Towards a sustainable fine chemical and pharmaceutical industry: screening and re-utilization of carbon-rich liquid wastes
SH7/2/14

Schweizerische Eidgenossenschaft
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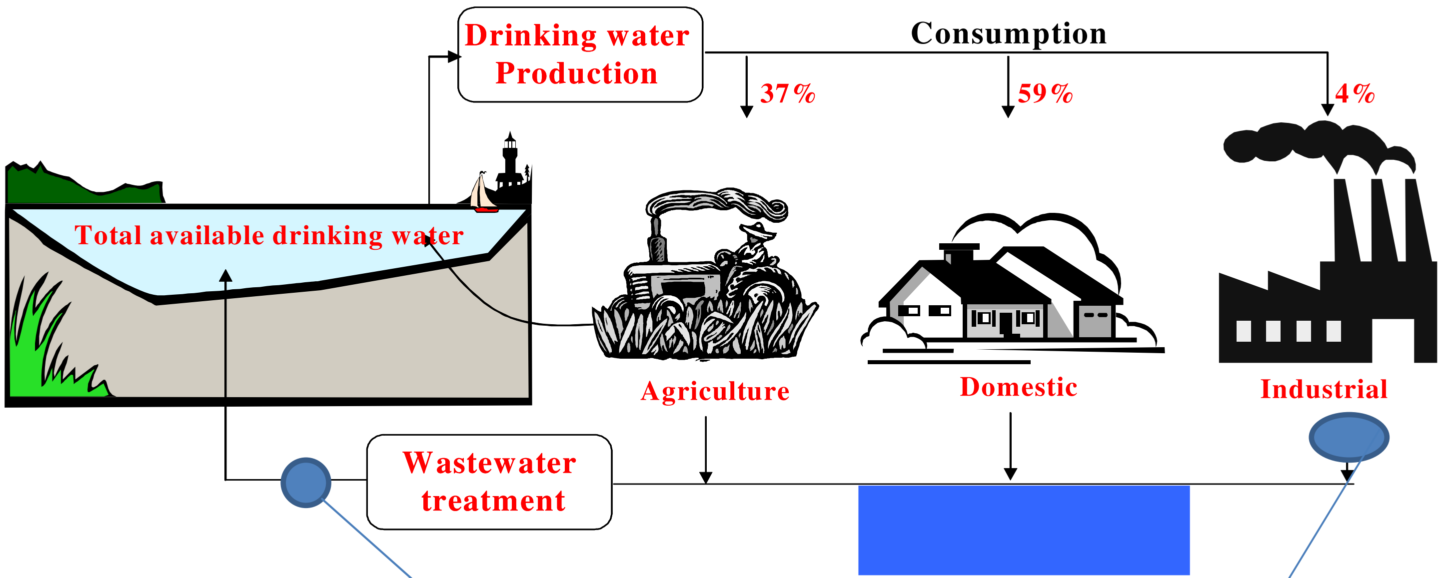
Swiss Contribution

HAS CER (former IOI), BME, BSW, GEOSAN and EPFL
Andrea Jobbágy, Gábor Tardy, Péter Mizsey, László Wojnárovits, Erzsébet Takács, Renáta Homlok, Antal Tungler, Magdolna Makó, Arezoo Hosseini, Szilvia Szikora Tarjányiné, Chamam Mounir, Balázs Pinke
Cesar Pulgarin, John Kiwi, Ruales Ceron Christina, László Kaszanyiczky, Natalia de la Cruz, Laura Esquius

Content of the presentation

- Introduction of the problem, previous project activities of consortium members
- Starting points of the project
- Testing and treatment methods
- Results in Biodegradation, VOC removal, Wet oxidation, Anaerobic digestion, High energy irradiation+oxidation, AOP processes
- Summary about „half-time” results

Water Cycle in the Center of Human Activities



Emergent organic contaminants (EOCs) are naturally or synthetic substances which:

- have the potential of entering the environment
- cause adverse ecological or negative effects on human health
- most of them are not regulated

Principal *sources* of EOCs are:

- wastewater treatment plants that treat domestic sewage
- wastewater from hospital effluents
- chemical manufacturing plants
- livestock and agriculture

Our activities in these sites

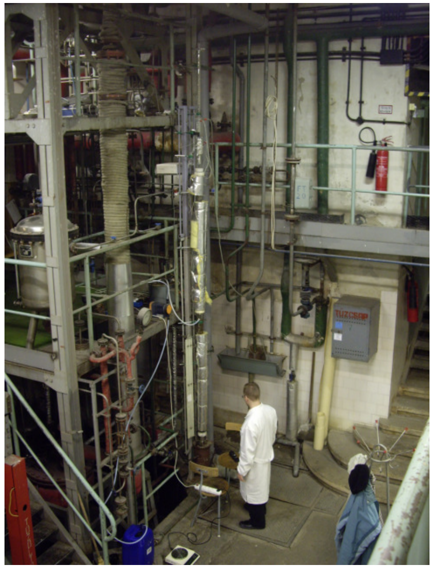
Previous activities of consortium members

Swiss participant, *EPFL*
AOP process development, combined chemical, catalytic oxidation and coupled biological treatment

Hungarian participants
Jedlik project: ***BME ABFS, CEPE, BSW, GEOSAN***
complex treatment of process wastewaters of pharmaceutical production
HAS IOI high energy radiation of wastewaters containing organic compounds, destruction of dyes, drugs.

Coupled solar-biological reactor at pilot scale

Pilot plant column Sulzer structured packing,4 m high N_{th}~10 - 15



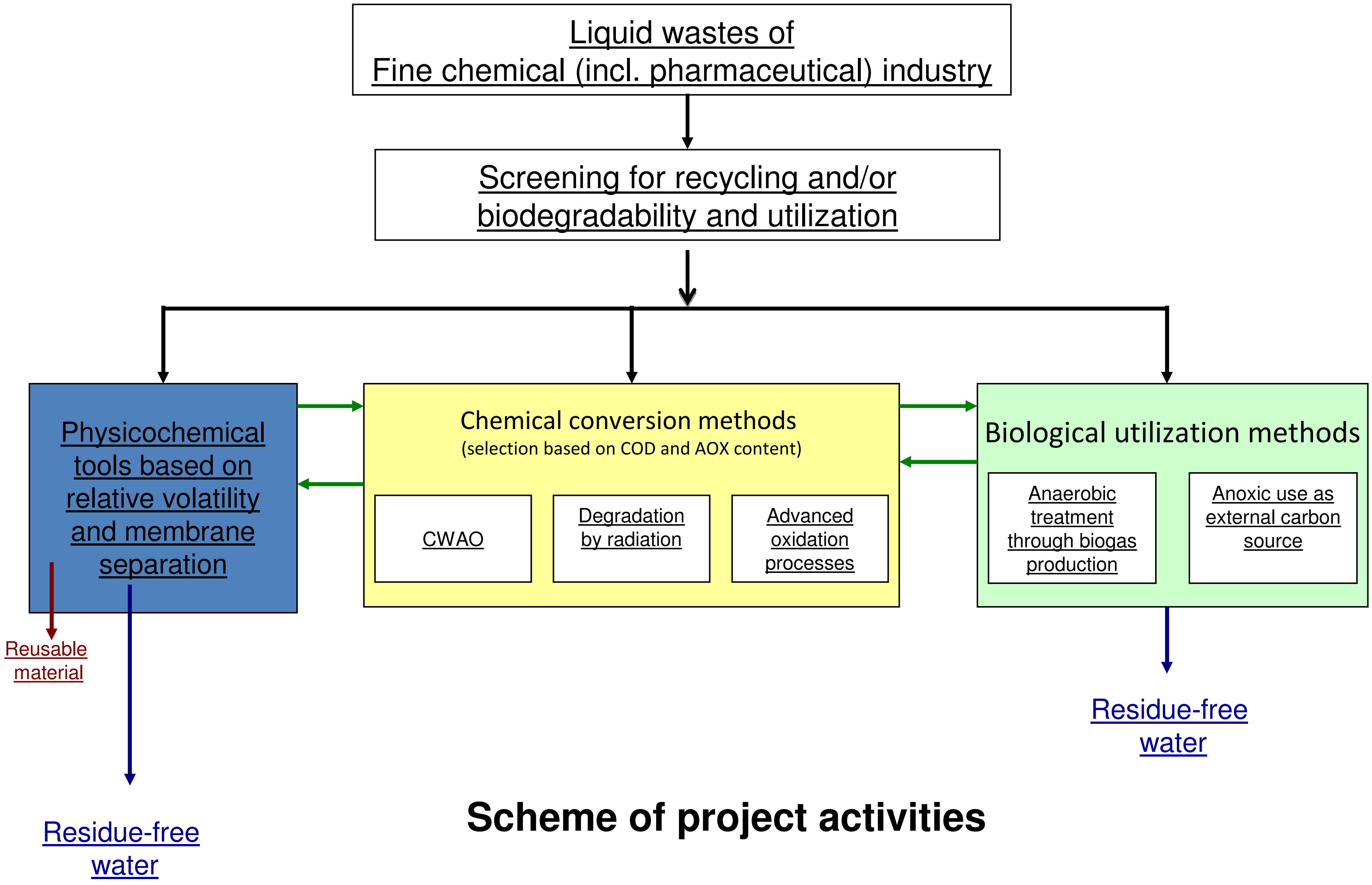
Pilot scale oxidation reactor GEOSAN Ltd Pétfürdő

Starting points of the project

The pharmaceutical industry is leading in Switzerland and it is one of the main components of the chemical industry in Hungary.
Increasing production may well be accompanied by increased amounts of byproducts and wastes, among others carbon-rich, liquid wastes, disposed mainly through incineration.

The basic idea of the proposed project is, that major part of the carbon-rich wastes could be utilised in biological N-removal as carbon source for denitrification in domestic wastewater treatment, or for anaerobic biogas production.

The purpose of the project is (i) to elaborate a novel biological screening methodology taking the concentration dependence of biodegradability and toxicity as well as possibilities offered by the co-treatment with domestic wastewaters into consideration,
(ii) to work out pretreatment procedures using physico-chemical separation processes, combined with chemical and/or catalytic methods in order to make originally non-biodegradable, toxic wastes utilisable and/or biodegradable, moreover remove residual bioactive compounds in treated water coming out from WWTP's.



Scheme of project activities

Primary elaborated selection method - respirometry

Test compounds used: diclofenac, dimethyl formamide

Investigated concentrations:

~300 mgCOD/l ~150 mgCOD/l

~75 mg COD/l

Minerals addition: NH_4Cl, KH_2PO_4, K_2HPO_4, $MgCl_2$, $CaCl_2$

Investigation of co-metabolism

co-substrate: peptone

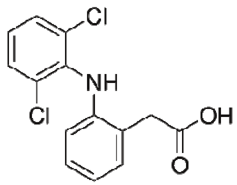
concentration: 20% of the test compound

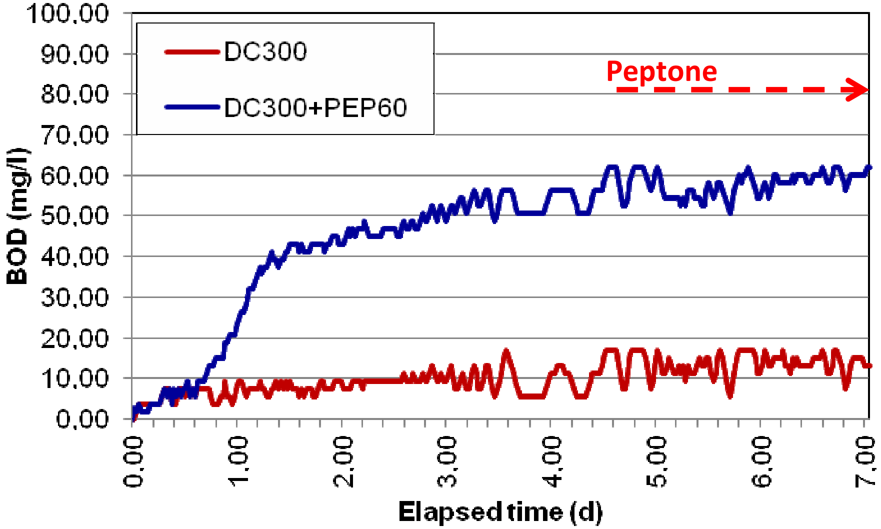
Origin of the seeding biomass: domestic WWTP

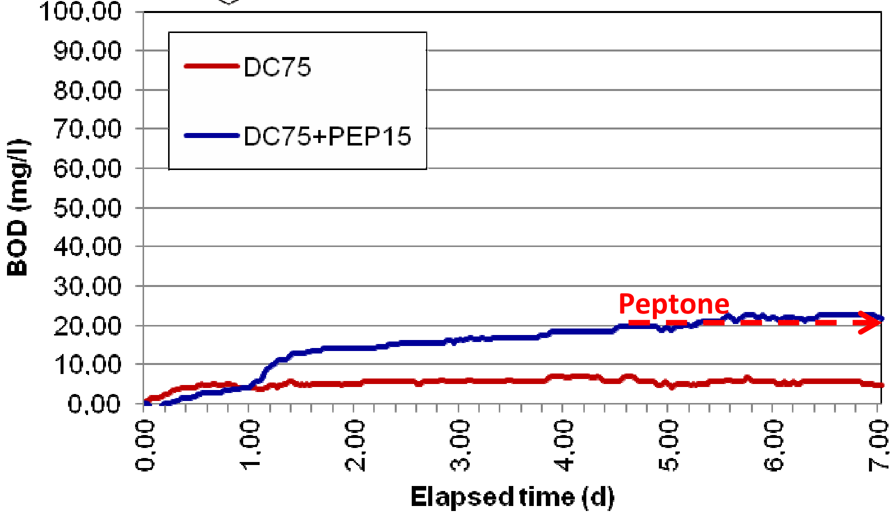
Temperature: 20 °C, **pH:** 7,4-7,8

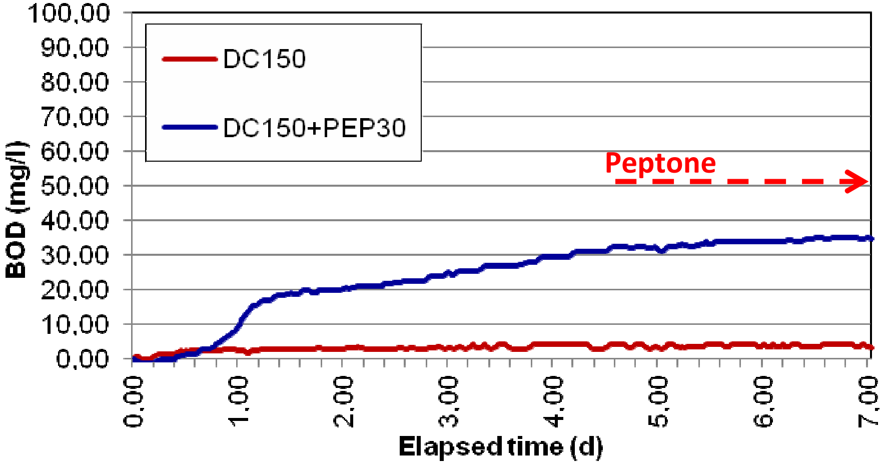
Real pharmaceutical wastewaters were also tested!

Test results for diclofenac



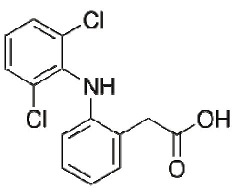


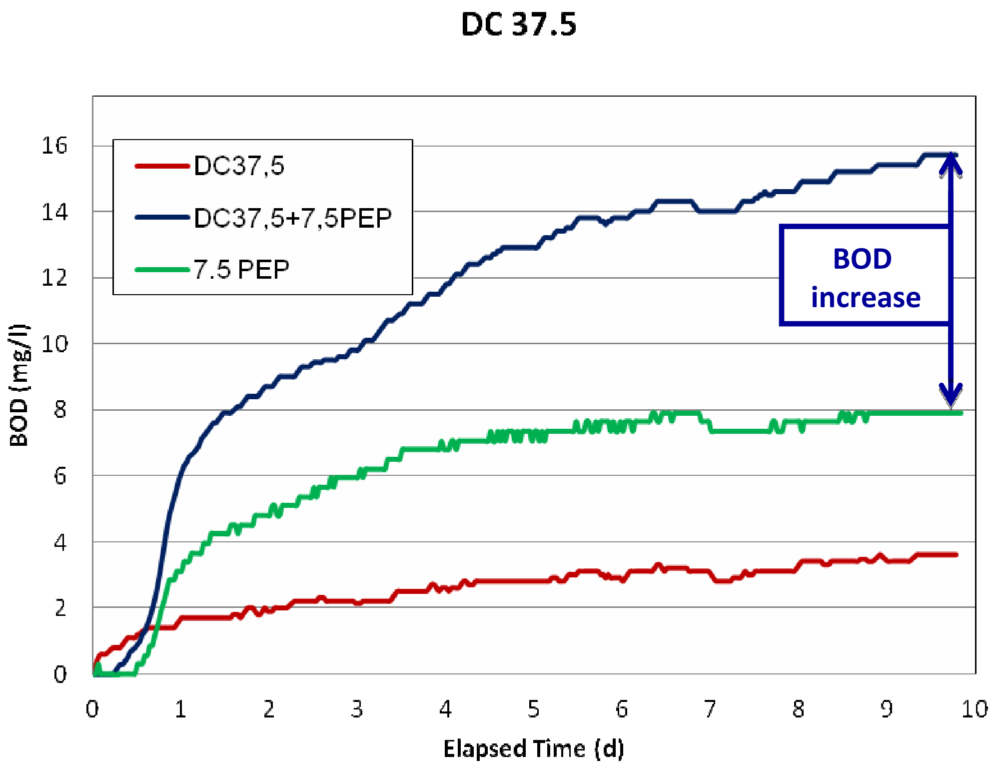


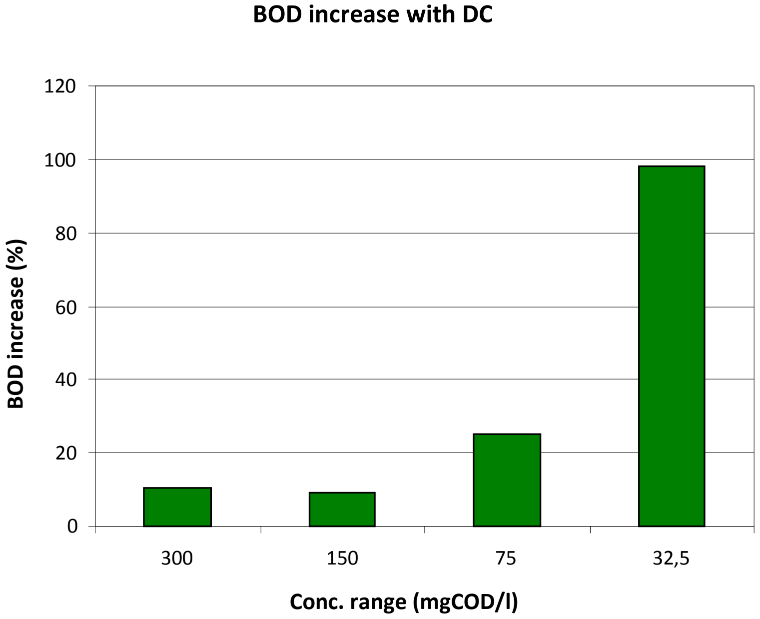


BOD_7/COD ratio (%)	DC	DC + Peptone	Theor. peptone
Diclofenac conc.			
283 mgCOD/l	4,6	17,8	19,4
146 mgCOD/l	2,2	20,3	23,9
83 mgCOD/l	6,7	25,9	28,6

Diclofenac biodegradation with seeding biomass originated
from domestic WWTP with 20 % industrial influent







Biodegradation of pharmaceutical real liquid wastes
Waste „B" – Total COD ~ 410 000 mg/l

Basic components:
Benzylamine HBr
Benzylamine HCl
Toluene
Dilution~1500x

	BOD_{10}/COD (%)	COD removal (%)	Final COD (mg/l)
B300+PEP60	84	88	41
B300	96	86	33

Biodegradation of pharmaceutical liquid wastes
Waste „II" – Total COD ~ 265 000 mg/l

Basic components: Sodium methyl sulphate, PEG, Methanol Dilution ~1000X

COD removal efficiency with peptone cofactor >80%

Biodegradation of pharmaceutical liquid wastes
Waste „XX" – Total COD ~ 455 000 mg/l

Basic components: Methanol, Morpholine Dilution~1000x

COD removal efficiency with peptone cofactor >60%

Determination of anaerobic biodegradability

Anaerobic sludge spiked with sample and the blank are stirred at mesophile or thermophile temperature for 5-28 days.

The OXI-Top C heads measure the pressure differences in the bottles for calculating biogas production.

According to the biogas productions the anaerobic biodegradability of different samples can be compared.

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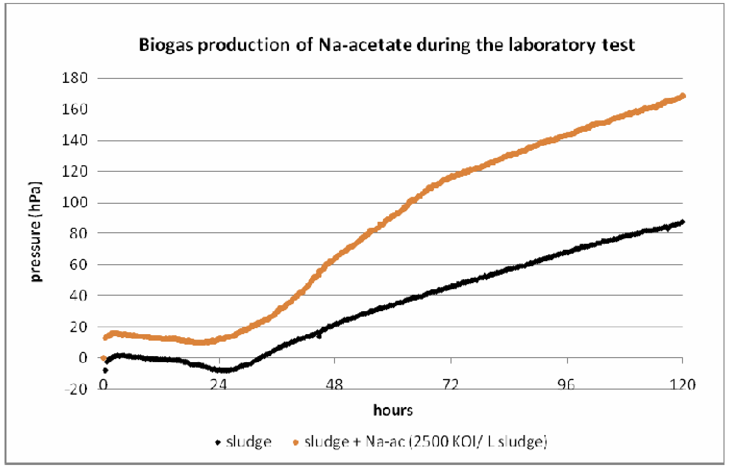
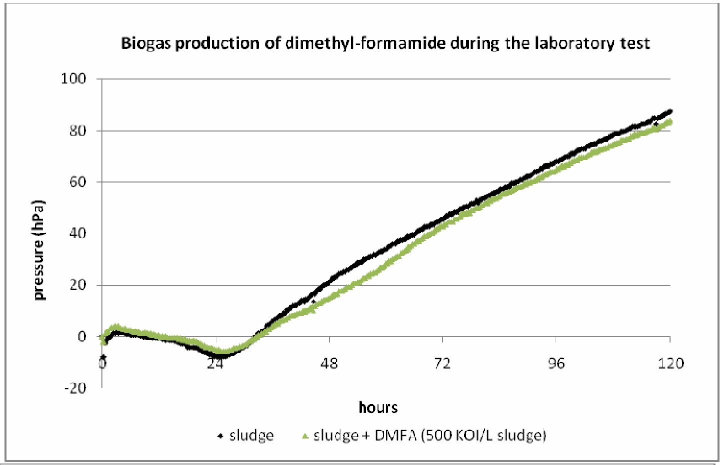
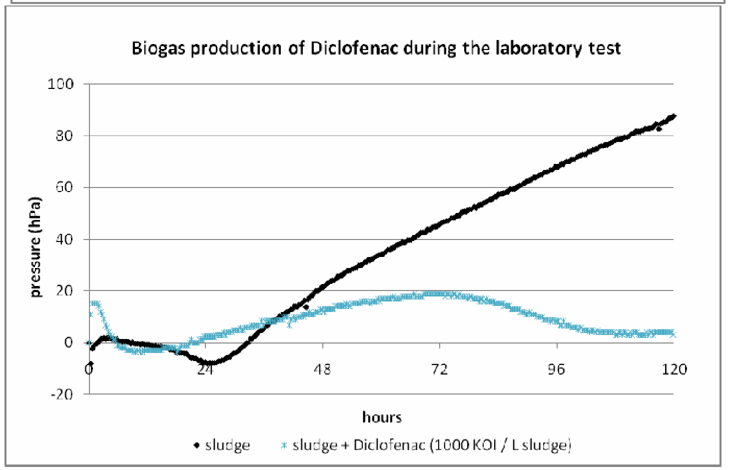
Biogas production



Anaerobic biodegradable Model comp. Na acetate



Anaerobic non-biodegradable DMF



Anaerobically toxic

EGIS wastewaters are all anaerobic non-biodegradable!!!

Conclusions of biodegradability tests

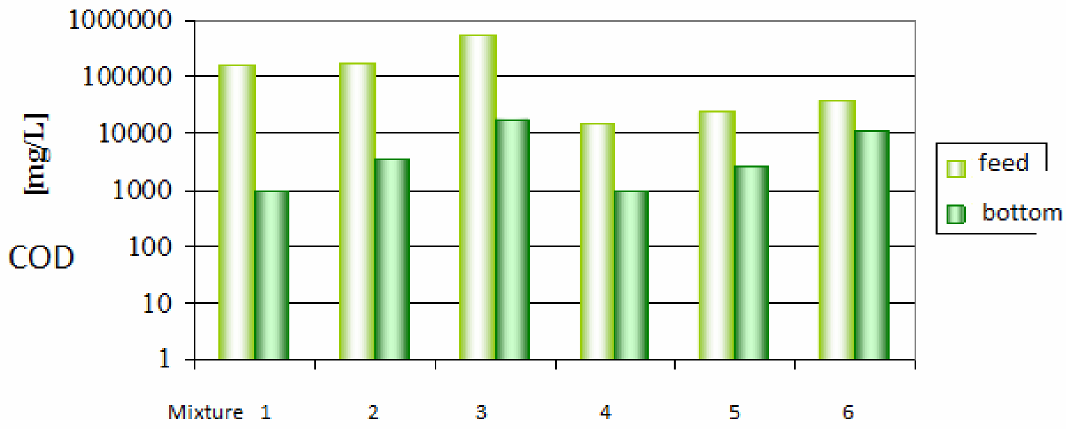
- **Elaboration of screening methods** for determining the biodegradability of liquid wastes and toxic materials has been **completed**.
- Selected methods: r**espirometry, Zahn-Wellens test, anaerobic digestion test**
- Test compound diclofenac (DFC) has proved to be non-biodegradable and showed toxic effect on biomass adapted to domestic wastewater. With **WAO** application, residues of diclofenac were found to be readily **biodegradable**, already after 1 hour pretreatment time. **Biomass adapted to wastewater containing 20% industrial effluent could degrade DFC in small concentration.**
- Adaptation phase required for dimethylformamide biodegradation, could be significantly reduced both by peptone added as co-substrate and with WAO pretreatment.
- In **anaerobic digestion DMF** was not biodegradable, **DFC** was toxic as well. Pharmaceutical wastewaters were all **non degradable**.

Presence of VOC's in Process waste waters

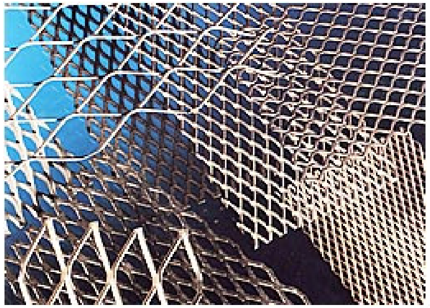
- PWWs have special feautres, from fine chemical industry,
- In our project basically from pharmaceutical industry, organic pollutants, many of them volatile or forms heteroazeotrope with water
- The volatile organic pollutants can cause high Chemical Oxigen Demand (COD, **VOC-COD**), higher than 100,000 mg O_2/lit.
- Adsorbable Organic Halids (AOX) other problems, they usually form heteroazotrope with the water, or highly volatile e.g. dichlormethane
- AOX can be problematic at other treatment alternatives
- Emission limits: COD 1000 mg O_2/lit, AOX: 8 ppm

Comparison of rectification and stripping with air..
Removal of volatile pollutants (VOC-COD)
Removal of AOX
Design of AOX removing distillation (reectifying) column.

Membrane treatment
Non-VOC

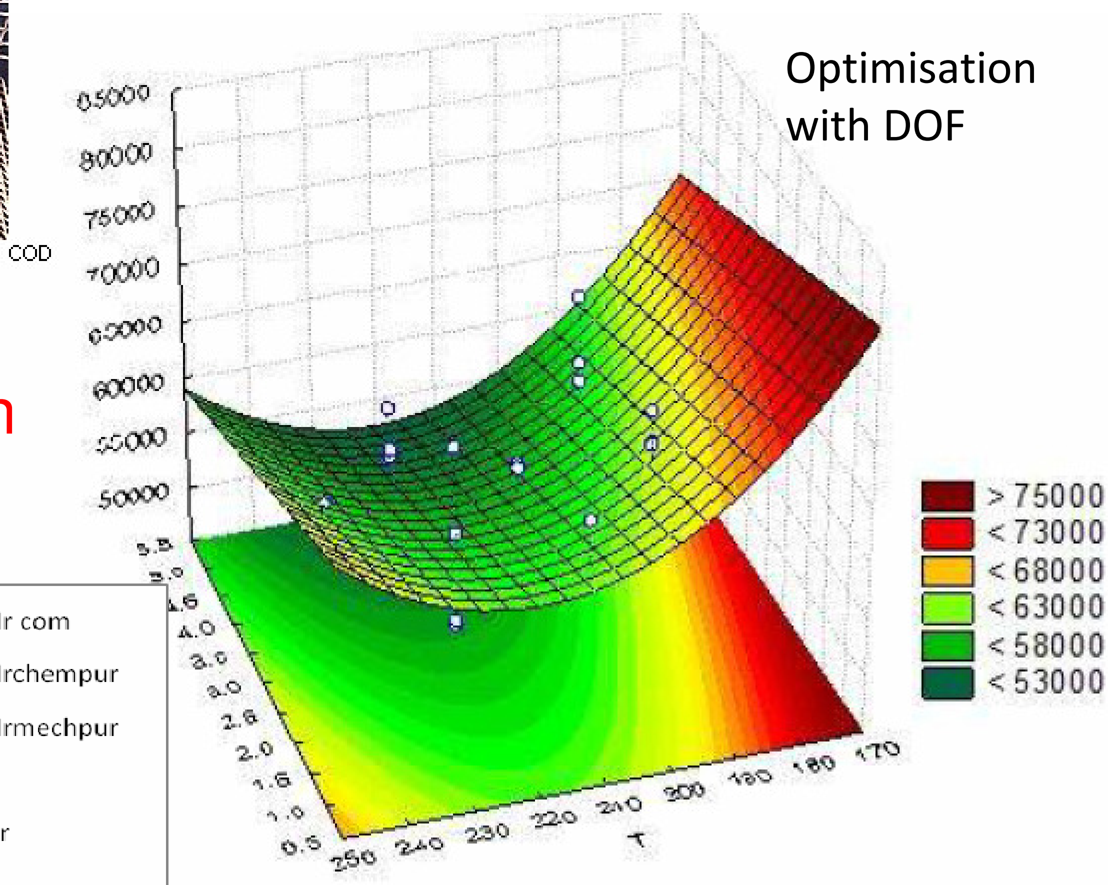


AOX < 8 ppm

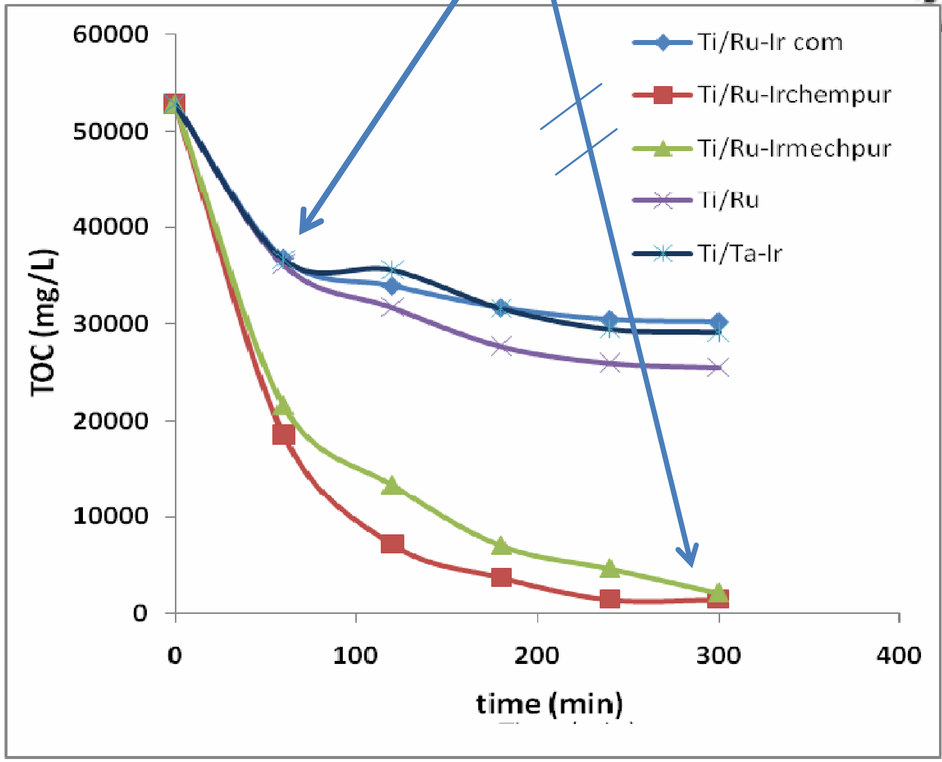


Wet oxidation of a process wastewater

Optimisation with DOF



No complete mineralization !!!



Catalytic wet oxidation at temperatures above 200°C and 50 bar pressure

Analyzed treated wastewater from Lausanne WWTP:

Family/Function		Substances	LOQ (ng L^{-1})	Wastew. (ng L^{-1})
Pharmaceuticals	**Lipid regulators**	Bezafibrate	8	426
		Gemfibrozil	2	25
		Simvastatin	15	nd
	Antidiabetic drug	Metformin	15	**1,027**
	Antiepileptic drugs	Carbamazepine	9	263
		Gabapentin	7	**1,737**
	Analgesics	Diclofenac	15	518
		Ibuprofen	15	112
		Ketoprofen	10	123
		Mefenamic acid	15	291
		Naproxen	30	178
		Paracetamol	50	nd
		Primidone	5	49
	Beta Blockers	Atenolol	7	669
		Metoprolol	5	179
		Sotalol	5	260
	Antibiotics	Azithromycin	40	295
		Ciprofloxacin	15	129
		Clarithromycin	3	518
		Metronidazole	50	456
		Norfloxacin	15	27
		Ofloxacin	15	41
		Sulfamethoxazole	5	578
		Trimethoprim	5	131

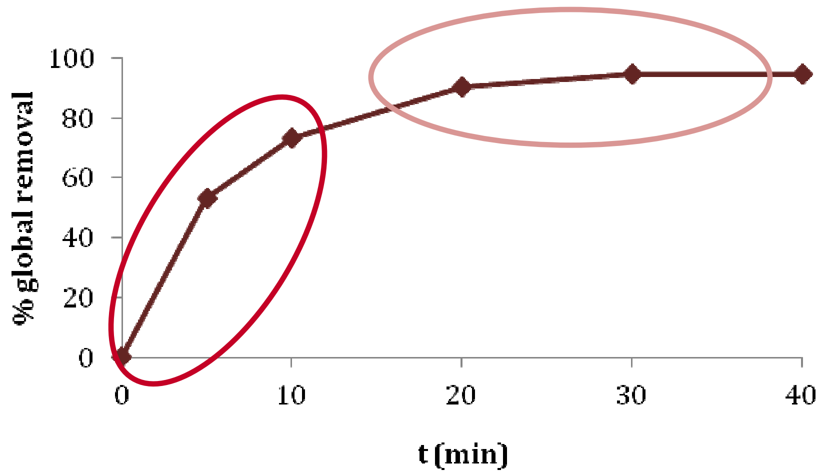
Family/Function		Substances	LOQ (ng L^{-1})	Wastew. (ng L^{-1})
Pharmaceuticals	**X-Ray contrast media**	Iohexol		**10,920**
		Iomeprol		**4,268**
		Iopamidol	240	**1,716**
		Iopromide	600	nd
Corrosion inhibitors		Benzotriazole	19	**2,781**
		Methylbenzotriazole	10	**1,535**
Biocides / Pesticides	**Biocide**	Triclosan	50	135
	Herbicides	Atrazin	4	9
		Diuron	40	57
		Isoproturon	10	nd
		Mecoprop	5	34
	Algicides	Irgarol	3	nd
		Terbutryn	3	19

Treated wastewater:
37 micropollutants were assessed at real concentrations (ng/L)
28 pharmaceuticals, 2 corrosion inhibitors and 7 biocides/pesticides
32 were found at the effluent of the MWTP → AOPs are required

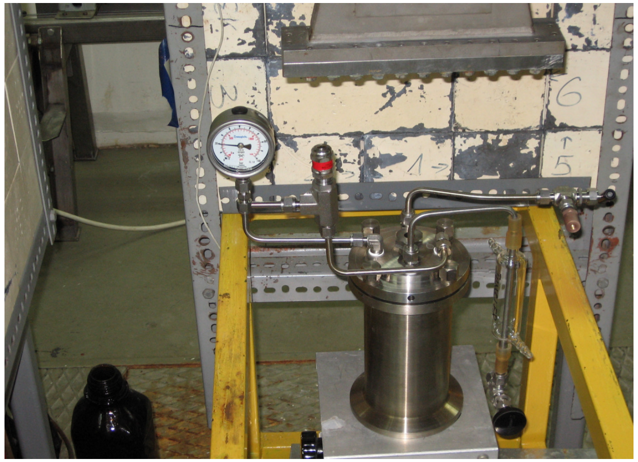
Effect of the differents versions of photo and photo-Fenton processess

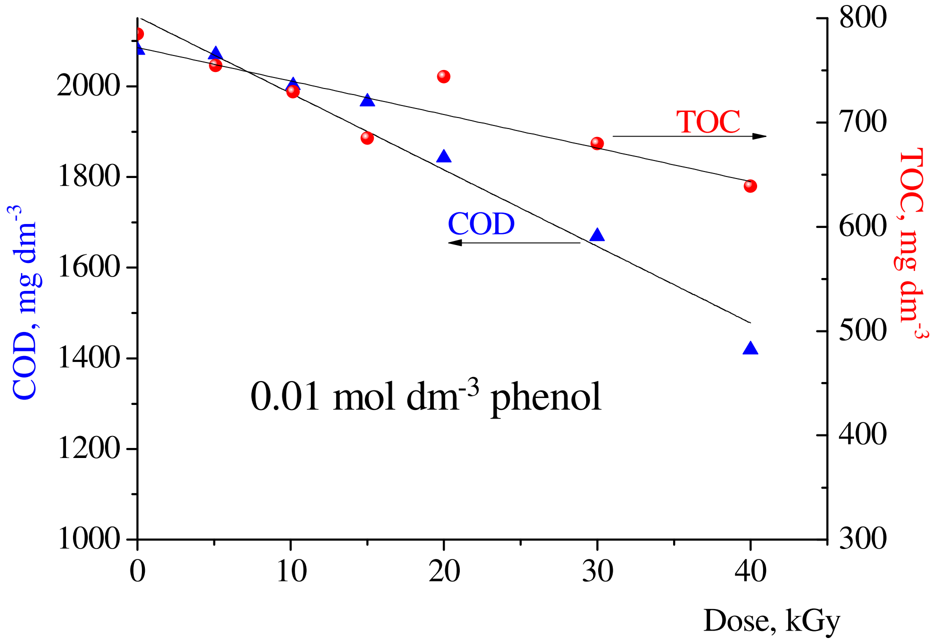
	UV	UV + H_2O_2 (10 mg/L)	UV + H_2O_2 (10 mg/L) + Fe (5mg/L)
Pollutants degradation (30 min)	80 %	96 %	95 %

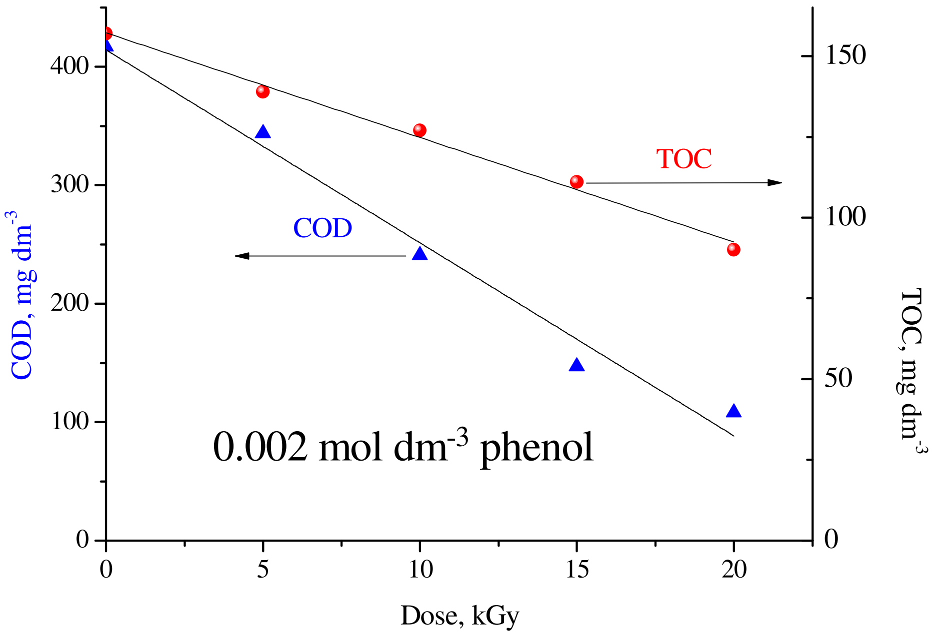
% global removal vs time



Irradiation (EB) combined with (catalytic) wet oxidation







Significant reduction of WO temperatures!

Publications **EPFL**

Degradation of 32 emergent contaminants by uv and neutral photo-fenton in domestic wastewater effluent previously treated by activated sludge, N De la Cruz, J Giménez, S Esplugas, D Grandjean, L.F de Alencastro, C Pulgarín, Water research, in press

Emergent contaminants degradation by neutral photo-Fenton in domestic wastewater effluent previously treated by activated sludge. N. De la Cruz, J. Giménez, S. Esplugas, L.F. De Alencastro and C. Pulgarín. Mediterranean Congress of Chemical Engineering, Shaping the future of Chemical Engineering, Barcelona, Spain, November 15-18 2011,

High power impulse magnetron sputtering (HIPIMS) and traditional pulsed sputtering (DCMSP) Ag-surfaces leading to E. coli inactivation, O. Baghriche1, A. P. Ehiasarian2, E. Kusiak-Nejman1,3, C. Pulgarin1, R. Sanjines4, A.W. Morawski3, J. Kiwi, Journal of Photochemistry and Photobiology A: Chemistry 227 (2012) 11– 17

Hungarian participants

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J. Tóth, F. Gergely, P. Mizsey: Physicochemical treatment of pharmaceutical wastewater: distillation and membrane processes, Periodica Polytechnica, 2011, 55/2, [IF: 0,042]

J. Tóth, P. Mizsey, Reduction of PWWs AOX, and COD values with physicochemical tools, http://www.hidrologia.hu/vandorgyules/29/dolgozatok/toth_andras_jozsef.html

Antal Tungler, Arezoo M. Hosseini, Zoltán Schay, Sándor Szabó, János Kristóf, Éva Széles, Comparison of noble metal oxide/titanium monolith catalysts in wet oxidation of process wastewaters, Europacat X., Glasgow, 27 08 2011-02 09 2011

Chamam, M., Földváry, C.M., Hosseini, A.M., Tungler, A., Takács, E., Wojnárovits, L., Mineralization of aqueous phenolate solutions: a combination of irradiation treatment and wet oxidation. Radiation Physics and Chemistry accepted. doi: 10.1016/j.radphyschem.2011.11.013

Summary

- Project implementation according to schedule: project component 1 (characterization) completed
- Four scientific sessions with the Swiss partner up till now,, consensus in program planning, good complementarity
- Good results in biodegradation (project component 4, 5) , VOC removal (project component 2) , WO (project component 3) , AOP (project component 6)
- Pilot scale and industrial devices for distillation (operation at a pharma company), oxidation (project component 7), biodegradation (at Geosan) and biogas production (at BSW), coupled AOP and biodegradation (EPFL).


Thank you for your kind attention!
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