3. COD conversion to CH_4

What is Chemical Oxygen Demand (COD) ??

The “theoretical COD” calculation of organic compound

$C_nH_aO_bN_d$

is based on a complete oxidation.
The amount of required O_2 depends on the oxidation state of C:

$$C_nH_aO_bN_d$$

+a

-2b

-3d

Oxidation state:

$(2b + 3d - a)/n$

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Chemical Oxygen Demand (COD)

The number of electrons made free per atom C in the complete oxidation of $C_nH_aO_bN_d$ amounts to:

$$4 – (2b+3d-a)/n \qquad (\text{or } 4n + a - 2b - 3d)$$

as +4 is the most oxidized form of C (CO_2)

The required number of O_2 molecules for the complete oxidation is:

$$C_nH_aO_bN_d + \tfrac{1}{4}\,(4n+a-2b-3d)\ O_2 \rightarrow n\ CO_2 + \tfrac{1}{2}(a-3d)\ H_2O + d\ NH_3$$

→ 1 O_2 accepts max. 4 electrons

Chemical Oxygen Demand (COD)

In the standardized COD test with bichromate as oxidizer (150°C) almost all organic compounds

$$C_nH_aO_bN_d$$

are completely converted in CO_2 and H_2O

→ But: organic N stays reduced and is converted in NH_3

The required number of O_2 molecules for the complete oxidation is:

$$C_nH_aO_b + \tfrac{1}{4}\,(4n+a-2b)\ O_2 \rightarrow n\ CO_2 + \tfrac{1}{2}a\ H_2O$$

That is Chemical Oxygen Demand (COD) !!

1 “mol” of organic matter demands:

¼ (4n+a-2b) moles O_2 or 8(4n+a-2b) g O_2

Theoretical COD calculation:
COD_t = 8(4n+a-2b)/(12n+a+16b) mg COD/mg $C_nH_aO_b$

$$C_nH_aO_b + \tfrac{1}{4}(4n+a-2b)\,O_2 \rightarrow n\,CO_2 + \tfrac{1}{2}a\,H_2O$$

What is Total Organic Carbon (TOC) ??

Organic matter measured as CO_2 after incineration
(corrections needed for inorganic carbon in waste sample)

TOC_t = 12n / (12n + a + 16b) g TOC/g$C_nH_aO_b$

g COD and g TOC per g organic compound

Ratio COD / TOC: $8(4n+a-2b)/(12n) = 8/3 + 2(a-2b)/(3n)$

Compound	n	a	b	g COD ($g\ C_nH_aO_b$)	g TOC ($g\ C_nH_aO_b$)	COD/TOC ratio
Oxalic acid	2	2	4	0.18	0.27	0.67
Formic acid	1	2	2	0.35	0.26	1.33
Citric acid	6	8	7	0.75	0.38	2.00
Glucose	6	12	6	1.07	0.40	2.67
Lactic acid	3	6	3	1.07	0.40	2.67
Acetic acid	2	4	2	1.07	0.40	2.67
Glycerine	3	8	3	1.22	0.39	3.11
Phenol	6	6	1	2.38	0.77	3.11
Ethylene glycol	2	6	2	1.29	0.39	3.33
Benzene	6	6	0	3.08	0.92	3.33
Acetone	3	6	1	2.21	0.62	3.56
Palmitic acid	16	32	2	3.43	0.75	3.83
Cyclohexane	6	12	0	3.43	0.86	4.00
Ethylene	2	4	0	3.43	0.86	4.00
Ethanol	2	6	1	2.09	0.52	4.00
Methanol	1	4	1	1.50	0.38	4.00
Ethane	2	6	0	3.73	0.80	4.67
Methane	1	4	0	4.00	0.75	5.33

Calculating the Theoretical Methane Production

Theoretical methane production depends on:
- the biodegradability of the substrate
- the oxidation state of the organic compound

Oxidation state of biodegradable compound:

$C_nH_aO_bN_d$

+ a

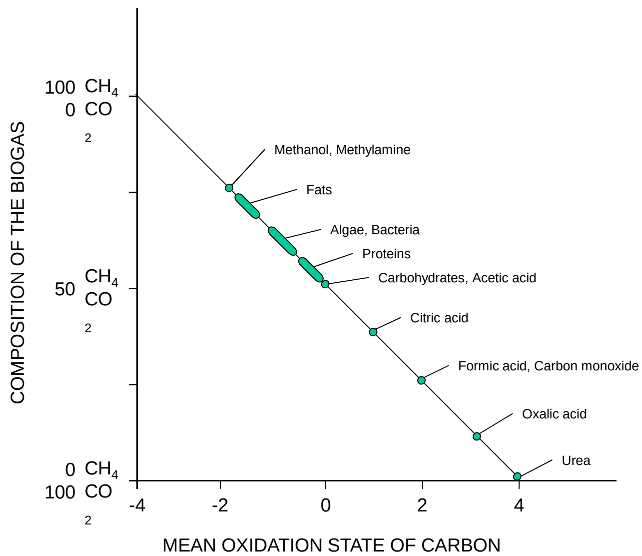
- 2b

- 3d

Oxidation state:

$$\frac{2b + 3d - a}{n}$$

Theoretical CH_4 / CO_2 production of various organic compounds



Methane Production from $C_nH_aO_bN_d$

Basic principles:

- part of C will be completely oxidized
- the other part of the C will be completely reduced
- N and O stay completely reduced
- the average oxidation state of C stays the same

Methane Production from $C_nH_aO_bN_d$

Assumption:
- fraction X of C goes to CH_4 (oxidation state C = -4)
- fraction (1-X) of C goes to CO_2 (oxidation state C = +4)

Since the oxidation state does not change:

$$-4X + 4(1-X) = \frac{2b + 3d - a}{n}$$

$$\rightarrow \boxed{x = (a - 2b - 3d)/8n + 4/8}$$

Methane Production from $C_nH_aO_bN_d$

so $C_nH_aO_bN_d$ is converted in:

$\rightarrow$ $n.x.CH_4$

$\rightarrow$ $n.(1-x).CO_2$

$\rightarrow$ $d\ NH_3$

substitution of x gives:

……

$$\rightarrow \boxed{x = (a - 2b - 3d)/8n + 4/8}$$

Methane Production from $C_nH_aO_bN_d$

$$C_nH_aO_bN_d \rightarrow n \cdot X\ CH_4 + n \cdot (1-X)\ CO_2 + d\ NH_3$$

$(n/2 + a/8 – b/4 – 3d/8)\ CH_4$

$(n/2 – a/8 + b/4 + 3d/8)\ CO_2$

Buswell's formula

$$\boxed{x = (a - 2b - 3d)/8n + 4/8}$$

Buswell's formula

Theoretical CH_4-yield for a compound $C_nH_aO_bN_d$ follows from:

$$C_nH_aO_bN_d + (n – a/4 – b/2 + 3d/4)\ H_2O \rightarrow$$

$$(n/2 + a/8 – b/4 – 3d/8)\ CH_4 + (n/2 – a/8 + b/4 + 3d/8)\ CO_2 + d\ NH_3$$

Actual methane production differs owing to:

- Limited biodegradability of compounds
- Part of organic matter is used for cell growth (bacterial yield)
- Possible presence of alternative electron acceptors
- High solubility of CO_2 / HCO_3^- in the water fraction

COD 'consumed' by alternative electron acceptors

Required COD to be calculated from complete reduction reaction

1. COD oxidation with sulphate

$$COD + SO_4^{2-} \rightarrow H_2S + CO_2$$
$$8e + S^{6+} \rightarrow S^{2-}$$

2. COD oxidation with sulphite

$$COD + SO_3^{2-} \rightarrow H_2S + CO_2$$
$$6e + S^{4+} \rightarrow S^{2-}$$

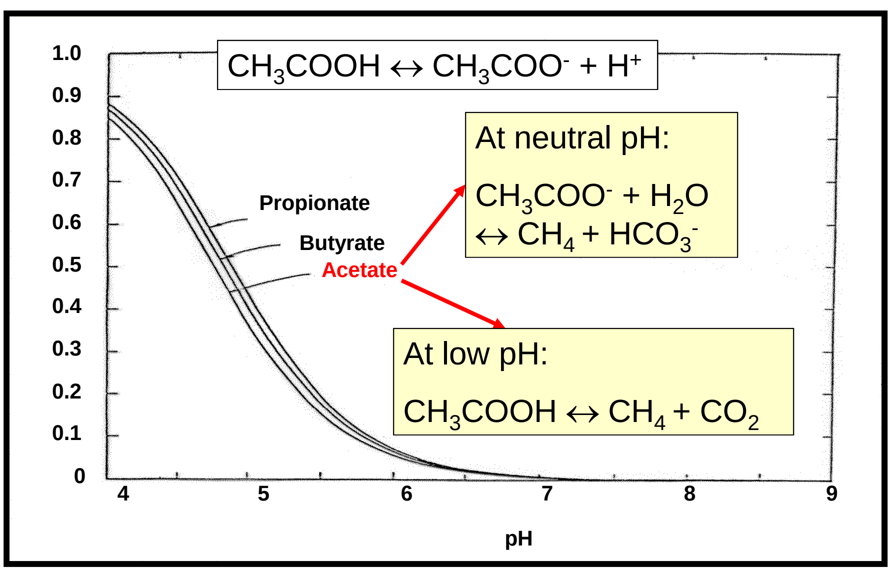
3. COD oxidation with nitrate

$$COD + 2NO3^{-} \rightarrow N_2 + CO_2$$
$$5e + N^{5+} \rightarrow N^{0}$$

Stochiometric calc.:	1 mol SO_4^{2-}	~2 mol O_2
	1g SO_4^{2-}	=> 0.67 g COD
	1 g SO_3^{2-}	=> 0.6 g COD
	1 g NO_3–N	=> 20/7 g COD = 2.86 g COD

(1 g NO_3 => 0.65 g COD)

The ratio of unionised VFA to total VFA as a function of pH



Metabolism generated alkalinity from protein degradation: decrease in biogas CO_2

$$C_nH_aO_bN_d + (n - a/4 - b/2 + 3d/4)\,H_2O \rightarrow$$
$$(n/2 + a/8 - b/4 - 3d/8)\,CH_4 + (n/2 - a/8 + b/4 + 3d/8)\,CO_2 + d\,NH_3$$

$+$

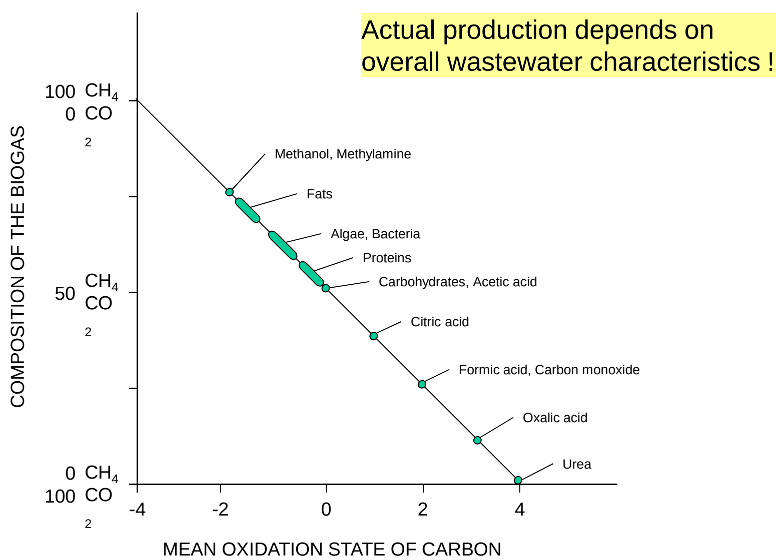
$H_2O \leftrightarrow OH^- + H^+$

$\downarrow\uparrow$

$\boxed{d\,NH_4^+}$

$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$

Theoretical CH_4 / CO_2 production of various organic compounds



Conversion CH_4 production - COD

The oxidation of CH_4 requires 2 moles of O_2:

$CH_4 + 2\ O_2 \rightarrow CO_2 + 2H_2O$

$x = (a - 2b - 3d)/8n + 4/8$

Since "the fraction X" of the compound $C_nH_aO_bN_d$ will go to CH_4,

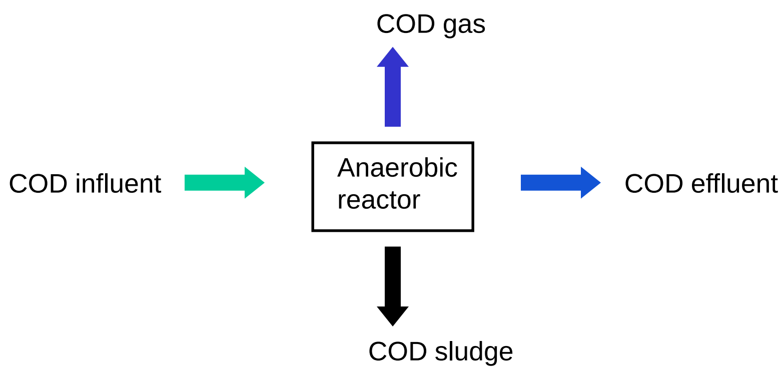
The COD of compound $C_nH_aO_bN_d$ is 2 • "fraction X" mol O_2/l or:

$2 \cdot (n/2 + a/8 - b/4 - 3d/8)$ mol O_2/l

The "overall" oxidation state of organic compounds will not change during anaerobic conversion:

A COD balance can be made: COD-in = COD-out

COD-Balance



$COD_{influent} = COD_{effluent} + COD_{gas} + COD_{sludge}$

Balance always fits !!!

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Measurable COD fractions in various compartments

COD influent:
- COD soluble
- COD solids
- COD colloidal

COD effluent:
- COD soluble organic
- COD soluble inorganic (e.g. H_2S)
- COD solids
- COD dissolved reduced gases

COD gas:
- COD CH_4
- COD H_2S
- COD H_2

COD sludge:
- COD entrapped solids
- COD newly grown biomass
- COD entrapped

Working with the COD Balance

COD equivalents in produced gas:

1 mol CH_4 = 2 mol O_2
22.4 l (STP) CH_4 = 64 g O_2 or 64 g COD
1 l CH_4 (STP) = 64/22.4 = 2.86 g COD

Or: 1 g COD = 0.35 l CH_4 (STP)

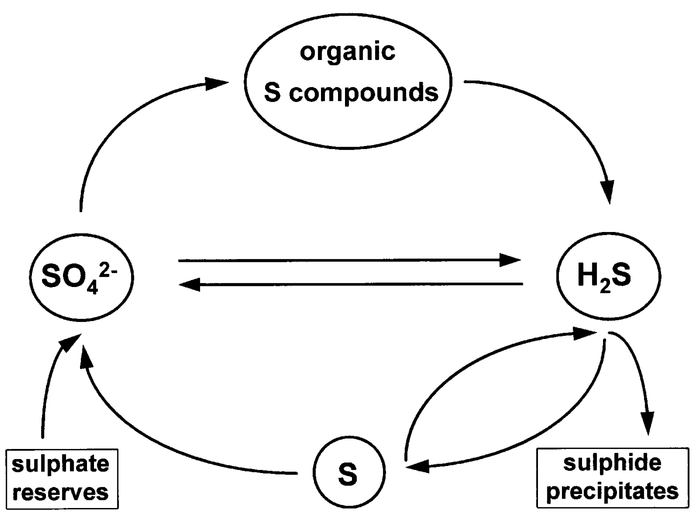
COD equivalents in sludge:

1 g sludge - VSS = 1.42 g COD
(based on heterotrophic biomass:
$C_5H_7O_2N \Rightarrow$ 113 g VSS per mol X)

Question: what is the biogas and sludge production in a UASB treating sugar mill wastewater:
- Q = 500 m^3/day
- COD = 3.5 kg/m^3
- Sludge Yield = 10%
- Efficiency = 90%

4. Impacts of SO_4^{--}

THE BIOLOGICAL SULPHUR CYCLE



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1. Introduction: bio-chemical properties of C and S

Similarities:

Appearance in various states of oxidation,

C: (-4) – (+ 4) ➔ $CH_4 - CO_2$
S: (-2) – (+ 6) ➔ $H_2S - H_2SO_4$

Can both act as electron acceptor / donor in anaerobic systems

Reduced end-product is gaseous

Possible formation of precipitates: MeS, $CaCO_3$

Bacteria using either S or C as electron acceptor may compete for the same substrate

1. Introduction: Sulphate, sulphite and nitrate as electron acceptors

1. Oxidation with oxygen

$$COD + O_2 \rightarrow H_2O + CO_2$$
$$4e + O_2 \rightarrow 2O^{2-}$$

2. Oxidation with sulphate

$$COD + SO_4^{2-} \rightarrow H_2S + CO_2$$
$$8e + S^{6+} \rightarrow S^{2-}$$

3. Oxidation with sulphite

$$COD + SO_3^{2-} \rightarrow H_2S + CO_2$$
$$6e + S^{4+} \rightarrow S^{2-}$$

4. Oxidation with nitrate

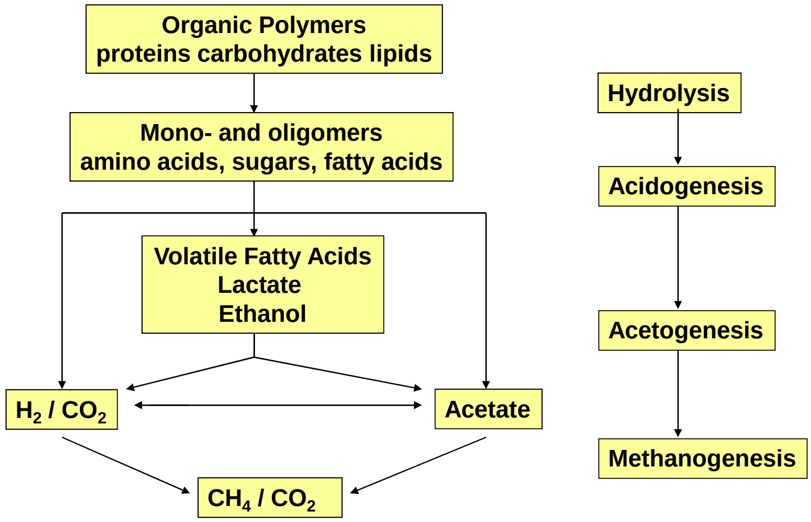
$$COD + 2NO3^{-} \rightarrow N_2 + CO_2$$
$$5e + N^{5+} \rightarrow N^0$$

Conclusions:

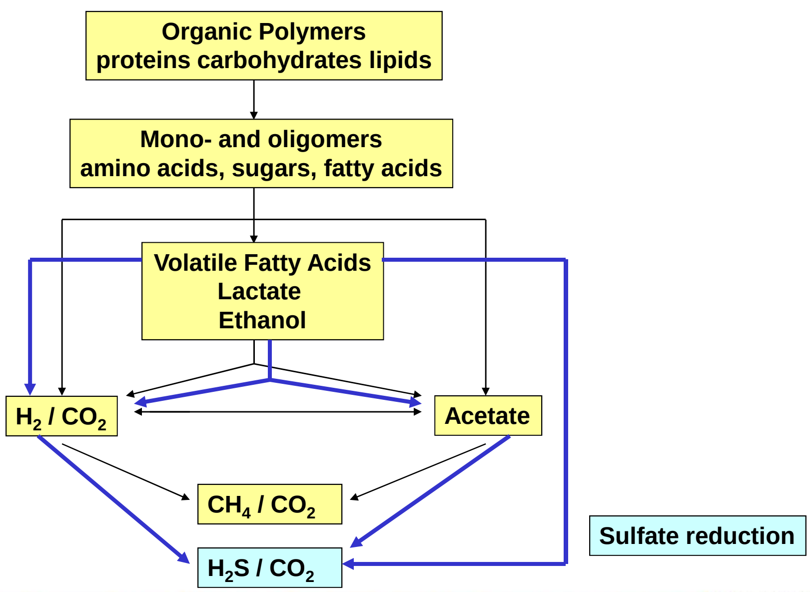
1 mol SO_4^{2-}	~2 mol O_2
1g SO_4^{2-}	=> 0.67 g COD
1 g SO_3^{2-}	=> 0.6 g COD
1 g NO_3—N	=> 20/7 g COD = 2.86 g COD

(1 g NO_3 => 0.65 g COD)

Anaerobic Conversion of Organic Matter



Anaerobic Conversion of Organic Matter with Sulfate



Problems Associated With Sulphate Reduction

- **Negative effect on energy balance of anaerobic reactor**
  - => Lower methane yield per unit organic waste
  - => Biogas treatment required (H_2S removal)

- **Maintenance Costs Increase**
  - => Malodor
  - => Corrosion to engines, boilers, reactor parts, pipes,..

- **Effluent Polishing Required**
  - => S^{2-} increases effluent COD (1 mol S^{2-}= 2 mol O_2)
  - => Bulking of activated sludge (successive post-treatment)

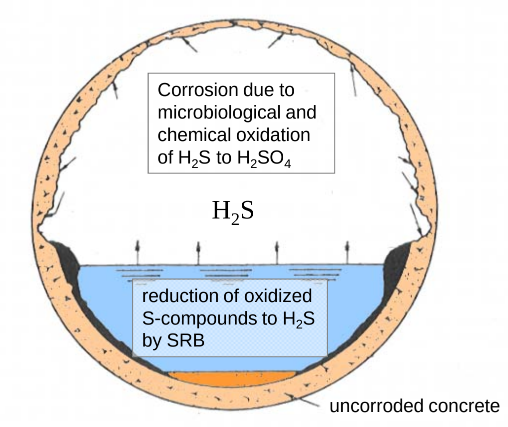
Odour and human toxicity

- H_2S is a colorless, very flammable, toxic gas. It is heavier than air.
- In low concentrations it smells like "rotten eggs“. Low-level exposures usually produce local eye and mucous membrane irritation
- At levels of 300 ppm the olfactory nerve loses sensitivity. At first the "rotten egg" odor is detected but on the second or third breath, the odor is no longer noticed.
- At 600 ppm, breathing is inhibited, as the lungs fill with the gas. Exposures of 700-800 ppm or greater usually result in death
- The Netherlands: MAC-value = 10 ppm (15 mg/m^3)

Corrosion above the water level

"sulfuric acid attack"

Concrete sewer pipe



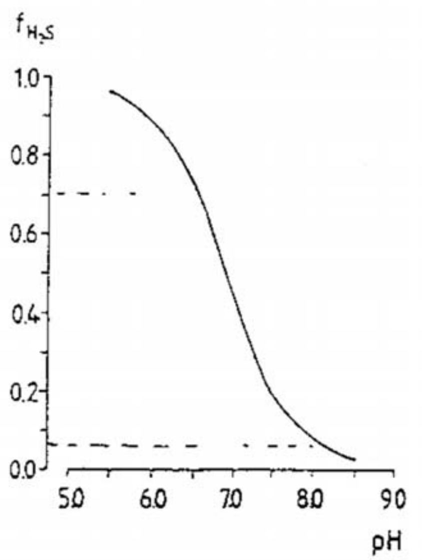
Iron influent distribution box of a UASB treating domestic sewage

Inhibition Phenomena

Sulfide toxicity

- Only undissociated H_2S is toxic
- diffuses 'freely' through cell membrane
- Denatures proteins and enzymes (sulfide cross-linking)
- Effect internal cell pH
- **Inhibition of methane producing bacteria**

pH dependent toxicity



$$H_2S_{gas} \Leftrightarrow H_2S_{aq}$$

$H_2S_{liq} = K_H * pH_2S$

$$H_2S \Leftrightarrow HS^- + H^+$$

Fraction of total dissolved sulfide present as undissociated H_2S: f_{H2S}, (30 °C).

$f_{H2S} = H_2S/(H_2S + HS^-)$
$= 1/(10^{pH-pKa} + 1)$

Sulfide inhibition at various pH, temp., and different sludge types

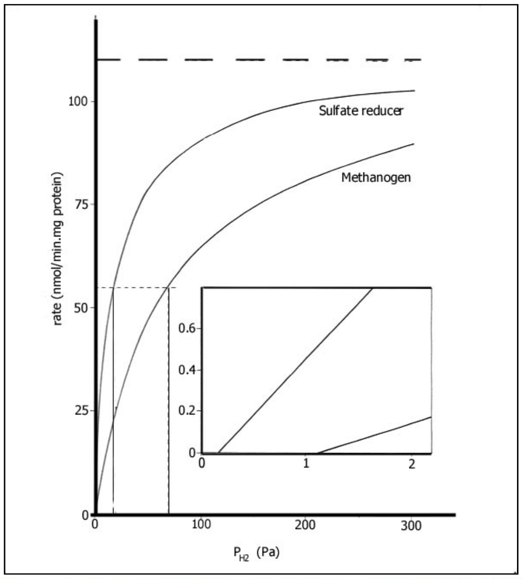
H_2S and Total-sulfide (TS) concentrations causing a 50 % inhibition of acetotrophic methanogenesis.

Sludge type	pH	T °C	H_2S	TS mg.l^{-1}	Ref
suspended	6.5-7.4	30	100	---	1
	7.7-7.9		125	---	1
	6.3-6.4	55	18	33	2
	7.1-7.2		21	78	2
	7.9-8.0		24	400	2
granular	6.4-6.6	30	246	357	3
	7.0-7.2		252	810	3
	7.8-8.0		50	841	3
	6.3-6.4	55	54	81	2
	7.1-7.2		75	338	2
	7.9-8.0		24	450	2

1. Oleskiewicz et al. 1989, 2. Visser et al. 1993e, 3. Koster et al. 1986.

Competition between SRB – MPB: Hydrogen

Clear kinetic and thermodynamic advantage of SRB over MB



Competition between SRB – MPB: Acetate

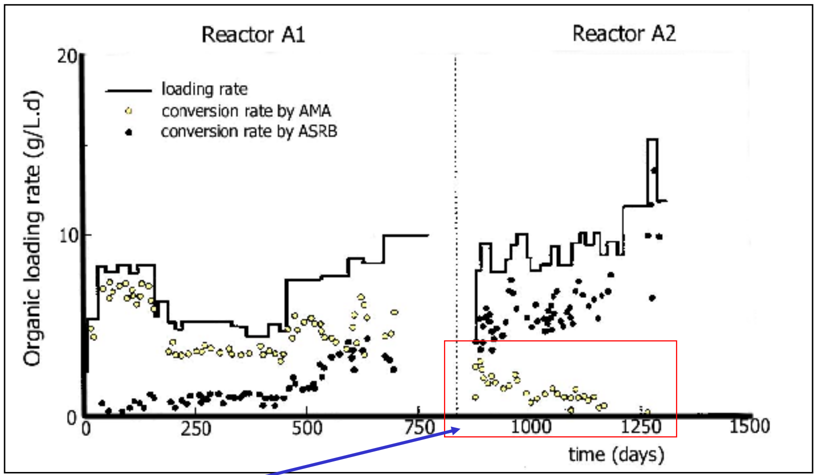
General Observations:

- Without the presence of SO_4^{--}: 70% of COD is degraded via acetate
- In presence of SO_4^{--}: Acetate is still converted into CH_4,
  → even in excess of sulfate

Competition is affected by:

Influent composition:
- Acetate concentration
- Sulfate concentration (mass transfer limitation)
- COD/sulfate ratio
- Iron concentration
- Toxic compounds

Competition of SRB and MB for Acetate



Gradual conversion of a methanogenic bioreactor in a sulfidogenic reactor

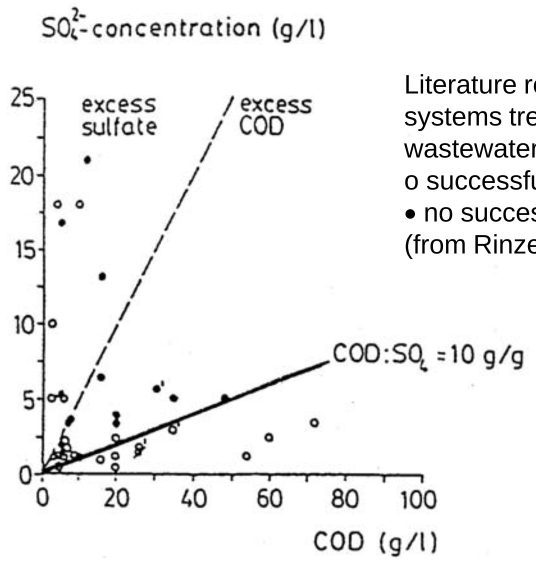
Treatment of sulfate rich wastewaters

- Removal of sulfate

COD/SO_4^{2-}	=	0.67	Enough sulfate for COD removal by SRB Enough COD for sulfate removal by SRB
COD/SO_4^{2-}	<	0.67	Extra COD should be added for complete SO_4^{2-} removal
COD/SO_4^{2-}	>	0.67	Complete COD removal only if also Methanogenesis takes place

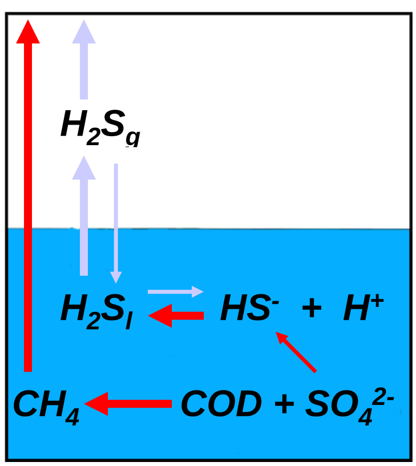
Objectives of treatment should be set:
- Removal of organic matter and/or sulfate
- Removal of organic matter

COD/SO_4 ratio as guidance for successful treatment



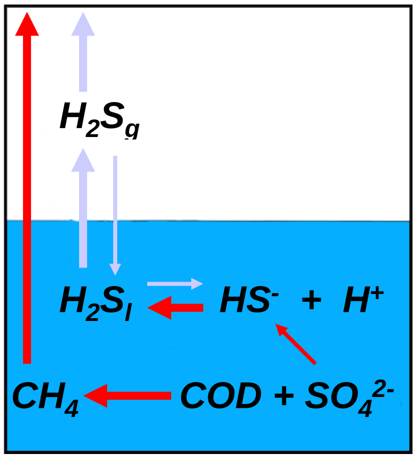
Literature results of anaerobic treatment systems treating sulfate containing wastewater.
o successful treatment,
• no successful treatment
(from Rinzema and Lettinga, 1988)

Toxicity relieve through sulfide stripping by produced biogas



H_2S-stripping by biogas at high COD/SO_4-ratio's

Toxicity relieve through sulfide stripping by produced biogas



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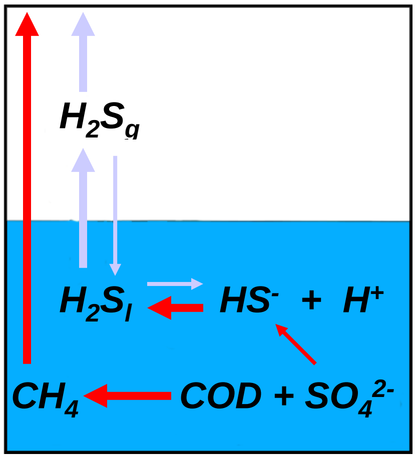
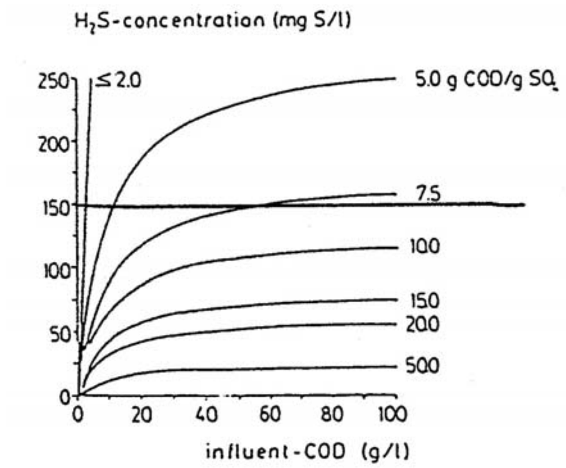


H_2S-stripping by biogas at high COD/SO_4-ratio's

Toxicity relieve through sulfide stripping by produced biogas



Reactor hydrogen sulfide concentration as a function of the COD-influent at various COD/SO_4 ratios (from Rinzema and Lettinga 1988)

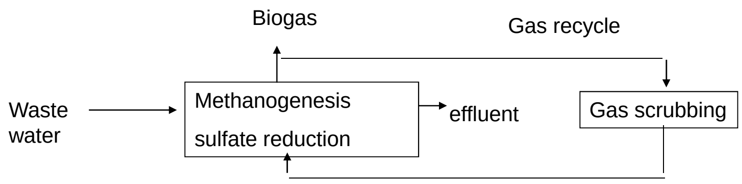
Methods for reducing H_2S concentration in UASB

1. Stripping of H_2S from the solution
2. Dilution of wastewater
3. Increase of the pH of the reactor

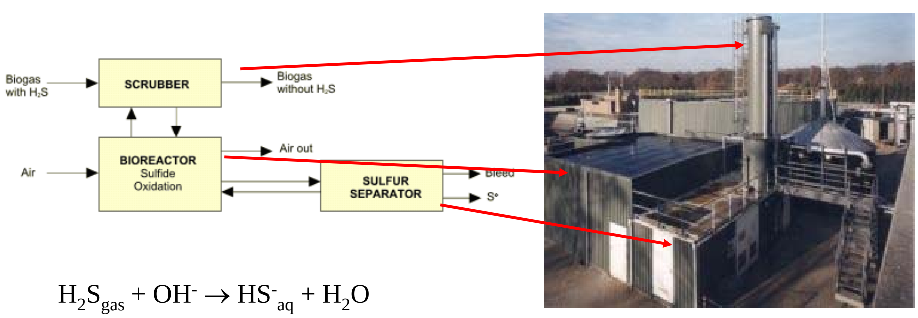
Toxicity relieve by H_2S stripping / removal

- addition of Fe-salts in the reactor

- stripping H_2S by biogas recirculation and biogas scrubbing



Biological biogas scrubber



$$H_2S_{gas} + OH^- \rightarrow HS^-_{aq} + H_2O$$

$$HS^- + ½\ O_2 \rightarrow S^0 + OH^-$$

THIOPAQ®- Bioscrubber for H_2S removal from biogas produced in papermill UASB, The Netherlands

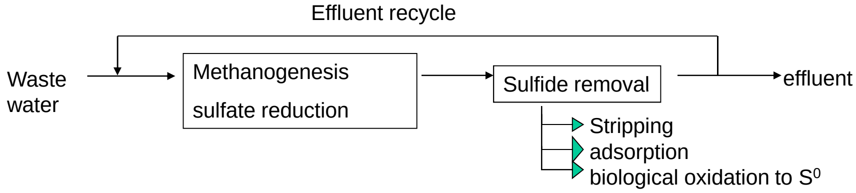
Low chemical consumption (90% chemical savings

High efficiency (99%)

S production

Toxicity relieve by dilution with H_2S-free effluent

Effluent Recirculation After Sulfide Removal



Preventive measure: separation of sulfide production and methanogenesis