Towards a sustainable fine chemical and pharmaceutical industry: screening and re-utilisation of carbon-rich liquid wastes

Intensification of WAO, catalysis, parameter optimisation, ionizing radiation

Removal of volatile components of real process wastewaters

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Peter Mizsey

SH7/2/14 19-20 04 2012 Lausanne

Topics of the presentation

Investigation of monolith catalysts

Design of experiments-Parameter optimisation

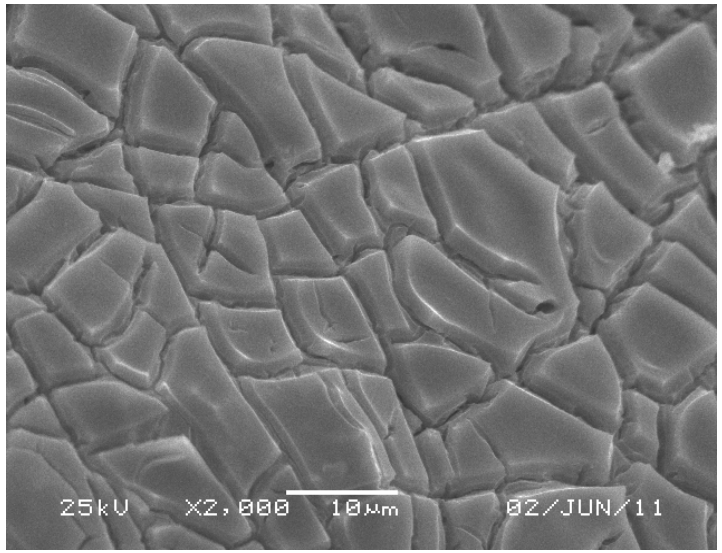
Effect of high energy radiation

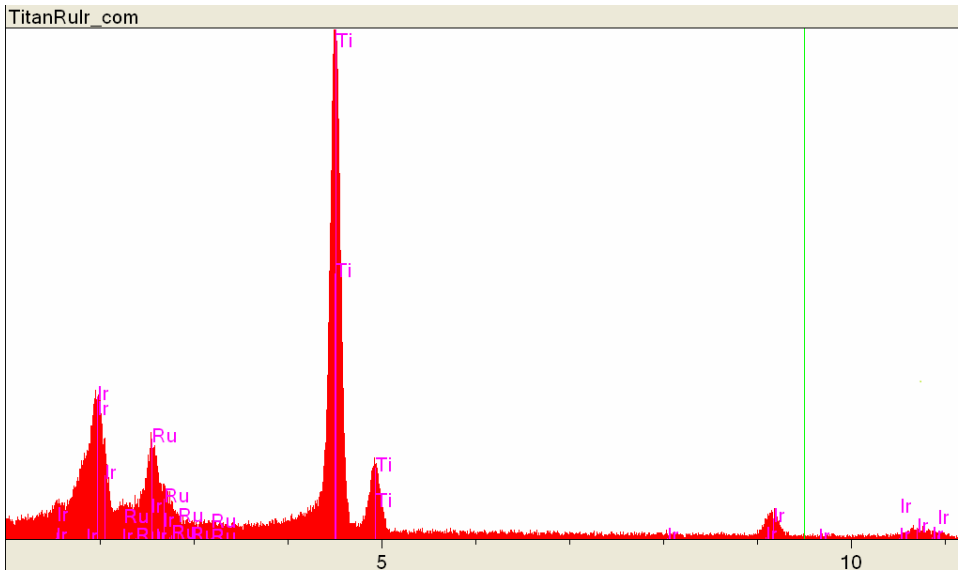
Tested monolith catalysts

Sample No.	Added components	Ru m%*	Ir m%*	Pd m%*	Cd ppm	V ppm	Cr ppm	Ta ppm
1	Ru, Ir	0.14	0.35		3			
1a	Ru, Ir	0.21	0.40					
1b **	Ru, Ir	0.20	0.23		1			
A/I	Ru, Ir	0.11	0.1					
A/I ***	Ru, Ir		360 ppm		0.5			
A/II	Ru	0.11				210		
A/III	Pd			0.12		230		
B/I	Ru, Ir	0.1	0.052		0.1	340	430	
B/II	Ir, Ta		330 ppm			200		19

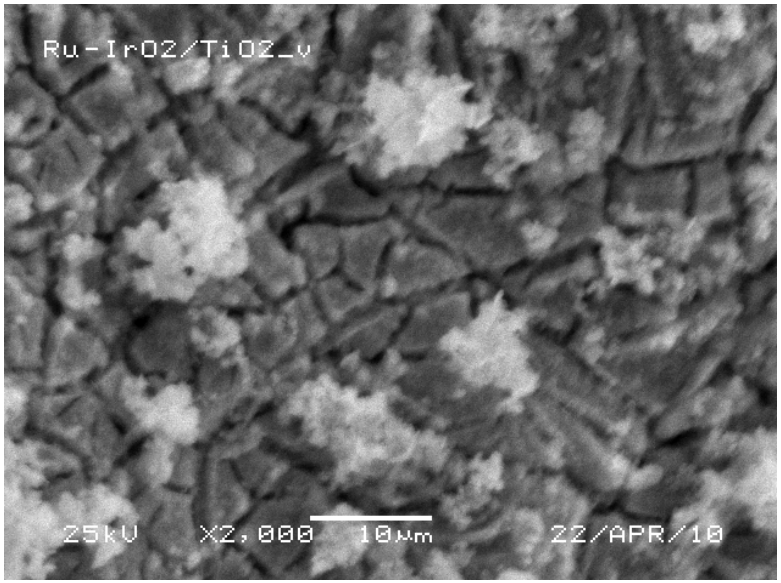
1-commercial sample, A-chemically purified Ti mesh, B-mechanically purified Ti mesh, * calculated on Ti mass, ** after 170 hours operation, ***after 100 hours operation

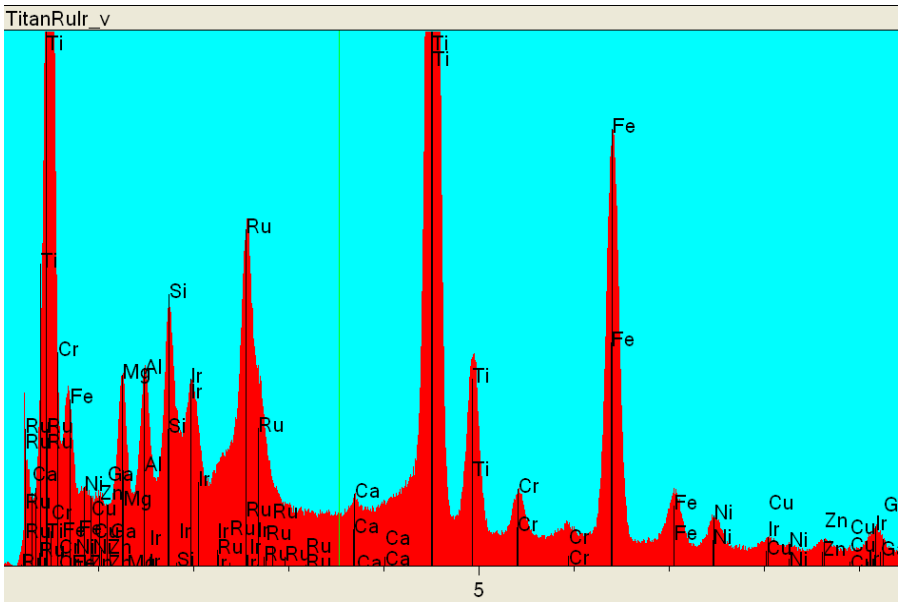
Surface of commercial Ru-Ir oxide/Ti mesh



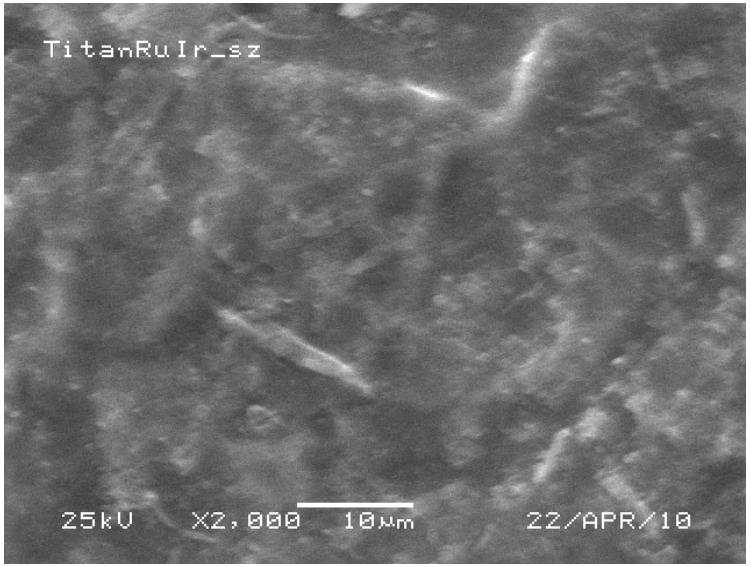


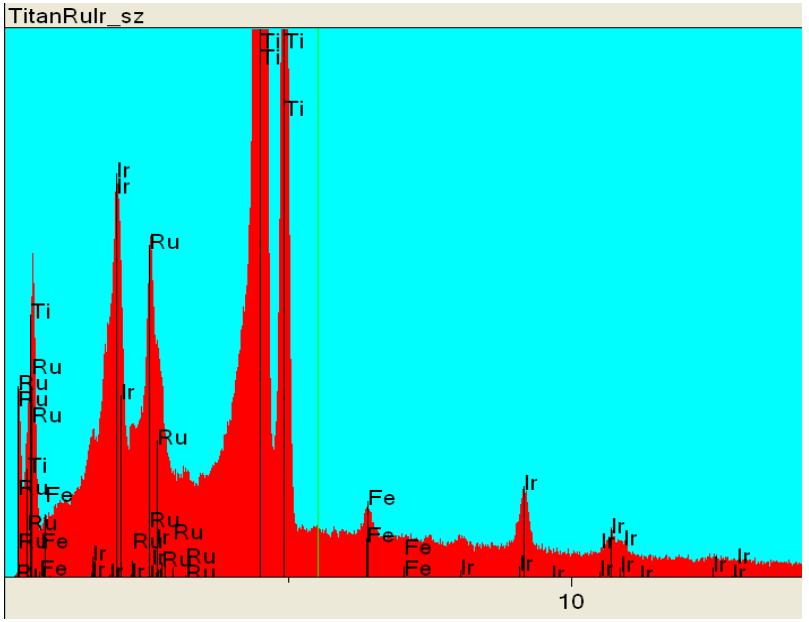
Surface of commercial Ru-Ir oxide/Ti mesh after ~200 hour usage



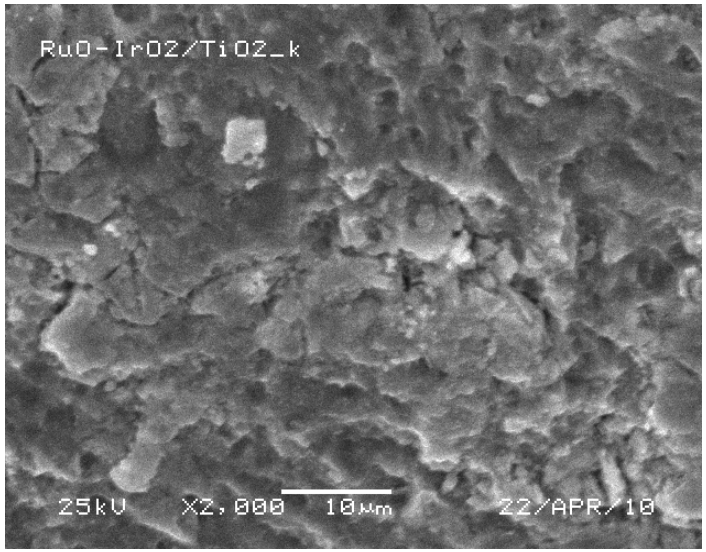


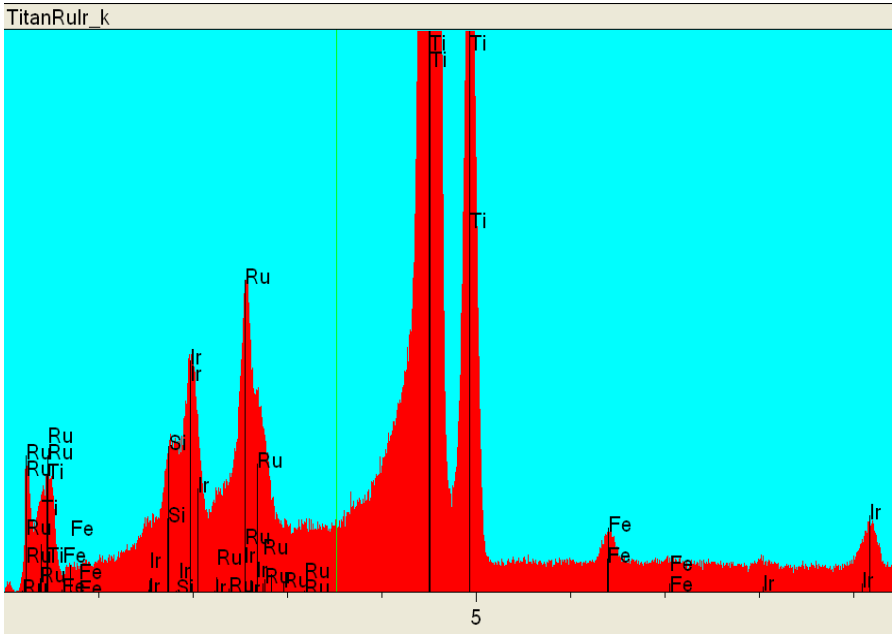
Surface of Ru-Ir oxide/Ti mesh purified by chemical method



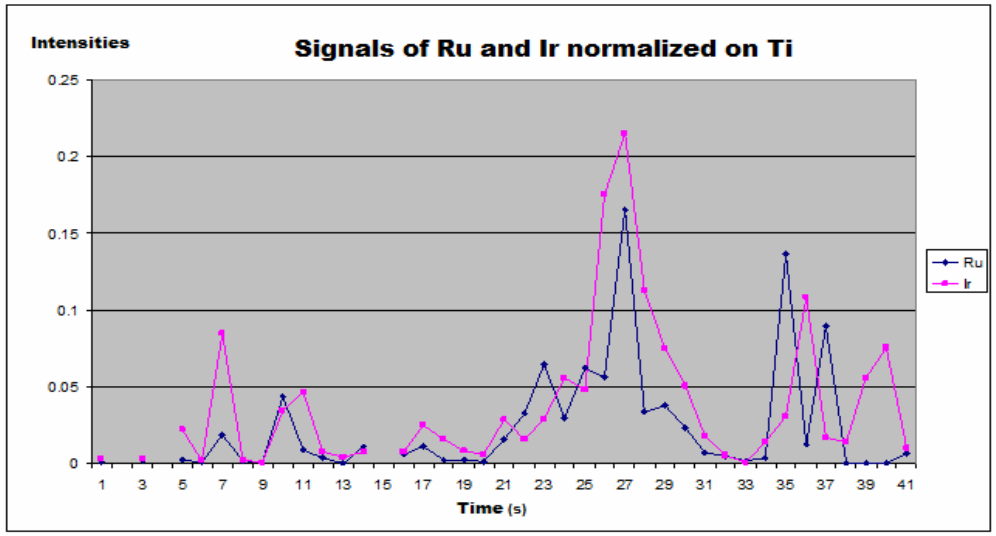


Surface of Ru-Ir oxide/Ti mesh purified by mechanical method





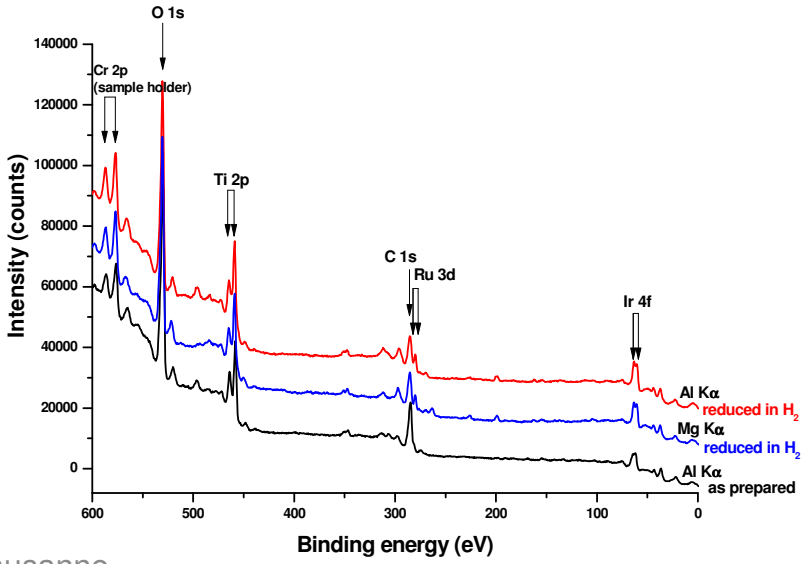
LA-ICPMS results, Ru and Ir distribution in the surface layer of the commercial catalyst



Comparison of noble metal oxide/titanium monolith catalysts in wet oxidation of process wastewaters

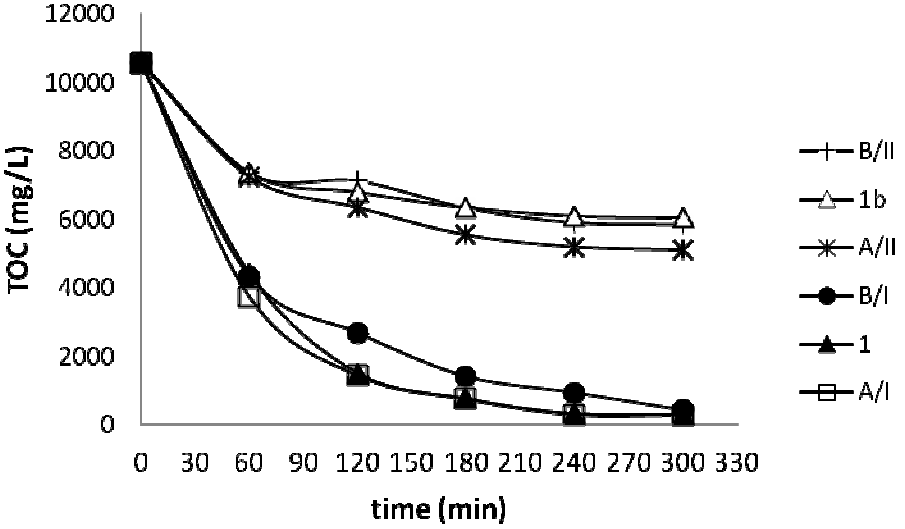
Antal Tungler, Arezoo M. Hosseini, Zoltán Schay, Sándor Szabó, János Kristóf, Éva Széles, Europacat X. Glasgow, 2011 08 27-09 02

XPS spectrum of commercial Ru-Ir oxide/Ti mesh



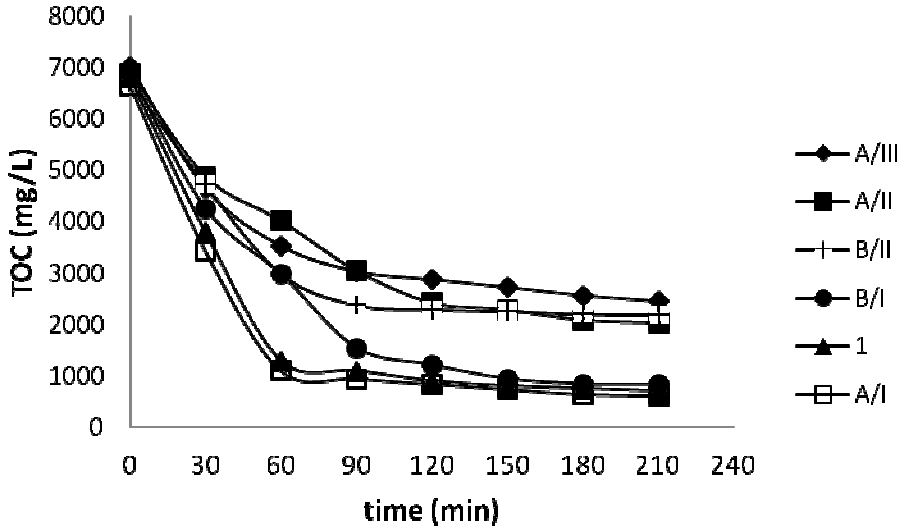
Comparison of different catalysts in wet oxidation

Oxidation of a real wastewater, TOC vs. Time (a), oxidation of phenolate solution, TOC vs. time (200°C, 50 bar) (b) with different monolith catalysts.



a

b



Design of experiments Parameter range

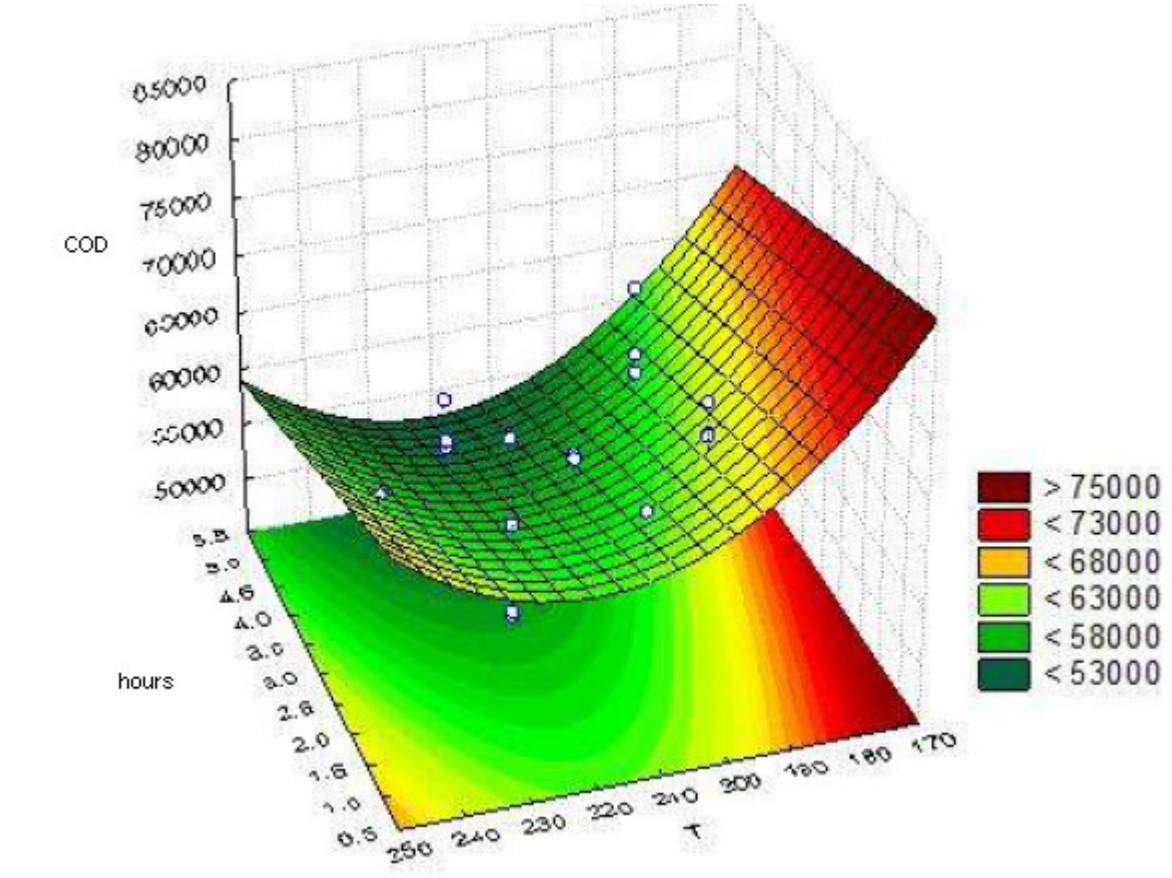
	5227	NaPH	DMF	DFA
Temperature (°C)	180 – 240	150 – 190	180 – 220	180 – 220
Oxygen partial pressure (bar)	7 – 27	10 – 26	8 – 24	8 – 24
Reaction time (h)	1 – 5	1 – 5	1 – 5	1 – 5
RPM of mixing (1/min)	150 – 1350	150 – 1350	750	750

Decrease of COD and TOC

	COD decrease		TOC decrease	
	min	max	min	max
5227	15 %	39 %	18 %	47%
NaPH	17 %	94 %	14 %	82 %
DMF	5 %	79 %	3 %	59 %
DFA	32 %	72 %	25 %	66 %

Choosing of parameters was good, the conversion values are in a wide range.

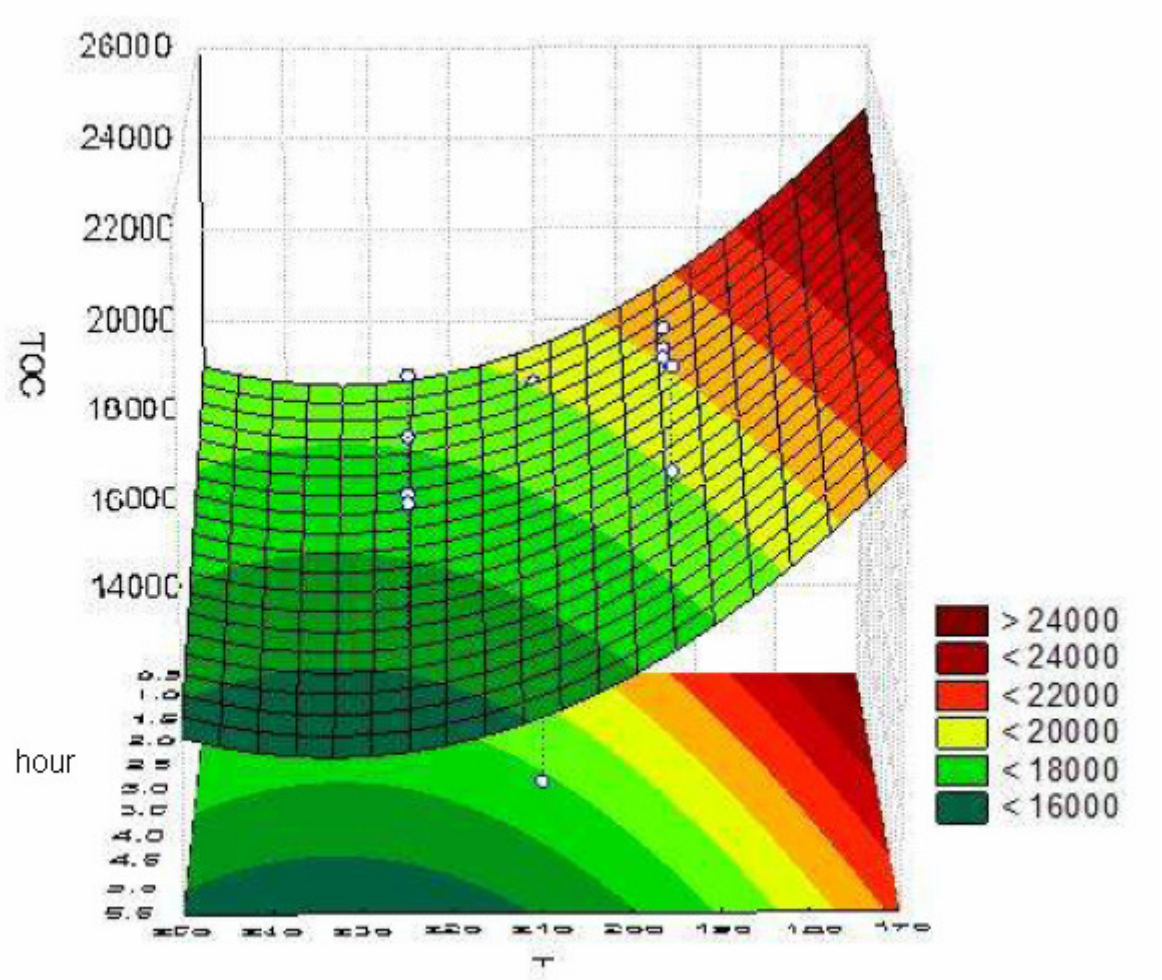
Wet oxidation of a process wastewater 5227
COD decrease in the function of temperature and time



$$\Delta COD = 466936{,}6 - 3456{,}5T + 7{,}2T^2 - 1873{,}2t - 74{,}8n + 0{,}4Tn$$

T (℃), t reaction time (hour), n rpm (1/min)

Wet oxidation of a process wastewater 5227
TOC decrease in the function of temperature and time



$$\Delta TOC=128296,2-840,4T+1,5T2-660,3t-36,4n+0,2Tn$$

Comparison of model structures for COD and TOC decrease

sample	T	T^2	p	t	t^2	n_mix	Tp	Tt	Tn_mix
5227	✓	✓		✓		✓			✓
NPH	✓	✓	✓	✓	✓		✓	✓	
DMF	✓			✓					
DFA	✓	✓	✓	✓	✓			✓	

Present work: same series of experiments in the presence of monolith catalyst.

Wet oxidation of real process wastewaters time 3h, temp. 230°C

Sample	Starting TOC(mg/L)	Starting COD(mg/L)	Catalyst	TOC (mg/L)	COD (mg/L)
EGIS B (5000X)	**136200 27.2**	**423470 84.7**	-	1-22,5(1h) 3-20(3h)(25%)	1-59,6 3-58(31%)
EGIS II (1000X)	**80900 80.9**	**279250 279.3**	-	1-61,3(1h) 2-61,3(2h) 3-55,5(3h)	1-191,4 2-176,8 3-229(18%)
EGIS II (1000X)	**80900 80.9**	**279250 279.3**	Ru-Ir/Ti mesh	1-65,0(0) 4-14,8(81%)	3-80,5(71%)
EGIS B (5000X)	**136200 27.2**	**423470 84.7**	Ru-Ir /Ti mesh	1-22,2(0h) 2-20,9(1h) 3-20,3(2h) 4-16(3h)(40%)	2-76,7 3-60,1 4-46,3(45%)

WO of dimethyl formamide, Starting TOC 6153, COD 7954 mg/L

Time (h)	Temp. (°C)	Cat.	TOC (mg/L)	COD (mg/L)
3 h	230	-	1-4841(0t) **2-**2662 **3-**1631(73%) **4-1105(82%)**	2-2805 3-2235 **4-1642(79%)**
4h	230	Ru-Ir mesh	1-5020(0t) 2-1806(71%) 3-751(88%) 4-468(92%) **5-332(95%)**	2-2502 4-1742 5-1294(84%)
3h	200	-	1-5645(0t) **2-**5380 **3-**4639(25%) **4-3833(38%)**	2-6599 3-5665 **4-4542(43%)**
3h	200	Ru-Ir mesh	1-5580(0t) 2-4581 **3**-3275(47%) **4-2228(64%)**	2-6164 3-5235 **4-3898(51%)**

Complete conversion with catalyst at 230 °C

WO of diclofenac, Starting TOC 543, COD 1398 mg/L

Time (h)	Temperature (°C)	TOC (mg/L)	COD (mg/L)
3h	230	1-431 2-91.55(1h) 3-67.6(2h) **4-43,85(3h)**	2-220(82%) 3-114,7(92%) **4-114,7(92%)**
3h	200	1-285(1h) 2-142(2h) 3-101(3h)(81%)	1-597 2-245 3-188(86%)
Up to 230	-	337	807
1h	230	120	291
3h	230	70.5	190

Not one phase!

High conversion without catalyst!

WO of Chloramphenicol
Starting TOC 129, COD 287 mg/L

Time (h)	Temperature (°C)	TOC (mg/L)	COD (mg/L)
3h	230	28,6(78%)	70.0(76%)

High conversion without catalyst!

Wet oxidation of real process wastewaters

EGIS II Starting TOC 539, COD 1862 mg/L
EGIS B Starting TOC 681, COD 2117 mg/L

	Time (h)	Temperature (°C)	TOC (mg/L)	COD (mg/L)
EGIS II	3h	230	378 (30%)	1137 (39%)
EGIS B	3h	230	547(20%)	1677(21%)

Low conversion! How does biodegradability change?

Effect of high energy radiation on wet oxidation at elevated temperatures, combination of the two methods generating radicals

First results are promising!

The present task is to carry out experiments on elevated temperatures under irradiation.

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

-Katalin Koczka, Péter Mizsey, New area for distillation: wastewater treatment, Periodica Polytechnica, Chemical Engineering, 54/1 (2010) 41–45, doi: 10.3311/pp.ch.2010-1.06,

Arezoo Mohammad Hosseini, Vince Bakos, Andrea Jobbágy, Gabor Tardy, Peter Mizsey, Magdolna Makó, Antal Tungler, Co-treatment and utilisation of liquid pharmaceutical wastes, Periodica Polytechnica, Chemical Engineering, 55:(1) pp. 3-10. (2011)

-A.M.Hosseini, A.Tungler, V. Bakos, Wet oxidation properties of process waste waters of fine chemical and pharmaceutical origin, Reac. Kinetics, Mechanism and Catalysis, DOI: 10.1007/s11144-011-0315-2, 103:(2) pp. 251-260. (2011)

-Tóth, A. J., F. Gergely, P. Mizsey, Treatment of pharmaceutical process waste waters with physicochemical tools, Technical Chemistry Days-2011, ISBN 978-615-5044-07-6, p. 112, Veszprém, Hungary, 2011.

-Nagy, R., E. Csefalvay, P. Mizsey, Concentration of sugar sorghum liquid with membrane separation, Technical Chemistry Days-2011, ISBN 978-615-5044-07-6, pp. 191, Veszprém, Hungary, 2011.

-Pauer V., E. Csefalvay, P. Mizsey, Treatment of soya process waste water with environmental friendly operations, Technical Chemistry Days-2011, ISBN 978-615-5044-07-6, pp. 201, Veszprém, Hungary, 2011.

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

Thank you for your attention!

Timetable of the project implementation reports

Starting: 15 10 2010
First period until 14 04 2011 Report PIR1 15 05 2011
First completion of documents VATI 15 06 2011, Pharmawater consortium 30 06
Second completion of documents VATI 30 07 2011, cons. 21 09 2011
Acceptance of PIR1 06 11 2011, money transfer 06 12 2011

APR1 VATI 21 10 2011, cons. 12 28 2011 (two corrections needed)

Second period until 14 10 2011 Report ready 30 11 2011 PIR2 excel table sent by VATI 02 04 2012 !!! Deadline for PIR2 is 02 05 2012.

Third period until 14 04 2012 PIR3 deadline (according to guidelines) 15 05 2012

In September 2012 financial audit is needed.

Quod licet Iovi, non licet bovi! "What is legitimate for Jove (Jupiter), is not legitimate for oxen."

PIR1

	Actual expenses this period (HUF) (2.15)	Expenses total to date (HUF) (2.16)	Planned total (HUF) (2.17)	
Salary for the Principal Investigator	1 153 154	1 153 154	7 207 837	
Employment (salary for part-time or full-time investigator or technician)	6 832 800	6 832 800	50 453 025	
Investigator work contract	1 829 447	1 829 447	14 415 471	
Miscellaneous work contract	0	0	4 036 764	
Student employment	2 727 522	2 727 522	20 888 776	
Per diem	0	0	865 079	
Administration costs	513 003	513 003	5 767 535	
Management	0	0	3 443 182	
All personal costs	13 055 926	13 055 926	107 077 669	
Travel, conferences	85 891	85 891	7 426 096	
Consumables	3 606 423	3 606 423	14 851 172	
Miscellaneous costs	896 591	896 591	21 777 925	
Overhead	3 456 403	3 456 403	16 689 644	
All material costs	8 045 308	8 045 308	60 744 836	
Investments (equipment)	1 362 380	1 362 380	13 986 297	
Total cash eligible expenses (2.19)	22 463 614	22 463 614	181 808 802	12,36%
Own contribution (2.20)	5 831 273	5 831 273	22 453 915	25,97%
Co-financing (2.21)	3 360 042	3 360 042	15 110 838	22,24%
Own contribution and co-financing % (2.22)	40,92%	40,92%	20,66%	-
Swiss grant (2.23)	13 272 299	13 272 299	144 244 049	9,20%
Non-eligible expenses (2.24)	0	0	-	-
Contingencies (2.25)	-	-	-	-

Partners					
HAS IOII	4126653	3682183	3600053	0	82 130
II	3730763	3730763	3415322	0	315 441
III	4838386	4838386	3382847	0	1 455 539
HAS IOI total	12695802	12251332	10398222	0	1 853 110
EPFL total	6632710	6556498	725225	5831273	0
BME ABFS total	3655784	3655784	2148852	0	1 506 932
Sum	22984296	22463614	13272299	5831273	3 360 042
	Brutto	**Cash eligible exp.**	**Swiss grant**	**Own cont.**	**Co-financing**

Expences of money transfer ~150.000 HUF

	Actual expenses this period (HUF) (2.15)	Expenses total to date (HUF) (2.16)	Planned total (HUF) (2.17)	
Salary for the Principal Investigator	1 084 035	2 237 189	7 207 837	
Employment (salary for part-time or full-time investigator or technician)	10 274 784	17 107 584	50 453 025	
Investigator work contract	0	1 829 447	14 415 471	
Miscellaneous work contract	0	0	4 036 764	
Student employment	12 457 403	15 184 925	20 888 776	
Per diem	0	0	865 079	
Administration costs	513 001	1 026 004	5 767 535	
Management	0	0	3 443 182	
All personal costs	24 329 223	37 385 149	107 077 669	
Travel, conferences	860 779	946 670	7 426 096	
Consumables	5 155 552	8 761 975	14 851 172	
Miscellaneous costs	2 579 329	3 475 920	21 777 925	
Overhead	2 921 948	6 378 351	16 689 644	
All material costs	11 517 608	19 562 916	60 744 836	
Investments (equipment)	1 451 578	2 813 958	13 986 297	
Total cash eligible expenses (2.19)	37 298 409	59 762 023	181 808 802	32,87%
Own contribution (2.20)	10 902 861	16 734 134	22 453 915	74,53%
Co-financing (2.21)	3 365 462	6 725 504	15 110 838	44,51%
Own contribution and co-financing % (2.22)	38,25%	39,26%	20,66%	-
Swiss grant (2.23)	23 030 086	36 302 385	144 244 049	25,17%
Non-eligible expenses (2.24)	-	-	-	-
Contingencies (2.25)	-	-	-	-

Partners					
HAS IOI 1a	2223918	2223918	1422074	0	801844
HAS IOI 1b	1505743	1505743	554201	0	951542
HAS IOI 2	551577	551577	551577	0	0
HAS IOI 3	1795410	1795410	1679107	0	116303
HAS IOI total	6076648	6076648	4206959	0	1869689
EPFL 1a	7169673	7169673	3260713	3908960	0
EPFL 1b	3695007	3695007	1853532	1841475	0
EPFL 3	7501470	7501470	4137270	3364200	0
EPFL total	18366150	18366150	9251515	9114635	0
BME ABFS 1	533294	469794	182794	0	287000
BME ABFS 4	7953827	8011674	6983646	0	1028028
BME ABFS total	8487121	8481468	7166440	0	1315028
BSW total	3982919	3576447	1788221	1788226	0
SUM	36912838	36500713	22413135	10902861	3184717
	Brutto	**Cash eligible exp.**	**Swiss grant**	**Own cont.**	**Co-financing**

EPFL exp. 9251515 HUF, HUF/CHF= 229.58 Grant for EPFL 40298 CHF
Expences of money transfer ~850.000 HUF

Tasks for the third half year	HAS IoI	EPFL	BME ABFS	BSW	Geosan
Testing of model wastewaters in WO, AOP and high energy radiation assisted oxidation	+	+			
Testing of model wastewaters in biological degradation		+	+	+	
Chemical and biological characterization of PWWs from pharmaceutical companies COD, BOD, TOC volatile content, AOX, digestion properties, toxicity oxidation properties	+ + + + +	+ + + +	+ +	+ +	
Investigation of the optimal removal methods of volatile content of PWWs	+				
Detailed testing of selected toxic, non-biodegradable PWWs in chemical (WO, AOP) degradation	+	+			
Detailed testing of selected non-toxic, biodegradable PWWs in biological degradation, anaerobic digestion		+	+	+	
Advanced oxidation processes, (Photocatalysis, AOP, high energy radiation) for destruction of recalcitrant components after biological treatment, HAS IOI treatment of toxic and recalcitrant compounds with high energy radiation	+	+			
Pilot scale reactors and scale-up of laboratory processes.				+	+

Tasks of the third half year

Participants	HAS IOI	BME CEPE	BME ABFS	BSW	Geosan
Tasks	Oxidation Irradiation and oxidation	Distillation	Determination of bio-degradability	Anaerob digestion	Pilot plant experiments
Materials and details	DMF	EGIS waters	DMF	EGIS waters	Putting into operation of oxidation and biological treatment pilot-plant
	DFC		DFC		
	EGIS waters		EGIS waters	oxidated EGIS waters	
			oxidated EGIS waters		

Planned CHF 2011 10 15-2012 04 14

Project components	HAS IOI CHF	BME ABFS CHF	EPFL CHF	BSW CHF	Geosan CHF	Sum CHF
1	18.148	30.327	8.000			56.475
2	24.318					24.318
3	15.000		23.088			38.088
4		13.068				13.068
5				9.044		9.044
6	7.124		24.052			31.176
7				11.520	13.200	24.720
8						
9						
Sum	64.590	43.395	55.140	20.564	13.200	196.889

Planned spending ~ 196.889 CHF
co-financing + own contribution~41.352 CHF, support ~ 155.537 CHF
The sums not spended in the first year have to be added to these sums!