow scheme of this process.

Figure 3: Simplified flow scheme of Royal Hulshof WWTP.



The influent is a mixture of different streams containing COD, sulfate, ammonium and some metals amongst which chromium.

The influent is fed to the anaerobic IC® reactor in which COD is converted to methane gas and sulfate is reduced to sulfide. From the anaerobic reactor the water is led to a flotation unit in order to separate colloidal matter such as undissolved proteins from the water flow. To minimize sulfur production in this unit biogas is used as the flotation medium.

From the flotation unit the slurry containing up to 10% dry matter, is led to the digester in which over 50% of the more complex solid fractions is degraded. The water from this digester is recycled to the influent. The water from the flotation unit is brought into an aerobic sulfur reactor in which the sulfide is oxidized to elemental sulfur.

After the sulfur removal with a tilted plated settler the water flow is led to a partial nitrification reactor in which part of the ammonium is oxidized to nitrite. Finally the flow is led to the Anammox reactor in which the produced nitrite together with the other part of the ammonium is converted anaerobically to nitrogen gas. Now the water is ready for discharge. Table 4 gives the details of influent and effluent streams for the Royal Hulshof WWTP.

Table 4: Influent and effluent details for the Royal Hulshof WWTP.

Variable	Unit	Design	Effluent
Flow	m^3 / hr	30	30
CZV	mg / l	7750	< 500
Sulfate	mg / l	1100	< 300
N-total	mg / l	610	< 50
Cr	mg / l	15	< 1
PH		8 – 10	8 – 9
Temperature	°C	25	

The Royal Hulshof WWTP was started very recently. An update on the performance of the process will be given during the conference.

Conclusion

A number of market drivers is forcing companies to meet tightening discharge limits on waste waters that are becoming more complex in nature. Integration of the different anaerobic water treatment technologies for COD, sulfur and nitrogen removal offers a number of advantages. On the investment side, costs can be saved in the optimization of the pre- and post treatment sections. On the operational side, chemicals addition and solids handling can be optimized. Three full-scale references are briefly discussed to show the benefits of this approach.

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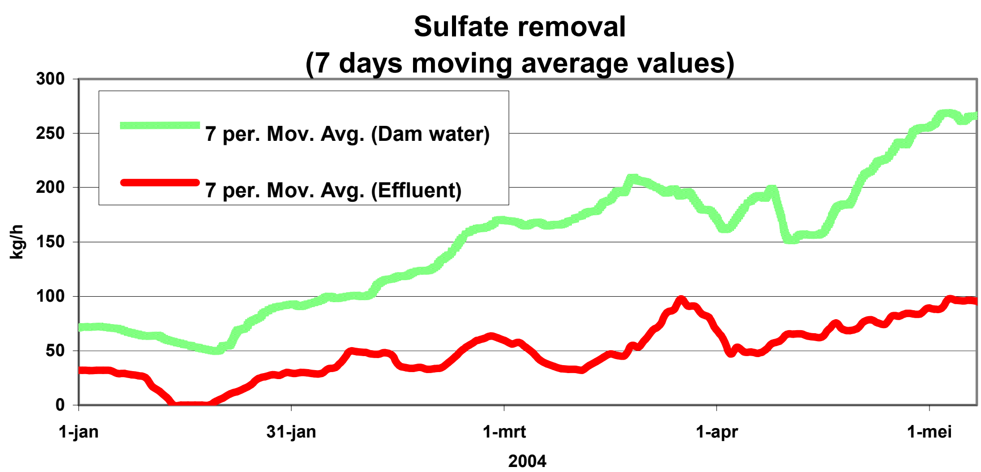
Appendix 1: Picture and performance of the SACE WWTP

Graph 1: Sulfate load removed during first 5 months of 2004.



Note: The plant capacity is building up to design capacity. As soon as design capacity is reached, the plant will be optimized based on desired effluent quality.

Appendix 2: Lenzing WWTP startup data and picture.

Picture of Lenzing WWTP during installation.

Graph of Lenzing start up data: Development of removal capacity.