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Bio-recalcitrant Pollutants Removal from Wastewater with Combination of the Fenton Treatment and Biooxidation

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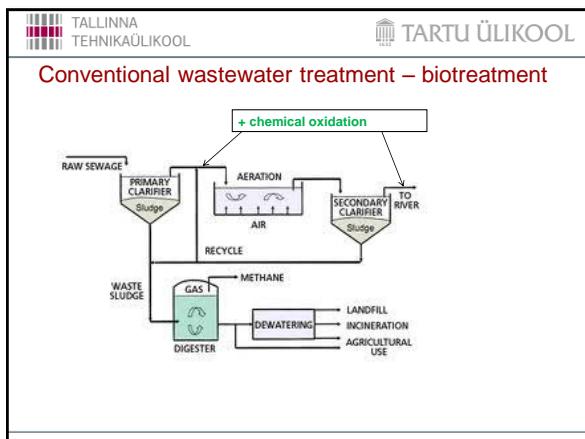
Introduction

The pollution load to the water bodies in Estonia was constantly decreasing during last 20 years. However, the total values characterizing the pollution load in year 2013 remained notable:

814 tons of BOD ₇	6650 tons COD
2461 tons of suspended solid	1228 tons of N _{total}
66.4 tons of P _{total} were discharged into receiving water bodies.	

Some industrial wastewaters in Estonia contain considerable amount of organics that are totally **refractory** to biotreatment or their biotreatment efficacy is quite low.

The biodegradability of wastewater could be enhanced by introduction of chemical oxidation or other chemical-physical processes as an additional step in wastewater treatment schemes.



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Objective of the study

To develop strategies for implementation of **combined** chemical and biological treatment: upgrade the classical wastewater treatment scheme (primary settling – aerobic biotreatment – secondary settling – anaerobic biotreatment of sludge) introducing the **chemical treatment step** for degradation of recalcitrant organics, improvement of biodegradability and wastewater purification degree, and, thus, lowering total pollution load.

The target was to remove over 80 % of organic load (COD) and improve other wastewater characteristics at least by 50 %.

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Chemical treatment

Coagulation (iron- or aluminum salts)

Fenton-process

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}\cdot + \text{HO}\cdot \quad (1)$$

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2\cdot + \text{H}^+ \quad (2)$$

Persulphate

$$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightarrow 2\text{SO}_4^{\cdot-} \quad (3)$$

$$\text{S}_2\text{O}_8^{2-} + \text{activator} \rightarrow \text{SO}_4^{\cdot-} + (\text{SO}_4^{\cdot-} + \text{SO}_4^{\cdot-}) \quad (4)$$

Ozonation (O₃)

Direct reaction with ozone (acidic conditions)
 Reaction with (hydroxyl)radicals (basic conditions)

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Table 1. Main Characteristics of Studied Wastewaters

Parameters	Municipal landfill leachate (MLL); landfill operated since 2003	Hardwood soaking basin wastewater from plywood industry (PWW)	Leachate from shale oil processing semicoke landfill area (SCL)	Discharge limits set by Estonian legislation
COD, mg/L	5900-15700	5100-7800	1000-2100	125 (250; 1250)
BOD ₇ , mg/L	3100-10970	1600-3500	175-196	15 (125)
Recalcitrant COD, %	15	7	15	
Total nitrogen, mg/L	710-2000	11-69	10-42	10-60 (75)
Total phosphorous, mg/L	19	33-60	40-42	0.5-2
Inhibition of oxygen consumption, I ₅₀ %	No	25.5	No->20	
Inhibition of nitrogen consumption, I ₅₀ %	5.9	17	16	

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The treatment schemes tested:

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    graph LR
        A[Chem] --> B[Bio]
        B --> C[Chem]
        D[Bio] --> E[Chem]
        F[Wastewater] --> G[BIO]
        G --> H[FENTON]
        H --> I[BIO]
        I --> J[Effluent]
    
```

Chemical (the Fenton) Treatment
High potential for degradation (mineralisation) of organics

Biological Treatment
Sustainable, cheap and efficient when operating under suitable conditions

The target is high efficacy and low (acceptable) cost!

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The Fenton treatment

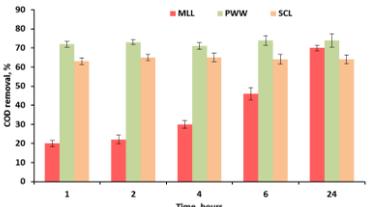



Fig.1. COD removal with the Fenton treatment (MLL – municipal landfill leachate, COD/H₂O₂/Fe²⁺, g/g/g, 1/3,45/0,7; PWW – pre-coagulated hardwood soaking basin wastewater from plywood industry, COD/H₂O₂/Fe²⁺, g/g/g, 1/1/0,2; SCL – leachate from oil shale processing semicoke landfill area, COD/H₂O₂/Fe²⁺, g/g/g, 1/1/0,2).

Cost of the chemicals 4-25 EUR/m³!!!

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Municipal landfill leachate (MLL)



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Municipal landfill leachate (MLL)

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    graph LR
        A["COD = 6790±50 mg/L  
BOD7 = 4700±300 mg/L  
Ntotal = 840±40 mg/L  
C(phenols) = 33 mg/L"] --> B[BIO]
        B --> C[FENTON]
        C --> D[BIO]
        D --> E[discharge]
    
```

COD = 550±30 mg/L (↓ 92%)
 BOD₇ = 213±13 mg/L (↓ 95%)
 N_{total} = 500±20 mg/L (↓ 40%)
 C(phenols) = 2.4 mg/L (↓ 93%)

COD = 1840±19 mg/L (↓ 73%)
 BOD₇ = 330±30 mg/L (↓ 93%)
 N_{total} = 510±10 mg/L (↓ 39%)
 C(phenols) = 15.8 mg/L (↓ 52%)

COD = 400±34 mg/L (↓ 94%)
 BOD₇ = 19.4±9 mg/L (↓ 99%)
 N_{total} = 371±30 mg/L (↓ 56%)
 C(phenols) = n.d. (↓ ca 100%)

The cost of the treatment (7.5 €/m³ ; 70 %) compare to 4.33 €/m³ + transportation for the local WWTP

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Hardwood soaking basin wastewater from plywood industry (PWW)



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    graph LR
        A["COD = 6830±250 mg/L  
BOD7 = 3530±275 mg/L  
Ntotal = 69.3±3.5 mg/L  
C(phenols) = 94±6 mg/L"] --> B[BIO]
        B --> C[FENTON 1]
        B --> D[FENTON 2]
        C --> E[BIO]
        D --> F[BIO]
        E --> G[discharge]
        F --> H[discharge]
    
```

COD = 460±30 mg/L (↓ 93%)
 BOD₇ = 164±40 mg/L (↓ 95%)
 C(phenols) = 5.9±0.4 mg/L (↓ 94%)

COD = 180±8 mg/L (↓ 97%)
 BOD₇ = 20±2 mg/L (↓ 97%)
 N_{total} = 6.2±0.5 mg/L (↓ 90%)
 C(phenols) = n.d. (↓ 100%)

COD = 1490±120 mg/L (↓ 78%)
 BOD₇ = 300±40 mg/L (↓ 92%)
 N_{total} = 8.5±0.7 mg/L (↓ 88%)
 C(phenols) = 15.4±0.5 mg/L (↓ 84%)

COD = 220±30 mg/L (↓ 97%)
 BOD₇ = 102±10 mg/L (↓ 97%)
 C(phenols) = n.d. (↓ 100%)

COD = 90±3 mg/L (↓ 99%)
 BOD₇ = 10±1 mg/L (↓ 99.7%)
 N_{total} = 6.0±0.2 mg/L (↓ 90%)

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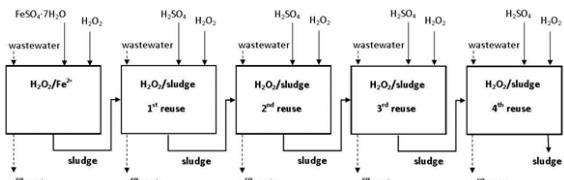
Leachate from oil shale processing semicoke landfill area (SCL)



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The Fenton-based treatment – sludge reuse



The high efficacy of the iron-containing sludge without any regeneration enables to carry out the Fenton-based treatment **waste-free!**
 More details in Bolobajev et al., *Chemical Engineering Journal*, 2014, 255:8–13.

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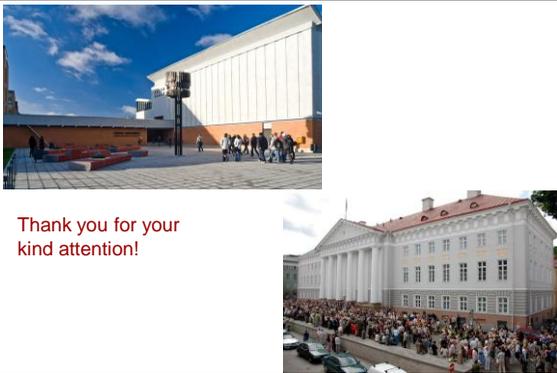


BIO-CHEM-BIO scheme has been successfully applied for MLL in pilot scale. The removal efficiency was even **higher** compared to the lab-scale study.

Acknowledgements

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Thank you for your kind attention!