Institute of Sanitary Engineering & Waste Management

Leibniz Universität Hannover

Systematic determination of the inert COD of industrial wastewaters in the context of COD fractionation

WaReIp
Water Reuse in Industrial Parks

GEFÖRDERT VOM
Bundesministerium für Bildung und Forschung

NaWaM WavE

12th IWA International Conference on Water Reclamation & Reuse in Berlin 2019

- Innovative Treatment Technologies & Applications -
Disruptive technologies for hard-to-treat wastewater

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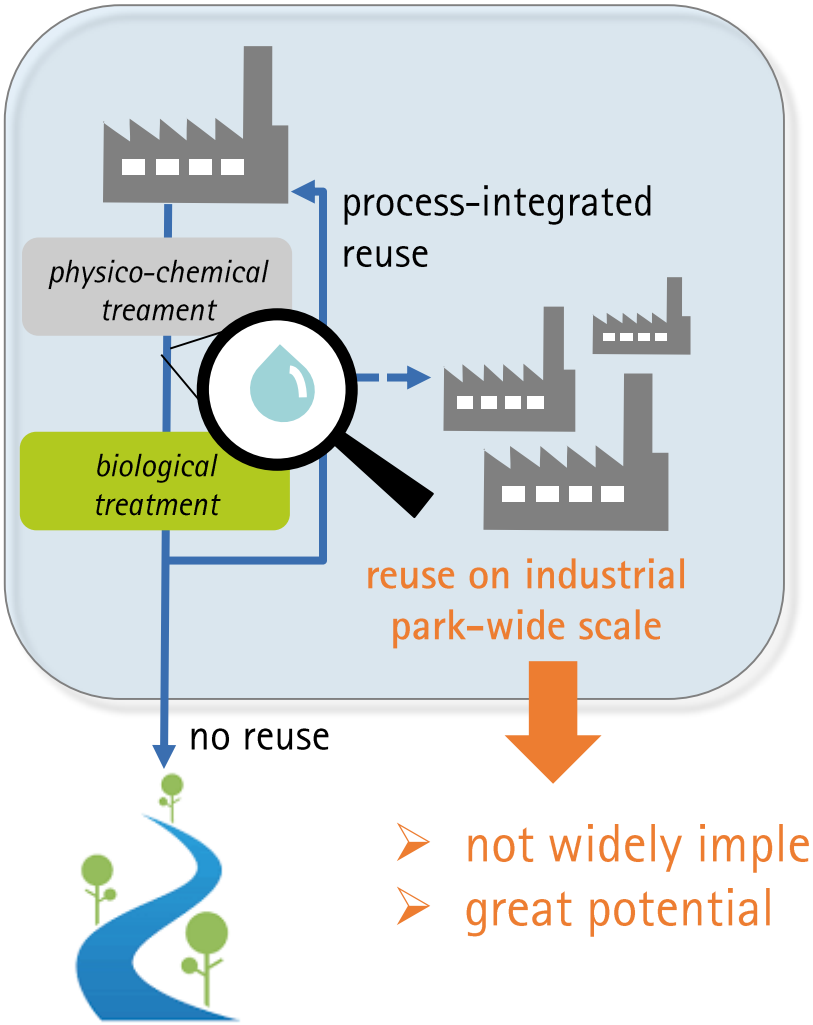
Introduction

Water Reuse in Industrial Parks



- not widely implemented
- great potential

Challenges for biological treatment

- salt concentrations
- toxic substances
- high concentrations & fluctuations
- **poor biodegradability**

What is „poor“ biodegradability?

- apparent poor biodegradability due to
  - Toxins
  - Harsh conditions (pH, salt, etc.)
  - Nutrient deficiency
- very, very slow degradation rate
- concurrent substrates (diauxie)
- refractory nature of the substances (e.g. anthropogenic origin)

Relevance of biodegradability

(Poor) biodegradability…

- of industrial wastewaters is **crucial** for reuse implementation
- can lead to **accumulation** of non-biodegradables in the reuse cycle
- is especially important for the **biological treatment** process due to its advantages in terms of **energy & costs**
- assessment & definition are **not harmonized** and often **time-consuming**
  - BOD_5/COD ratio
  - Zahn Wellens Test (DIN EN ISO 9888)
  - OECD Biodegradability Tests (301, 302, 303, 310)

Comparison difficult!

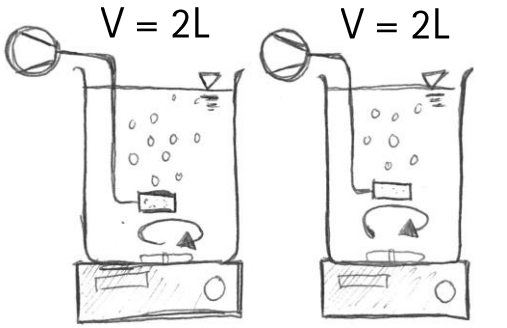
Objectives

- **identify** important **industrial sectors** with regard to poor biodegradability
- **gather data** on **inert COD and DOC** from literature and lab experiments

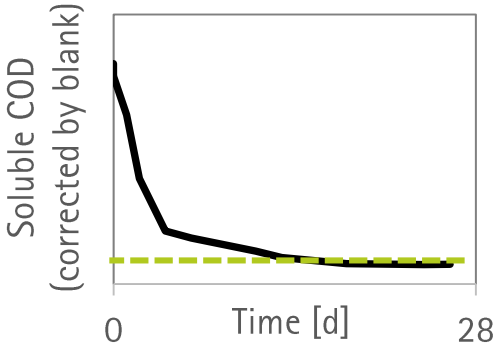
- identify **influencing factors** on the outcome of biodegradability tests
- Which measurement method is most suitable for…
  - **designing** (reuse) treatment concepts?
  - **operation monitoring?**

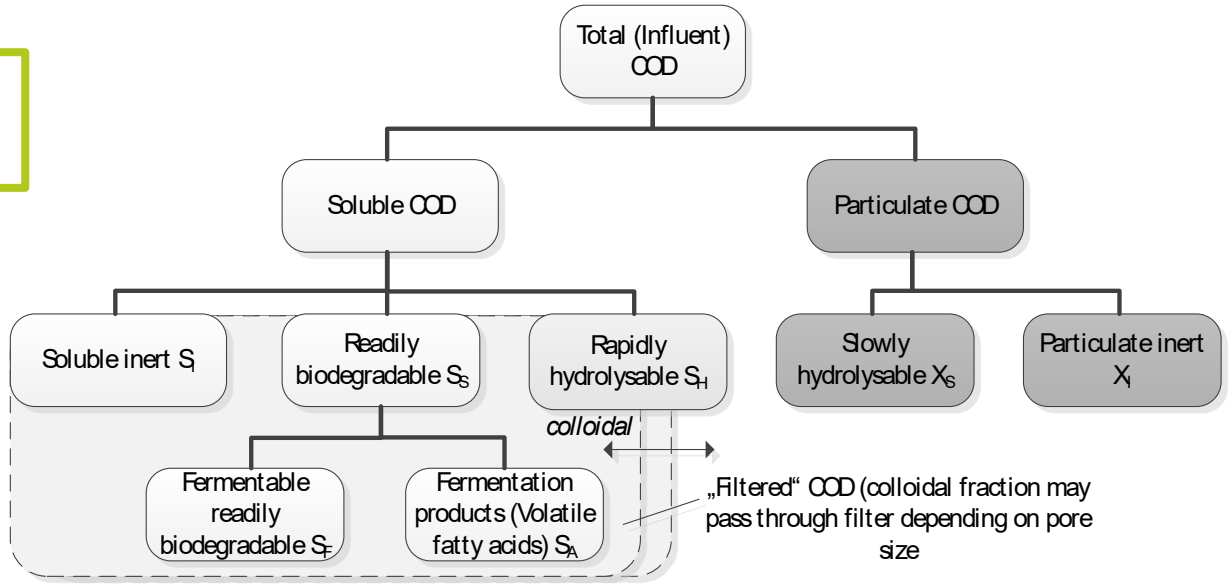
How can we determine COD fractions?

Experimental Set Up for (modified) Zahn Wellens Test



Resulting degradation curve





Soluble inert S_I	Readily biodegradable S_S	Rapidly hydrolysable S_H	Slowly hydrolysable X_S	Particulate inert X_I
Zahn-Wellens Test (DIN EN ISO 9888) Effluent sCOD of a CAS Reactor in lab- or large-scale (DWA A131)	Oxygen Uptake Rate (OUR) (Ekama et al., 1986) Flocculation-filtration (Mamais et al., 1993) Ultrafiltration (Dold et al., 1986)	$S_{total} - S_I - S_S$	$X_{total} - X_I$	Modified Zahn-Wellens Test with unfiltered samples (Orhon et al., 1993) CAS Reactor coupled with computational model and calibration of sludge production through X_I) (Henze et al. 1987)
	Fermentable S_F: $S_S - S_A$	Volatile fatty acids S_A: Gas Chromato-graphy		

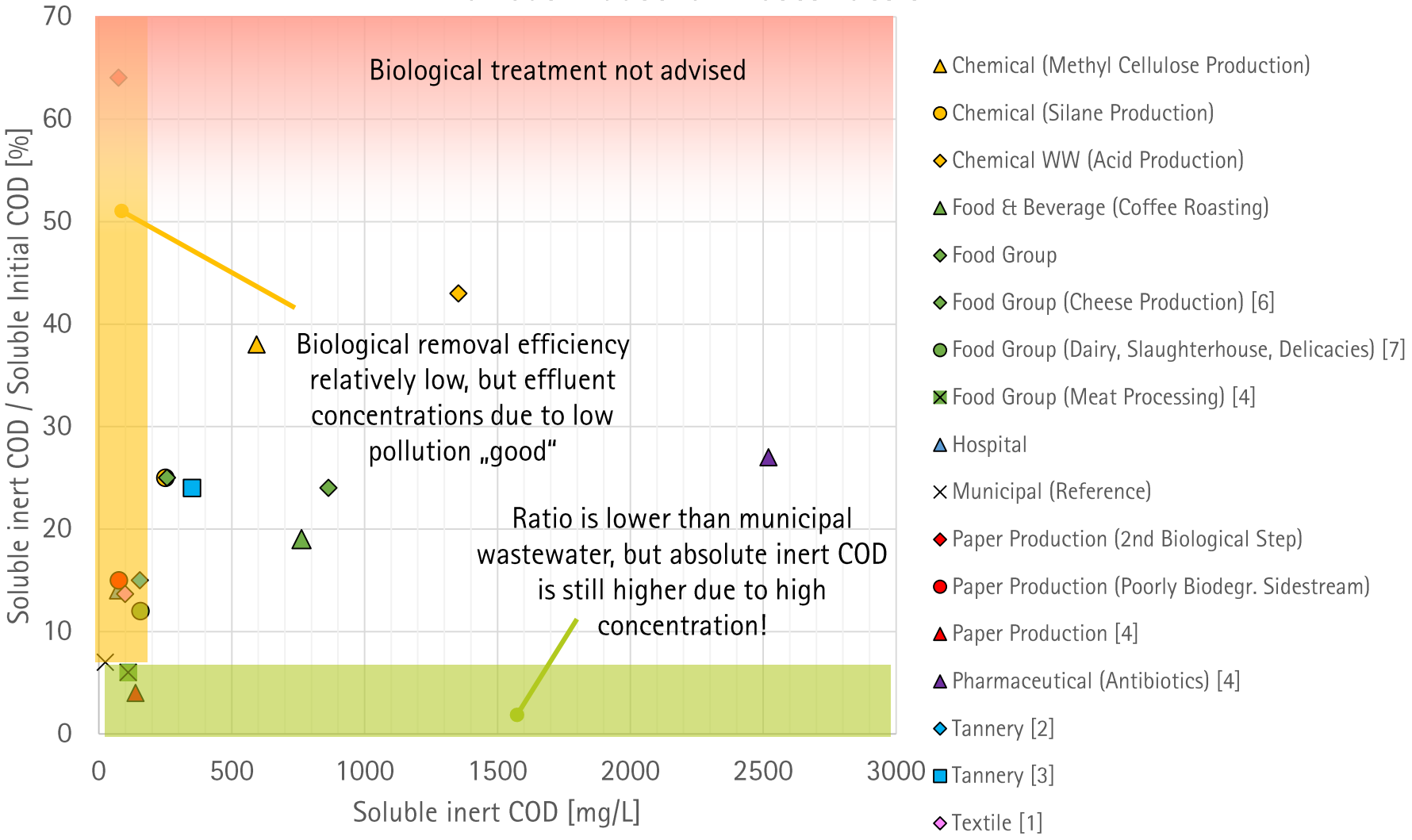
Figure & Table: Influent COD fractionation model according to Henze et al. [8] and suggested methods for determination of the fractions

Industrial wastewater „screening“

Important sectors with poorly biodegradable wastewaters

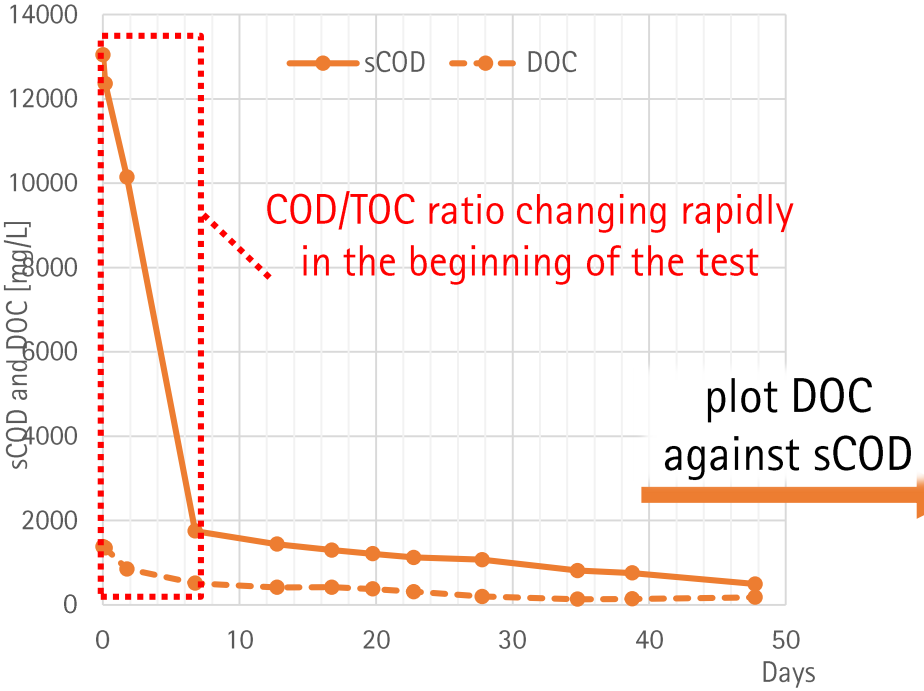
- molasse-based industries, such as **yeast production** and **alcohol production** [9], [10], [11]
- **paper and cellulose** production containing lignins, cellulose and additives ([12], [13])
- **textile industry** containing polymers and carboxy methyl cellulose (sizing agents)
- **chemical/ pharmaceutical industry** with numerous compounds, such as methyl cellulose (thickening agent)
- in **coal gasification wastewater** 40 to 50% of the total COD originates from poorly biodegradable phenols [14]

Industrial wastewater „screening“



COD/TOC ratio as online-monitoring parameter

- COD/TOC ratio is specific for each substance and wastewater



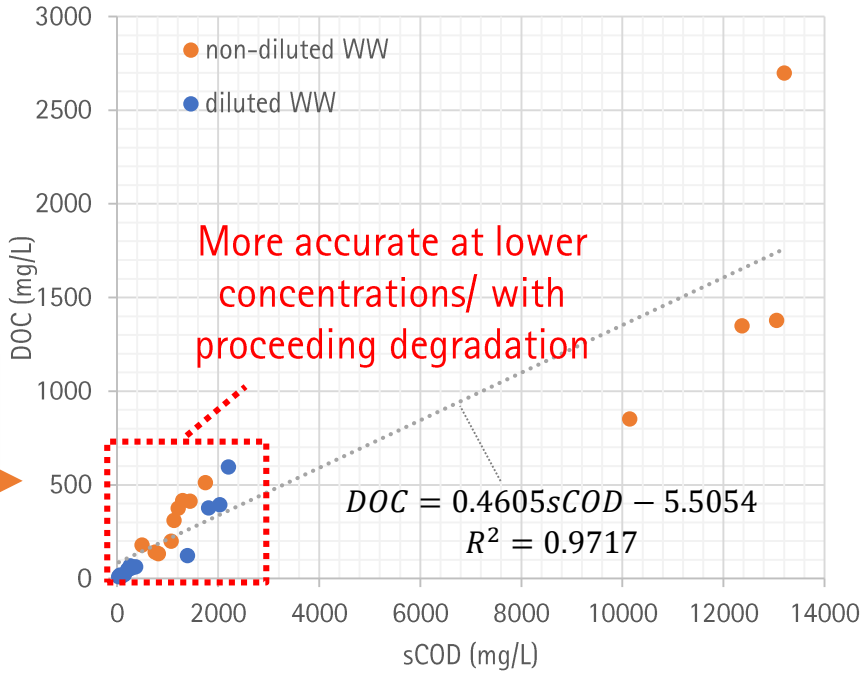


Figure 1: COD and DOC Degradation test (modified Zahn Wellens Test) of a industrial wastewater containing thickening agents (CMC and MC)

Figure 2: Regression analysis for COD and DOC of a industrial wastewater

➢ change in the influent COD/TOC ratio is an indicator for changing biodegradability characteristics → **monitoring parameter**

Zahn Wellens Test – variability and influencing factors

Wastewater Sample	Dilution	F/M Ratio [mg COD/ mg TSS]	Initial Soluble COD [mg/L]	Inert Soluble COD [mg/L] (→ undiluted)	Inert Soluble COD [%]	
Industrial Plant Stream 1 (CMC and MC)	1:1	0.5	13,200	492	3.7	1)
Industrial Plant Stream 1 (CMC and MC)	1,6:10	0.5	2,200	32 → 192	1.45	
adapted sludge: Industrial Plant Stream 2 (MC)	1:1	0.5	8,640	257.6	3.27	1)
adapted sludge: Industrial Plant Stream 2 (MC)	1:10	0.5	1,956	39.8 → 398	1.7	
*Industrial Plant Stream 2 (MC)**	*1:10*	*0.5*	*1,956*	*127.1 → 1271*	*6.89*	2)

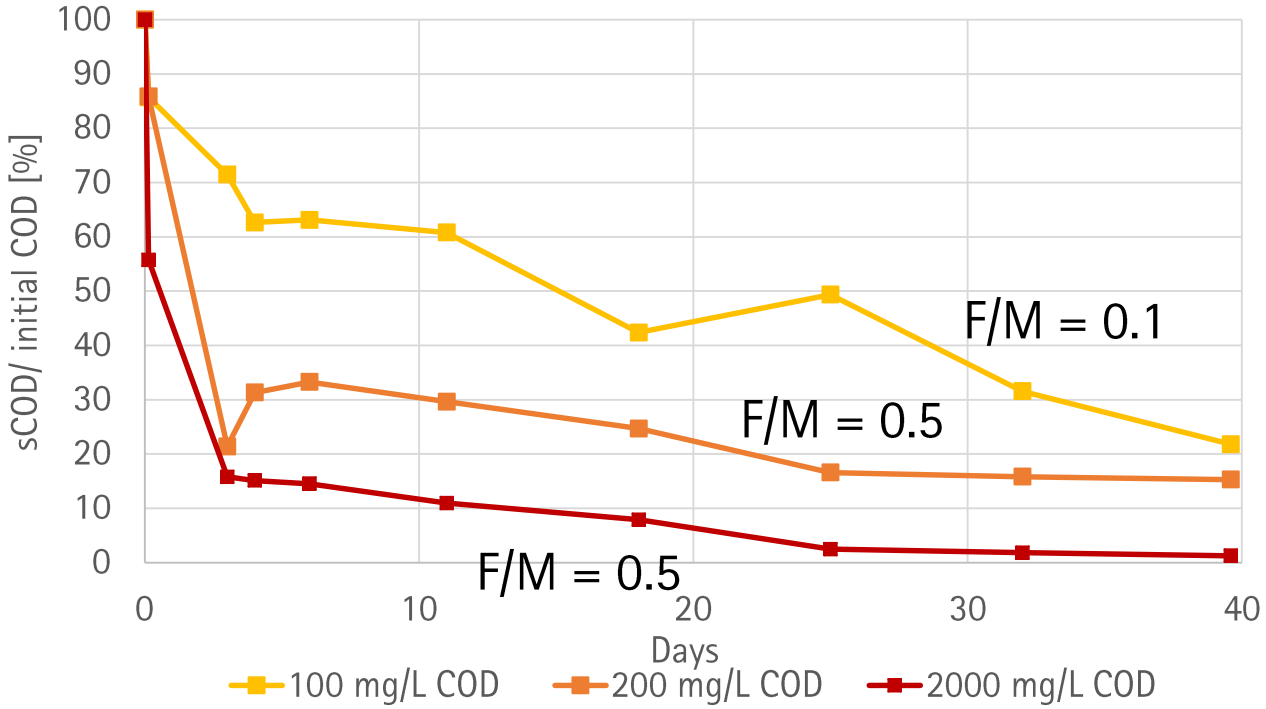
Degradation results are influenced positively by...

1) Dilution
2) Adaptation of the sludge
   - ➢ Convergence towards same value in the end?

**test ongoing (35 days)*

Zahn Wellens Test – variability and influencing factors

- test series on **Tannic Acid and varying Food/Microorganism Ratios** [mg COD / mg TSS] and dilutions



- F/M ratio has influence on degradation rate but also on the outcome of the test

Conclusions

- Many industrial sectors, e.g. chemical, textile & yeast industry have significant poorly biodegradable fractions
  - ➢ assessment of inert fractions is necessary – especially with regard to water reuse and an economic design of the reuse plant
- Provided industrial wastewater screening data can be used in the early planning stage and in benchmark analysis

- Need for harmonization of biodegradability tests
- Understanding the variances in the Zahn Wellens Test results increases the knowledge of the basic microbiological processes
  - ➢ Knowledge can be transferred into operational parameters for optimizing biological treatment processes

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Thank you for your attention!

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