Catalytic wet oxidation of real process wastewaters

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Abstract CWO and WO were carried out for oxidizing different industrial wastewaters of pharmaceutical production, at 230°C and 250°C and total pressure of 50 bar, with oxygen, in stainless steel autoclaves. The catalysts were titania supported precious metal (Pt, Pd, Ru, Rh) oxides and copper sulfate. Samples were analyzed with respect to their TOC, COD (BOD) content. The tested wastewaters, some of them mother liquors, could be oxidized , but with rather different conversions. Even at the hard-to-oxidize wastewater the COD decrease hit the 50 % during 4 hours, this procedure decreased the COD/BOD ratio. The Ru oxide-titania catalyst proved to be the most active in this process, yet in the non-catalytic reactions significant conversion was detected also, due to the Fe or Cu ion content of the wastewaters.

Keywords: Catalytic wet oxidation; mixed real industrial wastewater**,** Ru oxide-titania catalyst, Pd oxide-titania catalyst

1. Introduction

Wastewaters, process waters and mother liquors produced in many industrial processes often contain organic compounds that are toxic and non biodegradable. Treating of these streams has become a technological, ecological, and economical problem. One of the present technologies used for high organic content waste streams is Wet (Air) Oxidation. Wet Oxidation is a process widely used for water treatment, by which the pollutants are converted into easily biodegradable substances or completely mineralized.

An alternative is catalytic wet (air) oxidation (CW[A]O). Soluble transition metal salts (such as copper and iron salts) have been found to give significant enhancement of the reaction rate [1, 2], but a post treatment is needed to separate and recycle them. Heterogeneous catalysts have the advantage that they can be used without the problem of separation and for continuous operation. Mixtures of metal oxides of Cu, Zn, Co, Mn, and Bi are reported to exhibit good activity, but leaching of these catalysts was detected [3, 4, 5].

On the other hand, heterogeneous catalysts based on precious metals deposited on stable supports are less sensitive to leaching [2, 6, 7, 8, 9, 10]. Pt and Ru on ceria and zirkonia-ceria supports [11] were tested in oxidation of acetic acid which was accompanied by the loss of activity. In a following paper [12] the same authors described the reason for deactivation of Pt catalyst, the accumulation of carbonate species on the surface.

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Recently activity of Ru oxide on different oxide supports in acetic acid oxidation was reported. The mixed Zr, Ce oxide supported catalyst proved to be the most active [13].

In the last decade significant need was revealed [14, 15] toward treatment of highly concentrated wastewaters of chemical, pharmaceutical production, as well as residual sludges. The wastewaters, process waters and mother liquors which arise during the operation of chemical and pharmaceutical plants contain high amount of organic and inorganic material which has to be treated before releasing them to the environment or sewage system. If these wastewaters are toxic and/or non-biodegradable, so there is a significant need for oxidative degradation. CW(A)O has been applied to many different model effluents, but relatively few works have been devoted to real and complex industrial wastes [1, 6, 16, 17, 18]

In a recent paper [19] a complex approach of treatment has been outlined, the optimal combination of physical-chemical, wet oxidation and biological disposal methods. Depending on the toxic and volatile content of the individual process wastewater the use any of these methods can be the solution for the treatment.

The oxidation properties of process wastewaters of pharmaceutical origin [20] were studied in thermal and in catalytic wet oxidation, the latter with a monolith type catalyst. The tested PWW's could be oxidized but with rather different conversions, some effluents were converted with remarkable rate due in some cases to their Fe or Cu ion content, in other cases to the Ti mesh supported precious metal oxide catalyst.

In this research work real waste waters of chemical production and a sludge from treatment plant were oxidized, which contained numerous organic and inorganic components. These mother liquors were reacted with oxygen at 230-250°C temperatures, at total pressures (O_2+water vapour pressure) up to 50 bar with powder formed titania supported precious metal oxide catalysts, with copper sulfate and without catalysts.

The aim was not the complete oxidation but to attain a certain level of conversion, where the toxicity ceased, but reaction mixture still contained simple organic compounds, for example sufficient amount of carboxylic acids, like acetic acid, which then could be used as a carbon source for denitrification.

2. Experimental

2.1. Catalyst preparation

Different titania supported precious metal oxides were prepared. The general procedure was: 2g (10 g) TiO_2 support (Evonik [Degussa] P-25, surface area: $50 m^2 g^{-1}$) was suspended in 30 ml (100 ml) distilled water and the precious metal salt ($PdCl_2$ in cc HCl, H_2PtCl_4, $RuCl_3$ and $RhCl_3$ dissolved in distilled water, in amounts to ensure 2w% metal content for the catalysts) was added and mixed with the support. The pH of the mixture was then adjusted to 10 by introducing proper amount of 10% Na_2CO_3 solution. After 2 hours mixing, the catalyst was filtered, the filtrate was washed with distilled water, and finally it was calcined at 800°C in air for 6 hours.

2.2. Catalyst characterization

The Pd and Ru containing catalysts, which turned to be the most active ones, were characterized by TPR, SEM, XRD and XPS. Their metal contents were determined by ICP-MS (ELEMENT2 Thermo Electron Corp.) after dissolving them in HF(50%)-HCl(37%)-HNO_3 1:0.5:0.2 mixture at 90^{o}C. TPR was carried out in a sorptometer device developed in our laboratory. SEM images were made on a JEOL JSM 5600 LV instrument. Powder XRD measurements were performed with Cu Kα radiation using a Bruker AXS D8 Discover horizontal X-ray diffractometer equipped with a two dimensional GADDS detector system. The beam diameter was about 500 μm.

The surface composition of these catalysts was analysed by a KRATOS XSAM800 XPS machine using Al-Kα source with 120 W X-ray power and 40 eV pass energy. To avoid any artifacts the catalysts were placed onto the XPS sample holder and analysed in the form as prepared (calcined at 800^{o}C) as a sieve fraction. The Ru oxide/TiO_2 sample was additionally reduced *in situ* at 500^{o}C in hydrogen flow at atmospheric pressure for 1 hour in a catalytic reactor attached to the XPS machine. The VISION software from KRATOS was used in spectrum fitting and calculation of surface compositions. As the Ru3d spin pair and the C1s peak overlap, the position, FWHM and area of the Ru $3d_{3/2}$ peak was constrained to the $Ru3d_{5/2}$ peak. C1s at 285 eV and $Ti^{4+}2p_{3/2}$ at 458.8 eV were used for charge compensation.

2.3. Oxidation procedure

The wastewater samples and model solutions were oxidized in a 250 and in 850 ml stainless steel high pressure autoclave equipped with a magnetic stirrer (rpm 700), at 230, 250°C temperature and 50 bar total pressure. Usually during oxidation the pH decreases, therefore the non-basic (pH<8) wastewaters were basificated to basic values, above 8-9 with solution of 20% NaOH before the oxidation. Wastewater and sludge samples were loaded to the autoclave and they were pressurized with oxygen and heated up to the desired temperature. At the end of each experiment samples were taken and then analyzed.

In case of CWO experiments catalyst was added to the solution before feeding it into the reactor. For determining the conversion-time relationship liquid samples of approximately 3 ml were periodically withdrawn from the reactor through a tube located at the bottom of the reactor. The outer section of the tube was water-cooled in a jacket for decreasing the sample temperature. Before taking each sample, the dead volume of the tube (about 7 ml) was let out.

Beside the oxidation of real wastewaters, in order to verify the activity of our catalysts and to compare the non catalytic and catalytic experiments, oxidation of water solution of acetic acid and phenol in the form of their Na salts was carried out (model solutions). Acetic acid is one of the most, phenol is a least resistant compound towards wet oxidation.

Prior to oxidation experiments COD, TOC and pH (in some cases BOD_5) of the wastewater samples were measured. Dilution experiments were carried out in order to observe precipitation upon adding water or NaOH solution for neutralization, basification, and on the basis of these results the wastewaters were treated in different ways.

The adding of NaOH solution before starting the reactions was a necessity in order to avoid corrosion of the autoclave material, which was a highly corrosion resistant stainless steel (equivalent to 316L). Even at basic pH moderate corrosion was experienced, which was highly accelerated with decreasing pH.

2.4 XRF measurements

The metal content of wastewaters was detected by X-Ray fluorescence spectroscopy using one point calibration (device Canberra Si(Li) SSL 8013 detector, surface area 80 mm^2, thickness 5 mm, resolution 150 eV (at 5,9 KeV energy, Fe-55 line). Measuring part DSA 1000 type signal processor, exciting source I-125, in 20-60 atomic number, and Fe-55 10-25 atomic number). It turned out that there are different amounts of metal ions present in these wastewaters, mostly Fe and Cu, which could act as catalyst.

Table 1 X-ray fluorescence analysis of the metal content of the wastewaters

Sample	Fe ppm	Ni ppm	Cu ppm	Mo ppm	Cr ppm	Ce ppm	Zn ppm
B1	10	-	-	1-2	10	-	-
B2	100	-	30	-	-	500	-
B3	1.0%	100	100	-	-	-	-
F3	1000	-	100	-	-	-	100

2.5. TOC, COD and BOD measuring methods

Liquid samples taken from the reactor during the CWO experiments were analyzed measuring the TOC and the COD values, some wastewaters and their final reaction mixtures were tested with respect to their BOD value. The TOC was determined by a Shimadzu TOC analyzer whose operation was based on catalytic combustion and non dispersive infrared *(NDIR)* gas analysis. TOC values were obtained by subtracting measured inorganic carbon (IC) from measured total carbon (TC). COD was determined by the standard dichromate method. BOD_5 was measured according to DIN EN 1899-1, with an OxiTop device.

3. Results and discussion

3.1. Catalyst characterization

In oxidation of Sample A (an acetic acid containing sample) it turned out that our Pt and Rh containing catalysts have small activity, therefore Pd and Ru oxide-titania catalysts were used in further reactions and characterized in detail.

The colour of the Ru containing catalyst was gray, its Ru content 0.62% according to ICP-MS. This is in good agreement with the TPR results (fig 1, 2), because the metal content calculated from the 79 micromole consumed hydrogen /g catalyst, supposing Ru^{III}, is 0.6%. Similarly, the Pd content of the Pd oxide/TiO_2 (colour light brown), from ICP-MS was 1.7%, from TPR 1.6%. The significant Ru loss (~1.4%) can be attributed to the volatility of Ru oxide at the calcination temperature of 800^oC.

The particle size of the catalysts was in the 10-50 μm range, the crystallite size in 0.1 μm order of magnitude according to SEM images (Figure 3, 4).

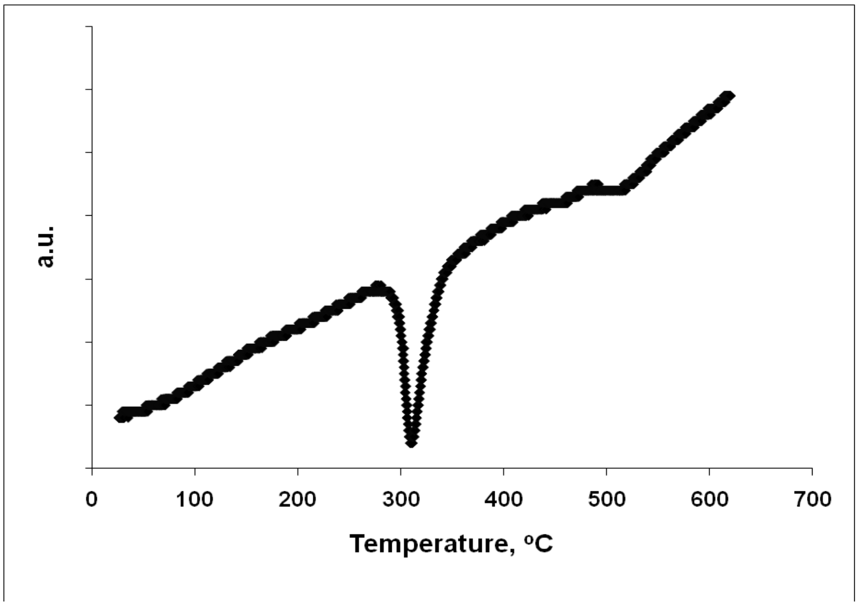

Figure 1 TPR Curve of Ru oxide/TiO_2, consumed hydrogen: 79 micromole/g with 310 and 520°C peak maxima.

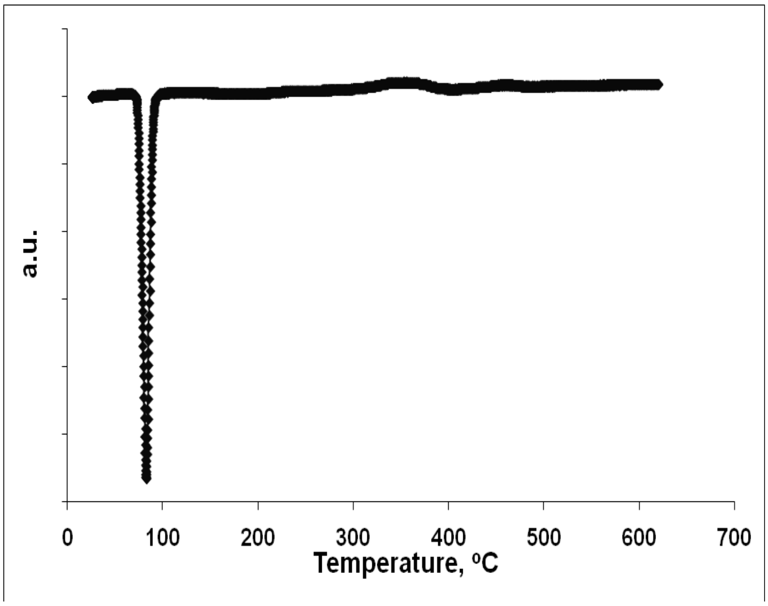

Figure 2 TPR Curve of Pd oxide/TiO_2, consumed hydrogen; 151 micromole/g with 83°C peak maximum.

The recorded XRD spectra are presented in Figure 5. Most of the peaks can be identified as TiO_2, either rutile or anatase peaks. Further peaks, denoted by arrows, can be found in the spectrum of the Pd oxide/TiO_2 sample, they can be identified as the peaks of the tetragonal palladinite (PdO, JCPDS Card No 41-1107). No other peaks except TiO_2 ones are present in the spectrum of the Ru oxide/TiO_2 sample, which is in accordance with the low Ru content.

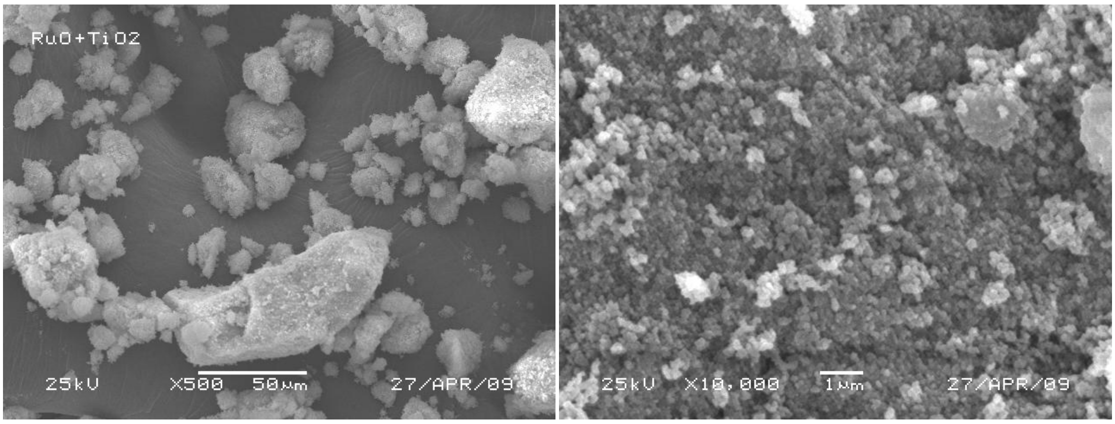

Figure 3 SEM pictures of Ru oxide/titania catalyst (magnification 500x, 10000x)

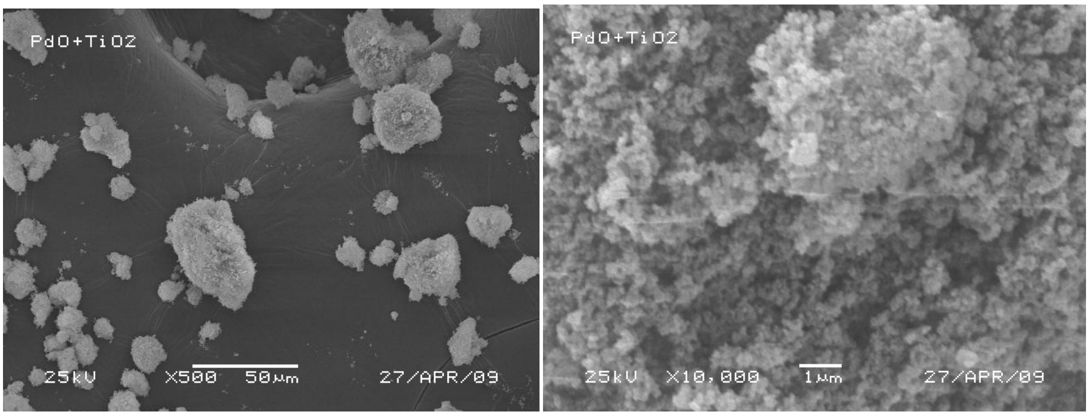

Figure 4 SEM pictures of Pd oxide/titania catalyst (magnification 500x, 10000x)

Table 2 XPS results of the Pd oxide/TiO_2 and Ru oxide/TiO_2 catalysts

Catalyst	O/Ti atomic ratio	C/Ti atomic ratio	Pd or Ru peak position (eV)	Pd/Ti or Ru/Ti atomic ratio*100
Pd oxide/TiO_2 calcined	2.8	0.4	336.6	1.4
Ru oxide/TiO_2 calcined	2.7	0.89	282*	0.55*
Ru/TiO_2 reduced *in situ*	2.2	0.069	279.6	0.3

*uncertain due to the large C1s peak

The XPS results are summarized in Table 2. Both catalysts were fully oxidized in the form as prepared. The overlap in the Ru oxide and C peaks and the high amount of carbon in the as prepared catalyst resulted in an uncertainty in the calculation of the surface concentration of Ru (Figure 6/**a**). To overcome this difficulty the sample was reduced *in situ* resulting a shift of the $Ru3d_{5/2}$ peak to a lower binding energy and a separation from the C1s peak (Figure 6/**b**). Simultaneously most of the carbon was removed by hydrogen and this also improved the reliability of the fitting. The XPS results are also in good agreement with the metal contents, determined by ICP-MS and TPR.

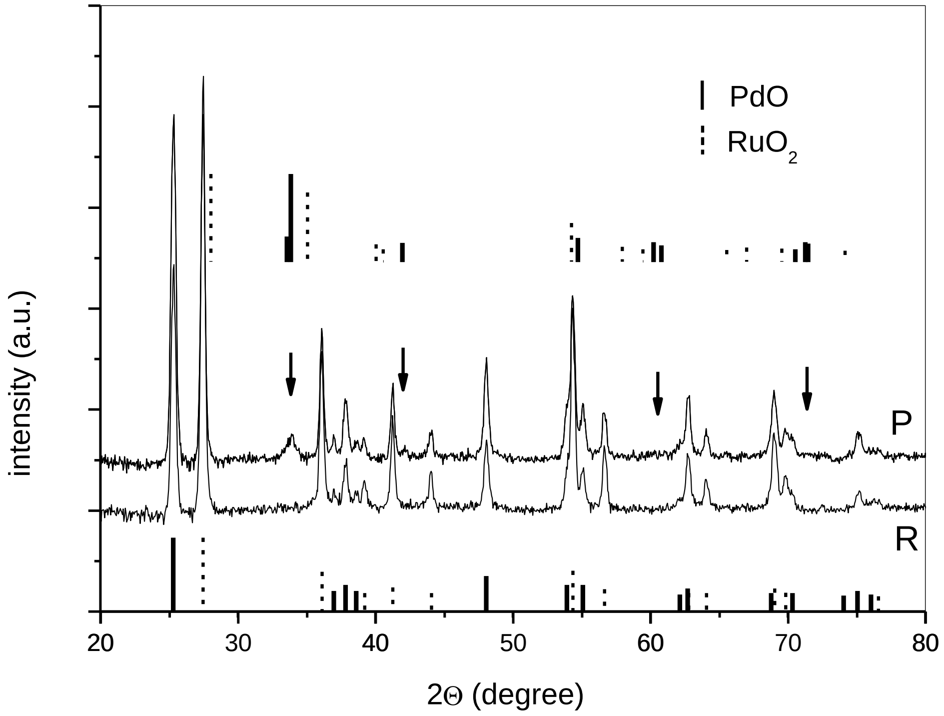

Figure 5 XRD spectra of samples PdO/TiO$_2$ (P) and RuO$_2$/TiO$_2$ (R). Peak positions of anatase (solid lines) and rutile (dashed lines) are given at the bottom of the figure. Peaks of the Pd oxide/TiO$_2$ spectrum other than TiO$_2$ ones are denoted by arrows. For comparison, peak positions of PdO (solid lines) and RuO$_2$ (dashed lines) are presented in the upper part of the figure.

3.2. Catalytic wet oxidation experiments

Sample A, a high COD value (>1 000 000) waste was oxidized in diluted form., it was an acetic acid solution containing <5% water, diluted (23x) before loading it to the reactor. Reactions performed during 4h at 50 bar total pressure and 250°C were chosen as standard operating conditions for this sample. This experiments served for distinguishing between four noble metal oxides on titania, including Pt, Pd, Ru, Rh and Fe^{III} and Cu^{II} catalysts. Liquid samples were then analyzed with respect to their TOC and COD content. (Table 3)
Sample A contained different organic compounds which were at least partly precipitated when the sample was diluted and basificated. Comparing COD values at the end of each experiment, there was 62% decrease in COD, 23% in TOC with Ru oxide/TiO$_2$ and it proved to be the most efficient in the CWO. The other effective catalysts are Pt and Pd oxides, with similar COD decrease, but Pd is superior in TOC reduction (37%). The added metal salts (Fe, Cu) didn’t increase reaction rate.

As part of the catalyst characterization, comparative experiments were carried out, the wet oxidation of acetic acid and phenol at basic pH, without and with Ru oxide and Pd oxide on titania catalysts (the most active ones according to oxidation of sample A, Table 3). Data in Table 4 indicate that in spite of its lower metal content, Ru oxide-titania catalyst is more active in both oxidations. Oxidizing phenol the catalysts seem to decrease the induction period, great differences are in the 2 hour results.

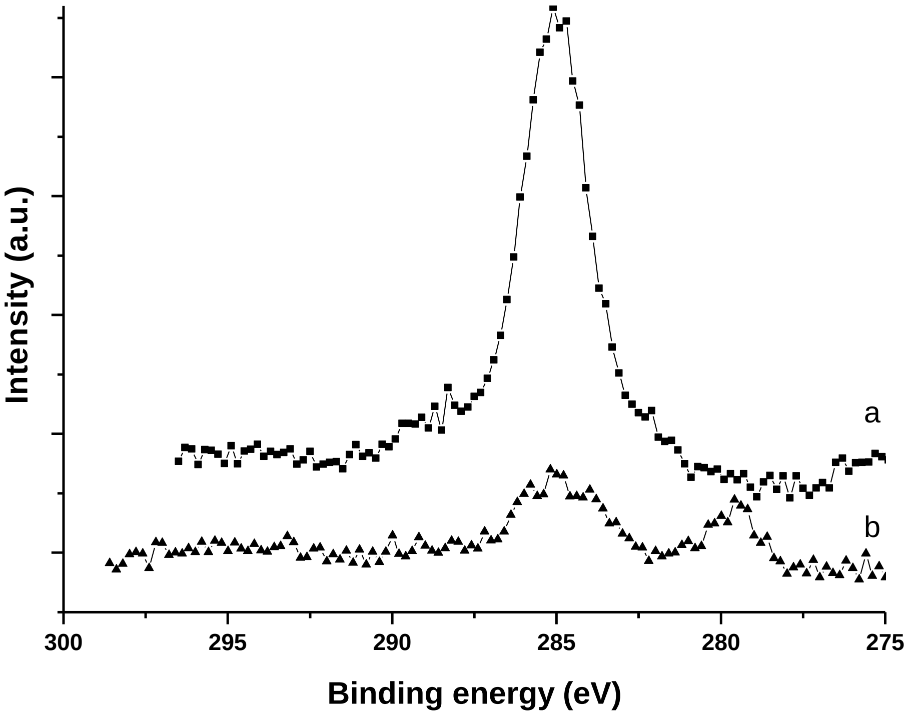

Figure 6 XPS curves of Ru containing catalyst, **a**/ as prepared state, **b**/ after reduction in hydrogen at 500°C

The oxidation results of F2, which was an industrial wastewater and F3, which was sewage treatment plant sludge, (20% solid matter) are presented in Table 5 and 6. For determining the TOC value, the sludge had to be filtered before introducing it to the TOC analyzer, so the non-soluble part of the organic matter content was filtered out and the remaining liquid was analyzed.

Sample F2, 50 g was basificated with NaOH solution to pH=10 and oxidized at 250°C, 50 bar total pressure, for 4 hours with heterogeneous and homogeneous catalysts in order to compare the activity of the catalysts. Data in Table 5 indicate that the reaction rate is somewhat higher with Ru and Pd catalysts.

Sample F3, a sludge, 50 g was oxidized at 250°C and 50 bar pressure for 4 hours with Pd oxide-titania and Cu sulfate catalyst (Table 6). The COD decrease was much higher than the TOC decrease (its values uncertain), which can be due to the formation of carboxylic acids, acetic acid concentration measured by gas-chromatography after oxidation was 1213 ppm. Catalytic WO has no excess effect, which can be due to the significant original Fe ion content of the sample (1000 ppm).

Finally three B coded wastewaters were tested at 250˚C and 230˚C temperature and 50 bar pressure in presence or absence of catalyst. B1 had extremely high COD concentration because of its ethanol content (751 800 mg/L). B1 and B2 were diluted, 10x, 5x respectively, before each experiment. Ru oxide/TiO_2 was used as catalyst. Samples were analyzed with respect to their TOC, COD and BOD content (Table 7).

Table 3 Oxidation of sample A

Catalyst	TOC (mg/L)	COD (mg/L)	TOC reduction (%)	COD reduction (%)
A	**344000**	**1218000**	-	-
diluted, starting	**15000**	**53000**	-	-
-	14600	28670	2.7	46
0.6 g Pt oxide/TiO_2	12970	22920	13.5	57
0.6 g Ru oxide /TiO_2	11565	20280	23	62
0.6 g Rh oxide /TiO_2	13485	38940	10	26.5
0.6 g Pd oxide /TiO_2	9430	23465	37	56
0.5g $FeCl_3$	12310	28670	18	46
80 mg $CuSO_4$	11650	29150	22	45

Table 4 Oxidation results of acetic acid and phenol.
(Na acetate 3x H_2O solution, 84g/L, phenol solution 9.4g + 4 g NaOH/L, total pressure 50 bar)

Temp.(°C)	Catalyst	Reaction time hour	TOC(mg/L)	COD(mg/L)
substrate solution acetic acid			**15070**	**34600**
230	-	2	14740	34263
		5	13440	31200
230	Pd oxide/TiO_2 0.5 g	2	15000	34190
		5	14580	32400
230	Ru oxide/TiO_2 0.5 g	2	15000	26350
		5	14860	23440
substrate solution phenol			**7850**	**20830**
120	-	2	7290	19430
		5	7110	17630
120	Pd oxide/TiO_2	2	7360	20050
		5	7140	19790
120	Ru oxide/TiO_2	2	7140	20060
		5	7160	19790
180	-	2	7090	20200
		5	1150	2050
180	Pd oxide/TiO_2	2	1640	6980
		5	1170	3980
180	Ru oxide/TiO_2	2	1620	3710
		5	1230	2200

The B samples were oxidized at two temperatures, with Ru oxide-titania catalyst. Conversion rate increased for B1 and B2 with increasing temperature (230 to 250°C). It was surprising that the oxidation rate of B3 was higher at lower temperature (230°C), although this 20°C difference means 12 bar increment in oxygen partial pressure. (At total pressure of 50 bar and at 230°C the partial pressure of O_2 is ~22 bar, water vapor pressure ~28 bar, at 250°C 10 bar and 40 bar, respectively). The oxidation rate of B3 seems to be more sensitive to oxygen partial pressure than that of samples B1 and B2, but latter ones are more susceptible to reaction temperature. The heterogeneous catalytic effect was again small or negligible. According to TOC and COD profiles (Figures 6-9) in the first period of the reactions, during heating up and in the first ½ or 1 hour the conversion rate is higher, we think this is the accumulation phase of the carboxylic acid intermediates. The smaller TOC and the higher COD change indicate this.

Table 5 Oxidation of sample F2

Catalyst	TOC (mg/L)	COD (mg/L)	TOC reduction (%)	COD reduction (%)
starting	**34000**	**113600**	-	-
-	15 940	41 700	53	63
0.3 g Pd oxide/TiO_2	11 640	29 600	65	74
0.3 g Ru oxide/TiO_2	13 920	36 300	59	68
0.3 g TiO_2	14 940	36 100	56	68
16 mg $CuSO_4$	11 760	36 000	65	68

Table 6. Oxidation of sample F3

Catalyst	COD (mg/L)	COD reduction (%)
starting	**53000**	
-	4880	91
0.3 g Pd oxide/TiO_2	6130	88.4
16 mg $CuSO_4$	6430	87.9

4.Conclusion

The tested process wastewaters and the sludge could be oxidized at 50 bar total pressure, with oxygen, up to 250°C temperature, but with rather different conversions. Even at the hard-to-oxidize wastewater the COD decrease hit 50%. For B3 waste the lower temperature (230°C) - higher oxygen partial pressure (22 bar) was more beneficial than the higher temperature (250°C) lower oxygen partial pressure (10 bar), with respect to the attainable conversion rate. The diversity of such wastes, mother liquors is obvious, the optimal parameters of oxidation treatment including the use of catalysts have to be determined individually. The catalytically active metal ion, Fe, Cu content of these wastes has to be taken into account.

The small or negligible reaction rate change upon adding of the powder form catalysts prepared in our laboratory can be explained with various reasons. (i)The metal content, especially at the Ru containing catalyst was too low. (ii) The noble metals in oxide form are not the optimal catalysts for WO. (iii) The real wastewaters are not so easy to oxidize as of model effluents. Their metal ion content can poison the heterogeneous precious metal oxide catalysts.

Therefore the study of oxidation of real wastewaters is unavoidable towards the development of disposal technologies. This also explains why the Zimpro and Athos technologies are working at more severe conditions than most described oxidation on model waters.

For the heterogeneous catalysts, the following trend could be observed in their effectiveness in oxidation of sample A of high acetic acid content:

$$\text{Ru oxide/TiO}_2 > \text{Pd oxide/TiO}_2 > \text{Pt oxide/TiO}_2 > \text{Rh oxide/TiO}_2$$

The performance of added $CuSO_4$ and $FeCl_3$ was rather poor in oxidizing the samples, this is understandable as the pH of the reaction mixtures was adjusted to basic values, moreover the wastes contained these metal ions even before treatment. Beside the beneficial catalytic effect, these metal ions can deteriorate the activity of the heterogeneous catalysts as they can act as poisons, adsorbing on the surface of the precious metal oxides.

The oxidation improved or, at the well biodegradable samples, did not change biodegradability (BOD/COD ratio increased or remained unchanged). In the oxidized wastewaters significant amount of carboxylic acids were accumulated, specifically acetic acid, and this can act as carbon source for the denitrification process.

Acknowledgement

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Table 7 Oxidation results of samples B1, B2 and B3

Sample	Temp. (°C)	Catalyst	TOC (mg/L)	COD (mg/L)	BOD/COD %	TOC reduction (%)	COD reduction (%)
B1	**-**	**-**	**208000**	**751000**	**94**	-	-
diluted, starting			**20800**	**75100**	**-**	-	-
	230	-			-	43	51
	250				100	54	56
	250	Ru ox./TiO$_2$			100	49	58
B2	**-**	**-**	**52850**	**178180**	**21**	-	-
diluted, starting			**10570**	**35640**	**-**	-	-
	230	-			-	30	38
	250	-			62	46	52
	250	Ru ox./TiO$_2$			82	47	59
B3	**-**	**-**	**41 200**	**117 000**	**91**	-	-
	230	-	21 200	54 270	-	49	54
	230	Ru ox./TiO$_2$	21500	54500	90	48	53
	250	-	25 690	62 270	90	38	47
	250	Ru ox./TiO$_2$	22 300	69 890	92	46	40

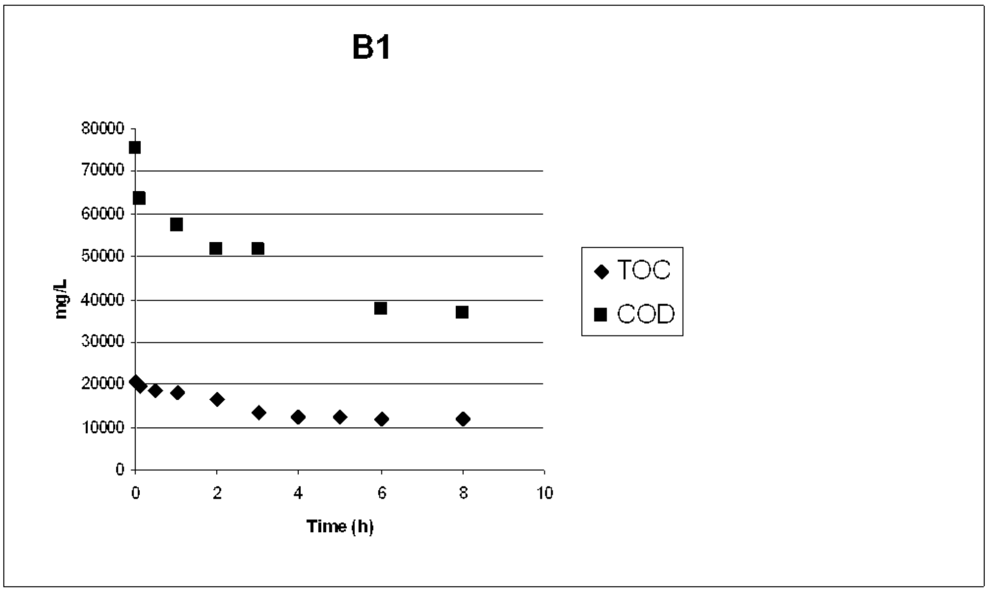

Figure 7 Oxidation of B1, TOC and COD profiles at 230^{o}C

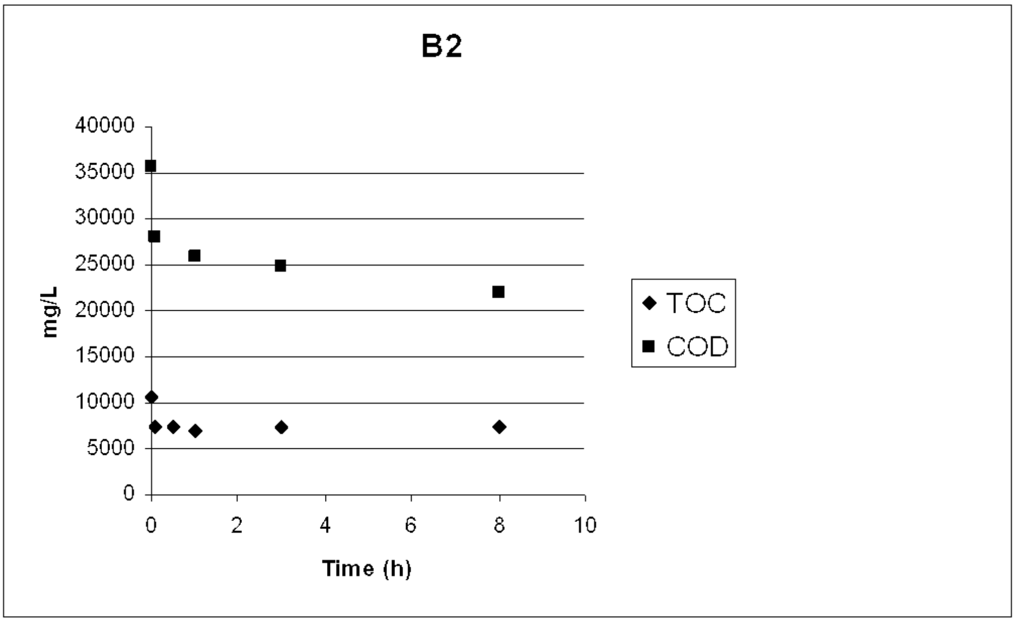

Figure 8 Oxidation of B2, TOC and COD profiles at 230^{o}C

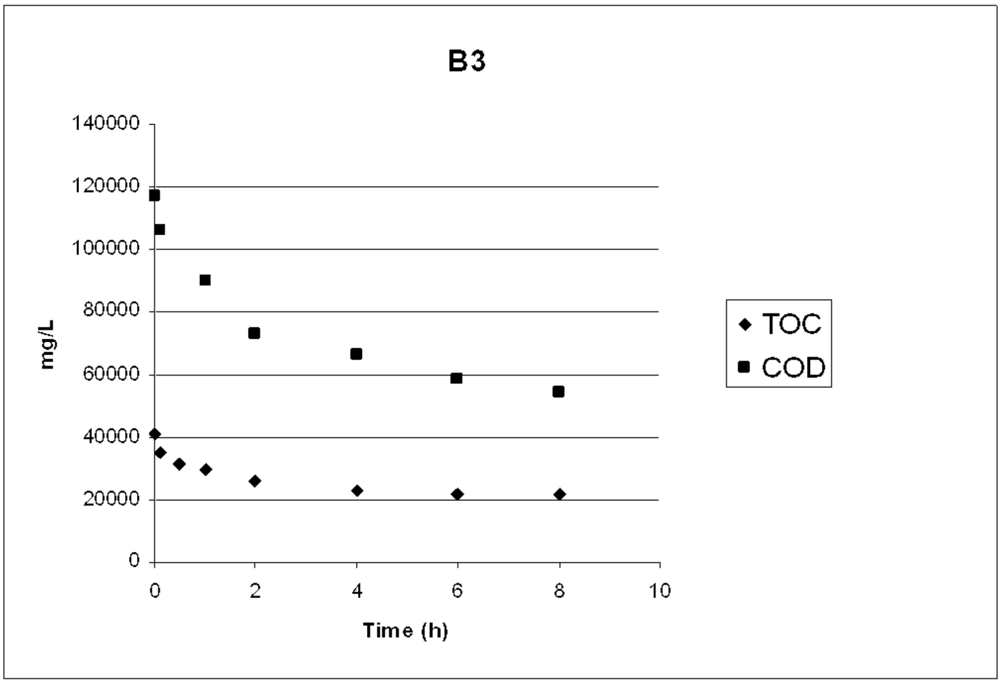

Figure 9 Oxidation of B3, TOC and COD profiles at 230°C

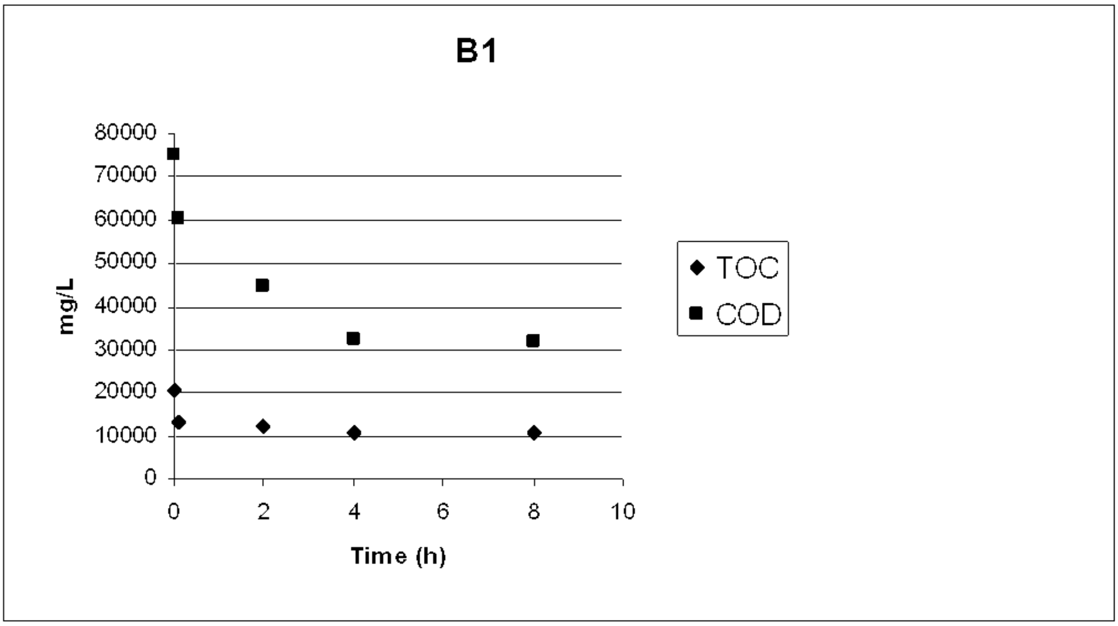

Figure 10 Catalytic oxidation of B1, TOC and COD profiles at 250°C

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